CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION
INTERNATIONAL CO-OPERATIVE PROGRAMME ON ASSESSMENT AND MONITORING
OF AIR POLLUTION EFFECTS ON FORESTS

and

EUROPEAN UNION SCHEME
ON THE PROTECTION OF FORESTS AGAINST ATMOSPHERIC POLLUTION

United Nations
Economic Commission
for Europe

European Commission

FOREST SOIL CONDITION IN EUROPE

Results of a Large-Scale Soil Survey

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Abstract

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This technical report presents the results of the first European large-scale forest soil survey. The aim of the survey was to assess basic information on the chemical soil status and on other soil properties which determine the soil vulnerability to air pollution. **Part** I of the report discusses the transnational comparability of data, the influence of climate and soil characteristics on soil chemistry, the effects of atmospheric deposition on soil chemistry and assesses the ecological quality of forest soils in Europe. The forest soil condition in most European countries is summarised in concise national reports in **Part** II.

Keywords: forest soil, monitoring, data comparison, soil chemistry, air pollution

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Preface

At European level two programmes are dealing with the protection of forests against atmospheric pollution:

1) The convention on Long-Range Transboundary Air Pollution (LRTAP), which lays down the general principles of international co-operation for air pollution abatement and brings together research and policy, was the first internationally binding instrument to deal with problems of air pollution on a broad regional basis. The convention constitutes a framework within which international actions are undertaken. The International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests in the UN/ECE region (ICP Forests) was established in 1985 in response of the widespread damage to forests observed in the late 70s and early 80s.

2) The European Union Scheme on the Protection of Forests against Atmospheric Pollution (EEC Regulation no. 3528/86) was established by the Council in 1986 in order to protect forests against atmospheric pollution and to contribute, in particular, to safeguarding the productive potential of agriculture by monitoring the forest condition in Europe and by carrying out pilot and demonstration projects in the field.

A close co-operation between both programmes has developed which includes annual crown condition assessments on a uniform 16x16 km transnational grid composed of more than 3000 plots in the European Union and more than 5000 plots over the whole of Europe.

The results of the crown condition assessments and other studies indicate that the effects of air pollution on the soil, in particular acid deposition, may be an important stress factor predisposing the forest to damage and loss of vitality. Therefore, at the annual Task Force Meeting of ICP Forests in 1989, the establishment of a Forest Soil Experts Panel (FSEP) was mandated. The FSEP presented in 1992 a submanual on methods and criteria for monitoring of forest soils, which was adopted by the Task Force (ICP Forests). For the EU Member States, the technical details were laid down in Commission Regulation (EEC) no. 926/93. The submanual and the Regulation contain a selection of mandatory and optional parameters and outline reference procedures for sampling, analysis and reporting. Thirty-one European countries are participating in the large-scale soil monitoring activities of level I. Today, the transnational Forest Soil Condition Database stores the soil information from 4532 observation plots in 23 European countries. The data of 8 other participating countries are either in the process of collection, or have recently been submitted and are currently verified.

For the processing of the soil data, observed at the level I monitoring plots, a Forest Soil Co-ordinating Centre (FSCC) was set up in November 1993 at the Laboratory of Soil Science of the University of Gent. The major activities of FSCC are storage, quality control, interpretation and presentation of collected soil data on level I plots. FSCC collaborates with other Expert Panels of the ICP Forests and the European Commission. The collected data of 23 countries, comprising all 15 EU-Member States and 8 non-EU countries, are presently stored in a relational database linked to a GIS, and presented in this forest soil condition report.

Summary

The European *Forest Soil Condition Database* contains information on 4532 plots in 23 countries, and will be extended with more than 1000 plots from 8 countries in the coming years, with the possibility for further data from other countries. Most observation plots are situated at the intersection points of a 16x16 km grid, and are shared with the *Forest Crown Condition Database*. The main objective of this European-wide soil survey is the assessment of basic information on the chemical soil status and on other soil properties which determine the soil vulnerability to air pollution.

For each plot, the database consists of general information, such as FAO soil classification name, chemical and physical data of organic and mineral soil layers. The mineral soil was sampled at two or three fixed depths between 0 and 20 cm. Data are available in the majority of plots for the following parameters: pH ($CaCl_2$), organic carbon, nitrogen for both mineral and organic layers, and total amounts of P, K, Ca and Mg for organic layers. Total concentrations of Na, Al, Fe, Cr, Ni, Mn, Zn, Cu, Pb and Cd and cation exchange properties were less frequently reported. In addition, information on soil parent material and some physical soil properties (texture, coarse fragments content and bulk density) was provided on a voluntary basis.

Although a common methodology for sampling and analysis was adopted before the start of the monitoring activities in most countries, differences in national methods exist. In order to verify the data quality of the reported analysis results, two standard samples were provided to all laboratories, participating in the survey. The results of the standard samples showed a moderate to high variability even among laboratories using the same methods. Fortunately, a relatively low interlaboratory variability was observed for the most relevant parameters in this study (23% for pH, 10% for total N and 10% for base saturation).

The quality of the chemical data was further controlled by subjecting the national data files to an integrity check. Integrity rules were defined by plausible value ranges and acceptable differences between overlying layers, and take into account soil type specific properties. Reported data, violating one or more integrity rules, were flagged and cross-checked by the National Focal Centre.

Soil chemical parameter results were divided into five classes. Nonparametric factor analysis of variance was conducted using differences in climate, atmospheric deposition load, soil type, parent material class, textural class, or humus type as criteria to cluster observation plots. In order to study the soil condition in relation to atmospheric deposition, the survey area was divided in four regions based on the spatial distribution of the measured acid deposition load in Europe in 1988/1989. This procedure resulted in the clustering of observation plots in four groups, based on their geographical location.

Approximately half of the observed soil types in European forests are Podzols and Cambisols. Leptosols, Arenosols and Regosols are also common. European forest soils are often marginal for agriculture, due to physical limitations such as stoniness, sandy texture and high carbonate content. The majority of the forest soils are derived from sedimentary rocks.

Soils with peat or mor humus accumulate large amounts of organic matter at the soil surface, as a result of a slow decomposition rate, and are dominant in northern Europe. Mull humus, characterised by a fast turnover rate and an intimate mixture with mineral soil materials, is the most frequently observed humus type in southern Europe. Next to climate, soil nutrient availability influences the decomposition rate of organic matter and the distribution of humus types. In climatic zones, where both mor and mull types are found, mor humus is usually found on nutrient-poor soils, containing organic matter with a wide C/N ratio, whereas C/N values are lower and nutrient contents are higher in soils underlying mull humus.

Soil texture, parent material type and climate largely determine the cation exchange properties of forest soils. Cation exchange capacity is usually less than 10 cmol(+) kg^{-1} in mineral subsurface layers of coarse textured soils, but increases with increasing clay content; values of more than 10 cmol(+) kg^{-1} are dominant in fine textured soils. The exchange complex of calcareous soils, which comprise 14% of the European forest soils, is completely saturated with basic cations. On the other hand, basic cations occupy 15% or less of the cation exchange sites of the mineral surface layer of about one quarter of the European forest soils. Average base saturation values of carbonate-free soils increase from north to south, as well as from west to east in Europe, following the climatic gradient of a precipitation surplus in north-western Europe to an evapotranspiration deficit in eastern Europe and the Mediterranean area.

Results show a correlation between soil chemistry and atmospheric deposition of nitrogen, acidity and heavy metals:

- A higher nitrogen content in the organic layer of forest soils is observed in the area receiving a high atmospheric deposition load, as compared to remote areas in Europe. Nitrogen deposition, decreasing the C/N ratio of humus layers, has probably disturbed organic matter and nutrient cycling. Unusually high N contents in the organic layer, indicated by a lower ratio in this layer compared to the mineral layer, were observed in 17 % of the plots.
- Acid topsoil conditions, i.e. base saturation of 20% or less, or pH values below 3.5 are reported in 42% of the plots. Results indicated a relationship between acid deposition and pH, but for base saturation such a direct relationship could not be substantiated. This may be due to the fact that other factors, such as climate and soil type, strongly influence base saturation. Extremely acid topsoil conditions, i.e. having a mineral surface layer pH ($CaCl_2$) value below 3.0, are reported for 80 plots (1.9% of all plots), located almost exclusively in the region receiving a very high atmospheric deposition load. A common characteristic of these soils is a low reserve of basic exchangeable cations (BCE of 2.0 cmol(+) kg^{-1} or less), indicating a low buffering capacity against acidification.
- Atmospheric deposition has resulted in high levels of heavy metals in strongly industrialised areas. Concentrations of certain heavy metals, particularly lead and zinc, in humus layers and topsoils show regional gradients reflecting atmospheric deposition patterns. The majority of plots having an organic layer with high lead or zinc concentrations is found in the region with the highest deposition load. Contaminated soils may accumulate more than 100 mg kg^{-1} of lead in the organic layer and are commonly observed in central Europe. However, critical concentrations of Pb (500 mg kg^{-1}), Zn (300 mg kg^{-1}) and also Cd (3.5 mg kg^{-1}), are exceeded in less than 1% of the plots for which values have been reported. Exceedences of critical organic layer concentrations of Cr (30 mg kg^{-1}) and especially Cu (20 mg kg^{-1}) have been reported more frequently, in 9% and 19% of the plots respectively.

The chemical soil data allowed an assessment of the soil's capacity to perform its ecological functions within the forest ecosystem. The capacity to supply nutrients (N, P and basic cations), the sensitivity to acidification, and the capacity to immobilise heavy metals (Zn, Pb and Cd) are important indicators of forest soil quality in strongly industrialised regions. An evaluation of the transnational soil data has resulted in a classification of individual monitoring plots, based on calculated indicator values for nutrient availability, soil acidification and metal availability.

The indicator values for nutrient availability show an overall north-south gradient. A generally low nutrient supply probably contributes to the slow tree growth observed in northern Europe. The association of humus type and nutrient availability is confirmed, whereas soil texture appears to largely determine the soil supply of cationic nutrients.

National report summaries on the forest soil condition in 23 countries are also presented in this report. A short informative text on national survey activities was prepared for 8 other participating countries, that have not yet completed the interpretation of national soil condition data. At national level, various forms of damage to the chemical status of forest soils have been reported; most common forms are soil acidification, nutrient imbalances and heavy metal contamination. Among the damaging agents atmospheric deposition of acids, nitrogen and heavy metals, historical land use and forest fire are mentioned, although relationships with tree vitality are difficult to prove. Liming is often used to remediate strongly acidified soils, but alternative measures which have less influence on biological processes, such as woodash fertilisation and silvicultural measures (mixed stands, deep-rooting trees), are tested in several countries. Some national datasets on soil condition have been confronted with results of crown condition, however, significant correlations between level I soil condition parameters and tree vitality could generally not be found.

The Soil Condition Database offers numerous application possibilities, such as the investigation of soil stress factors on tree condition, the improvement of critical load calculations, estimation of weathering rates and the extrapolation of soil data to sites where no information is available. However, this first European-scale survey also revealed some limitations: (i) a high interlaboratory variability for several parameters, (ii) a low reliability of calculated nutrient pools, and (iii) the unavailability, for many plots, of parameters that are important in the study of soil changes induced by atmospheric deposition, such as exchangeable cations in the organic layer. Further efforts to improve data quality and a revision of the soil manual should precede future large-scale soil monitoring activities.

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Definitions

Organic 0-layer	layers dominated by organic material, consisting of undecomposed or partially decomposed litter, such as leaves, needles, twigs, moss and lichens, which has accumulated at the soil surface; they may be on top of either mineral or organic soils. 0-layers are not saturated with water for prolonged periods.
Organic H-layer	layers dominated by organic material, formed from accumulations of undecomposed or partially decomposed material at the soil surface which may be underwater. All H-layers are saturated with water for prolonged periods or were once saturated but are now artificially drained.
Surface mineral layer	consists of the uppermost mineral soil layer, i.e. the ***0-5*** cm, 0-10 cm or in a few cases the 0-20 cm layer;
Subsurface mineral layer	consists of the sampled mineral soil layer between 10 and 20 or between 10 and 30 cm.

Soil Parameters and Units

All soil analysis results are based on oven-dry weight.

Org. **C**	Organic carbon	g kg^{-1}	**BS**	base saturation	%
OrgLay	Organic layer weight	kg m^{-2}	**Na**	sodium	mgkg"
N	Total nitrogen	g kg^{-1}	**Al**	Aluminium	mg kg^{-1}
P	phosphorus	mgkg"	**Fe**	iron	mg kg^{-1}
K	potassium	mg kg^{-1}	**Cr**	chromium	mg kg^{-1}
Ca	calcium	mg kg^{-1}	**Ni**	nickel	mg kg^{-1}
Mg	magnesium	mg kg^{-1}	**Mn**	manganese	mg kg^{-1}
$CaCO_3$	Calcium carbonate	g kg^{-1}	**Zn**	zinc	mgkg''
CEC	cation exchange capacity	cmol(+) kg^{-1}	**c u**	copper	mgkg"
BCE	exchangeable basic cations	cmol(+) kg^{-1}	**Pb**	lead	mg kg^{-1}
ACE	exchangeable acid cations	cmol(+) kg^{-1}	**Cd**	cadmium	mg kg^{-1}
AcExc	exchangeable acidity	cmol(+) kg^{-1}			

Country Codes

FR	France	**LX**	Luxembourg	**CR**	Croatia
BE	Belgium	**SW**	Sweden	**CZ**	Czech Republic
NL	Netherlands	**AU**	Austria	**ET**	Estonia
DL	Germany	**FI**	Finland	**SL**	Slovenia
IT	Italy	**RO**	Romania	**BL**	Belarus
UK	United Kingdom	**PL**	Poland	**BU**	Bulgaria
IR	Ireland	**SR**	Slovak Republic	**LA**	Latvia
DK	Denmark	**NO**	Norway	**UR**	Ukraine
GR	Greece	**CH**	Switzerland	**YU**	Yugoslavia
PO	Portugal	**HU**	Hungary		
ES	Spain	**LI**	Lithuania		

Climatic Regions

AN	North Atlantic	**HN**	Mountain (North)
AS	South Atlantic	**MD**	Higher Mediterranean
B	Boreal	**ML**	Lower Mediterranean
BT	Temperate Boreal	**S**	Subatlantic
H	Mountain (South)		

Other Abbreviations

MIN	Ministry
NFC	National Focal Centre
NC	National Co-ordinator of the forest soil survey
EU	European Union
EC	European Commission
ICP Forests	International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests
UN/ECE	United Nations Economic Commission for Europe
FSCC	Forest Soil Co-ordinating Centre
FSEP	Forest Soil Experts Panel

INTRODUCTION

The Soil Component in Forest Ecosystems

Soil has a major ecological role in forest ecosystems, involving many organisms and individual chemical processes. It provides moisture, nutrients and physical support for plants, and serves as a filter for toxic substances and a receptor for natural wastes. In forestry, soil is the resource, whereas trees are merely a crop.

The forest cover and the resultant forest floor provide a micro-climate and a spectrum of organisms different from those associated with most other soils. Differences between agricultural and forest soils derive, in part, from the fact that often the most "desirable" soils have been selected for agricultural use and the remainder left for native vegetation such as forest. Fortunately, soil requirements for forest trees frequently differ from those for agricultural crops. Poor drainage, steep slopes, or the presence of large stones are examples of soil conditions that favour forestry over agricultural use.

Objectives

The aim of this first European-wide soil survey, at which 31 countries participated, is the assessment of basic information on the chemical soil status and on soil properties which determine the soil vulnerability to air pollution. The importance of chemical properties to tree growth has gained considerable attention in recent years, largely because of greater demands placed on forest soils in terms of productivity, but also because of indications that the recent decline in forest health may be related to soil changes induced by atmospheric pollution. The collected information of 23 countries is currently stored in a transnational Forest Soil Condition Database. In this report, four major objectives are pursued.

(1) Intercomparability of data

The development of more reliable soil tests as diagnostic tools and an improving knowledge of soil chemistry have contributed to the increased interest in the chemical status of forest soils. **A** major concern in this survey, where soil samples were collected by different national or regional teams and analysed in local laboratories, is the transboundary data comparability. Although a common methodology for sampling and analysis was adopted before the start of the monitoring activities in most countries, differences in national methods exist.

In order to control the quality of the collected data of the survey, two standard samples have been analysed by most participating laboratories, together with the collected samples of the inventory plots. The variation among the reported standard sample results give an indication of the possibilities and limitations of a transnational comparison of the collected data.

(2) Influence of climate and soil characteristics on soil chemistry

The chemical properties of soils are the result of weathering of their mineral components, decomposition of organic materials, and the activity of plants and animals (Kimmins, 1987).

Physical weathering of mineral materials, breaking down rocks into increasingly smaller particles, largely determines soil texture. Chemical weathering releases nutrients and may result in the formation of clay minerals. Both clay and colloidal organic matter exert a dominant influence over the chemical properties of soils. The ability to absorb and hold nutrient cations is perhaps their major contribution to soil chemical properties.

Parent material affects soil chemistry, but the extent of its influence can be modified by climate. For example, soils derived from a similar parent material, but developed under different climatic conditions, may have vastly different properties, because of variations in weathering rate, leaching of nutrients, and accumulation of organic matter.

Soil chemistry is further influenced by forest management practices. Many European forest lands have been managed rather intensively for centuries. Few truly virgin forests exist today in Europe. The conversion of forest to crop land and back to forest has gone through many cycles in some areas of Europe.

The contribution of chemical properties to tree growth has traditionally been believed to be largely overshadowed by physical properties (Pritchett and Fisher, 1987). This assumption was largely based on observations that most forest trees possess deep, efficient root systems capable of exploiting large volumes of soil and that the nutrients obtained from soil depths are effectively cycled to promote long-term growth with a minimum drain of nutrient reserves. However, the significance of the chemical soil status becomes obvious with a few examples. On many northern European sites, restricted rooting and slow nutrient cycling may result in nutrient deficiencies. Slow tree growth in quartz sand soils often results from strictly chemical factors.

(3) Effects of atmospheric deposition on soil chemistry

A possible reason for the loss of vitality of the European forests is the persistent input of atmospheric pollutants, which might affect forests indirectly through changes of the soil (Matzner and Murach, 1996). Soil damage forms associated to atmospheric deposition, of particular concern in European forests, are soil acidification, nutrient imbalances, and heavy metal contamination.

Natural soil forming processes in humid regions lead to acidification, but atmospheric deposition of sulphur compounds and nitrogen (both reduced and oxidised) compounds may accelerate this process (Erisman et al., 1995). Because soils contain various compounds that may buffer acidification processes, it usually takes some time before negative effects of acid deposition, i.e. nutrient depletion, become apparent. The buffering capacity of a soil is largely determined by its amount of exchangeable basic cations and weatherable minerals content. Initially, the replacement of calcium, magnesium and other cations by hydrogen ions might increase the availability of nutrients and uptake by plants. After a point, the essential cations may be largely replaced by hydrogen or by other acid cations in the soil. With continued deposition of acids soil pH may ultimately decrease, which makes some nutrients such as P less soluble and may mobilise potentially toxic elements such as aluminium and several heavy metals.

Since the beginning of industrialisation, nitrogen deposition has promoted tree growth. Increased levels of nitrogen in forest soils due to atmospheric deposition may lead to a more vigorous vegetation growth. This should be particularly true for trees in the Boreal zone where N is often limiting. A continuous high input of N may adversely affect ecosystem stability due to increased demands of nutrient cations and water, and an increased sensitivity to natural stress factors, such as frost, fungi attack and wind throw (Ulrich, 1995; Matzner and Murach, 1996). Nevertheless, it is unlikely that nitrogen will adversely affect tree properties in the presence of adequate supplies of other essential nutrients.

Anthropogenic emissions of heavy metals have enhanced the concentrations of these elements even in remote areas in Europe (Andreae, 1996). As a filtering medium, soil removes many of the elements that reach it in solution. When their normal concentrations in soils are exceeded, a new situation arises which may have serious harmful effects on the environment. Chemical immobilisation mechanisms in the topsoil may protect plants against direct toxic effects, but are responsible for a long-term accumulation of heavy metals within the rooting zone, resulting in enhanced heavy metal exposure of plant roots and decomposer communities (Tyler et al., 1989). Because soil pH plays a major role in the adsorption processes of metal cations, input of acidifying compounds can have a triggering effect on heavy metal availability. The long-term impact of metals will largely depend on rates of acidification, which in time may even result in the contamination of groundwaters with the more mobile metals, such as Cd and Zn.

Because most soils have a certain buffering capacity, it usually takes some time before negative effects of pollution become apparent. The buffering capacity depends on the nature of the pollutant and is a function of many soil properties.

(4) Soil quality assessment

The collected soil data can be used to assess the soil's capacity to perform its ecological functions within the forest ecosystem. The capacity to supply nutrients (N, P and basic cations), the sensitivity to acidification, and the capacity to immobilise heavy metals (Zn, Pb and Cd) are important indicators of forest soil quality, in particular in strongly industrialised regions. Calculated indicator values for nutrient availability, soil acidification and metal availability allow the identification of monitoring plots where ecological risks, such as nutrient deficiency, soil acidification and/or metal toxicity may occur.

Structure of the Report

This report gives an overview of the data collected during the inventory, both at transnational and national level. Part I presents, discusses and evaluates the soil information on 4532 observation plots in 23 European countries, which currently comprise the transnational database. Chapter 1 of Part I describes the methods applied to check the quality of the data and to statistically analyse the results. Chapter 2 presents and discusses the results of all parameters covered by the inventory. The discussion of the results focuses on interrelations between individual parameters and on relationships with external variables, such as climate, parent material and atmospheric deposition load. An in-depth evaluation of the soil condition is presented in chapter 3. The observation plots of the large-scale inventory are evaluated in function of their ecological qualities, such as the availability of macronutrients (nitrogen, phosphorus and basic cations), the availability of heavy metals and the sensitivity to acidification.

In Part II, the results of national inventories are presented. National report summaries consist of (i) a concise description of the survey methods applied in the national inventory, (ii) a description of the data evaluation procedures, (iii) a report on the forest soil condition which is often related to tree vitality, and (iv) a discussion of the measures taken to restore damaged soils (when applicable).

In the Conclusions and Recommendations reference is made to the objectives stated in this introduction, in order to draw conclusions and to formulate recommendations for future activities in relation to the European Forest Soil Condition Database.

PART I.

TRANSNATIONAL INVENTORY

1. MATERIALS AND METHODS

1.1 Soil Survey Methods

1.1.1 Selection of Sample Plots

In most participating countries, the forest soil condition inventory was carried out at the observation plots of the annual tree vitality assessment. The forest observation plots were selected by means of a systematic sampling technique, outlined in the Commission Regulation (EEC) no. 1696/87 (CEC, 1987): plots were installed wherever a forest was encountered at the intersection points of a uniform 16x16 km grid. This approach guarantees complete coverage of the forest population in Europe and prevents sampling preferences for particular parts of the population (Crépin and Johnson, 1993). Theoretically, this systematic grid technique results in a density of 1 sample plot for every 256 (= 16x16) km^2 of forest area.

In several countries, national soil survey activities were initiated before the start of the transnational programme. In these countries, sample plot locations do not coincide with the EC 16x16 km grid intersections. In that case, the reported data correspond to an objectively selected subsample of the plots from a denser national network, simulating the 16x16 km grid density.

1.1.2 Soil Sampling and Analysis

The field and laboratory work of the large-scale forest soil condition inventory were co-ordinated out by the National Focal Centres (NFCs). The inventory methodology is outlined in the ICP Programme Manual (UN/ECE, 1994) and the Commission Regulation (EEC) no. 926/93 (CEC, 1993). Since the field work was a national activity, details on the applied field procedures are given in Part II (National Inventories).

Table I 1-1. Parameters of the large-scale Forest Soil Condition Survey and a short description of the reference analysis method.

Parameter	Unit	Reference method	Organic layer*	Mineral layer*
pH		extractant: 0.01M $CaCl_2$ measurement: pH-electrode	M	M
Org. C	g kg^{-1}	dry combustion	M	M
Total N	g kg^{-1}	dry combustion	M	M
P, K, Ca, Mg	mg kg^{-1}	digestion in aqua regia	M	O
$CaCO_3$	g kg^{-1}	calcimeter (if pH>6)	O	M
Weight of the organic layer	kg m^{-2}	volume (cylindrical) - dry weight	M	
Na, Al, Fe, Cr, Ni, Mn, Zn, Cu, Pb, Cd	mg kg^{-1}	digestion in aqua regia	O	
Exchangeable acidity (AcExc)	cmol(+) kg^{-1}	titration of a 0.1M $BaCl_2$ extraction to pH 7.8		O
Acid exchangeable cations (ACE)	cmol(+) kg^{-1}	sum of Al^{3+}, Fe^{2+}, Mn^{2+} and H^+ measured in a 0.1M $BaCl_2$ extraction		O
Basic exchangeable cations (BCE)	cmol(+) kg^{-1}	sum of Ca^{2+}, Mg^{2+}, K^+ and Na^+ measured in a 0.1M $BaCl_2$ extraction		O
Cation exchange capacity (CEC)	cmol(+) kg^{-1}	BCE + ACE, or BCE + AcExc		O
Base saturation	%	100 x BCE/CEC		O

* M : mandatory parameter; O : optional parameter

The parameters of the forest soil condition inventory and their reference analysis methods are given in Table I 1-1. Analysis results are usually reported for the following layers :

- 0 to 10 cm (M01); it was advised to sample 0 to 5 cm (M05) and 5 to 10 cm (M51) separately;
- 10 to 20 cm (M12).

M05 and MO1 are further referred to as mineral surface layers, M12 and M13 as subsurface layers.

The sampling and analysis methods applied in several countries deviate from the recommended methods. The National Focal Centres of these countries have made many efforts towards a harmonisation with the reference methods, for example through calibration tests organised at national level and eventual recomputation of obtained analysis results. For detailed information on the applied analysis methodologies we refer to Annex A (Interlaboratory Variability). The influence of the variability of national analysis methods on the transnational comparability is discussed in section 1.3.

1.1.3 Supplementary Information

NFCs were asked to provide, on a voluntary basis, additional data on physical soil parameters (parent material, texture, coarse fragments and bulk density) for plots of the large-scale inventory. The data are complementary to the data requested in the EC regulation no. 926/93 (CEC, 1993) and adopted in the ICP manual (UN/ECE, 1994). A description of the parameters and the procedure for data submission are given in Annex B.

1.2 Data Integrity Check

The submitted national forest soil condition data were subjected to a step-wise data integrity check.

- A visual examination of the data files checked whether all requested information was provided in the correct data format:
    - use of spaces for data field separation (no tabs are allowed);
    - number of decimals;
    - position of each data field.
- **A** first automatic integrity check was performed on the ASCII data files, before loading into the database. This integrity check detected illegal characters, undefined codes, impossible dates or co-ordinates and stored them in so-called “bad record files”. The involved NFC was next contacted for correction of the errors. Data files purged of undefined codes and impossible values were then loaded in the database.
- After loading the corrected data files in the database, the co-ordinates of the soil condition plots were compared with the co-ordinates of the annual crown condition databases of 1993 and 1994. In view of cause-effect studies, relating results of crown condition, soil condition and foliar analysis, links between the respective databases should be made possible. The primary key parameters that enable the connection between databases are plot number and plot co-ordinates. Therefore, each observation plot should have a unique number and unique co-ordinates.
- A final integrity check was performed in order to detect parameter results outside the expected range. The verification was based on simple relationships between individual soil properties. The relationships were defined in a set of rules that were applied on the database. Four types of rules are distinguished (details are given in Annex C):

  Type **A:** rules that check whether the ratio between two parameters are within the plausible range.

  Type B: rules that check whether parameter results are within the required range in the presence of a certain soil property. For example, Mollic and Umbric properties require an organic carbon concentration above 6 g/kg in the top soil.

Type C: rules that detect abnormal changes between overlying layers. These can be verified by setting a maximum permissible absolute difference (MPAD) between parameter values of overlying layers. When a parameter has a large range of possible results, the MPAD has to be set quite high in order to tolerate natural variations in the high value range. For example, it is not abnormal to measure a Ca concentration difference of 10,000mg/kg in overlying mineral layer in a calcareous soil. However, rules based on absolute value differences will not detect an abnormal change between layers having parameter results in the low value range. The same difference in Ca concentration in non-calcareous soils is quite unusual. Therefore, another set of type C rules checks the ratio between parameter results of overlying layers. This ratio is > 1 when the value in the overlying layer exceeds the value of the underlying layer. Parameters for which this is expected, such as Org. C and N, the maximum permissible ratio (MPR) is set relatively high compared to the minimum permissible ratio (mPR).

Type D: rules that verify whether CEC and BaseSat were correctly determined.

Records for which a violation is reported were stored in separate tables and sent to the respective NFC. After verification, the corrected records were permanently stored in the database.

7.3 Interlaboratory Comparison

1.3.1 Background

Quality control of analytical procedures for soils is of utmost importance to produce reliable and reproducible analytical data (Houba et al., 1996). In order to control the quality of the collected data of the Forest Soil Condition Inventory, the Soil Expert Panel decided in 1991 to proceed with a First Intercalibration Exercise. Twenty two countries participated in this study that was finalised in November 1992. It assessed the amount of variation introduced by the use of different analysis methods and established the need for harmonisation of the methodologies. The participating laboratories received 4 standard soil samples, two acidic mineral soil samples, one calcareous mineral soil sample and one organic layer sample from a calcareous soil. It was recommended to repeat the analyses of each sample at least three times. Guidelines for reporting the replicate results on prepared forms were provided.

Due to missing information and inaccurate method descriptions, the First Intercalibration Exercise was restricted to a statistical comparison of grouped analysis results obtained with similar methods. In a first stage, all reported methods of each parameter were grouped. Next, the results obtained by the same method group were clustered. The statistical analysis consisted of an analysis of variance (ANOVA) and of Tukey's honest significance test. The variation between the results obtained by different methods was high (Van der Velden and Van Orshoven, 1992). Several national methods were identified as producing strongly deviating results. As a consequence, certain countries decided to use the recommended instead of national methods or adapted their national methods in order to improve the harmonisation.

However, even laboratories using the same analysis method often recorded strongly differing results. In 1993, the Soil Expert Panel decided to proceed with a Second Intercalibration Exercise. A new set of two standard samples (A and B) were sent to the laboratories of the participating countries of the soil condition inventory (Annex A). These samples were to be analysed together with the collected samples of the inventory plots, hereby enabling a constant quality control of the submitted data. Laboratories using national methods were recommended to analyse the new standard samples with both the national and the reference method, in order to provide a basis for method comparison.

A list of applied analysis methods is given in Annex A.

1.3.2 Transnational Comparability

The variation among the reported standard sample results illustrates the importance of quality control measures in international programmes of chemical soil condition monitoring and emphasises the need for a better laboratory control/quality and wider use of reference methods. Several of the recommended reference methods require the use of expensive laboratory instruments, unavailable in many laboratories. Another reason for applying methods deviating from the reference methods, is related to the fact that national soil analysis methods have been established in most countries. Changing national methods would have the undesirable consequence of producing data that may not be comparable to values previously measured with a national method. Simultaneous analysis of samples with both national and reference methods has been reported by many NFCs to be financially unfeasible.

Table I 1-2. Summary of the interlaboratory variability between standard sample results.

Parameter	unit	median reference value	average absolute deviation	average relative deviation	standard sample	number of participating laboratories
pH		3.4	0.1	17%*	A	22
Org. C	g kg^{-1}	205	23	11%	A	22
N	g kg^{-1}	9.1	1.0	11%	A	22
P	mg kg^{-1}	432	83	19%	B	20
K	mg kg^{-1}	3738	1809	48%	B	20
Ca	mg kg^{-1}	1430	457	32%	B	19
Mg	mg kg^{-1}	3415	425	12%	B	20
Na	mg kg^{-1}	104	45	44%	B	8
Al	mg kg^{-1}	19428	3621	19%	B	10
Fe	mg kg^{-1}	22101	3484	16%	B	12
Cr	mg kg^{-1}	28	17	61%	B	7
Ni	mg kg^{-1}	20	7	33%	B	7
Mn	mg kg^{-1}	341	50	15%	B	14
Zn	mg kg^{-1}	166	24	14%	A	11
Cu	mg kg^{-1}	12	3	26%	B	11
Pb	mg kg^{-1}	77	24	31%	A	10
Cd	mg kg^{-1}	3.2	0.9	28%	A	8
AcExc	cmol(+) kg^{-1}	5.4	1.4	27%	A	9
ACE	cmol(+) kg^{-1}	6.1	2.0	33%	A	11
BCE	cmol(+) kg^{-1}	5.4	0.7	13%	A	14
CEC	cmol(+) kg^{-1}	11.6	2.0	17%	A	13
BaseSat	%	46	4	9%	A	13

* : based on delogarithmised results

Table I 1-2 gives a summary of the standard sample results and the calculated variation between laboratories. For each parameter, the number of observations, the median of the reported values and the average deviation from the median are given for the most representative standard sample. When studying interlaboratory variability in a relative way, it is appropriate to use the results of samples for which high values are reported. Results near detection limit would automatically lead to high relative deviations due to inherent limitations of the analytical instrument. The standard samples are used in a complementary way. Sample A is rich in organic matter, and was used to assess the variation of parameter results related to organic matter content, such as organic carbon, nitrogen, cation exchange properties and trace elements associated with organic colloids. Sample B, organic matter poor but richer in native elements associated with soil minerals, was used for the assessment of the variation of most total element concentrations.

The average relative deviation can be used as an estimate for the degree of comparability that may be expected among the national soil condition results. High deviation values are measured for trace elements, present in small amounts in the standard sample. For example, measured concentrations of Na, Cr, Ni, Cu, Pb and Cd are lower than the concentrations of Al, Fe, Mn and Zn. Consequently, relative deviations are generally higher. The high deviations observed in K and Ca results cannot be explained by low concentrations in the sample. The macronutrients were measured by more laboratories, using many different methods. The high variability in applied methods is reflected by strongly deviating standard sample results, in particular for K and Mg. Because the same methods were applied in the national surveys, a relatively high analytically caused variation in the concentrations of K, Ca and probably also of P and Mg may be expected in the transnational database.

Although the absolute deviations of logarithmic pH measurements are usually very low, relatively high relative deviations are observed among the delogarithmised values, due to the extremely low proton concentrations in the equilibrated solution during measurement. Nevertheless, because pH is expressed on a logarithmic scale, the results may be regarded quite reliable. Organic carbon and total nitrogen contents in sample A are very high, which largely explains the relatively low deviations from the median value. The variation of the sample B results for Org. C and N is several times higher.

The intercalibration results of the cation exchange properties are rather promising, because the average deviation observed for base saturation, probably the most important of the cation exchange parameters in the framework of atmospheric pollution, is low. Apparently, a method measuring high, or low, exchangeable cation concentrations often does so for all measured cations. Because the concentrations of individual cations are usually added to obtain BCE, ACE, AcExc and CEC, this addition results in an accumulation of absolute deviations from the median values of individual cations. Consequently, relatively high deviations from the median may be observed in the intercalibration results of BCE, ACE, AcExc and CEC. Fortunately, base saturation expresses exchangeable cation concentration as a ratio, and therefore differences between methods partly disappear. The average relative deviation from the median base saturation result of sample B is only slightly higher (13%). On the other hand, a German study (Konig and Bartens, 1995), comparing the German and European reference methods for CEC, found that the amounts of basic cations Ca, Mg and Na are nearly the same for both methods, but the amounts of acid cations Al, Fe and H and CEC are nearly 60% lower when samples were analysed with the European reference method. As a result, German results of base saturation may tend to be lower than results obtained with the reference method, whereas ACE and CEC values may be higher.

The results of the intercalibration exercises demonstrate that transnational comparison of data should be made with great care. The results may be compared across national boundaries with a fairly high degree of confidence for some of the major parameters, such as pH, N, Org. C, BCE and BaseSat. However, the high variation coefficients for many of the extracted elements, in particular K, Ca, Na, Cr, Ni and Pb, indicates that a transboundary comparison is very tentative for these parameters.

It is worthwhile to note that the variability assessed by the intercalibration exercises is related to differences in applied methods and instrumentation, whereas it ignores data variability associated with differences in sampling methodologies and sample preparation. Particularly differences in sampling design and sample handling in the field may cause a substantial variation in the final analysis results.

The occurrence of significant differences between national sampling methodologies is illustrated by Figure I 1-1, which shows the distribution of OrgLay values of O layers for each country. According to literature, accumulation of soil organic matter reflects the effects of moisture and temperature on the balance between primary production and decomposition (Waring and Schlesinger, 1985). Dry weights of forest floors usually increase along a moisture gradient from low values at dry sites to high values at the wet end of the gradient. In contrast to the high levels of organic matter accumulation in cool temperate forests, tropical forests have low storages of carbon because of the high rates at which organic matter is broken down and incorporated into the mineral soil. In other words, the rate of decomposition and nutrient turnover is more rapid in warm climates (Pritchett and Fisher, 1987). Since net primary production shows the opposite trend, the accumulation of soil organic matter is largely due to differences in decomposition.

Thus, the weight of the organic layer is expected to gradually decrease from relatively high values in northern Europe, where thick accumulations of litter on the soil surface is common, to low values in southern Europe, where higher temperatures result in a faster turnover of litter. Figure I 1-1 shows that OrgLay values are indeed lower in some Mediterranean countries, such as Portugal and Spain, than in Sweden and Finland. However, it also shows that median OrgLay values of 10 kg per square meter or more were measured in the Netherlands, Italy, United Kingdom, Denmark and Greece, whereas more than 50% of the plots in France, Portugal, Spain, Luxembourg, Norway, Hungary and Croatia have O layer accumulations of less than 2 kg m^{-2}. This variation cannot be explained by differences in climate or vegetation type, but is likely to be determined by differences in sampling approaches, or by the use of corrected or uncorrected OrgLay values (a correction factor, based on organic matter content, may be used to exclude mineral materials from the organic layer weight). Neighbouring countries with similar climatic conditions, often reported very different OrgLay values. For example, O layer weight of approximately 50% of the Slovakian plots is 2 kg m^{-2} or less. For the Czech Republic such low OrgLay values have been reported for less than 5% of the plots having O layers.

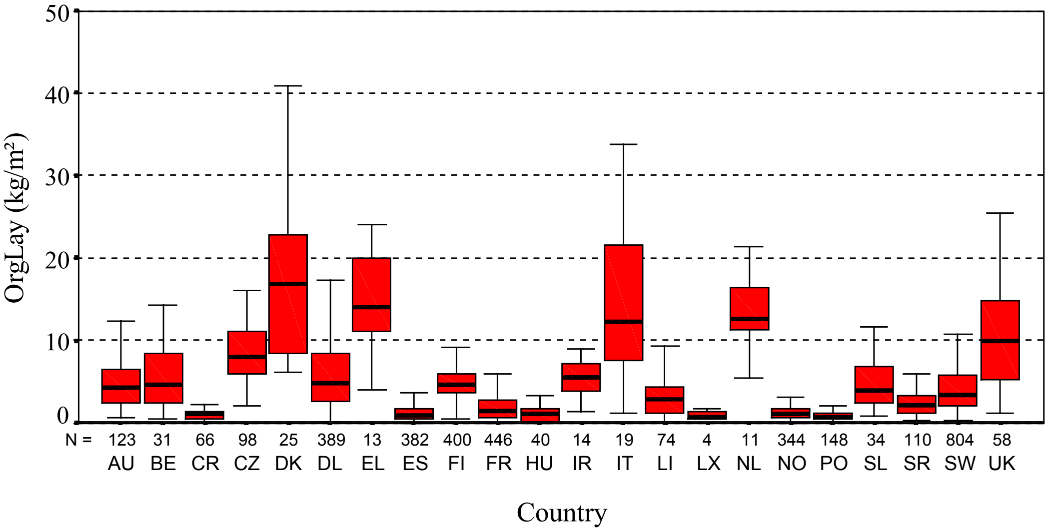


Figure I 1-1. Distribution of OrgLay values (weight of the organic layer) of O layers, grouped per country.

1.4 Data Processing

1.4.1 Data Classification

Presentation of the results of the soil condition parameters on maps requires a selection of classes. The number of classes is limited to 5 for all parameters. Except for heavy metals, the class limits are selected in function of the frequency distribution of the parameter results. The determination of class limits of heavy metal concentrations is based on normal and ‘toxic’ ranges stated in literature, while observed frequency distributions are partly ignored. Class limits are given in Annex D.

In case the results approximate a normal distribution (e.g. Org. C, total N and P in the organic layer), class limits were chosen more or less symmetrically around a central class. The difference between upper and lower class limits was kept constant, consequently most results are assigned to the middle class. Classes 1 (lowest values) and 5 (highest values) have the least members.

Most parameter results are not normally distributed. The distributions are often positively skewed, showing a tail towards larger values (Figure I 1-2). In order to obtain a distribution of results among the classes similar to normally distributed parameters, the difference between upper and lower class limits was gradually increased. The following principle was mostly applied: the upper limit value of classes 2, 3 and 4 is exactly two times the lower limit value. In the example of Mg, the upper limit value of class 2 (1000 mg kg^{-1}) is two times its lower limit value (500 mg kg^{-1}); intervals of classes 3 and 4 are 2000-4000 and 1000-2000 mg kg^{-1}, respectively.

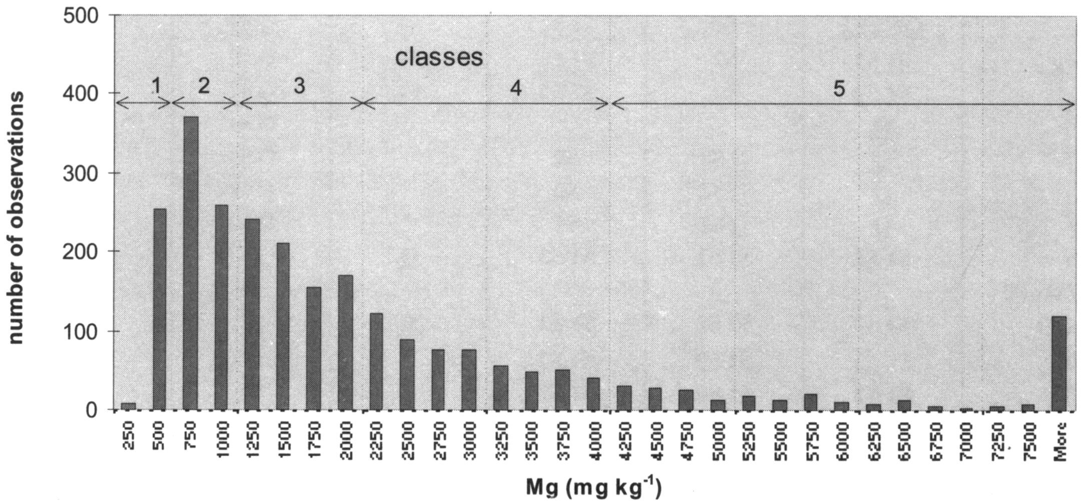


Figure I 1-2. Classification of positively skewed parameter results (example: Mg content of organic layers).

Table I 1-3. Derivation of lower class limit values for heavy metals: based on frequency distribution (F), 'toxic' concentration for mineral soil (T_m), critical concentration for mineral soil (C_m), or critical concentration for humus layer(C_h).

	Lower limit value of			
Heavy metal	**class 2**	**class 3**	**class 4**	**class 5**
Cr	F	F	C_h	C_m
Ni	F	F	F	C_m
Mn	F	F	T_m	T_m
Zn	F	F	C_m	C_h
Cu	F	F	C_h	C_m
Pb	F	F	C_m	C_h
Cd	F	F	F	C_h

For the classification of elevated heavy metal concentrations, use was made of available 'toxic' values found in literature and critical values derived from so-called Lowest Observation Effect Concentration (LOEC) data in field and laboratory studies of soil microbiota (see also discussion on page 80). Table I 1-3 shows that the lower class limits of classes 2 and 3 are based on the observed frequency distribution, whereas critical values are mostly used as limit values of classes 4 and 5. When critical values for both the humus layer and mineral soil are available, the lower of the two values is used as the lower limit value of class 4, the higher as the limit value of class 5. In the case of Cr and Cu, critical values for humus layers are lower than those for mineral layers, whereas for Zn and Pb the opposite is true.

1.4.2 Clustering Soil Observation Plots

Soil chemical properties usually vary within a wide range of values. They are influenced by many external factors such as climate, soil parent material, age of the soil material and vegetation type. Evaluation of the soil condition at a large number of observation sites involves the study of relationships between individual soil properties and between soil properties and external influencing factors. In order to investigate these relationships statistically, the need arises to compare groups of individual soils, having similar properties.

Table I 1-4. Investigated relationships between chemical soil parameters in organic (O), mineral surface (S1) and subsurface layers (S2), and the 6 defined clustering criteria.

	Soil Type	Parent Material	Texture Class	Climatic Region	Atmosph. Depos.	Humus Type
pH	O S1 S2	S2	S1 S2	S1	O S1	O S1
Corg	S1 S2	S2	S1 S2	S1	O S1	O S1
N	S1 S2	S2	S1 S2	S1	O S1	O
P	S1				O S1	O
K	O	O S2	S2		O S1	O
Ca	O	O S2	S2		O S1	O
Mg	O	O S2	S2		O S1	O
C/N	S1 S2	S1 S2	S1 S2	O	O S1	O S1
Ca/Mg/K					O	O
$CaCO_3$	S1 S2	S1 S2	S1 S2	S1	S1	
CEC	S1 S2	S1 S2	S1 S2		S1	
ACE	S1 S2	S1 S2	S1 S2		S1	
AcExc	S1 S2	S1 S2	S1 S2		S1	
BCE	S1 S2	S1 S2	S1 S2		S1	
BaseSat	S1 S2	S1 S2	S1 S2	S1	S1	
Na		S2	S2			O
Al		S2	S2			O
Fe		S2	S2			O
Cr		S2	S2		O S1	O
Ni		S2	S2		O S1	O
Mn		S2	S2		O	O
Zn		S2	S2		O S1	O
Cu		S2	S2		O S1	O
Pb		S2	S2		O S1	O
Cd		S2	S2		O S1	O

relationships significant at 0.01 level are given in bold, those discussed in Chapter 2 are underlined

Considering the site factors that determine forest soil conditions and limitations associated with data availability, the following criteria for clustering soil observation plots were used:

- climate;
- atmospheric deposition load;
- soil type;
- parent material class;
- texture class;
- humus type.

For reasons of comprehensibility, data are never clustered following more than one criterion at the same time. Unfortunately, a direct causal interpretation is mostly impossible due to the interdependent nature of the clustering criteria. For example, the climatic Subatlantic region (1.4.2.1) largely coincides with the region receiving the highest acid deposition load (1.4.2.2). The interpretation is further complicated because several other factors influence the soil condition.

The expected relationships between chemical soil parameters and the clustering criteria were investigated for their statistical significance with the nonparametric ***Sample*** *Median* ***Test*** (see also Section 1.4.3). Although significant differences between the results of the above defined clusters were found for most investigated relationships (Table I 1-4), a causal connection could not always be demonstrated. The discussion in Chapter 2 is limited to relationships for which an explanation could be given.

1.4.2.1 Clustering based on climatic region

For the presentation of the annual crown condition results, a climatic classification was introduced with the 1993 report (UN/ECE-CEC, 1993). The same climatic classification system was used to classify the soil observation plots. A major problem with attributing climatic classes to soil observation plots is the fact that discrepancies of plot location and/or numbering exist between the crown condition and soil condition databases. For example, most Swedish soil plots do not coincide with the plots where annual tree condition is surveyed. Crown condition and soil condition databases share 2939 common plots, having an identical plot number, and a location discrepancy of less than 5 seconds (Figure I 1-3). If a difference of ***5*** minutes in either longitude or latitude is tolerated, **4** plots are added to the common database.

Table I 1-5. Distribution of plots, common in the soil and crown condition databases, over the climatic regions.

Climatic region	Number of common plots	% of total
Boreal	418	14
Temperate Boreal	158	5
North Atlantic	240	8
South Atlantic	244	8
Subatlantic	591	20
Continental	53	2
Northern Mountainous	251	9
Southern Mountainous	365	12
Higher Mediterranean	228	8
Lower Mediterranean	391	13
All regions	2939	100

The Boreal region has a cold temperate climate with low winter temperatures. The temperate Boreal region constitutes a transition between the Boreal climate and the temperate climate of the Atlantic and Subatlantic regions. The north Atlantic region has a moist and windy climate with moderate temperatures in both summer and winter, and with long transitional seasons. The climate in the south Atlantic region is rather warm temperate with high precipitation in winter, but very little frost and snow. The Subatlantic region comprises the largest group of common plots (Figure I 1-3). It has a typically temperate climate with larger differences between winter and summer temperatures and less wind as compared to the Atlantic regions. There is a gradient from higher winter temperatures in the west to low winter temperatures in the east. The climate of the Continental region grades from typically temperate to semi-arid and is characterised by high temperatures and dry periods in summer, and low temperatures in winter. The Mountainous regions share steep climatic gradients. The northern Mountainous region consists of the Norwegian mountains; the southern Mountainous region

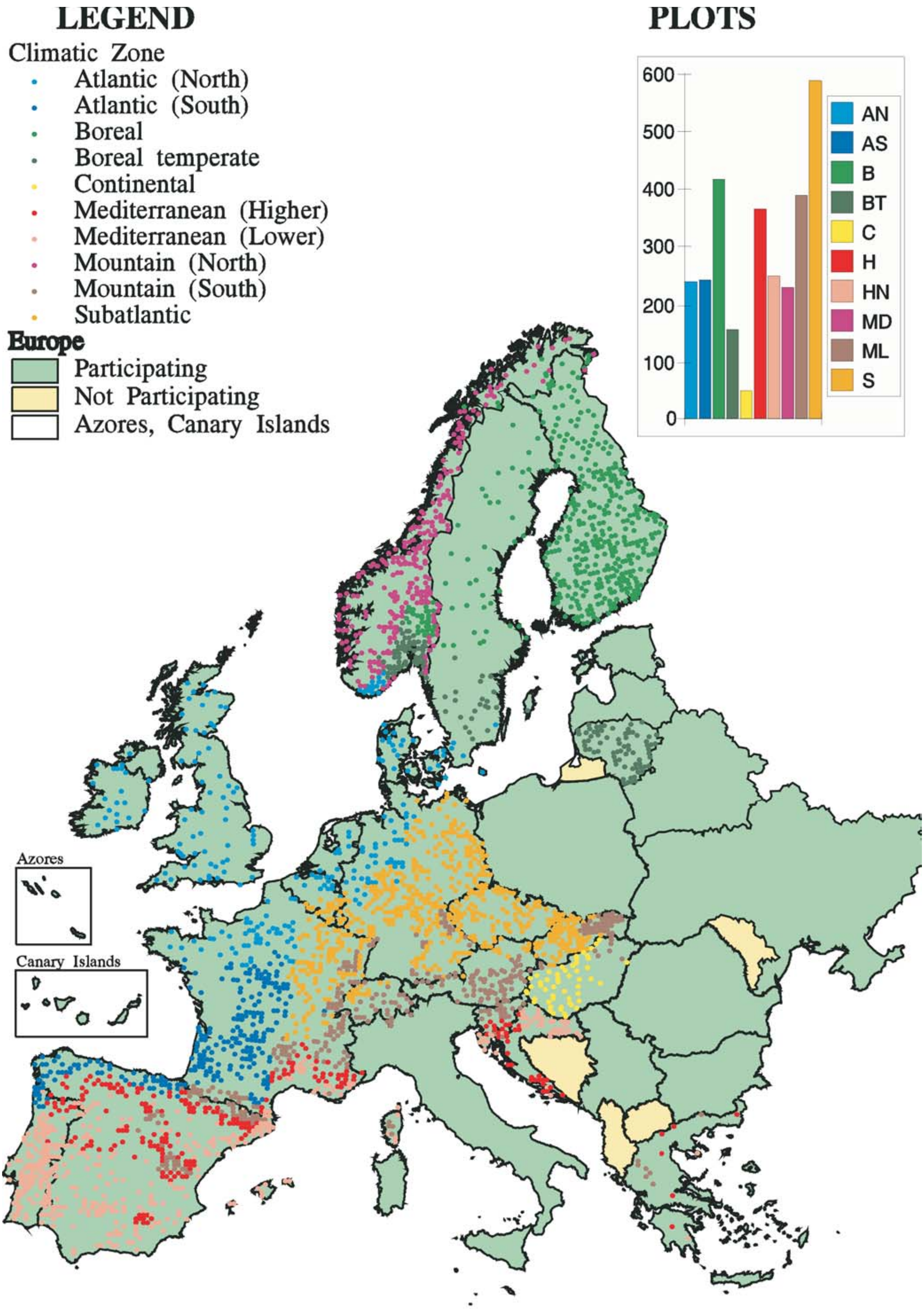


Figure I 1-3. Geographical distribution of the soil plots over climatic regions (each point represents a common plot of the crown condition and the soil condition database).

comprises the Alpine system (Pyrenees, Alps, Tatras, Carpathian and Balkan chains), several ridges in the Mediterranean countries and some highland areas. The climate of the lower Mediterranean region is characterised by hot summers and periods of extensive drought. Rainfall is mainly confined to the winter season. The higher Mediterranean region lies between 400 and 1000 m altitude and has a more humid climate as compared to the lower Mediterranean region.

1.4.2.2 Clustering based on regional variations in atmospheric deposition

The present load of atmospheric deposition strongly varies within Europe (Hettelingh et al., 1991). Based on the loads of acidity of atmospheric origin, computed for the EMEP grid cells (150x150 km) using the 1988/1989 deposition data, four *"atmospheric deposition regions"* were defined (Figure I 1-4):

- Region 1 has a high load of acidity (> 2000 mol(+) ha^{-1} yr^{-1}) and corresponds roughly to Central Europe;
- Region 2 forms a ring around the first region and has a computed load of acidity between 1000 and 2000 mol(+) ha^{-1} yr^{-1};
- Region 3 largely corresponds with northern Europe, which has a load of acidity that gradually decreases from about 1000 mol(+) ha^{-1} yr^{-1} in southern Scandinavia and the north-eastern part of the British Isles to less than 200 mol(+) ha^{-1} yr^{-1} in the most northern part of Europe;
- Region 4, with a low load of acidity (< 1000 mol(+) ha^{-1} yr^{-1}), covers most of the western Mediterranean area.

Heavy metal and nitrogen deposition may be expected to be correlated with acidic deposition in the sense that all these compounds usually emanate from industrial areas (de Vries and Bakker, 1996; van Pul et al., 1994). Moreover, the proposed clustering in four regions is rather rough, therefore a generalisation of regional differences in acidic deposition to overall atmospheric inputs is acceptable.

1.4.2.3 Clustering based on FAO soil unit

Soil classification systems tend to order or arrange soils in a hierarchy of classes based on the relationships between soils and between soils and the factors responsible for their character (Soil Survey Staff, 1975).

The FAO Soil Classification System (FAO, 1988) combines into one outline the major soil units which have been recognised in all parts of the world. As a result, the concepts on which the subdivisions in categories are based, are a compromise between approaches of existing classification systems. The FAO soil classification system distinguishes 28 major soil groupings, subdivided at the second level in 153 soil units. The soil units adopted were selected on the basis of the present knowledge on soil formation processes, characteristics and distribution of soils on the earth's surface, their importance as resources for crop production and their significance as factors of the environment. The differentiating criteria between soil units are measurable and observable properties. It should be noted that these differentiating criteria to properly classify soils differ from the parameters measured for this survey. In order to classify a soil according to the FAO system, analytical data for surface and deeper soil horizons are required, analysed with specific methods (e.g. cation exchange properties by 1M NH_4OAc at pH 7.0). Clusters of properties are combined in so-called 'diagnostic horizons' (FAO, 1988). Many key properties are relevant to soil use and have a practical value for application.

The FAO soil classification system often uses the presence or absence of diagnostic properties occurring in the subsoil as criteria to distinguish between classes, at a higher level than properties occurring in the surface horizon. In general, the analysis results of the large-scale soil condition inventory can be expected to relate better to properties of surface horizons than to those of subsurface horizons. Therefore, the soils of the Forest Soil

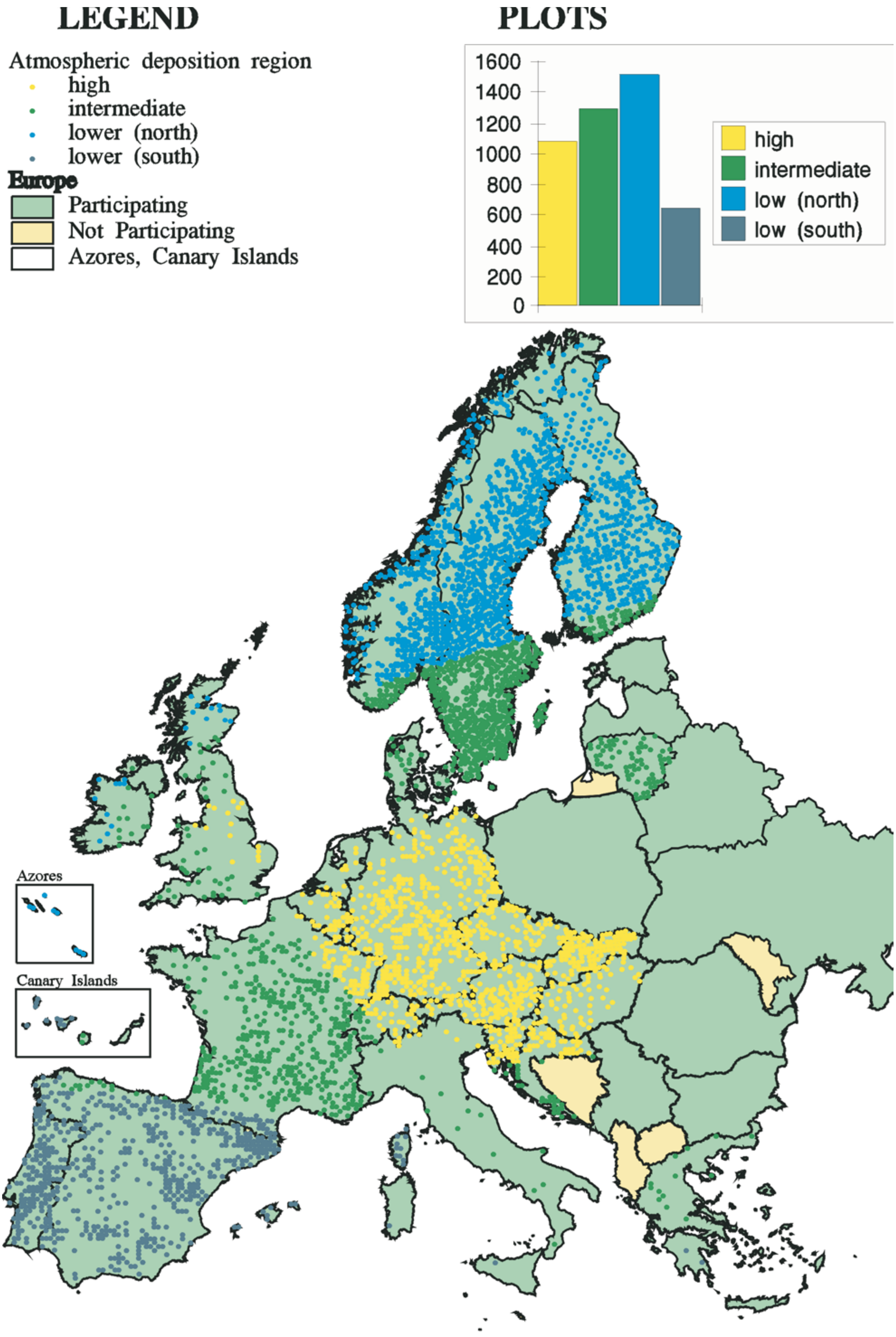


Figure I 1-4. Classification of observation plots in atmospheric deposition regions.

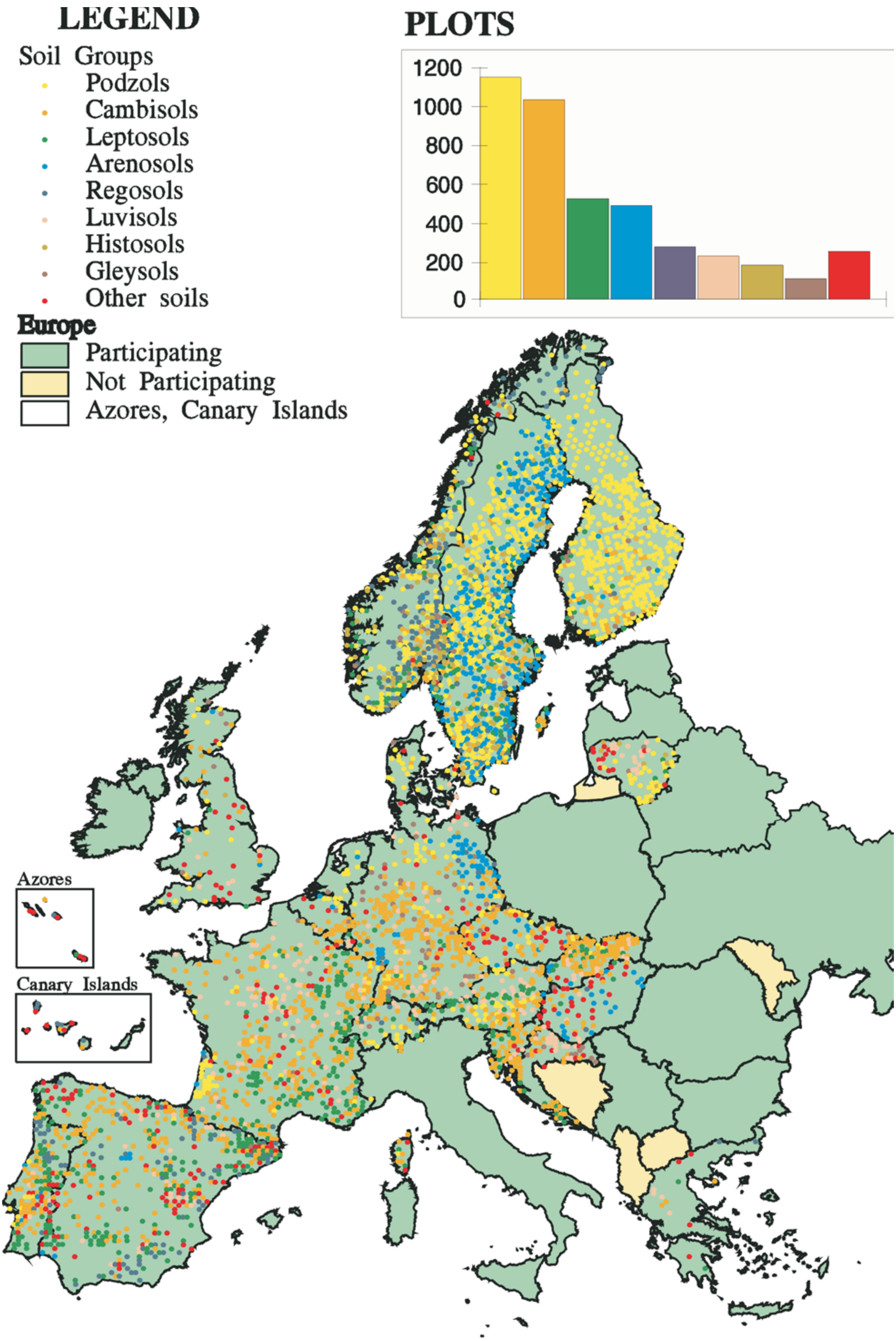


Figure I 1-5. Geographical distribution of the FAO Major Soil Groupings among the soil observation plots.

Condition Inventory were often regrouped in classes based on their topsoil properties, instead of using the **FAO** soil groupings (Table I 1-6).

Many diagnostic properties apply to the subsoil and are irrelevant when comparing topsoil chemistry. Other properties were disregarded because too few soils in the database, having these properties, could be identified to represent any statistical significance. The selected properties have been defined in terms of diagnostic horizons and/or properties, described in the revised **FAO** legend of the Soil Map of the World (FAO, 1988). Most properties have exactly the same definition as in FAO. However, Humic and Gleyic properties are somewhat broader defined.

Table I 1-6. Soil properties, derived from FAO soil unit, used as clustering criteria in the discussion of the results (diagnostic horizons and properties defined by FAO are given in italic).

Property	**Definition**	**Occurrence**
Histic	soils with an accumulation of organic soil materials near the soil surface; having a *Histic H horizon* or an *H* or *O horizon* of 40 cm or more, either extending down from the surface or taken cumulatively within the upper 80 cm of the soil;	192 plots (4 %)
Humic	soils with a high organic matter content; having a *Mollic*, an *Umbric* or a *Fimic A horizon* or having *Humic* properties;	405 plots (9 %)
Ochric	soils having an *Ochric A horizon,* which is generally poorer in organic carbon, or too thin to be a *Mollic* or *Umbric A horizon;*	2182 plots (48 %)
Spodic	soils characterised by an accumulation of sesquioxides and/or organic matter in the subsurface horizon; having a *Spodic B horizon;*	1149 plots (25 %)
Albic	soils with a horizon characterised by the removal of clay and free iron oxides; having an *Albic E horizon;*	586 plots (13 %)
Calcic	calcareous soils; containing at least 2% $CaCO_3$ or showing strong effervescence with 10% HCl in at least one horizon within 125 cm of the surface;	339 plots (7 %)
Gleyic	soils saturated with water at least during some period of the year; having *Gleyic properties* within 100 cm of the surface or *Stagnic properties* within 50 cm of the surface or *plinthite* within 50 cm of the surface;	640 plots (14 %)
Leptic	shallow soils; having *Continuous Hard Rock* or highly calcareous materials or a continuous cemented layer within 30cm of the surface, or having less than 20% of fine earth over a depth of 75 cm from the surface.	529 plots (12 %)

1.4.2.4 Clustering based on parent material

One of the key processes in soil nutrient cycling is the release of ions by weathering of mineral soil (Olsson, 1994). Weathering of soil minerals is the major long term source of cations to replace cations removed from the soil by leaching and by net uptake to the canopy, and it is an important factor for determining the chemical status of the soil (Sverdrup, 1990). When the basic cations depleted from the soil cannot be fully replaced by an equivalent amount of basic cations, the soil is said to acidify. Thus, soil mineralogy, and particularly the weathering rate of the mineral matrix, is a major factor in buffering processes against acidification and largely determine critical loads of acid deposition (de Vries, 1991).

Weathering of silicates buffers acid deposition (Ulrich, 1981; Sverdrup, 1990). Protons have the tendency to penetrate into the mineral lattice, thereby breaking Si-O-M bonds and expelling cations (M^+) from the silicate structure. Due to its weak strength, the resulting compound (silicic acid) removes H^+ irreversibly from the soil solution. The concentration of H^+ necessary for the substitution of M^+ by protons depends on the composition of the silicates, more precisely on the ratio between the stronger Si-0-Si bonds and Si-O-M bonds.

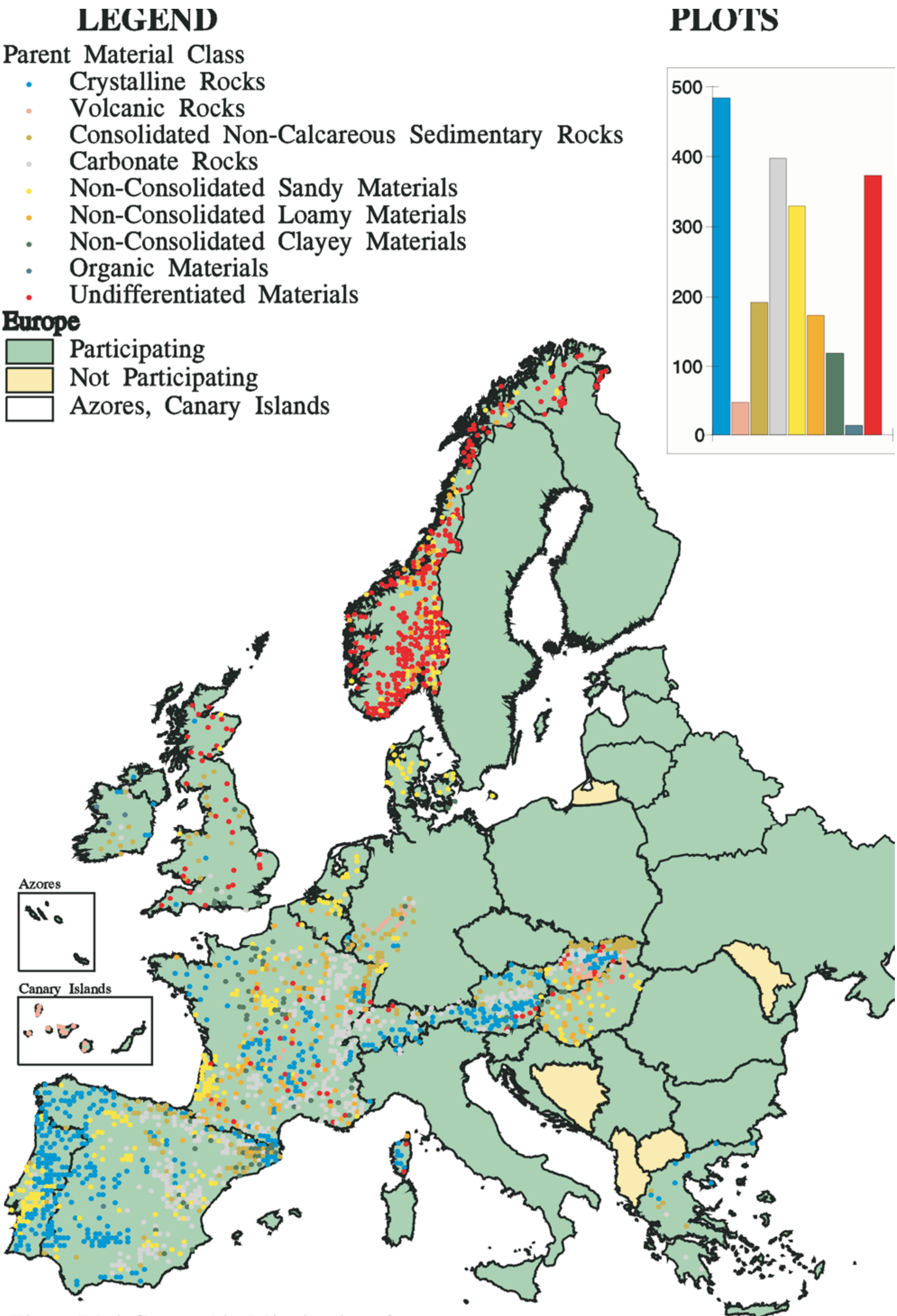


Figure I 1-6. Geographical distribution of parent material types (supplementary information submitted on a voluntary basis).

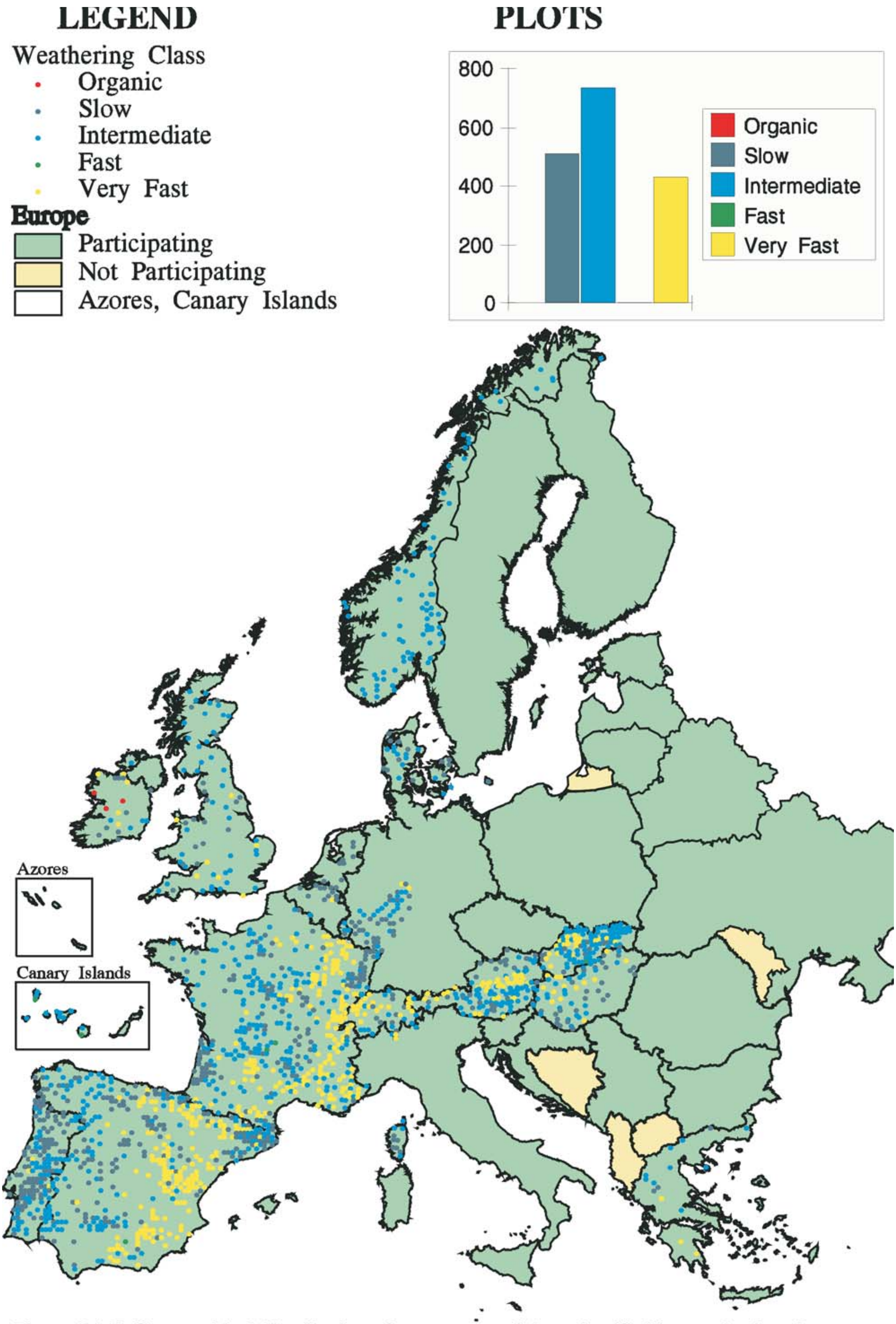


Figure I 1-7. Geographical distribution of parent materials reclassified in weathering classes (derived from supplementary information submitted on a voluntary basis).

Buffering through breakdown of silicates occurs in a broad pH field simultaneously with the process of removal of exchangeable cations (De Coninck and Van Ranst, 1993).

Parent material generally has a greater effect on mineral composition of soils than any other soil-forming parameter. However, the extent of the influence of parent material on chemical soil properties depends on climate. Soils derived from a similar parent material, but developed under different climatic conditions, may have vastly different properties because of variations in leaching of nutrients, accumulation of organic matter, and soil acidity. The distribution of parent material types observed at the level I plots is illustrated in Figure I 1-6 and discussed in Section 2.2.1.

The parent material codes (Annex F) were regrouped in 4 classes using the approximate weathering rate of the constituting minerals as a criterion (De Vries et al., 1992). Sverdrup and Warfvinge (1988) estimated field weathering rates, using reaction rate coefficients of rocks and minerals derived from laboratory studies. Carbonates (calcite, dolomite, magnesite) are considered as the fastest weathering minerals. Calcareous parent materials are therefore attributed weathering class 4. About one quarter of the plots for which information on parent material is available is located on soils developed in very fast weathering materials (Figure I 1-7). Other readily weatherable minerals are olivine, anorthite, garnet, diopside and nepheline. Parent material types dominated by these minerals are attributed weathering class 3. Such materials are not common in Europe; less than 1% of the soils have parent materials where these fast weathering minerals dominate. Parent materials dominated by minerals such as biotite, chlorite, amphiboles, pyroxenes, plagioclases (except anorthite) or apatite have an intermediate weathering rate (class 2). These parent materials form the largest group in European forest soils. Acidic parent materials consisting of very slow weathering minerals (K-feldspars, muscovite, a.o.) and inert minerals (quartz, rutile, a.o.) are attributed class 1. Almost 30% of the forest soils are formed in these rather chemically poor materials.

1.4.2.5 Clustering based on texture class

The particle size distribution of the mineral soil material is a key parameter in the assessment of the nutrient status of the soil. The coarser sand and silt particles differ strongly from the clay particles in mineralogy, nutrient retention properties and their capacity to form organo-mineral complexes. The small size and plate shape of clay particles greatly increase mineral surface area, which is important in determining the adsorption and release of nutrients by the soil solid phase (Barber, 1995). Due to the cation exchange properties of clay particles, fine textured soils have a higher nutrient availability than coarse textured soils.

The texture of the mineral soil further influences the site vulnerability to acid deposition, because it is theoretically essential to weathering rates in terms of the specific surface (Olsson, 1994). Figure I 1-8 shows the distribution of soil textural classes (defined in Annex B) among the level I plots in Europe.

1.4.2.6 Clustering based on humus type

Foresters generally use the term forest humus rather broadly for any organic portion of the soil profile, but they have long known that there are differences in humus beneath the various forest cover types and even beneath the same forest types growing on different soil types. The type of humus layer is controlled by chemical properties in both the organic and the mineral soil layers. The nomenclature used in describing the humus type strongly differs in various parts of the world. Humus type is recorded during the annual crown condition inventory of the large scale forest monitoring programme. Seven types are recognised (Figure I 1-9): *mull, moder, mor,peat, anmor, raw (roh)* and other . It should be noted that, being a parameter of the crown condition assessment, humus type may not have been determined by a soil scientist in the field, which could have consequences on the reliability of the data on humus type.

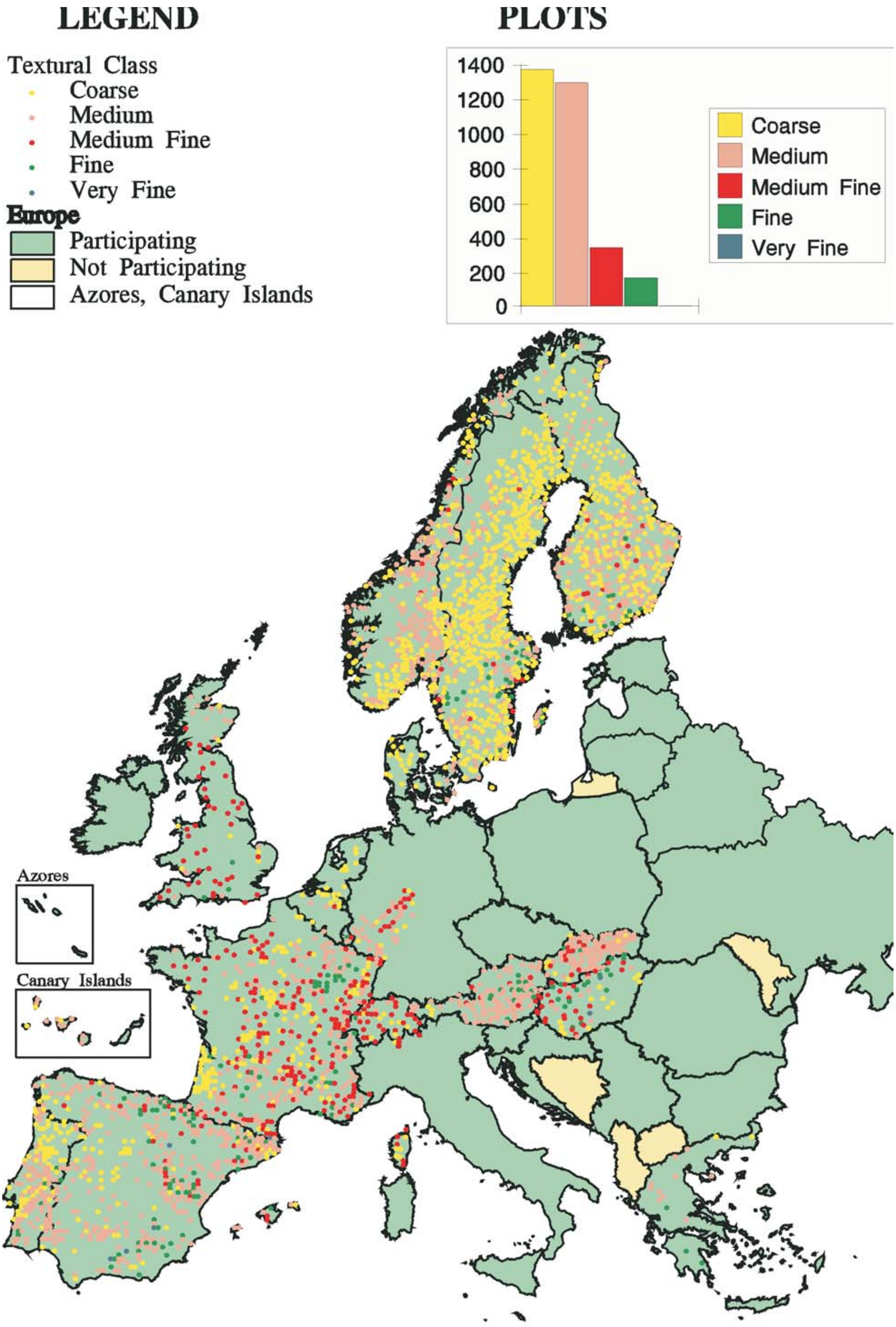


Figure I 1-8. Geographical distribution of soil texture classes (supplementary information submitted on a voluntary basis).

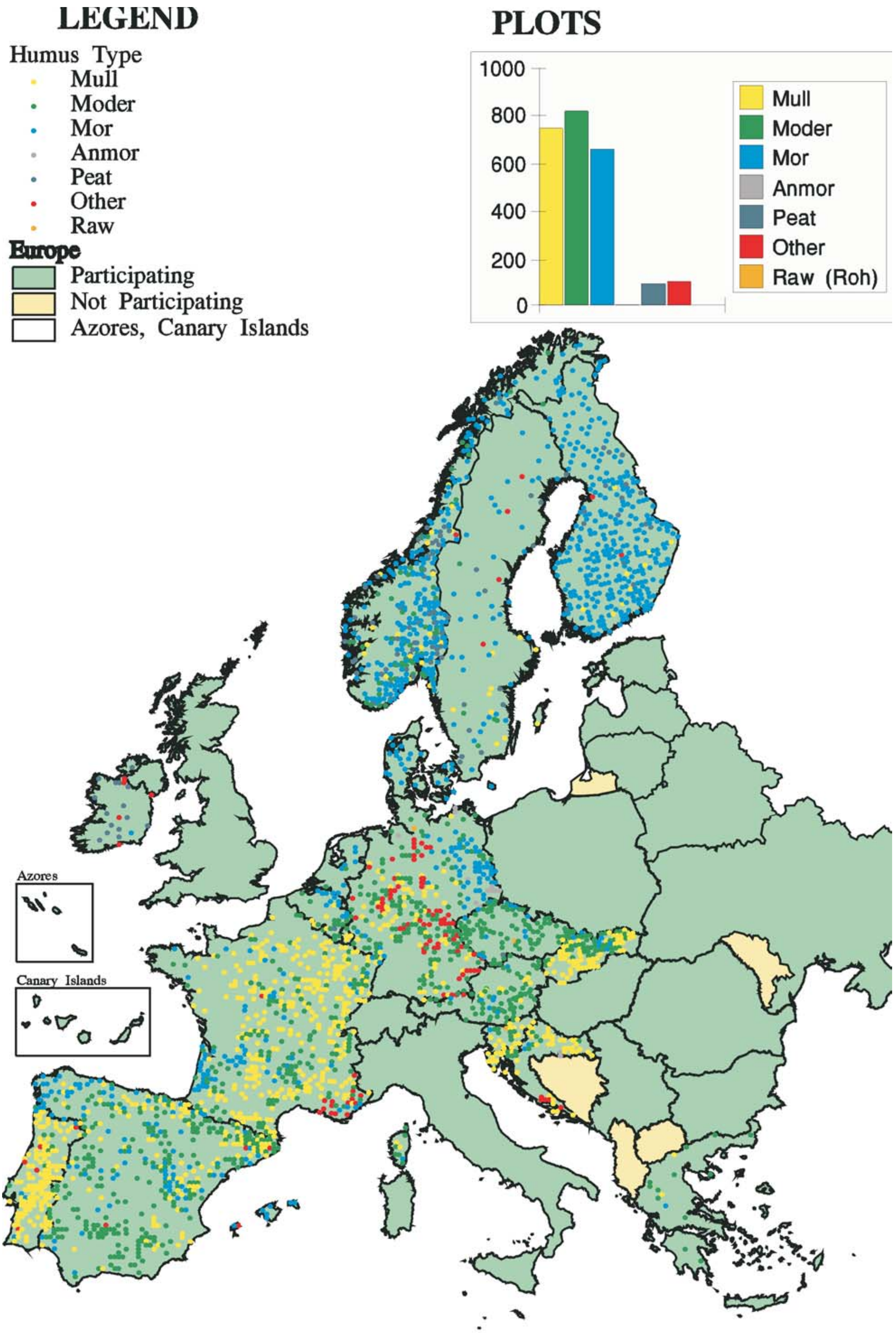


Figure I 1-9. Geographical distribution of the humus types (data obtained from the Crown Condition Database).

In a broad sense, two groups are recognised: the superficial deposit of mostly undecomposed organic remains is defined mor humus, while the intricate mixture of amorphous humus and mineral soil is named mull humus . Mor humus is usually acid and poor in basic cations. Faunal activity is low; plant materials are mainly decomposed by fungi. There is an abrupt transition from the forest floor to the underlying mineral soil (Kimmins, 1987). Mor humus generally occurs in cool, moist climates under temperate and boreal vegetation. Mull humus layers possess a diffuse lower boundary and a crumb-like or granular structure. Mull humus layers are generally less acid than mor humus. Consequently, bacteria and earthworms are more abundant, and are responsible for a rapid and complete decomposition (Pritchett and Fisher, 1987). Mull humus is characteristic of mild climates and fertile soils, conditions that promote rapid decomposition and vegetation that produces readily decomposable litter. There exists a gradual transition between these two extremes, collectively called moder

The term ***raw (roh)*** hummus indicates a thick accumulation of undecomposed litter, but is not often used; it has been recorded at only 4 plots. Typically, there are insufficient basic cations for the neutralisation of humic acids, resulting in a strong acid reaction and a less complete decomposition of organic residues associated with raw (roh) humus. Peat is composed of peat forming plant species (Spaghnum mosses, sedges, etc.) that accumulated under low base conditions and high water content. The development of peat may result from reduced microbial activity because of site wetness, especially where there is a plentiful supply of organic litter but a limited period with temperatures favourable for decay (Pritchett and Fisher, 1987). The term ***anmor*** humus is used in Germany, when humus content is between 15 and 30% and designates dark mixtures of mineral soil and organic materials accumulated under hydromorphic conditions.

The forest floor provides a filter and controlling mechanisms for water into the mineral soil profile. The litter layer absorbs incoming rainfall and throughfall, slowing down water percolation into the soil and providing time for elements in percolating water to be absorbed by organic matter. Water absorption thus reduces runoff and soil erosion (Ross, 1994c).

1.4.3 Statistical Methods

To analyse the significance of differences between the results of the above mentioned clusters, statistical methods were applied. The most popular test to analyse population differences is the so-called Analysis of Variance procedure, abbreviated as *ANOVA.* However, the analysis-of-variance procedure requires a number of assumptions to be met, that are not always satisfied. To avoid the above assumptions, statistical procedures that do not require any assumptions are used :

The ***Kruskal-Wallis Test*** and the ***Sample Median Test*** can be used to test differences among populations. These tests are distribution-free or so-called nonparametric tests and therefore these procedures do not require any assumptions from the considered populations.

The ***Kruskal-Wallis Test*** is also known as the Kruskal-Walllis one-way analysis of variance and is an extension of the ***Mann-Whitney Test,*** also known as the ***Wilcoxon Test.*** To compute the test, the observations from the different samples are first combined and ranked from the smallest to the largest value. The statistic for testing the hypothesis that the distributions are equal is the sum of the ranks for each of the groups. If the groups have the same distributions, their sample distributions of ranks should be similar. If one of the groups has more than its share of small or large ranks, there is reason to suspect that the underlying distributions are different. The Kruskal-Wallis H statistic is computed from these sums. The H statistic has approximately a chi-square distribution under the hypothesis that the groups have the same distribution.

The ***Sample Median Test*** is used to determine whether populations have the same median (SPSS, 1993). The samples are combined and the median for the total distributions is calculated. The number of observations above this median, as well as the number of observations less than or equal to this median, is counted for each sample. The test statistic is based on these counts. A difference is significant when the counts of one of the populations is distinctly different from the counts of at least one other population.

Subpopulation differences are often graphically illustrated by a *boxplot* (Figure I 1-10). The boxplot displays summary statistics for the distributions of the values, separately for each subpopulation. A boxplot displays the median, the 25th percentile, the 75th percentile, and values that are far removed from the rest.

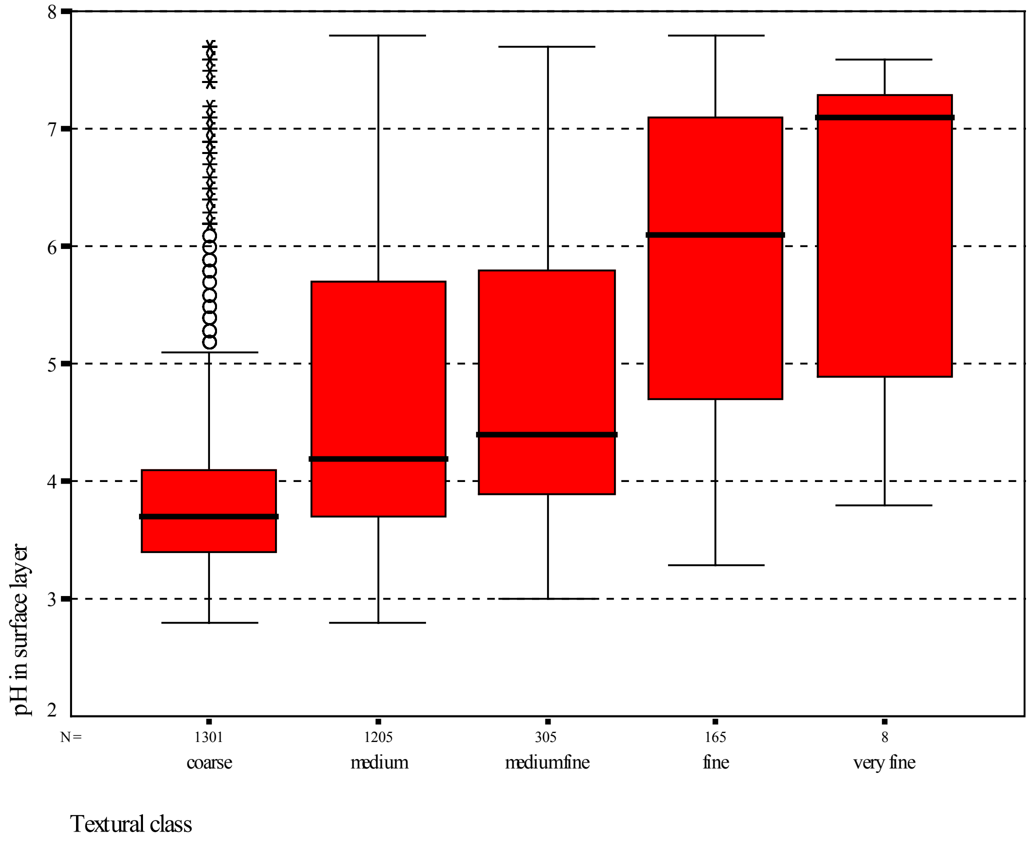


Figure I 1-10. Presentation of results in a boxplot (example: pH of surface layer grouped by soil texture class).

The lower boundary of the box is the 25th percentile and the upper boundary is the 75th percentile. The horizontal line inside the box represents the median. Fifty percent of the cases has values within the box. The length of the box corresponds to the interquartile range, which is the difference between the 75th and the 25th percentile. Outliers are defined as values that are more than 1.5 box lengths from the upper or lower edge of the box. The largest and smallest values observed that are not outliers are shown as lines, drawn from the ends of the box to these values.

2. RESULTS AND DISCUSSION

2.1 Data Availability

2.1.1 Participating Countries

Thirty-one European countries participated in the large-scale forest soil condition inventory (level I). The institutes involved in the monitoring work at national level are listed in Annex G. In the original planning of the programme, submission of national datasets to **FSCC** was foreseen before the end of 1995. Due to various reasons, this deadline has not been met by several **NFCs.**

Table I 2-1. **Availability of soil condition results in the 23 countries presented in this report** (percentages in last line express the relative availability in comparison to the total number of plots).

Country	**Number of soil plots**	**Soil unit**	**pH, Org. C, N**		**$CaCO_3$**	**P**		**K, Ca, Mg**		**Optional aqua regia extractions**	**Cation exchange properties**
			Org	Min	Min	Org	Min	Org	Min	Org	Min
Austria	131	1	1	1	1	1	1	1	1	Al, Fe, Cr, Ni, Mn, Zn, Cu, Pb, Cd	1
Belgium	31	1	1	1	1	1	0	1	0		(1)
Croatia	87	1	(1)	1	1	(1)	0	(1)	0	(Fe, Mn, Zn)	0
Czech Rep.	100	1	(1)	(1)	1	1	0	1	0		0
Denmark	25	1	1	1	1	1	1	1	1	Na	0
Finland	442	1	1	1	1	1	0	1	0	Na, Al, Fe, Cr, Ni, Mn, Zn, Cu, Pb, Cd	1
France	517	1	1	1	1	1	0	1	0		1
Germany	416	1	1	1	1	1	(1)	1	(1)	(Na), Al, (Fe, Cr, Ni, Mn), Zn, Cu, Pb, Cd	1
Greece	15	1	1	1	1	1	0	1	0		0
Hungary	67	1	1	1	1	1	0	1	0	Al, Fe, Mn	(1)
Ireland	22	0	1	1	1	1	1	1	1		0
Italy	20	0	1	1	1	1	0	1	0		0
Lithuania	74	1	(1)	(1)	1	0	0	0	0	Fe, Cr, Ni, Mn, Zn, Cu, Pb, Cd	1
Luxembourg	4	1	1	1	1	1	0	1	0	Mn	1
Netherlands	11	1	1	1	1	1	1	1	1	Na, Al, Fe, Cr, Ni, Mn, Zn, Cu	1
Norway	440	(1)	1	1	1	0	0	0	0		1
Portugal	157	1	1	1	1	1	0	1	1	Na, Al, Fe, Cr, Ni, Mn, Zn, Cu, Pb, Cd	1
Slovak Rep.	111	1	1	1	1	1	0	1	1	Na, Al, Fe, Mn, Zn, Cu	1
Slovenia	34	1	1	1	1	0	0	1	0		1
Spain	464	1	1	1	1	1	0	1	0		0
Sweden	1249	(1)	1	1	1	0	0	0	0		(1)
Switzerland	48	1	(1)	(1)	1	1	1	1	1	Na, Al, Fe, Cr, Ni, Mn, Zn, Cu, Pb, Cd	1
United Kingdom	67	1	1	1	1	1	0	1	0	Na, Al, Fe, Cr, Ni, Mn, Zn, Cu, Pb, Cd	0
Total	*4532*	*95%*	*81%*	*93%*	*84%*	*56%*	*13%*	*56%*	*11%*	*20 - 31%*	*62%*

1: available for at least 90% of the plots; (1): available for less than 90% of the plots; 0: unavailable; Org: organic layer; Min: mineral layer.

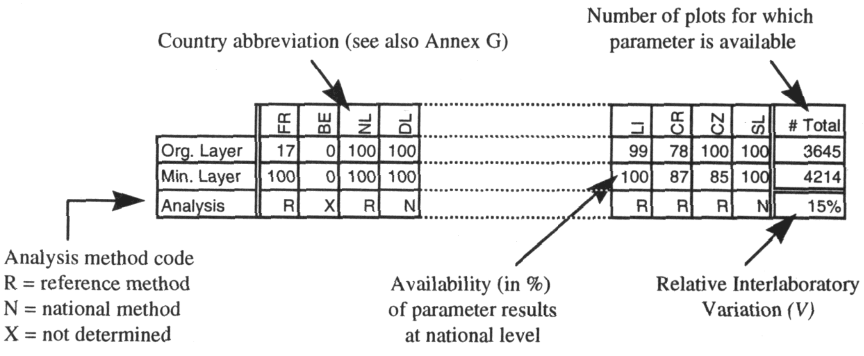
The following discussion is based on soil data inventoried by 23 NFCs (Table I 2-1) in the framework of the level I programme of ICP Forests and of the large-scale monitoring programme of the EC, and reported to FSCC before the 1st of April, 1996. Corrections, resulting from verifications made after the data integrity check and reported to FSCC before the end of October 1996, were taken into account for the final run of data processing. Results, presented and discussed in this chapter, are based on the data that were stored in the database on November 1, 1996. The data of the remaining participating countries are either in the process of verification (Romania, Bulgaria, Estonia and Poland), or haven't been submitted yet (Belarus, Yugoslavia, Latvia and Ukraine).

2.1.2 Mandatory and Optional Parameters

The monitoring programme is flexible in a way that it allows NFCs to decide, based on national financial and technical capabilities, which combination of parameters is measured. Consequently, the amount of data received varies substantially among countries. In general, information on mandatory parameters is provided by all countries, apart from a few exceptions. Data on optional chemical parameters are more scarcely available. In the caption of maps and tables with country indications, showing optional parameter results or derived values, reference is made of the optional character of the presented data. Table I 2-1 presents the availability of soil condition results in the current European database.

At the beginning of each of the following sections, a table, similar to the one presented in Figure I 2-1, illustrates the data availability for the parameter under discussion. The first line of the table lists the 23 countries comprising the database. The second and third line informs the reader of the relative data availability for organic (if relevant) and mineral layers, expressed as a percentage of the total number of plots in each country. In the case of chemical parameters, a fourth line indicates whether the reference or a national analysis method was used. For parameters covered by the Second Intercalibration Exercise, the table also gives an estimation of the relative interlaboratory variation between the results. This estimated value *(V)* compares the variability observed between the results of the Second Intercalibration Exercise (see also Section 1.3, Table I 1-2, and Annex A) with the range of values observed in the database:

$$V = 100 \cdot \frac{average\ deviation\ from\ median\ value}{90^{th}\ percentile - 10^{th}\ percentile}$$



	FR	BE	NL	DL	LI	CR	CZ	SL	# Total
Org. Layer	17	0	100	100	99	78	100	100	3645
Min. Layer	100	0	100	100	100	87	85	100	4214
Analysis	R	X	R	N	R	R	R	N	15%

Figure I 2-1. Schematic presentation of data availability per parameter.

The variability of the intercalibration results may seem large, especially when it is expressed as the percentage of the absolute deviation from the reference value. Indeed, the results show that the nationally applied analysis methods require further harmonisation. However, the same absolute variation may be less important within the range of observed values. For example, the average relative deviation of the Cr results of standard sample B is very high (62%). However, if the average absolute deviation (17 mg kg^{-1}) from the reference value (28 mg kg^{-1}) is added to the latter value, it would change the attributed class value with one level, from class 3 (11-30 mg kg^{-1}) to class 4 (31-75 mg kg^{-1}). Subtracting the average deviation from the reference value wouldn't change the class value at all. In other words, the measured Cr concentrations, obtained by most laboratories, result in attributing the same Cr-class 4 to sample B, although this parameter showed the highest variability in the Second Intercalibration Exercise. The estimated value V places the intercalibration results within the observed range of parameter values. Of course, this approach remains a rough estimation of the transboundary comparability. A really good insight of the interlaboratory variability of analysis results requires the participation of all laboratories to an extended ring test with more samples, representative for the entire range of observed values for all measured parameters.

Table I 2-2 lists the countries that submitted supplementary information on parent material, texture, coarse fragments and bulk density.

Table I 2-2. **Availability of supplementary soil information on parent material, texture, coarse fragments and bulk density** (percentages in last line express the relative availability in comparison to the total number of plots).

Country	Parent Material	Texture	Coarse Fragments	Bulk Density
Austria	1	1 J	1 J	0
Belgium	(1)	(1) J	(1) J	(1) M
Denmark	1	1 M	1 J	1 M
Finland	0	1 M	1 M	1 M, E
France	1	1 J	1 J	(1) M
Germany	(1)	(1) J	(1) M	(1) M
Greece	1	1 J	0	0
Hungary	1	1 J	1 J	1 M
Ireland	1	0	(1) J	1 J
Luxembourg	1	1 J	0	0
Netherlands	1	1 J	1 M	1 E
Norway	(1)	1 J	(1) J	1 J
Slovak Republic	1	1	1 J	1
Spain	1	1 M	1 M	1 M, E
Sweden	1	1 J	0	0
Switzerland	1	1 J	1 J	0
United Kingdom	1	1J	0	0
Total	*45%*	*77%*	*52%*	*48%*

1: available for at least 90% of the plots; (1): available for less than 90% of the plots; 0: unavailable; M: measured data; J: expert judgement; E: derived from pedotransfer function.

2.1.3 FAO Soil Unit

The availability of information on FAO soil unit is illustrated in Table I 2-3.

Table I 2-3. **FAO soil unit - data availability** (see **also** Figure I 2-1 for interpretation).

F	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
100	97	100	99	0	100	0	100	100	100	98	100	85	100	100	100	100	98	100	100	100	100	100	4284

Podzols and Cambisols each represent approximately one quarter of the forest soils in Europe (Figure I 2-2). Haplic Podzols alone cover 12% of the forest soils and are mostly found in Sweden and Norway. Ferric Podzols (6%) occur frequently in Finland and Lithuania. Cambic Podzols (3%) and Carbic Podzols (3%) are less common. The second largest group, Cambisols, occur extensively in Europe: Eutric (5%) and Calcaric Cambisols (2%) are very common in southern Europe, Dystric (12%) and particularly Gleyic (1%) and Humic Cambisols (1%) are typical for more humid areas.

Other common soil groupings are Leptosols, Arenosols, Regosols, Luvisols, Histosols and Gleysols. Leptosols, especially the Lithic subgroups (3%), are often found in mountainous areas. Haplic Arenosols (7%) are very common in Sweden. Dystric Regosols (4%) are the most common Regosols. Haplic Luvisols (2%) are the largest subgroup of the Luvisols. Histosols are largely confined to cool and cold climates. Organic soils with highly decomposed organic materials, Terric Histosols (3%), occur twice as often as Fibric Histosols, having weakly decomposed organic materials. Gleysols occur in alluvial plains throughout Europe; others are associated with slowly permeable subsurface horizons.

Together, the remaining 20 FAO major soil groupings represent only 6% of the forest plots. Soil groupings typical for humid tropical conditions, such as Ferralsols, Plinthosols and Nitisols, are not represented in the European forest soil database. Gypsisols and Solonchaks, soil groupings occurring in areas too dry for forest growth, are also absent in the database.

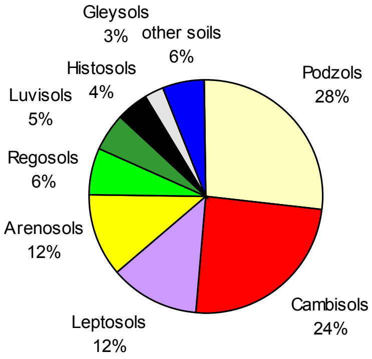


Figure I 2-2. Frequency distribution of major FAO soil types.

It is worthwhile to note that the observed distribution is not representative for the European soilscape in general. The most productive soils are preferentially used for the production of cereals and food crops. For example, Luvisols, in particular Haplic Luvisols, are important agricultural soils occurring throughout western and central Europe under a wide range of climatic conditions (CEC, 1985). However, only 5% of the forest plots are Luvisols. Other soil types, such as Chernozems and Kastanozems, have chemical and physical properties that are very favourable for agricultural use, but are rarely found under forest.

2.1.4 Humus Type

The availability of information on humus type is illustrated in Table I 2-4.

Table I 2-4. Humus type - data availability (see also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	98	94	100	82	0	0	95	96	100	90	96	100	6	58	75	100	83	0	0	0	76	100	82	2685

One third of the forest soils in Europe is covered by mor humus. The majority of soils with Spodic and/or Albic properties have mor humus layers (Figure I 2-3). Soils with Humic properties, having large amounts of organic material incorporated within the mineral soil, are more often associated with mull humus than soils with an Ochric horizon. Soils with abundant fauna have soft, mull-type humus. Soils with Leptic or Calcic properties are often rich in basic cations, resulting in an active fauna and a mull-type humus. After mor humus type, moder (31% of the plots) and mull (28%) are most often reported.

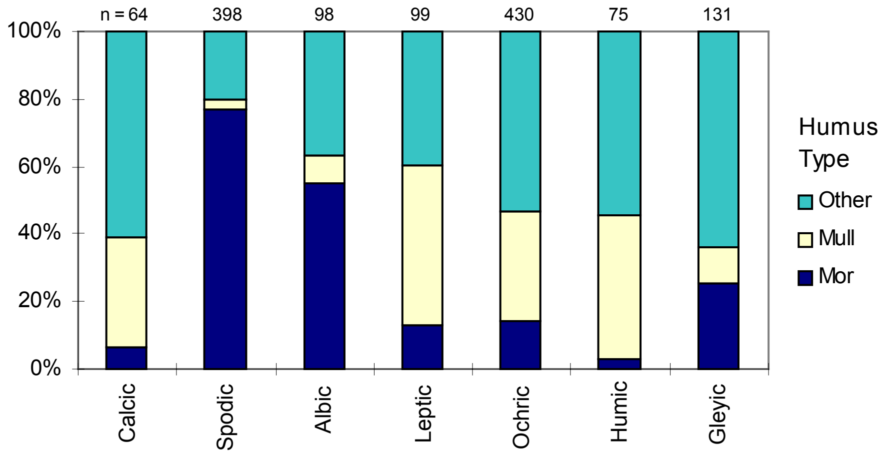


Figure I 2-3. **Relationship between humus type and soil properties** (n = number of observations).

Mor is the most frequently observed humus type in cool and humid regions. In the Boreal region it comprises 77% of the forest floors, with peat humus coming in second place. The share of mor in the total number of humus layers gradually decreases towards southern Europe. In the north Atlantic region, it is still the most common humus type with about 35% of the total, but it is superseded by mull in the south Atlantic and the Mediterranean regions. Moder humus is most often observed in the Subatlantic and Mountainous (south) regions, followed by mull and mor (Figure I 2-4).

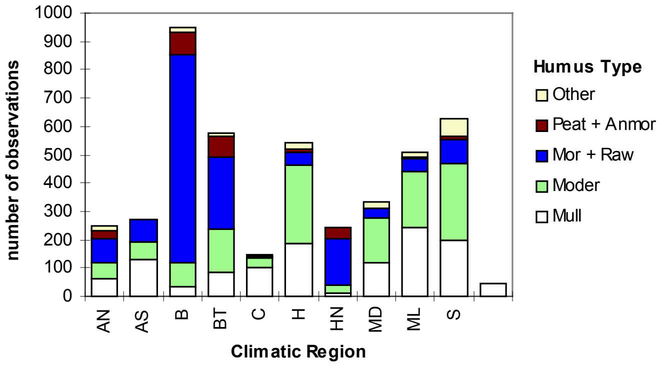


Figure I 2-4. **Distribution of humus types in the major climatic regions.**

2.2 Physical Soil Properties

2.2.1 Soil Parent Material

The availability of information on soil parent material is illustrated in Table I 2-5.

Table I 2-5. **Soil parent material (supplementary data submitted on a voluntary basis) - data availability** (see also Figure I 2-1 for interpretation).

FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
100	32	100	12	0	100	100	100	100	94	96	100	0	98	0	100	85	98	100	0	0	0	0	2044

Because of the deep rooting habit of trees, soil parent material is more important to foresters than to agriculturists. Soil parent materials are often classified according to their geological history; they may be igneous, metamorphic, or sedimentary.

Igneous rocks result from cooling of the magma from the earth's core. Slow cooling of the magma gives coarse-grained plutonic rocks. Fast cooling close to the earth' surface results in fine-grained volcanic rocks or glass. Plutonic rocks are mostly associated with the major mountain chains in Europe (see also Figure I 1-6). Reported forms include granite, granodiorite and gabbro, and represent 7% of the plots. Volcanic rocks are even less common in Europe: only 2% of the plots are reported having volcanic rocks, mainly andesite and basalt, as parent material.

Metamorphic rocks occur as a result of heat and pressure applied to sedimentary and igneous rocks over long periods of time. Gneiss is a laminated rock with a similar mineralogy as granite. Micaschists result from compression of shales. Marble is metamorphosed limestone, and quartzite is metamorphosed sandstone. Metamorphic rocks are reported as parent material in 17% of the plots; most common types are schists and gneiss.

Sedimentary rocks are much more important soil parent materials since they overlie most igneous and metamorphic formations. These rocks result from weathering of igneous and metamorphic rocks and their deposition in lakes and seas. Carbonate rocks result from deposition of $CaCO_3$ and $MgCO_3$, usually in marine environments and their eventual compression into hard rock. Limestones alone represent 14% of the parent materials of the soil plots. Other common forms of carbonate rocks are marls (2%) and dolomites (1%). Shales (1%) result from deposition and compression of loamy (8%) and clayey (4%) sediments. Sandstones and conglomerates **(7%)** result from deposition and compression of coarse textured sediments (14%). Loose materials of unspecified origin (alluvial, glaciofluvial, slope deposits, etc.) represent the largest group of parent materials (18%).

2.2.2 Soil Texture

The availability of information on soil texture is illustrated in Table I 2-6.

Table I 2-6. Soil texture (supplementary data submitted on a voluntary basis) - data availability (see also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Min. Layer	100	32	100	12	0	100	0	100	100	95	100	75	99	97	100	100	98	98	100	0	0	0	0	3493

A coarse texture is very common for forest soils in Europe (see also Figure I 1-8): 43% of the plots for which texture is reported, has a surface mineral layer that consists of more than 65% sand. Sandy soils are often avoided by farmers for their drought susceptibility. Soils having medium fine or finer textures are usually more productive and preferentially used for the production of food crops. Soils with a medium fine texture class have dominantly silt sized particles. Only 6% of the forest soils are clayey (fine or very fine texture class). The influence of soil texture on site productivity is more of an indirect than of a direct nature. Texture per se has little effect on plant growth as long as moisture, nutrients and aeration are adequate.

Soil texture is determined by the nature of the parent material. Most coarse textured soils are associated with unconsolidated sandy deposits of eolian or marine origin. These deposits are usually found at low altitude (Figure I 2-5): 54 % of the forest soils at an altitude below 500 m have a coarse texture. Above 500 m altitude medium textures are dominant. This texture class represents soil materials with particle diameters of all sizes in the 0-2 mm range. In the medium fine texture class silt sized particles are dominant; this is typical for soils that received a high input of eolian loams. 40% of the medium fine or finer textured soils are located at altitudes of more than 500 m, while this area covers only 29% of the forests.

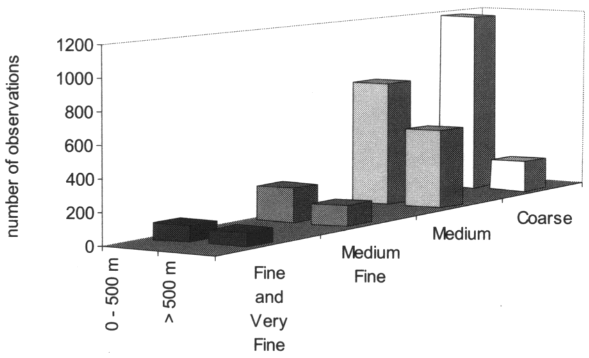


Figure I 2-5. Relationship between surface layer texture and altitude.

Most Podzols and almost all Arenosols are sandy soils (Figure I 2-6). The medium class is the dominant textural class for many soil types. Clayey textures are common for Cambisols, Leptosols, Luvisols and Gleysols. Remark also the relatively frequent occurrence of medium fine textures in Luvisols.

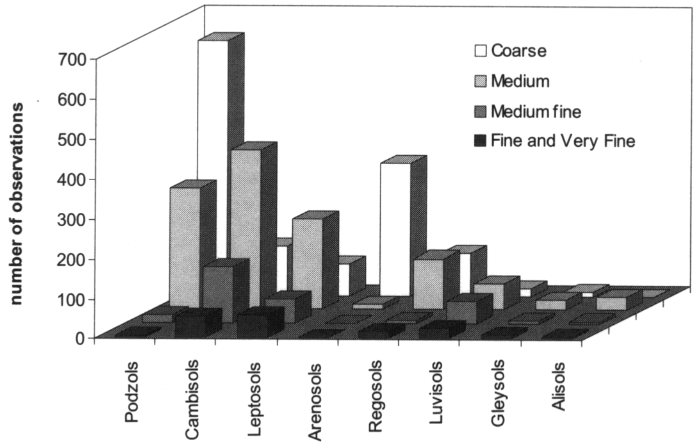


Figure I 2-6. Soil types and their surface layer texture.

A textural change within the top 20 cm of mineral soil is rather uncommon. Almost half of the 433 plots for which the reported texture class of the surface layer differs from the subsurface layer texture are Podzols, usually changing from coarse at the surface to medium texture in the subsurface layer.

Since sand and silt are dominantly quartz (SiO_2), these two fractions are generally quite inactive chemically. Other primary minerals which may contain nutrient elements in their lattice are generally so insoluble as to make their nutrient-supplying ability essentially nil (Brady and Weil, 1996). A poor nutrient status generally results in the development of mor humus types. More than 50% of the observed mor layers occur on sandy soils, while this texture class is associated with only 20% of the mull layers (Figure I 2-7). Most clay particles differ mineralogically from sand and silt, though they generally have developed from weathering of sand and silt particles. Surface area of clay minerals and the chemical and physical nature of their surface are important in determining the nature of adsorption and release of nutrients (Barber, 1995). Mull humus types are more frequently observed on clayey forest soils than any other humus type.

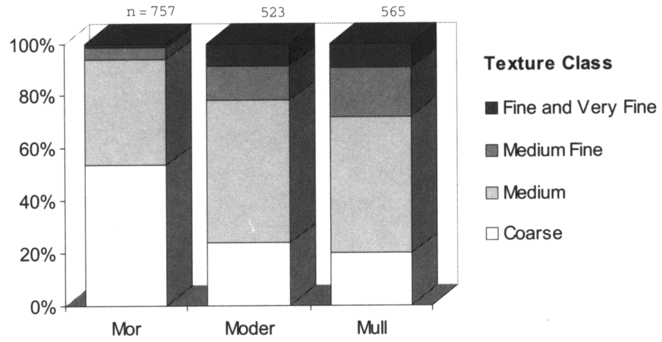


Figure I 2-7. **Effect of particle size distribution on humus type development** (n = number of observations).

2.2.3 Coarse Fragments

The availability of information on coarse fragments is illustrated in Table I 2-7.

Table I 2-7. **Coarse fragments (supplementary data submitted on a voluntary basis) - data availability** (see **also** Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Min. Layer	100	32	100	12	0	0	78	100	0	95	100	0	0	100	100	100	89	98	100	0	0	0	0	2375

Many forest soils are gravelly. Stones and gravel have a profound effect on both water and nutrient relations. Water moves quite differently through stony soil than it does through stone-free soils. Moreover, the volume of coarse fragments reduces proportionally the volume of plant available water per meter of soil depth, Likewise, although coarse fragments contain weathering minerals that release nutrient ions to the soil, the volume of coarse fragments reduces proportionally the plant available nutrient content on a whole soil basis.

Fifteen percent of the 2375 soils for which the content of coarse fragments is reported, is free of coarse fragments in the mineral surface layer. The fact that almost one tenth of these soils contain more than 50% of coarse fragments, shows that trees can grow on very stony soils. Coarse fragments are very common in recent soil types, such as Leptosols and Regosols (Figure I 2-8). Lithic Leptosols have the highest average coarse fragments content. Soils with a longer history of soil formation, such as Luvisols, Alisols, Lixisols and Planosols usually have low amounts of coarse fragments. Also Arenosols are frequently free of stones.

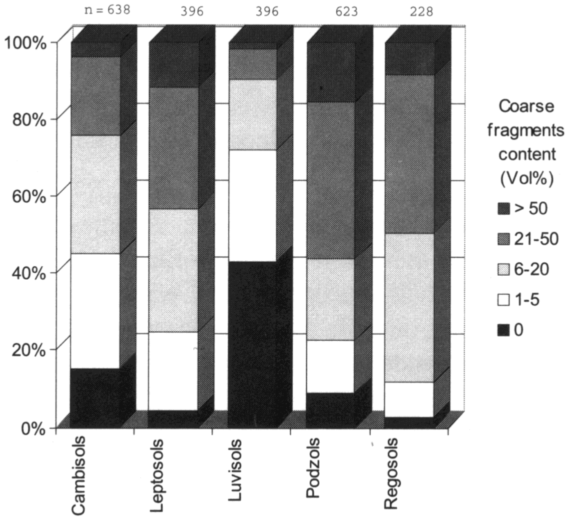


Figure I 2-8. **Occurrence of coarse fragments in the mineral surface layer.**

Coarse fragments are a common constituent of soils on steep slopes where the smallest mineral particles are frequently removed by erosion processes. Stony soils are found abundantly in mountainous areas (Figure I 2-9). Stony soils are also associated with glaciated landscapes throughout most of the boreal zone. In the Boreal region only 10% stone-free soils are reported, and stony soils have a higher average coarse fragments content than less glaciated areas such as the Atlantic region. Also in the dry Mediterranean region, coarse fragments are mostly present; they are reported in subsurface layers of about 90% of the plots.

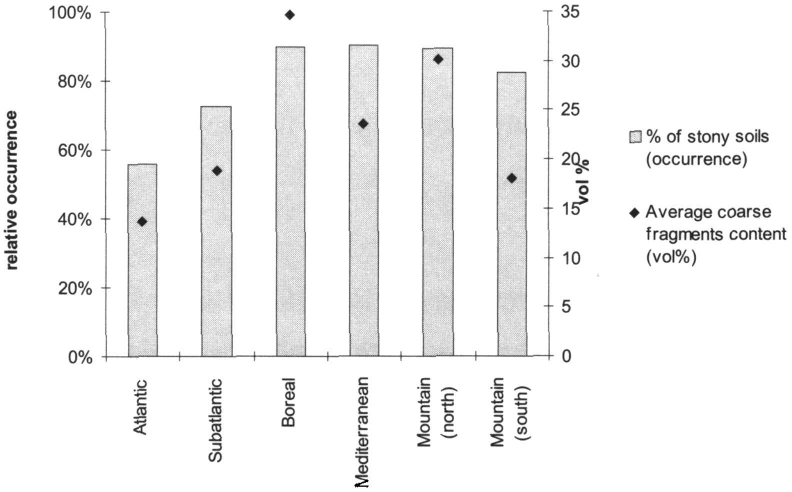


Figure I 2-9. **Regional distribution of stony soils** (relative occurrence of subsurface layers with coarse fragments and their average coarse fragments content).

2.2.4 Bulk Density

The availability of information on bulk density is illustrated in Table I 2-8. Bulk density has been determined by few countries. Most of the values were measured, although some countries, such as the Netherlands, Finland and Spain, also used published pedotransfer functions (e.g. Rawls, 1983; Tamminen, and Starr 1995) to estimate bulk density.

Table I 2-8. **Bulk density (supplementary data submitted on a voluntary basis) - data availability** (see also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Min. Layer	86	32	100	7	0	0	100	100	0	94	100	0	0	0	100	100	99	0	100	0	0	0	0	2192

The physical arrangement of soil components is important for determining the nutrient supply to plants. For example, a topsoil layer may contain 95% (w/w) inorganic and 5% organic matter. However, when expressed on a volume basis, which is important when considering nutrient flux, the same soil may be 38% (v/v) mineral, 12% organic matter, and 50% pore space (Barber, 1995).

Bulk density is defined as the mass (weight) of a unit volume of dry soil. The volume includes both solids and pores. Soils that are loose and porous have low bulk densities, while compact soils have high values. The bulk density of a soil is mainly determined by its organic matter, its coarse fragments content, and its texture. The average bulk density of surface mineral layers (0-5 cm or 0-10 cm) under forest in Europe is 1.05 kg dm^{-3}. Very stony soils (> 20% coarse fragments) have a an average fine earth density of 0.99 kg dm^{-3}, while the average density of stone-free surface soils is 1.12 kg dm^{-3}. Subsurface layers (10-20 cm or 10-30 cm) have a slightly higher average bulk density: 1.19 kg dm^{-3}. Sandy topsoils, free of coarse fragments and with low organic matter content generally have high bulk densities, up to 1.8 kg dm^{-3}. The bulk density of fine textured surface soils ranges from 0.8 to 1.6 kg dm^{-3}, depending on their organic matter and coarse fragments content. Soils rich in organic matter are comparatively well granulated, resulting in low bulk density values. Figure 12-loa shows that the organic matter content strongly affects bulk density of coarse textured soils. Texture seems to have a strong impact on the density of stony soils (Figure 12-lob): clayey topsoils with 2 to 5 % organic carbon have an average bulk density of 1.14 kg dm^{-3}, while sandy topsoils with similar organic matter content are much less dense (0.89 kg dm^{-3}).

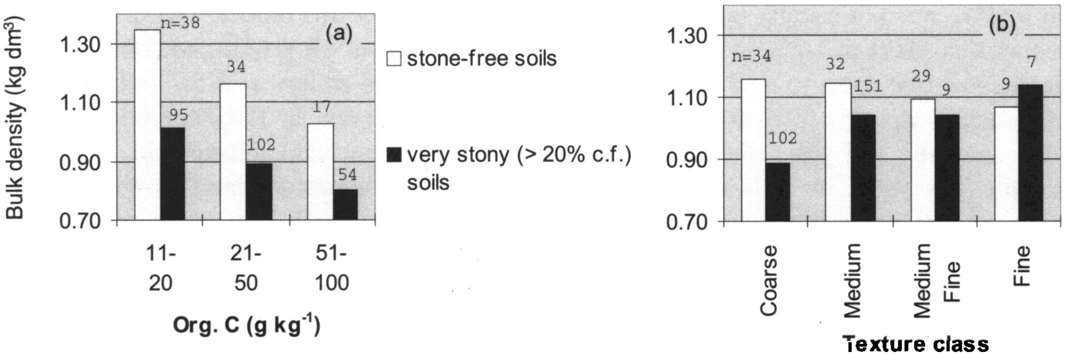


Figure I 2-10. Influence of organic carbon content (chart a) and texture (chart b) on the average bulk density of mineral surface layers. (a) constant texture (coarse); (b) constant organic *C* concentration (20 to 50 g kg^{-1}); n = number of observations.

Soil density above which roots do not penetrate varies with soil texture. Furthermore, the roots of some species are able to grow in moderately high soil densities where the roots of others cannot grow. Compacted sands with bulk densities exceeding 1.75 or clays with bulk densities exceeding 1.55 may prevent the penetration of tree roots (Pritchett and Fisher, 1987). Root penetration problems due to high density are likely to be more common in clayey soils. Bulk density values of 1.55 kg dm^{-3} or more in the subsurface layer of clayey soils were reported for 40 plots (12% of fine or very fine textured soils with known bulk density); values of 1.75 kg dm^{-3} or more in subsurface layers of coarse textured soils in only 14 plots (3% of coarse textured soils with known bulk density).

Bulk density has an indirect influence on the concentrations of air pollutants in the soil. Atmospheric deposition is more or less diffusely distributed over large surfaces. As a result, soils with a low bulk density are more heavily charged by atmospheric pollution.

2.3 *Soil Acidity*

The availability of information on pH values is illustrated in Table I 2-9.

Table I 2-9. Soil acidity - data availability (see also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	17	100	100	99	25	98	100	100	100	95	98	100	100	100	100	99	100	100	100	99	78	100	100	3649
Min. Layer	100	100	100	100	14	100	100	100	100	90	100	100	100	100	100	100	100	96	100	100	87	100	100	4218
Analysis	R	R	R	N	R	N	R	R	R	R	R	R	R	R	N	R	N	R	R	R	R	R	R	13%

Many soil chemical and biological reactions are controlled by the pH of the soil solution in equilibrium with the soil particle surface (Hendershot et al., 1993). High proton activity is not necessarily a disadvantage with respect to nutrient cycling and biomass growth. In fact, the vegetation itself is creating an acid micro-environment in the rhizosphere in order to increase nutrient availability.

Soil pH requirements for good tree seedling growth given in literature are generally between pH (H_2O) 5.0 and 7.0. Within this pH range, microbial activity and nutrient availability are considered optimal. Pritchett and Fisher (1987) suggested optimal ranges for conifers (pH 5.2-6.2) and for most broadleaves (pH 5.8-6.2). Tinus and McDonald (1979) and Landis (1989) considered a pH (H_2O) value between 5.0 and 6.0 for conifers and between 6.0 and

7.0 for broadleaves desirable. Lower pH values have also been recommended for conifers: e.g. between 4.5 and 5.0 by Brix and van den Driessche (1974). In a recent study, Rikala and Jozefek (1990) found pH (H_2O) conditions between 4.0 and 5.0 to be optimum for *Pinus sylvestris* and *Picea* abies seedlings. Plant roots, especially tree roots, can tolerate pH values in nutrient solutions as low as pH (H_2O) 4.0 (e.g. Bertram and Schleser, 1982). In more acid conditions, aluminium, manganese and other toxic metals are brought into soil solution, *so* that hydrogen is not usually the main factor affecting root growth (Barber, 1995). Taking into account that pH ($CaCl_2$) is approximately 0.5 units lower than pH (H_2O) and considering the tolerance of tree roots to acid conditions, pH ($CaCl_2$) values as low as 3.5 should not cause deficiency symptoms in soils with sufficient' nutrient reserves. In fact, many species will thrive at a low soil pH value, although the efficiency of nutrient uptake will decrease in strongly acid soils. In soils where the reserves of phosphorus, calcium, magnesium and potassium are inherently low, a significant decrease in soil pH may result in a nutrient deficiency of one of these essential elements. Moreover, aluminium, iron and manganese tend to be more soluble under acid conditions, sometimes affecting deciduous seedling growth.

Acid conditions are common in European forest soils, especially in surface layers (Figure I 2-11); values below pH 3.5 are reported in 42% of the organic layers, in 22% of the surface mineral layers, but in only 4% of the subsurface layers.

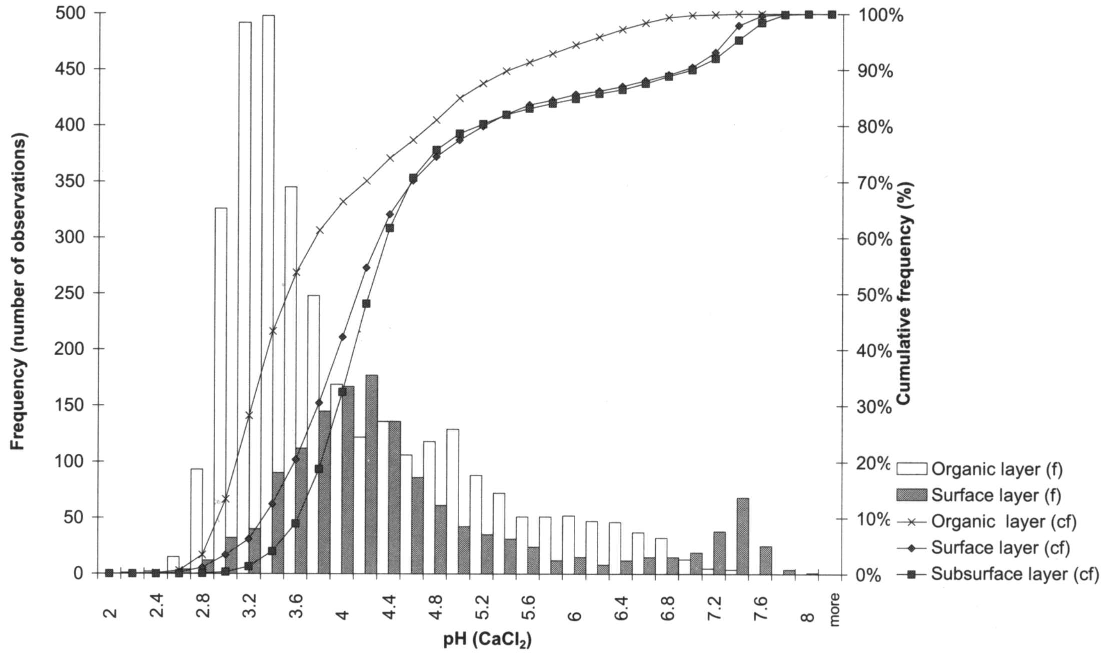


Figure 12-11. Frequency (f) and cumulative frequency (cf) distribution of pH ($CaCl_2$) values of organic and mineral layers.

The bimodal frequency distribution of pH values (Figure I 2-11) can be explained by the high pH values observed in calcareous soils. At this end of the acidity range, near neutrality, some species have difficulty obtaining sufficient iron and manganese for normal growth. Seedlings of most pine species are particularly subject to iron deficiencies in neutral and alkaline soils (Pritchett and Fisher, 1987), although some varieties, such as the austriaca (ssp. nigricans) and calbrica (ssp. laricio) varieties of Pinus nigra, are very tolerant to alkaline conditions.

Acid-base reactions are responsible for the actual H^+ concentration (or pH), caused by the acid reaction of the strongest acid present. Soil acidity is an important parameter for monitoring soils with a low buffering capacity which are exposed to acid precipitation (Ulrich, 1981). A buffer reaction only occurs when an acid or a base is added to a solution or a system. A pH-measurement gives an indication of which buffer reaction may take place. One of the most effective buffer systems in soils are the carbonate species. In the reaction of dissolved carbonate ions with the present protons, CO_3^{-2} is able to take up one H^+ and to form the soluble HCO_3^- (bicarbonate or better mono-hydrogen carbonate), resulting in a pH increase. $CaCO_3$ buffers between pH (H_2O) 6.8 and pH 8 or more (De Coninck and Van Ranst, 1993). In the presence of carbonates in the mineral soil, the pH is fixed within a rather narrow range: 80% of the reported pH values in calcareous subsurface layers lies between 6.3 and 7.7. The effect of carbonates persists in the overlying organic layer. The pH of organic layers overlying calcareous soils is significantly higher than the pH of organic layers overlying carbonate-free soils (Figure I 2-12).

More complex constituents like organic matter, clay minerals and silicates do not react as bases on a well-defined pH, but over a broad pH range (De Coninck and Van Ranst, 1993). These pH ranges overlap both each other either partly or completely and the pH ranges of simple buffering pairs. It is therefore not possible to distinguish well-defined pH fields, in which only one buffering system would act. In general, soils that have a low clay content are more easily acidified by natural or anthropogenic processes, resulting in significant differences in soil pH between coarse and fine textured soils. Many buffer systems may theoretically determine pH of non-calcareous soils, which would result in a wide range of observed pH values. However, also carbonate-free soils show a narrow, although distinctly lower, range of pH values: 80% of the subsurface layers free of carbonates has a pH between 3.6 and 4.8. This may indicate the presence of a common buffer system in non-calcareous forest soils, that buffers soil acidity around pH 4.2. Most probably, aluminium species in association with organic matter are the common soil constituent in non-calcareous soils, that are able to determine soil acidity in the observed pH range.

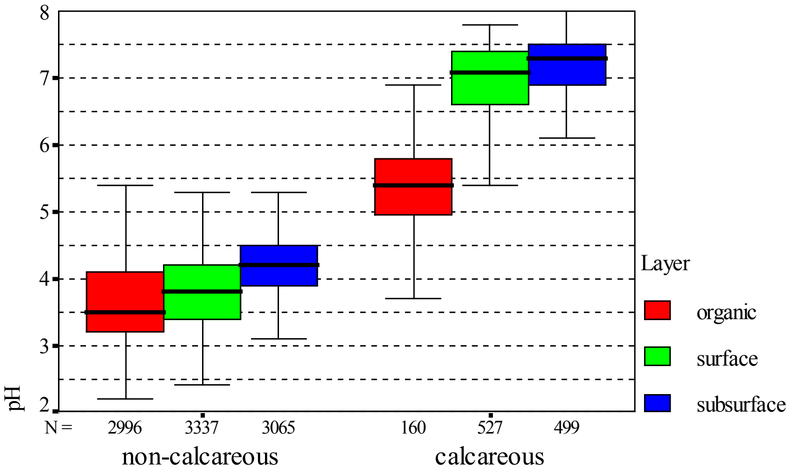


Figure I 2-12. Distribution of pH values in calcareous and non-calcareous soils in organic, and mineral layers.

The pH values of organic layers are usually 0.2 to 1.0 pH unit lower than those of the underlying mineral subsurface layer. As a result of the variable acid strength of organic materials, the pH of organic layers may vary within wide limits; 80% lies between 3.0 and 5.4. The type of vegetation growing on a soil is likely to have a marked influence on soil acidity because of the inherent differences in base content of their litter (Pritchett and Fisher, 1987). Soils supporting conifers tend to be more acid than those supporting broadleaves. This relationship is not always evident, nor is the cause-effect relationship always clear. Because of species differences in tolerance to soil acidity, soil conditions may influence the composition of the plant community more than the community influences soil reaction. For example, some *Quercus* species appear to have an optimum range near neutrality, while *Picea, Abies* and *Pinus* species grow best in acid soils, and, as a consequence, their litter is acid. Soil acidity may dictate the distributions of acid sensitive plants. The distribution of such indicator plants is not always a reliable guide to soil acidity, because of the modifying effects of climate and soil nutrient or moisture supply on tree growth.

Factors such as soil characteristics, climate and tree species that influence tree growth and rate of organic matter decomposition also affect the physical and chemical properties of the forest floor humus. Because the same humus type develops under wide ranges of tree species and soil types, the pH of the humus layer often varies within wide limits. A general observation is that mull layers are less acid than mor layers and peat (Figure 12-13): 78% of the mull layers have a pH above 4.0, while a pH above 4.0 occurs in only 18% of the mor layers. Average pH values of mor (3.6) and peat (3.4) are significantly lower than moder (4.3) and mull layers (4.8). Moder layers have a very broad range of pH values: 20% is very acid ($pH < 3.3$), 11% is neutral to alkaline ($pH > 6.0$). The pH in peat is strongly buffered around the pH_0 (pH at which the sum of the variable charge components is zero) of humic substances, resulting in a much narrower pH-range; 89% has a pH of 4.0 or less. Litter accumulates on the surface of acid soils because soil faunal activity is inhibited by low pH, resulting in acid mor humus rich in plant fragments. In neutral and alkaline soils, the plant debris is rapidly consumed by soil fauna and intimately mixed with soil minerals to give mull humus. The underlying mineral layer shows similar pH differences. The mineral surface layers below mor humus and peat are generally acid; average pH values are 4.0 and 4.2 respectively. Remark the rather abrupt change in pH at the contact between organic and mineral layers in peat soils. The mineral soil below mull humus has an average pH of 5.1.

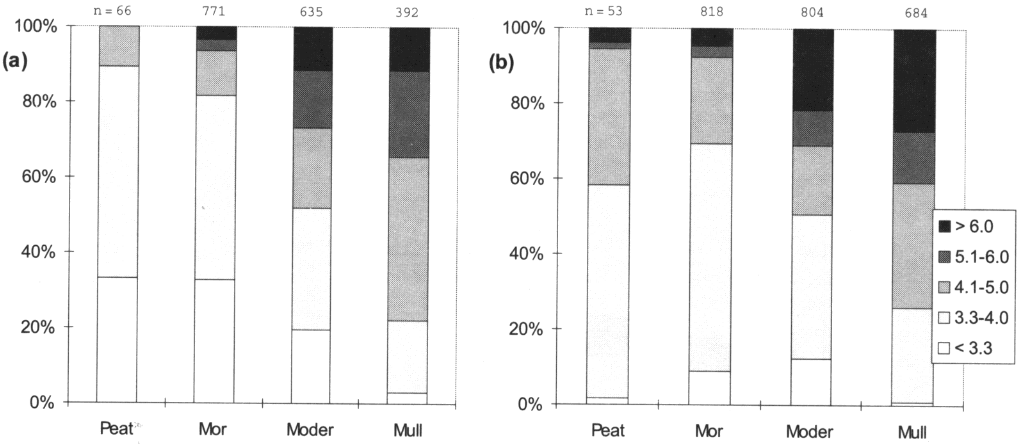


Figure I 2-13. Comparison of pH values in (a) organic and (b) surface layers of soils having various humus types (n = number of observations).

Table I 2-10. Percentile values for pH in mineral surface and subsurface layers (between brackets) of soils with Calcic, Spodic, Albic, Mollic and Umbric properties as compared to all soils of the database.

Plots grouped by soil properties	Percentile values of pH				
	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile
Calcic	5.5 (6.5)	6.6 (6.9)	7.1 (7.3)	7.4 (7.5)	7.6 (7.7)
Spodic	3.2 (3.6)	3.4 (3.9)	3.7 (4.2)	3.9 (4.4)	4.2 (4.6)
Albic	3.1 (3.5)	3.3 (3.8)	3.5 (4.1)	3.7 (4.4)	4.1 (4.6)
Mollic	5.7 (6.4)	6.5 (6.8)	7.0 (7.2)	7.4 (7.5)	7.5 (7.7)
Umbric	3.4 (3.8)	3.6 (4.0)	4.0 (4.2)	4.5 (4.4)	5.4 (5.1)
all soils	3.3 (3.7)	3.5 (4.0)	3.9 (4.3)	4.8 (4.8)	6.7 (7.0)

Mineral surface layers have intermediate pH values between those of organic and mineral subsurface layers in both calcareous and carbonate-free soils (Figure I 2-11). Also the width of the pH range in this layer is intermediate. In many soils, the FAO soil classification name can provide information on soil acidity level (Table I 2-10). The surface mineral layer of

Podzols is often very acid with some decrease in acidity with depth: 82% of the surface layers and 36% of subsurface layers of Spodic soils have a pH value of 4.0 or less. High acidity is even more closely associated with the removal of clay and sesquioxides in surface layers of soils with Albic properties: 88% of the surface layers and 48% of the subsurface layers of soils with Albic properties have a pH value of 4.0 or less. The presence of a Mollic A horizon occurs in high-pH soils, whereas Umbric A horizons are found in more acid soils. Median pH values of mineral surface layers with Mollic, respectively Umbric properties are pH 7.0 and 4.0.

The spatial distribution of pH values in the mineral surface layer (Figure I 2-14) reveals patterns related to the geological substratum in regions with shallow soils. High pH soils are usually associated with soils having calcareous parent materials. For example, the northern edge of the Alps in Austria and its western flank in France are characterised by limestone outcropping, which explains the occurrence of high pH soils in this area. Low pH soils are found throughout Europe on nutrient poor materials, but occur more frequently in north and central Europe.

2.3.1 pH Status and Acid Deposition

A major concern with acid deposition on forest soils having low buffering capacities is that the pH of these soils will ultimately decrease to levels at which toxic Al concentrations in the soil solution are reached. Extremely low pH values, i.e. values below pH ($CaCl_2$) 3.0, were reported for organic and mineral surface layers in 262 and 80 observation plots, respectively. Many of the extremely low pH values are observed in German plots. It should be mentioned that soil pH of German plots was determined in a 1M KCl solution, which may yield lower pH values as compared to the values obtained by the reference method (see also Annex A). Nevertheless, the difference between pH (KCl) and pH ($CaCl_2$) values becomes insignificant in the acid pH range (Backes, 1993).

Soil acidity levels as low as pH 2.9 or 2.8 in organic layers of forests producing acid litter may be reached under strongly leaching conditions. Many of the extremely low pH values in organic layers are observed in cool and humid regions of Europe. However, such low values are never reached in regions with both a moderate rainfall and low acid deposition load. Figure 12-15 shows that the majority of the plots, where extremely low pH values in the mineral surface layer have been reported, are located in the region within Europe receiving the highest acid deposition load. Soil types at these plots are Podzols (35), Dystric Cambisols (17), Dystric Gleysols (7) and Arenosols (5), i.e. soil types characterised by a low buffering capacity against acid deposition. A common characteristic of these soils is a generally low reserve of basic exchangeable cations and a low base saturation; at 62 sites (out of 72 for which exchange properties were measured) a sum of basic cations (BCE) of 2.0 $cmol_{(+)}\ kg^{-1}$ soil or less was measured, the base saturation in the surface layer of 40 sites is less than 20%. The coincidence of low pH, high acid load and low buffering capacity strongly suggests that acid deposition is the cause for the high soil acidity at these sites. It should be mentioned that historical land use of forests, such as forest litter utilisation and forest pasture, may also have contributed to soil acidification observed in certain regions in Europe (e.g. Austria).

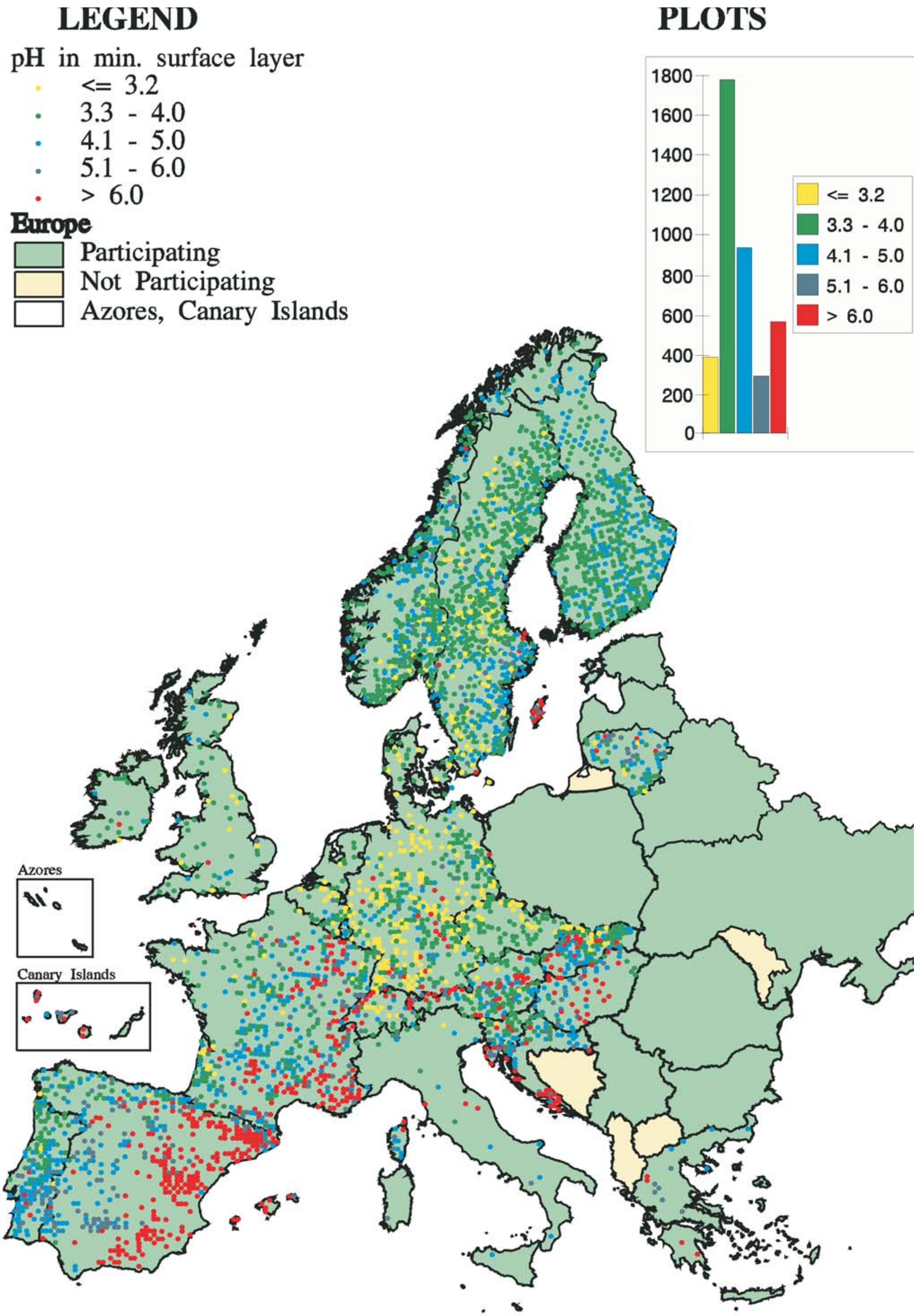


Figure I 2-14. Geographical distribution of pH values in the mineral surface layer.
The Relative Interlaboratory Variation (V) of pH values is estimated at 13%.

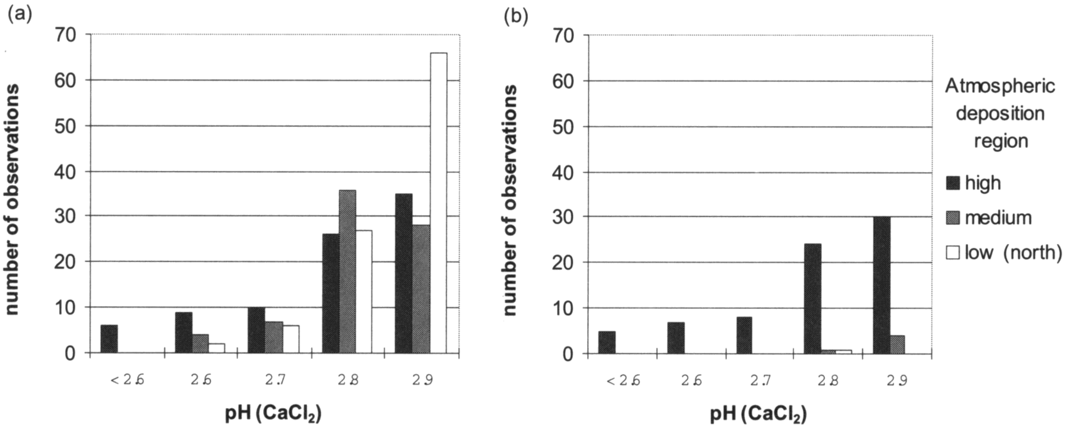


Figure I 2-15. **Distribution of pH values below pH (CaCl$_2$) 3.0 in (a) organic and (b) mineral surface layers over regions in Europe receiving different loads of atmospheric deposition.**

2.3.2 pH Gradient with Soil Depth

Considerable differences in acidity are often found among horizons of the same soil. Forest soils receiving a high input of acids, either through acid litter fall or through atmospheric deposition, may cause a steep pH gradient between the mineral surface layer and the underlying layer. A surface layer pH value that is more than 1.0 pH unit lower than the subsurface pH value is reported for 179 plots, which corresponds to 5% of all plots. The majority of these plots are located in Sweden (65 plots), Germany (51 plots), France (20 plots) and Norway (14 plots). Many of the pH differences in Germany may be explained by the particular sampling approach, where the 0-5 cm interval represents the surface layer and the 10-30 cm interval the subsurface layer. In areas with an evapotranspiration deficit, this phenomenon rarely occurs because basic cations, capable of neutralising acid input, are not leached from the surface layers.

In areas of low or moderate rainfall, a concentration of basic cations may occur at the surface of acid soils as a result of nutrient cycling, primarily through root absorption of basic cations from lower horizons and their return to the surface through litter fall. A slight decrease in soil pH from the organic to the mineral surface layer, may be explained by such an accumulation of basic cations at the surface through nutrient cycling. A pH decrease of 0.5 to 1.0 pH unit is observed in 184 plots. Very few of these observations are made in northern Europe.

Where a decrease in soil acidity is needed in production forests, additions of lime are usually made. For example, liming is a common practice in German forestry since the beginning of the 1980s in order to cope with acid deposition (Ulrich, 1995). The amounts of lime required to lower the acidity to the optimal level depends on the soil cation exchange capacity. Liming has also an immediate effect on the Ca and Mg concentration in soil solution. These managed forest soils usually have a steep pH gradient between the organic layer and the underlying acid mineral layer. In Germany (27 plots), the Slovak Republic (10 plots), Denmark (5 plots) and the United Kingdom (4 plots) a marked increase in organic layer pH (> 1.0 pH unit above mineral layer pH) is observed in some of the acid ($pH < 4$) plots. This pH gradient is probably the result of human intervention, but may also be due to natural factors, such as humus quality.

2.4 Organic Carbon

The availability of information on organic carbon concentration is illustrated in Table I 2-11.

Table I 2-11. Organic carbon concentration - data availability (see also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	93	100	100	99	25	100	100	100	100	95	100	100	100	100	100	99	100	75	93	99	78	100	100	4023
Min. Layer	100	100	100	100	25	100	100	100	100	95	100	100	100	100	100	100	98	79	100	100	87	100	100	4201
Analysis	N	R	N	R	R	N	N	R	N	N	R	R	R	R	N	N	R	R	R	R	N	N	R	28%

Plant materials are added to soils from living root systems, from dead roots and as litter added to the soil surface. Average plant tissue contains about 400 g C kg^{-1} on an oven dry basis. Before dead plant material reaches the soil as litter, most of the solubles and hemicelluloses have already been utilised, with C being released. as CO_2. Carbon is a common constituent of all organic matter. Organic materials on the soil surface undergo various changes during microbial digestion. The soil biota convert plant materials into humus, which is resistant to further rapid oxidation partly because of its chemistry, partly because of its interaction with clays, and partly because of its distribution in soils.

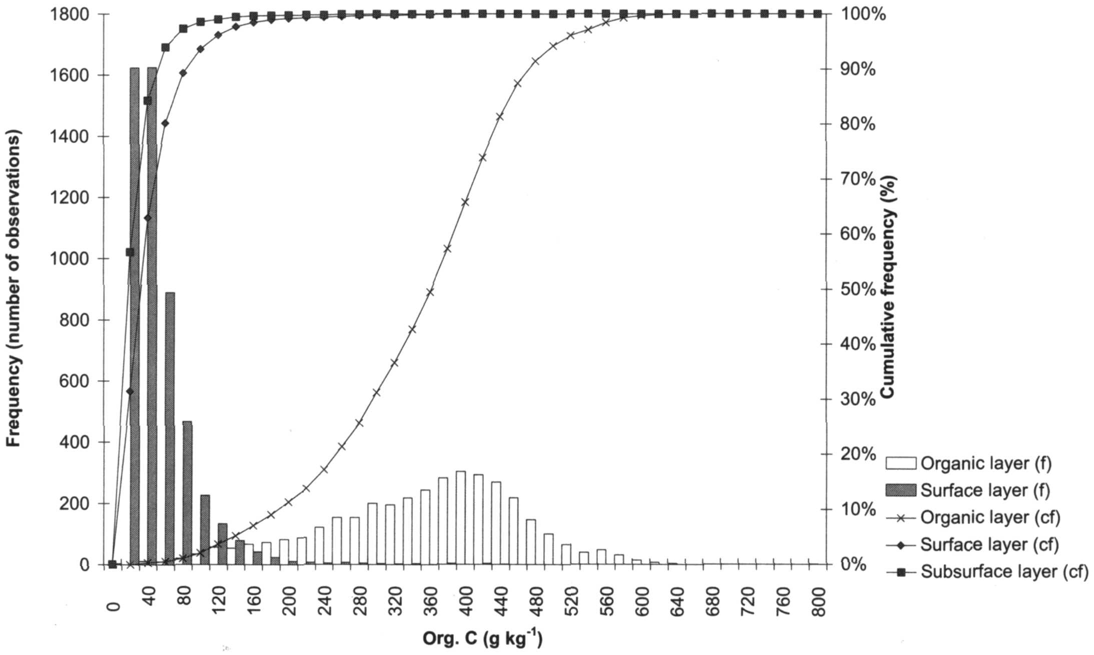


Figure I 2-16. Frequency (f) and cumulative frequency (cf) distribution of the organic carbon concentration in organic and mineral layers.

The composition of the organic fraction of the soil ranges from untransformed or slightly transformed plant remains to humic substances, which are large organic molecules. Humus **is** a general term for organic matter in soils for which the cellular organisation of plant material **is** not recognisable under a light microscope. It includes humic and non-humic substances.

Of the non-humic substances, carbohydrates are quantitatively the most important group, representing 100 to 250 g kg^{-1} of the organic C in soils. Carbohydrates are essential components of all living organisms, including micro-organisms and soil fauna, and are cycled rapidly compared with humic substances (Oades, 1989).

The humic substances compose the active fraction of the organic substances. Humic materials are in fact large organic molecules, mostly differentiated based on their solubility at different pH values. Because humic substances have a high CEC, they contribute to the acid neutralising capacity of the soil (Ulrich, 1981). The buffering capacity of humic compounds consists of the replacement of cations, which neutralise the negative charge of dissociated acidic groups, by added H^+ (De Coninck and Van Ranst, 1993). This reaction can take place within a broad pH range (pH 4 till 8).

Besides a high CEC, organic colloids have a strong chelating ability. High charged cations with a small diameter, such as Al^{+3} and Fe^{+3}, present in complexed form associated to humic substances are not easily exchanged. The tendency of metals to combine with chelating groups often results in a strong retention of heavy metals by organic matter.

2.4.1 Organic Materials in the Organic Layer

The majority of organic layers has an organic carbon concentration between 200 and 500 g kg^{-1} (Figure 12-16), which roughly corresponds with an organic matter content of 40 to 100%.Incorporation of mineral materials in the litter layer results from burrowing activity of soil fauna, which is favoured by high nutrient conditions (see also section 3.2).

Under permanently wet conditions, lack of oxygen prevents the decomposition of organic matter, resulting in the build-up of thick organic layers on the soil surface. H-horizons, which are saturated with water for prolonged periods during the year, accumulate much more organic matter than the drier 0-horizons (Figure I 2-17): the total Org. C pool in the organic layer exceeds 2 kg m^{-2} in 66% of plots with a H-horizon, but only in 23% of the plots with an 0-horizon. A similar observation is made when soils with Gleyic properties are compared with better drained soils. Half the soils with Gleyic properties accumulated more than 2 kg m^{-2} Org. C in the organic layer, whereas 53% of the better drained plots accumulate less than 1 kg m^{-2}.

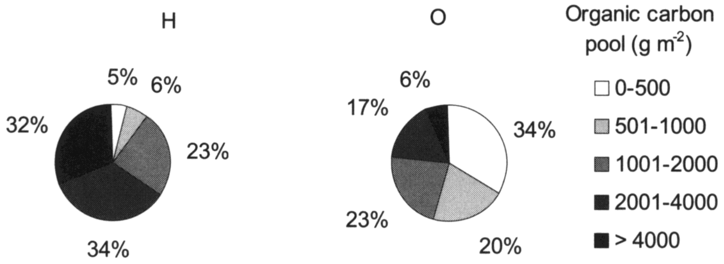


Figure I 2-17. Organic carbon pool in organic layers under waterlogged conditions (H layers) as compared to soils with O layers.

The majority of H-layers is peat (61%) or mor humus (27%), which confirms the observation that conditions favouring the accumulation of organic matter coincide with the development of these humus types. Figure I 2-18b reveals that peat layers store high amounts of organic carbon; 95% of the calculated Org. C pools varies between 1 and 30 kg m^{-2}. Organic carbon pools in mor and moder layers also vary within a wide range of values, but are about 10 times lower; from less than 0.1 to more than 3 kg m^{-2} (Figure I 2-18b). Organic carbon pools in mull layers are generally lower than 1 kg m^{-2}.

The burrowing activity of earthworms and arthropods in mull layers results in significant amounts of mineral materials within the organic layer, while peat and mor humus are essentially all organic matter (Figure I 2-18a). Organic layers with no or very little mineral materials are recognised by their high Org. C concentrations. Values of 500 g kg^{-1} C or more, which correspond to the average C content of soil organic matter, are found in about half of the peat layers and in 13% of the mor layers, but are almost never measured in mull humus. Assuming a factor of 1.7 for the conversion of Org. C to organic matter, more than 40% of the mull layers consists of more mineral materials on a weight basis than organic materials. Such intimate mixing of mineral and organic materials occurs in 34% of the moder layers, in 19% of the mor layers and in only 10%of the peat layers.

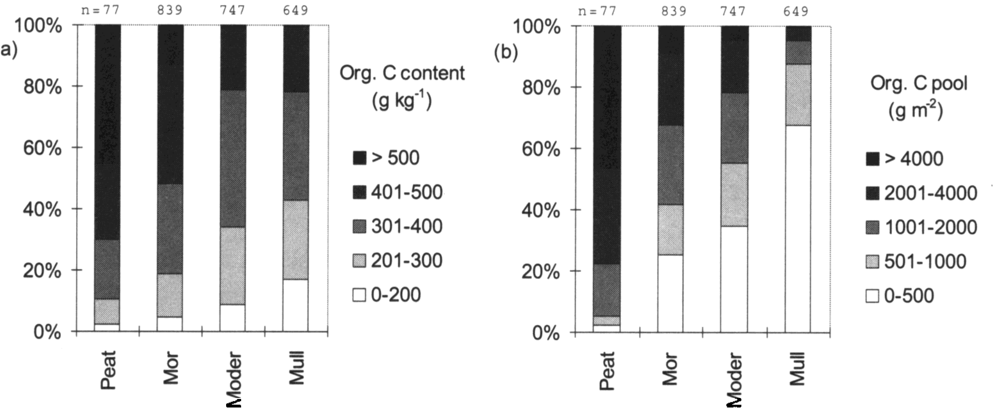


Figure I 2-18. **Relationship between humus type and (a) organic carbon concentration (g kg^{-1}) and (b) organic carbon pool (g m^{-2}) in the organic layer** (n = number of observations).

2.4.2 Organic Materials in the Mineral Layer

The organic carbon content in the mineral soil is generally much lower than in the organic layer, and decreases with depth (Figure I 2-16). The highest number of observations of organic C concentration in mineral layers is made in the 10 to 20 g kg^{-1} range. Soil organic matter content usually does not exceed 100 g kg^{-1}. Higher values are observed in 13% of the mineral surface layers and in less than 3% of the subsurface layers. Soils with a low biological activity are characterised by an abruptly decreasing organic matter content at the contact between organic layer and mineral soil. Burrowing animals bring organic matter in the mineral soil, which may result in an organic carbon enriched mineral surface layer of several decimetres thick. Such mineral surface layers are recognised in the FAO soil classification system as Mollic (high base saturation) or Umbric (low base saturation) A horizons. Soils with Mollic or Umbric A horizons and other soils with an increased organic matter content, as contained in the soil classification name, were grouped as having Humic properties. Although they comprise only 7% of the soil plots, half of the subsurface layers with more than 100 g kg^{-1} organic carbon are found in soils with Humic properties (Figure I 2-19). Sixty percent of these soils have more than 50 g kg^{-1} organic carbon in both the surface and subsurface layers, whereas a similar organic matter enrichment is achieved in only 12% of the other soils.

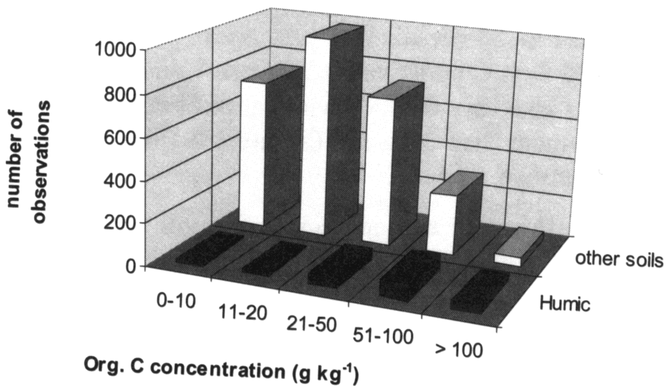


Figure I 2-19. **Comparison of organic carbon concentration in mineral subsurface layers between soils with Humic properties and other soils.**

Mollic and Umbric A horizons result from the activity of burrowing animals that transport organic materials from the surface and mix the latter with mineral soil. Soils having Mollic or

Umbric A horizons mostly underlie mull (52%) or moder (39%) layers. Mineral surface layers underlying mor humus are usually poor in organic matter (Figure I 2-20); only 21% of the surface mineral layers underlying mor layers have more than 50 g kg^{-1} Org. C. This concentration is exceeded in 39% of the surface mineral layers underlying mull humus. This difference in Org. C concentration largely disappears in the mineral soil below 10 cm. In other words, soils with mull humus are characterised by a gradual transition in the vertical distribution of organic matter between the litter and the mineral topsoil (0-10 cm), while soils with mor humus have an abruptly decreasing organic matter content at the contact between humus and mineral soil.

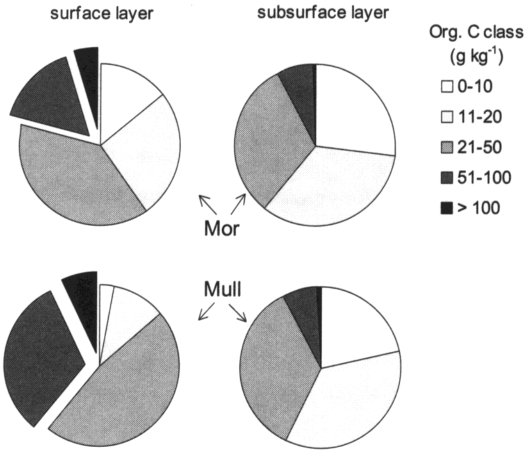


Figure I 2-20. Relationship between humus type and organic carbon concentration (g kg^{-1}) in the mineral layer.

In mineral soils, most humus is associated with inorganic materials, particularly clays. In some cases, particularly for non-polar organic molecules, the interaction forces are relatively weak, corresponding with physical adsorption only. However, polar or ionic organic species can enter into a wide variety of chemical reactions to form organo-mineral complexes (Hall, 1987). The interactions have profound effects on both the organic and inorganic materials (Oades, 1989). Clay particles are usually associated in domains. Adsorption of organic colloids tends to occur at the periphery of domains and has a stabilising effect on micro-aggregates (Greenland and Hayes, 1981). Because many of the organo-mineral associations involve charged clay minerals, organic matter content in mineral soil layers is positively related with clay content (Figure I 2-21). The correlation between organic matter and clay content in mineral soil may also be due to waterlogging in clay soils and reduced decomposition of organic matter. Average organic carbon concentration in mineral surface layers increases from 32 g kg^{-1} in coarse textured soils to 57 g kg^{-1} in fine and very fine textured soils.

Organic matter strongly affects the physico-chemical properties of the mineral soil (Campbell, 1978). The influence of organic matter on physical soil properties can be summarised as (Brady and Weil, 1996):

- encouraged granulation;
- reduced cohesion and plasticity;
- increased water holding capacity.

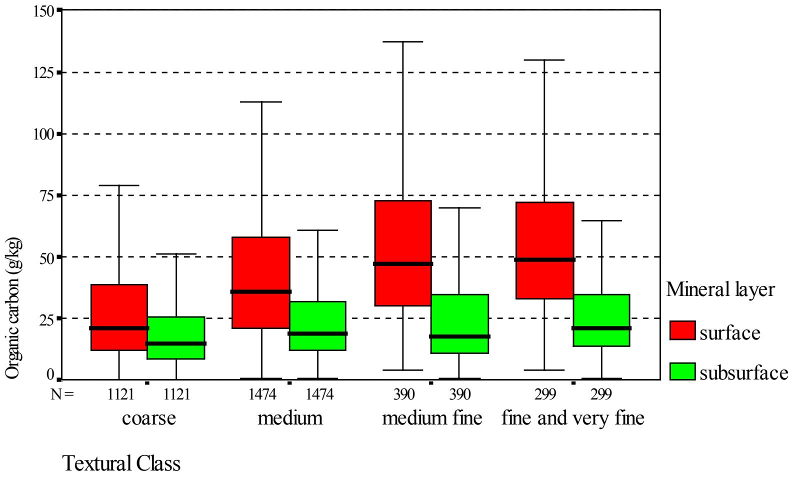


Figure I 2-21. Influence of texture on organic carbon concentration in mineral surface layers.

2.5 Macronutrients

Large quantities of nutrients circulate within a forest ecosystem. Part of the annual nutrient requirement for forest growth can be met by nutrient reabsorption before the loss of foliage (Waring and Schlesinger, 1985). The remaining amounts must be supplied by uptake from the soil or from deposition.

Three elements, nitrogen, phosphorus, and potassium, are used in relatively large amounts by plants and are the elements most often deficient in soils (Pritchett and Fisher, 1987). Calcium and magnesium are also used in large quantities, but are less often deficient in soils. Together, they are often called macronutrients.

Organic Matter and Nutrient Cycling

The majority of the nutrient pool that is available for uptake in many forests is derived from the decomposition of dead organic matter. Besides the main elements C, H and O, important amounts of other elements can be incorporated or fixed at the surface of organic substances. Nutrients are supplied through (Campbell, 1978):

- absorption of easily exchangeable cations;
- mineralisation of nitrogen, phosphorus and sulphur held in organic form; and
- extraction of elements from minerals by acid humus.

Relatively large quantities of nutrients are stored in the forest floor. In some chemically poor forest soils, the forest floor represents the major reserve of nutrients for tree growth (Pritchett and Fisher, 1987).

The release of nutrients is a complex process which is not fully understood. The release from organic matter takes place partly through leaching and partly through decomposition of structural components. Leaching is significant for elements not bound in structural components, i.e. Na, K, Ca, Mg and Mn, whereas decomposition is significant for elements like C, N and P. Cationic nutrients are held on cation exchange sites and are rapidly released from forest litter. Staaf and Berg (1982, in Waring and Schlesinger, 1985) found that particularly K, but also Ca and Mg are lost more rapidly than the disappearance of the organic mass of litter. Organic layers that are purely organic matter with very little mineral materials are very poor in these elements (Figure I 2-22 a). Organic layers that are well mixed with mineral soil are low in organic C, but distinctly richer in cationic nutrients. Rates of mineralisation do not usually determine the available quantities of these nutrients because they are adequately supplied by the mineral soil. N and P, on the other hand, are retained during the period of litter decay. Particularly nitrogen concentrations are positively related to the organic matter content of the organic layer (Figure 12-22 b and c).

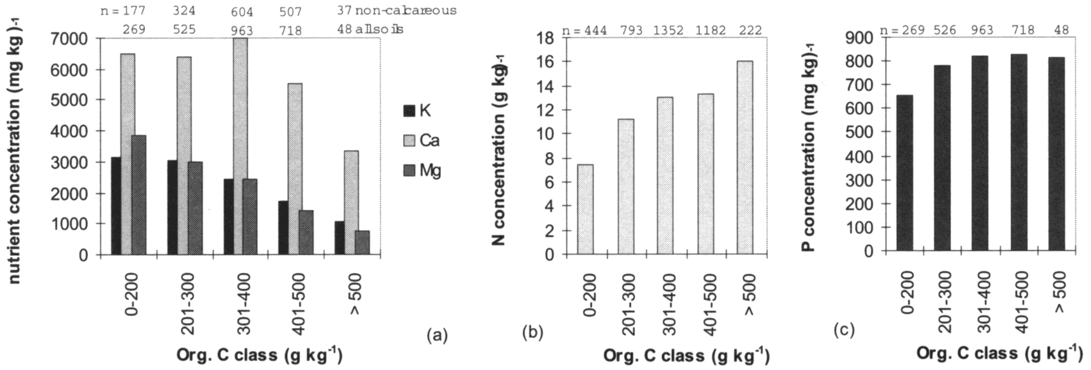


Figure I 2-22. **Relationship between organic matter and average nutrient concentrations in the organic layer;** (a) potassium, calcium (for non-calcareous soils, in order to eliminate Ca present in carbonate form) and magnesium, (b) nitrogen, and (c) phosphorus; n = number of observations.

Because the rate of decomposition and nutrient turnover is more rapid at high temperatures, the nutrient content of forest floors in warm regions is generally lower than that in cool regions.

Atmospheric Nutrient Input

The atmosphere is a source of nutrients which should be accounted for in ecosystem nutrient cycling. Large quantities of nitrogen are introduced into the atmosphere by industrial pollution. The actual inputs of nitrogen in many coniferous forests in central Europe exceeds 30 kg ha^{-1} yr^{-1}, if above ground uptake of N is included (Matzner and Murach, 1996). Potassium, calcium and magnesium additions to forest ecosystems via the atmosphere originate largely as aerosols over oceans and agricultural lands. These additions are usually larger in coastal areas than inland, especially for Na and Mg (Draaijers et al., 1996). The regional variation of total nutrient deposition values is considerable. Data from budget studies (e.g. Buttner et al., 1986; Hantschel, 1987; Hantschel et al., 1988; Federer et al., 1989; Zottl et al., 1989) indicate ranges of 0.07-2.38 kmol(+) ha^{-1} yr^{-1} Na, 0.02-0.24 kmol(+) ha^{-1} yr^{-1} K, 0.11-1.07 kmol(+) ha'' yr^{-1} Ca, and 0.05-0.63 kmol(+) ha^{-1} yr^{-1} Mg. The amounts are strongly dependent on the geographical distance to oceans, forest type (evergreen conifers vs. broadleaves), orographic conditions (luff vs. lee) and site altitude. In southern and south-eastern Europe, high Mg, Ca and K deposition results from a combination of wind erosion of calcareous and salt containing soils, agricultural practices, traffic on unpaved roads, and supply of Saharan dust (Draaijers et al., 1996).

Air pollution has changed needle and leaf chemistry (Hüttl, 1985a; Aronssen, 1985). This implies that the litter's chemical composition changes due to air pollution and that long-term decomposition rate is affected by decreased contents of Mg and K and increased contents of N. Decomposition of litter is initially determined by the content of nutrients. In later stages, the decomposition seems to be mainly regulated by the lignin content (Berg and Staaf, 1982). Factors regulating the decomposition of lignin are only partially known, but it seems that high initial nutrient contents in the litter might reduce lignin decomposition. As a result, the effect of nitrogen deposition might be harmful because it lowers long-term decomposition rate and hence the circulation of nutrients (Olsson, 1994). This is confirmed by the generally high N pool in soil ecosystems with low C/N ratio in organic and mineral layers.

2.5.1 Total Nitrogen

The availability of information on total nitrogen is illustrated in Table I 2-12.

Table I 2-12. **Total nitrogen concentration - data availability** (see also Figure I 2-1 **for** interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	93	100	100	99	25	100	100	100	100	95	100	100	100	100	100	99	100	75	93	99	78	100	100	4024
Min. Layer	100	100	100	100	25	100	100	100	100	95	100	100	100	100	100	100	98	79	100	100	87	100	100	4201
Analysis	N	R	N	R	R	N	N	R	N	N	R	R	R	N	N	N	R	R	R	R	N	N	R	20%

Contrary to the importance of soil organic C in the global C cycle, the amount of N in biota and soils is insignificant compared with amounts in the atmosphere. Gaseous nitrogen, however, is largely unavailable to higher plants. The forms most commonly assimilated by plants are the nitrate and ammonium ions (Pritchett and Fisher, 1987). Nitrogen is accumulated in the soils in the form of plant and animal residues, and a kind of equilibrium between the rate of accumulation and decomposition becomes established on each site over long periods of time.

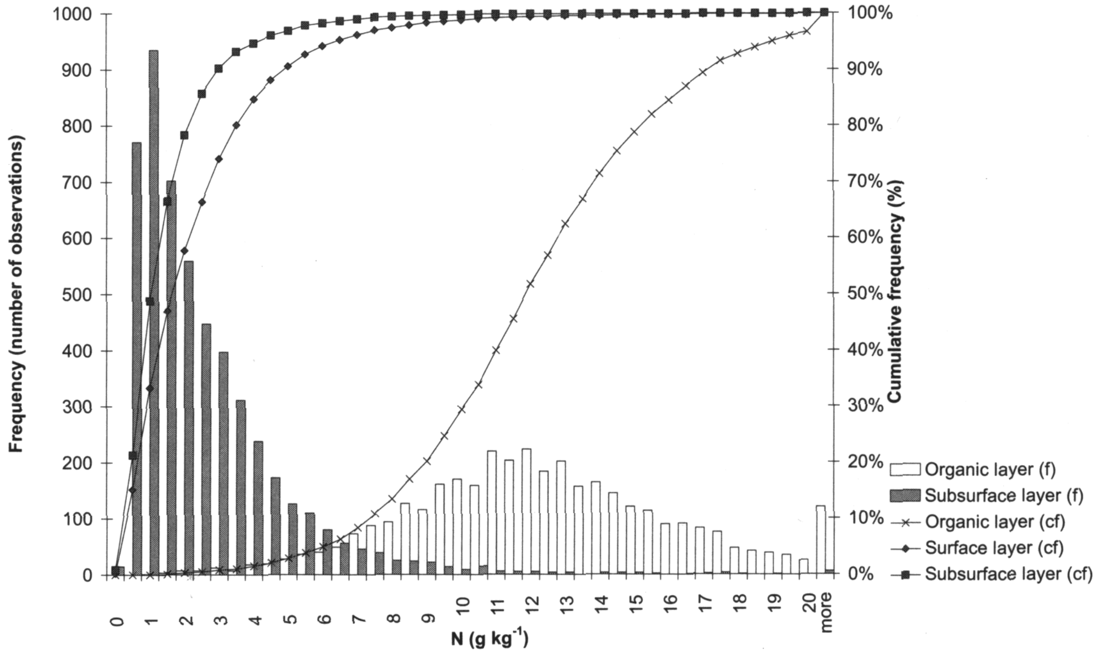


Figure I 2-23. Frequency (f) and cumulative frequency (cf) distribution of nitrogen concentrations in organic and mineral layers.

Nitrogen in forest soils is found largely in the humus layer and the surface mineral layer. The N concentration in forest floor materials varies within a rather narrow range, from 5 to 20 g kg^{-1}, in more than 90% of the plots (Figure 12-23). The variation is largely determined by the amount of mineral materials in the organic layer. The N concentrations in mineral layers also varies in function of organic matter content, but is always lower than the overlying organic layer. In mineral soil layers, 90% of the N values are less than 5.3 g kg^{-1} in surface layers and less than 3.0 g kg^{-1} in subsurface layers. Low values (< 1.0 g kg^{-1}) in surface layers are usually observed in highly permeable soil types, such as Arenosols and Podzols (Figure I 2-24).

The relationship between nitrogen and organic matter is expressed by highly significant correlation coefficients between total N and Org. C; r values for organic, mineral surface and subsurface layers are 0.50, 0.89 and 0.87, respectively. The nitrogen content of organic matter in organic layers, which ranges from untransformed to strongly transformed materials of various origin, is partly determined by vegetation type. In the mineral soil, most organic materials are in an advanced stage of humification and evolve towards a rather specific N content, characteristic for humic substances. As a result, the relationship between Org. C and N is more pronounced in mineral soil layers.

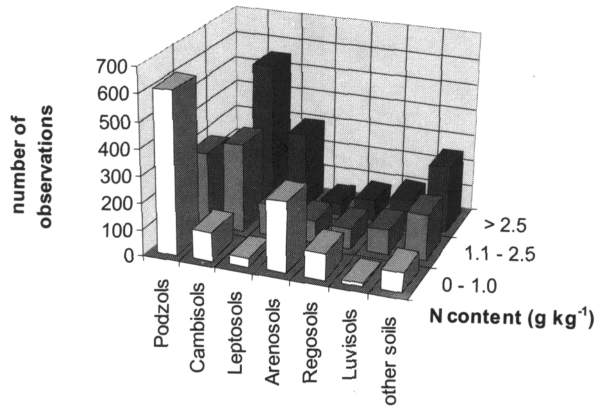


Figure I 2-24. Relationship between nitrogen concentration in the mineral surface layer and soil type.

The total amount or pool of N stored in the organic layer is determined by the equilibrium between litter production and organic matter decomposition. Total amounts of 750 g m^{-2} N and more in the organic layer were reported at 28 sites, all of which have waterlogged H layers. The combination of poor soil drainage (Gleyic property) and a cool climate usually results in high N pools in the organic layer. Total amounts in organic and mineral layers vary from no more than 100 g m^{-2} in some excessively drained sands to as much as 3000 g m^{-2} in some Boreal forests with a deep accumulation of humus (Weetman and Webber, 1972). Due to a slow decomposition of plant residues, most boreal forests are N limited, in spite of the large underlying pool size.

The average concentration varies little between the major humus types. The mean N concentration of mull layers (11.9 g kg^{-1}) is slightly lower than the N concentration of moder (13.1 g kg^{-1}) and mor layers (12.9 g kg^{-1}). About 70% or more of the plots having these humus types have an organic layer N concentration within a rather narrow range of 9 to 16 g kg^{-1} (Figure I 2-25a). Although mor layers have distinctly higher Org. C concentrations than mull layers, the similar N concentrations of mor and mull layers and the fact that nitrogen in litter **is** largely in organic form, must be explained by a difference in nature of the organic matter. The organic matter in mor layers is generally in a less transformed condition, and therefore has a lower nitrogen availability. The higher concentration observed in peat layers, having an average N concentration of 17.0 g kg^{-1}, is mostly a result of the near absence of mineral materials in these layers.

The difference between the major humus types lies in the pool of nitrogen in the organic layer (Figure I 2-25b). A generally lower turnover rate of organic matter in acid soils leads to accumulation of organic matter on the soil surface and a high nitrogen pool. The highest amounts are found in peat layers; 65% have a nitrogen pool of more than 100 g m^{-2}. A large part of the N pool in peaty soils is stored in the organic layer where it is largely unavailable for plant uptake. The majority of mull layers has a N pool below 20 g m^{-2}. Soils having mull humus quickly recycle nutrients stored in organic materials, due to a higher decomposition rate and an intricate mixture of the decomposition products with the mineral soil. The N pool in mor and moder layers varies within a very wide range.

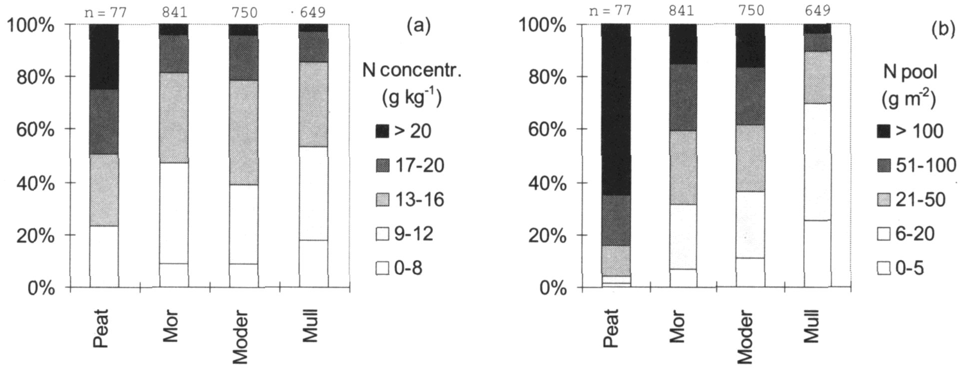


Figure I 2-25. Differences in nitrogen concentration (a) and total N pool (b) in the organic layer between major humus types (**n** = number of observations).

Nitrogen may be lost by denitrification in wet, poorly aerated soils. Denitrification is a biological process involving anaerobic bacteria that are able to use nitrate in place of oxygen as a hydrogen acceptor (Barber, 1995). It converts nitrates into N_2 which is lost to the atmosphere. Denitrification may account for a significant decrease in nitrogen in wet areas, following clear-cut harvesting and the associated rise in water table when transpiration is suddenly reduced (Pritchett and Fisher, 1987).

N Deposition

Nitrogen deposition is likely to be the cause for the higher N concentrations observed in organic layers in strongly industrialised regions as compared to more remote areas. Figure I 2-26 shows that 69% of the organic layers in the region with the highest load of atmospheric deposition has a N concentration of more than 12 g kg^{-1}. This value is exceeded in only 39% of the plots located in the area with a low deposition load.

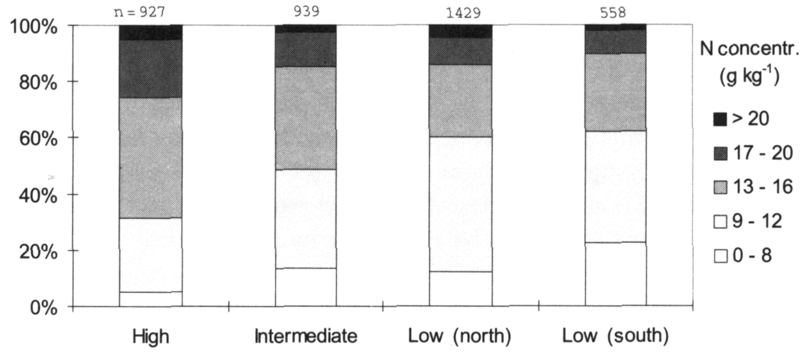


Figure I 2-26. Nitrogen concentration of the organic layer in different atmospheric deposition regions.

The increased N availability resulting from atmospheric deposition might lead to the situation that no longer N limits forest increment but the storage of nutrient cations, such as Mg and K, in the soil. The fast growth of young stands, pushed by N deposition, is than a factor that increases soil impoverishment and may result in an inadequate nutrient uptake (Ulrich, 1995). This is especially true for ammonium. If it is preferentially taken up, as is the case with spruce and pine (Arnold, 1992), it inhibits cation uptake by roots, its uptake acidifies the rhizosphere and it increases cation leaching.

2.5.2 Carbon/Nitrogen Ratio

During decomposition of dead plant material, most of the organic carbon is released as CO_2. The N, however, is retained, either complexed by plant polyphenols or incorporated into microbial tissue. Most organic residues entering the soil carry large amounts of C and comparatively small amounts of N. The C/N ratio in plant material ranges from 20 to 30 in legumes to as high as 100 in certain strawy residues. Soil micro-organisms ordinarily have a C/N ratio between 5 and 10 (Brady and Weil, 1996; Waring and Schlesinger, 1985). Bacterial tissue is in general richer in protein than fungi and consequently has a narrower ratio. During microbial decomposition of forest litter, the C/N ratio is gradually lowered. Because soils contain plant materials, in various stages of decomposition, and micro-organisms, the C/N ratio in soils is in between those of higher plants and micro-organisms. Ratios between the concentration of organic C and various nutrients can be used to follow nutrient immobilisation by microbes during the decomposition of litter. The C/N ratio gives an indication of availability of nitrogen in floor material and of its rate of decay.

The significance becomes obvious with an example (Brady and Weil, 1996). Suppose large quantities of organic residues with a wide C/N ratio are added to a soil with a much lower C/N ratio. The heterotrophic flora (bacteria, fungi and actinomycetes) quickly become active and multiply rapidly, yielding carbon dioxide in large quantities. Under these conditions, nitrate N practically disappears from the soil because of the insistent microbial demand for this element to build their tissues. At the same time, little nitrogen is available to trees, As decay occurs, the C/N ratio of the soil organic matter decreases since carbon is being lost and nitrogen conserved. Eventually enough C is lost that the C/N ratio of the residue is equivalent to that of bacterial and fungal tissues. When microbial activity slows, available N is released as NH_4^+ from dead microbial tissue. This mineralisation of N often commences with C/N ratios near 30:1 (Berg and Staaf, 1980).

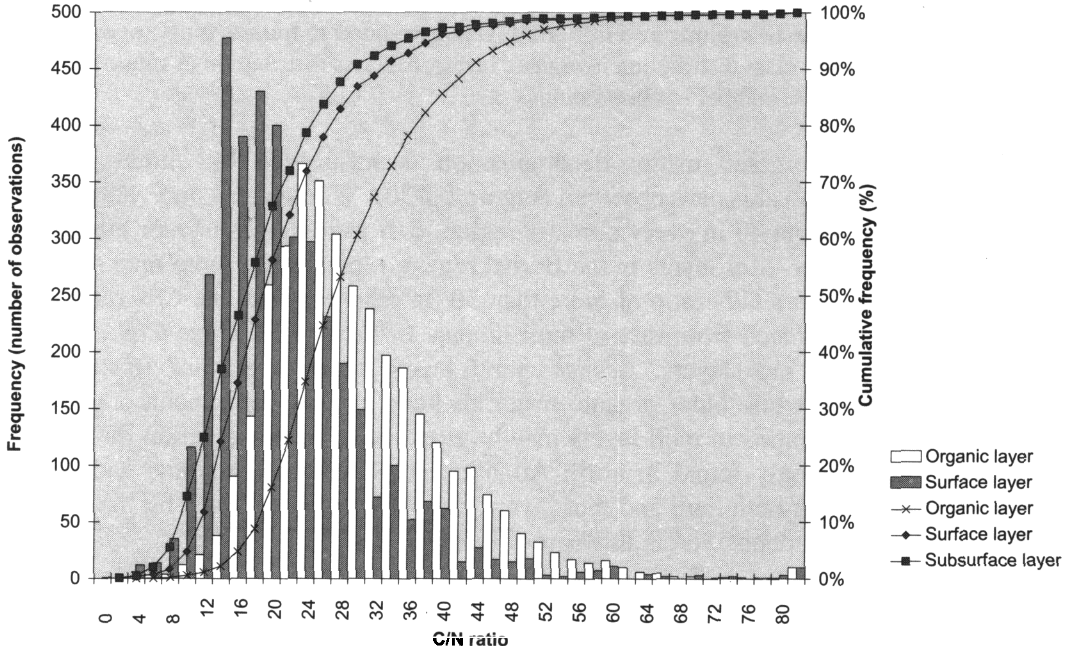


Figure I 2-27. Frequency (f) and cumulative frequency (cf) distribution of C/N ratios of organic and mineral layers.

In forest soils the C/N ratio is usually high in the organic layer and low in mineral subsurface layers where decomposition processes are in an advanced stage. In organic layers the ratio varies between 10 and 100, with few outliers on both sides of the range (Figure 12-27). The majority of C/N values are between 20 and 40. The N concentration in the residue of leaves increases as the mass of the original leaf material declines (Gosz et al., 1973, in Waring and Schlesinger, 1985). In mineral layers, the ratio is narrower for subsoils than for surface layers (Figure I 2-27). The range over which C/N ratio values vary in the mineral soil is distinctly lower, and decreases further with depth; 80% of the C/N ratio values in the mineral surface layer is from 12 to 33, whereas the 10- and 90-percentile values for subsurface layers are 10 and 30, respectively.

The average ratio in humus layers is 30. In general, the ratio is greater in mor and peat humus than in mull and moder humus. However, C/N ratio of mull layers may also be high because organic debris are relatively fresh compared to other humus types. The highest values are recorded in poorly decomposed mor layers (Figure I 2-28a); in 20% of the mor layers the C/N ratio exceeds 40. In the mineral soil the ratio decreases to an average of 20 in the surface layer and somewhat less in the subsurface layers. Due to a faster decomposition, the ratio **is** significantly lower under mull humus as compared to soils with mor humus. This difference related to humus type also persists in subsurface layers (Figure I 2-28c); 80% of the subsurface layers underlying a mull have a ratio of 16 or less, while these low values are measured in less than 25% of the subsurface layers underlying mor humus.

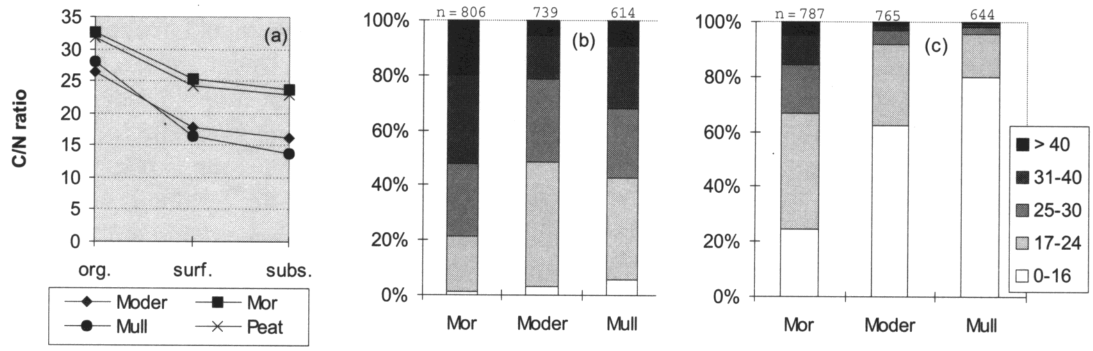


Figure I 2-28. C/N ratio in organic and mineral layers as related to humus type; (a) average ratio; (b) class distribution in organic layers; (c) class distribution in subsurface layers; n = number of observations.

Because the rate of organic matter decomposition is influenced by climate, regional differences in C/N ratio values are observed (Figure 12-30). Whereas median values of mull layers are between 20 and 30 in every climatic region, C/N ratio values of mor humus show more regional variability. Mor layers in the Boreal region, representing more than 40% of all mor layers, usually have a C/N ratio of more than 30. In other regions, the C/N ratio of mor humus does not differ much from that of mull humus. In fact, mull humus C/N ratios may even exceed those of mor layers. Because mull layers often consist of freshly fallen, undecomposed leaves, while older organic materials have already been incorporated in the mineral soil, high C/N ratios in mull layers may be explained. The observation that low C/N ratio values are commonly found in north Atlantic and Subatlantic regions, with average values of less than 27 in both mull and mor layers, may be partly explained by the high load of atmospheric nitrogen deposition in this part of Europe.

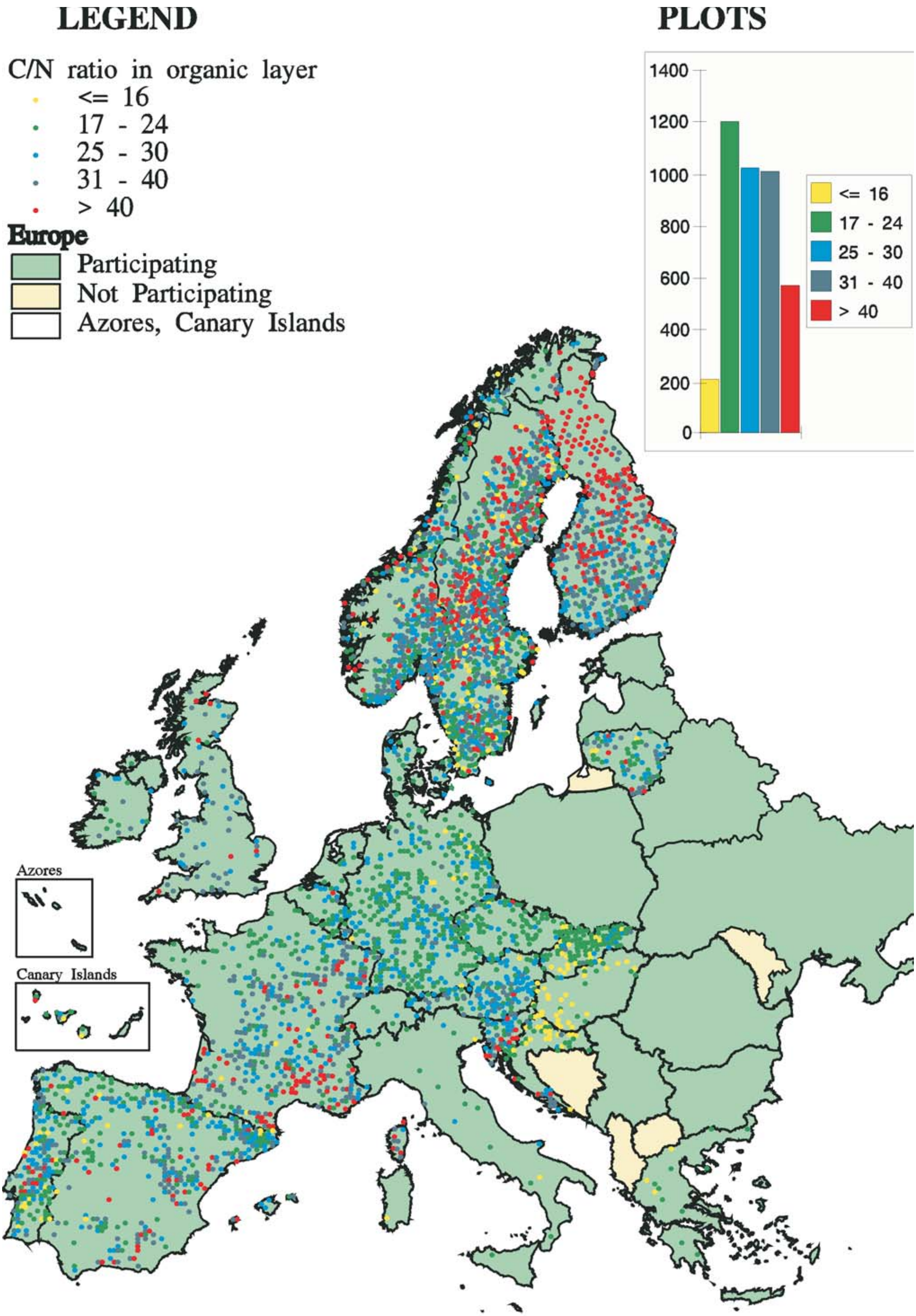


Figure I 2-29. Geographical distribution of C/N ratio values in the organic layer. The Relative Interlaboratory Variation (V) of Org. C and N contents is 28% and 20%, respectively.

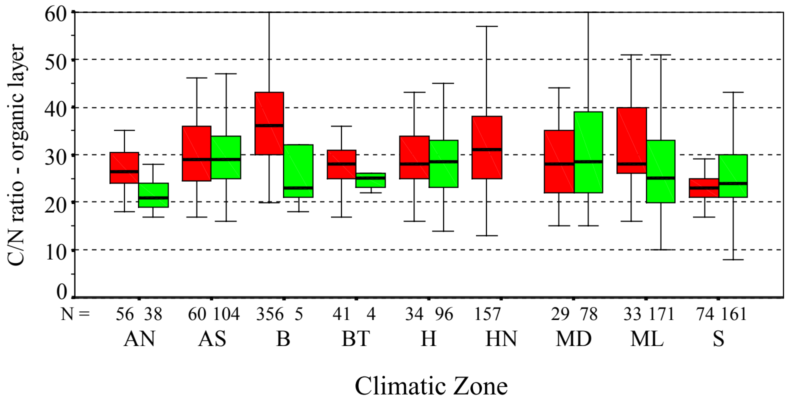


Figure I 2-30. Regional differences in C/N ratio of organic layers.

Figure I 2-29 shows that C/N ratios above 40 in organic layers frequently occur in northern Europe. In this area, wide C/N ratios are usually associated with mor organic layers and coniferous forests. High C/N values also occur, however less frequently, in the Mediterranean area, but they are nearly never found in the central European region. Many plots in central Europe have organic layers with a C/N ratio approaching 20, which confirms the observed increase in topsoil nitrogen content in areas with a high deposition load.

The national averages of the proportion of the C/N ratio of the organic layer over that of the mineral surface layer:

$$\frac{C/_{N}\,(organic\,layer)}{C/_{N}\,(\mathrm{min}eral\,surface\,layer)}$$

range between 1.0 in the Netherlands and 2.0 in France (Table I 2-13), but the proportions calculated for individual plots vary within a much wider interval (Figure I 2-31). Nitrogen deposition decreases the C/N ratio in the organic layer. In soils with a disturbed organic matter and nutrient cycling caused by nitrogen input the above defined proportion is smaller than 1. Such an unusual difference in C/N ratio between organic and mineral layer, which can probably be attributed to nitrogen deposition, occurs in 17% of the plots. A relatively high number of plots where the C/N ratio of the mineral surface layer exceeds that of the organic layer is mostly found in north-western Europe. The following countries, in decreasing order of relative occurrence, have a proportion < 1 in more than 20% of their total number of plots: NL, EL, NO, SW, DK, CZ, LX, UK, DL and BE (Table I 2-13). Except for Greece, these countries are located in a region with either a high deposition load (e.g. NL, CZ, LX, UK, DL, BE) or with cold and wet climatic conditions (e.g. NO, SW and DK). Figure I 2-31 also indicates that a low C/N ratio in the organic layer as compared to the mineral surface layer occurs frequently in the high deposition area, as well as in the low deposition area in northern Europe. Soils in the latter region are particularly vulnerable to a disturbance of the nutrient balance because the slow decomposition rate. Although the nitrogen input is low, these results indicate that the response of nitrogen deposition on the C/N ratio may be more pronounced in areas with a climate favouring slow organic matter decomposition.

Table I 2-13. Average (avg.) proportion of the C/N ratio of the organic layer over the C/N ratio of the mineral surface layer; number (n) and percentage (%) of plots for which C/N ratio of the mineral surface layer exceeds that of the organic layer.

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	all plots
avg.	2.0	1.2	1.0	1.4	1.5	1.4	1.6	1.1	1.2	1.6	1.9	1.4	1.2	1.5	1.6	1.5	1.2	1.2	1.5	1.7	1.8	1.2	1.8	1.5
n	15	7	5	93	0	16	1	8	5	24	13	1	200	5	12	16	112	0	1	9	12	25	2	582
%	3%	23%	45%	24%	0%	25%	6%	32%	38%	16%	3%	25%	34%	4%	3%	15%	35%	0%	3%	12%	20%	26%	6%	17%

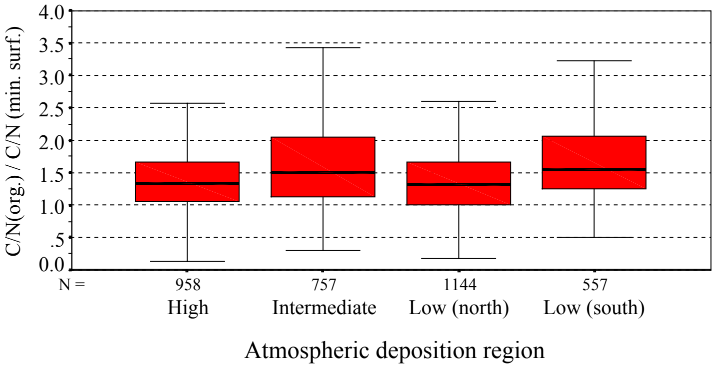


Figure I 2-31. Ratio of C/N of the organic layer over C/N of the mineral surface layer clustered by atmospheric deposition region.

2.5.3 Phosphorus

The availability of information on phosphorus is illustrated in Table I 2-14.

Table I 2-14. Phosphorus concentration (optional for mineral layers) - data availability (see also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	93	100	100	99	25	100	100	100	100	95	99	100	0	100	100	99	0	100	98	0	78	100	100	2539
Min. Layer	0	0	100	87	0	0	100	100	0	0	0	0	0	100	0	0	0	92	0	0	0	0	0	589
Analysis	N	R	N	N	N	N	N	R	N	R	N	R	X	N	N	R	X	N	R	X	R	R	N	11%

Phosphorus is an essential element for plant growth. The phosphorus present in the soil may be divided into (i) ions and compounds in the soil solution, (ii) phosphorus adsorbed on the surface of inorganic soil constituents, (iii) phosphorus minerals, and (iv) phosphorus as a component of soil organic matter (Barber, 1995). Organic matter is the principal source of phosphorus in many forest soils (Pritchett and Fisher, 1987). Phosphorus concentrations in soil solution are low, compared to nitrogen, potassium, calcium and magnesium. The most important phosphorus minerals in soils are calcium phosphates and iron and aluminium phosphates. In alkaline soils, calcium phosphate is dominant, while in acid soils iron and aluminium phosphates are the dominant forms. These forms are relatively insoluble, thus rendering the phosphorus unavailable for use by most plants.

Total phosphorus concentrations in organic layers vary between less than 50 mg kg^{-1} to more than 3000 mg kg^{-1}, but more than half of the reported values are within a narrow 500 - 1000 mg kg^{-1} range (Figure I 2-32). The values in the mineral soil are more equally distributed within a similar range of 50 to 3000 mg kg^{-1}. One half or more of the total phosphorus in the surface layer of soils may be present as organic phosphorus. Organic carbon content may explain about 15% of the variation of phosphorus concentration values in the surface layer (correlation coefficient of 0.39). The amount of phosphorus also depends on the degree of organic matter decomposition. As a consequence of organic matter decrease with soil depth, average P values decrease from 795 mg kg^{-1} in the organic layer to 453 and 391 mg kg^{-1} in mineral surface and subsurface layers, respectively.

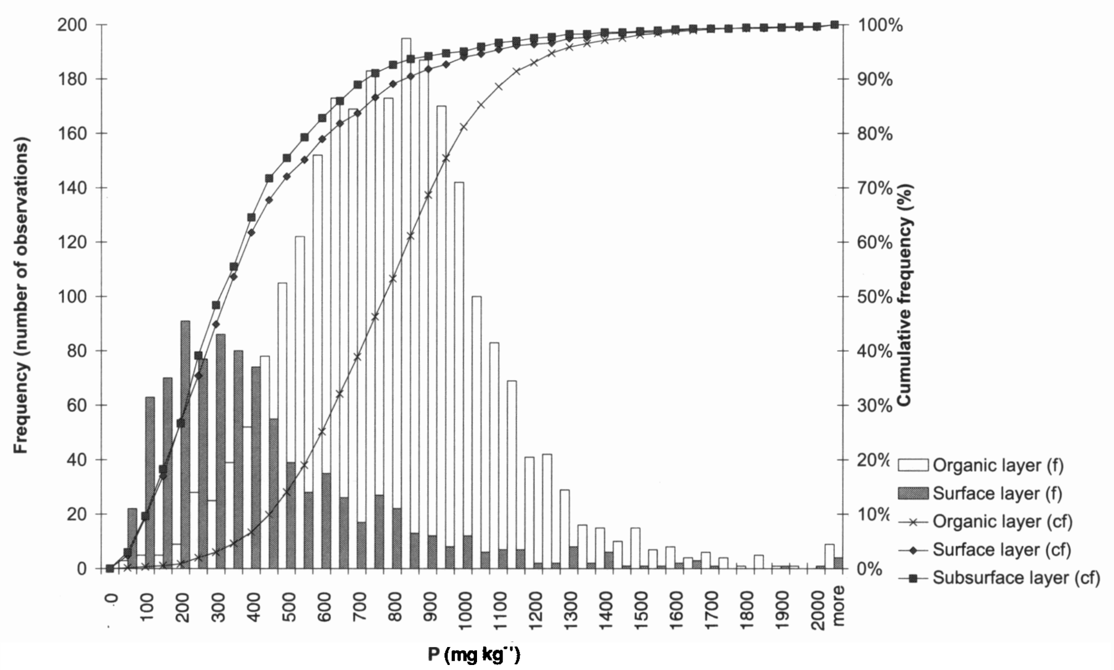


Figure I 2-32. **Frequency (f) and cumulative frequency (cf) distribution of phosphorus concentrations in organic and mineral layers.**

Soils with a fast decomposition rate of organic materials store low amounts of phosphorus in the organic layer, because phosphorus is mineralised soon after litter fall. The distribution of phosphorus concentration values in organic layers is similar for the major humus types (Figure I 2-33). However, mor, mull and moder humus types store different amounts of phosphorus, reflecting differences in decomposition rate. **A** total P pool of more than 1500 mg m^{-2} is observed in 23% of the mull layers. In plots having mor humus, this value is exceeded in 76% of the observations. Moder layers usually have intermediate total P concentrations.

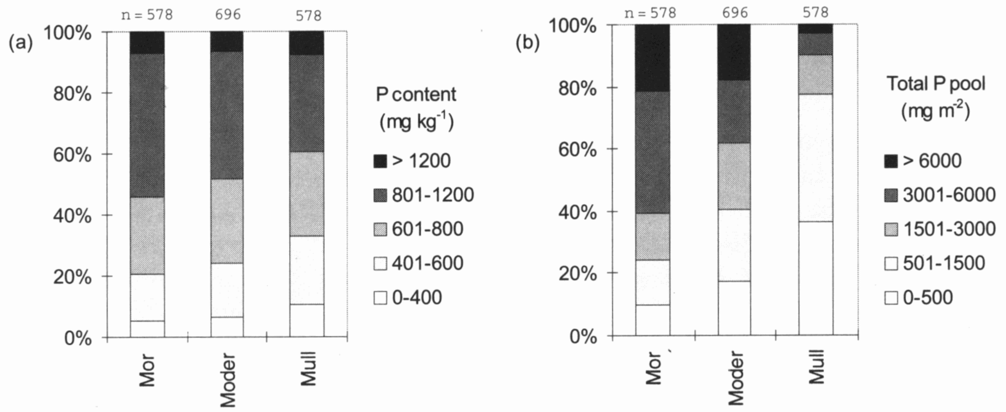


Figure I 2-33. **Differences in phosphorus concentration (a) and total phosphorus pool (b) in the organic layer between major humus types** (n = number of observations).

The overall symptom of phosphorus deficiency is retarded growth, rather than any striking foliar symptom. The majority of the phosphorus deficiencies occurs on poorly drained, acid sandy or loamy soils (Pritchett and Fisher, 1987). They contain very low concentrations of iron, aluminium and manganese; thus, most of the phosphorus has been leached to lower horizons. Much of the phosphorus leached from the surface of acid Podzols may be found as iron and aluminium phosphates in the Spodic horizon, where it may not be readily available.

The average P concentration of mineral surface layers of Gleyic Podzols (142 mg kg^{-1}) is distinctly lower than the overall average P concentration in these layers (453 mg kg^{-1}).

Phosphate-rich soils are often calcareous, due to the formation of crystalline calcium phosphate. Calcite surfaces are also able to adsorb phosphates specifically. Phosphate fixation is a well-known phenomenon associated with calcareous soils (Doner and Lynn, 1989). Consequently, soils with Calcic properties have a high average P concentration (632 mg kg^{-1}) in the mineral surface layer.

2.5.4 Potassium, Calcium and Magnesium

2.5.4.1 Potassium

The availability of information on potassium is illustrated in Table I 2-15.

Table I 2-15. **Potassium concentration (optional for mineral layers) - data availability** (*see* also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	93	100	100	99	25	100	100	100	100	95	99	100	0	100	100	99	0	100	98	0	78	100	100	2539
Min. Layer	0	0	100	39	0	0	100	100	0	0	0	0	0	100	0	100	0	92	0	0	0	0	0	501
Analysis	N	R	N	N	R	N	N	R	N	R	N	R	X	N	N	R	X	N	R	X	R	R	N	32%

Potassium is essential to many physiological functions and may be associated with the resistance of plants to certain diseases. Potassium is derived primarily from weathering of minerals such as feldspars and micas. A small portion is found as exchangeable ions' and an even smaller part may be present as a soluble salt (Pratt, 1965). A reasonable fraction of the aqua regia extracted potassium may be in non-exchangeable form. Non-exchangeable potassium is held between clay plates in positions that are not readily accessible for exchange with solution cations (Barber, 1995). Potassium present in silicate minerals may not be released during aqua regia extraction.

Potassium appears plentiful in most forest soils. It is rapidly and efficiently cycled in established forest stands. Concentrations of potassium vary from 100 to more than 25,000 mg kg^{-1} in organic layers (Figure I 2-34). However, half of the organic layers contain 1000 to 3000 mg kg^{-1} K. Mineral layer concentrations are more variable; values of less than 400 mg K kg^{-1} and values above 6,500 mg K kg^{-1} each represent approximately 10% of the plots.

Organic layer concentrations are largely determined by the contribution of mineral soil potassium. Organic soils are generally low in potassium, because of their low mineral contents (Barber, 1995). The median potassium concentration of the reported Histosols is 400 mg kg^{-1}. The influence of the mineral reserve of K on organic layer concentrations is further evidenced by a high correlation coefficient ($r = 0.59$) between organic layer and mineral layer K concentrations. Organic layer concentrations of K exceed those in the mineral surface layer in 46% of the plots for which both values are available. Most (61%) of these potassium accumulations in organic layers occur in soils that are relatively poor in potassium (K in mineral surface layer $<$ 1000 mg kg^{-1}).

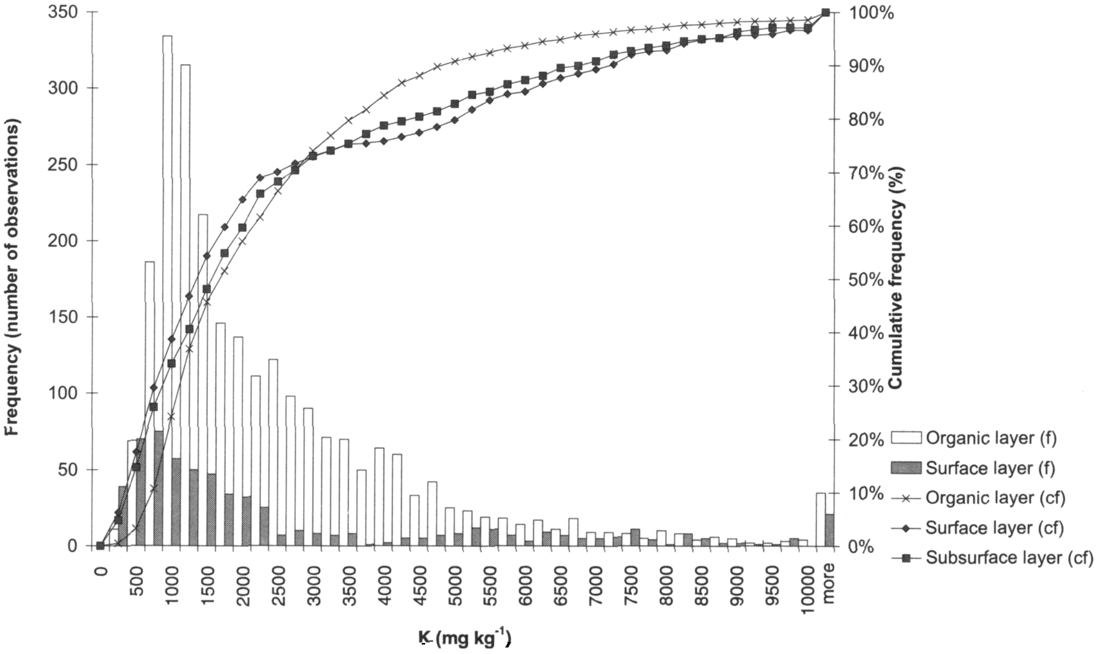


Figure I 2-34. **Frequency (f) and cumulative frequency (cf) distribution of potassium concentrations in organic and mineral layers.**

Deficiencies may occur in chemically poor acid sandy soils. Podzols and Arenosols have organic layers that are distinctly lower in potassium than soils in an early stage of weathering, such as Leptosols and Regosols. Median K amounts of the organic layer are: Podzols, 1000 mg kg^{-1}; Arenosols, 1200 mg kg^{-1}; Cambisols, 2000 mg kg^{-1}; Leptosols, 2300 mg kg^{-1}; and Regosols, 2900 mg kg^{-1}.

2.5.4.2 Calcium

The availability of information on calcium is illustrated in Table I 2-16.

Table I 2-16. **Calcium concentration (optional for mineral layers) - data availability** (see also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	92	100	100	99	25	100	100	100	100	95	99	100	0	100	100	99	0	100	98	0	70	100	100	2528
Min. Layer	0	0	100	38	0	0	100	100	0	0	0	0	0	100	0	100	0	92	0	0	0	0	0	498
Analysis	N	R	N	N	N	N	N	R	N	R	N	R	X	N	N	R	X	N	R	X	R	R	R	2%

Calcium is found in soils as cations and as a constituent of a variety of compounds (Heald, 1965). It exists in soils mostly in inorganic forms. Calcium-bearing minerals have varying degrees of solubility. Calcium sulphate and calcium carbonate are common soil minerals with high solubility. Gypsum (calcium sulphate) usually occurs only in arid soils (Barber, 1995). Most of the calcium held in silicate minerals will not be determined by the aqua regia method. The plant availability of calcium is mainly determined by the amounts of Ca^{2+}-ions held in exchangeable form.

The calcium content of a soil depends on its parent material and the degree of weathering and varies between wide limits (Figure I 2-35). Non-calcareous, coarse textured soils, such as Arenosols and Podzols, usually contain less than 2000 mg kg^{-1} calcium. Calcareous soils may have 50% or more calcium carbonate, so their calcium concentrations can be above 100,000 mg kg^{-1} (Barber, 1995).

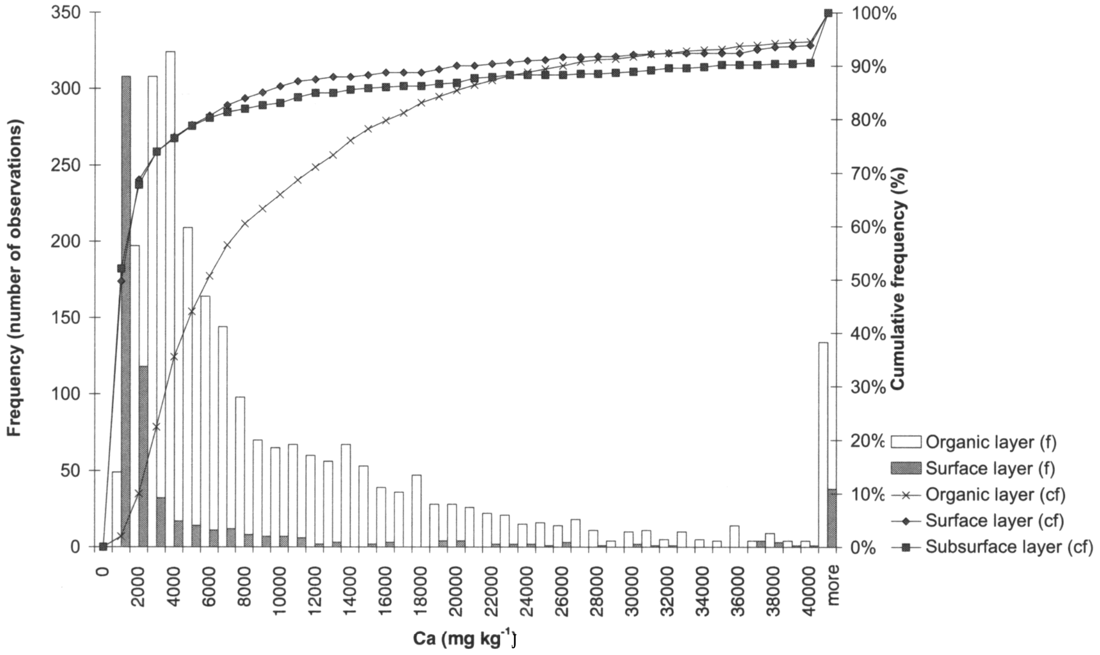


Figure I 2-35. Frequency (f) and cumulative frequency (cf) distribution of calcium concentrations in organic and mineral layers.

The calcium concentration of organic layers is mainly determined by the concentration in the underlying mineral soil, as evidenced by a highly significant correlation coefficient (r = 0.65) between organic and mineral subsurface layer concentrations. Median calcium concentrations in organic layers for different soils are: Leptosols, 18,000 mg kg^{-1}; Regosols, 13,000 mg kg^{-1}; Luvisols, 9000 mg kg^{-1}; Cambisols, 7000 mg kg^{-1}; Podzols, 3000 mg kg^{-1}; and Arenosols, 3000 mg kg^{-1} (Figure 12-36).

An adequate calcium supply is secured on soils with an appreciable cation exchange capacity (5 $cmol_{(+)}$ kg^{-1} and higher) and a pH-H_2O above 5.3 (Barber, 1995). The degree of growth restriction is related to the ratio of calcium to the other cations in solution. Leached acid soils are usually very low in calcium. Deficiency of calcium occurs in soils that are highly weathered, having a low pH and a low CEC (Barber, 1995).

Low levels of calcium can affect root growth (Barber, 1995). Roots only grow into soil where calcium is present. Deeper soil horizons normally contain more calcium than surface horizons. Deep-rooted trees with a high calcium requirement, tap calcium reserves in the subsoil and build up the concentration at the surface through annual leaf fall. This usually results in an accumulation of calcium in the organic layer: in 86% of the soils for which Ca concentrations are reported for both organic and mineral layers, the concentration in the organic layer exceeds that in the mineral layers. Although about 50% of the mineral surface layers contains less than 1000 mg kg^{-1} Ca, organic layers rarely (< 5%) contain such low Ca amounts. Soils having higher Ca concentrations in the mineral surface layer are almost exclusively calcareous soils.

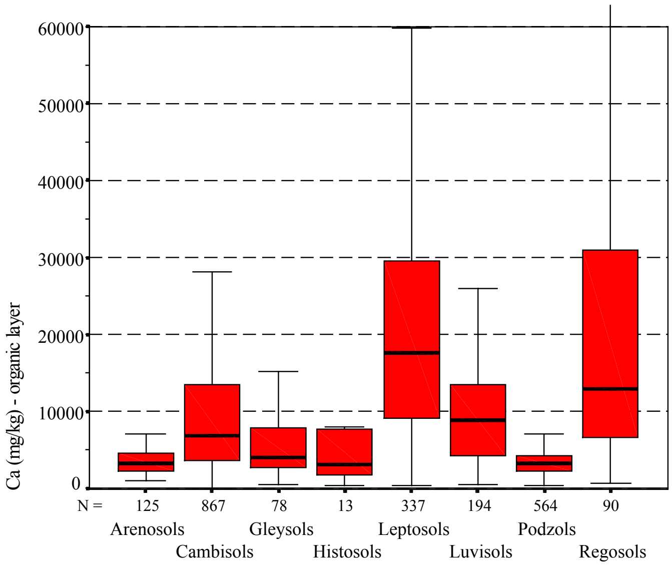


Figure I 2-36. **Distribution of calcium concentration values in the organic layer of major soil types.**

2.5.4.3 Magnesium

The availability of information on magnesium is illustrated in Table I 2-17.

Table I 2-17. **Magnesium concentration (optional for mineral layers) - data availability** (see also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	93	100	100	99	25	100	100	100	100	95	99	100	0	100	100	99	0	100	98	0	70	100	100	2532
Min. Layer	0	0	100	39	0	0	100	0	0	0	0	0	0	100	0	100	0	92	0	0	0	0	0	501
Analysis	N	R	N	N	R	N	N	R	N	R	N	R	X	N	N	R	X	N	R	X	R	R	R	4%

Magnesium is found in soils as exchangeable cations and as a constituent of organic litter and mineral compounds. The mineral compounds range from soluble forms such as magnesite and dolomite, to very insoluble primary and secondary minerals (Heald, 1965). Soils low in exchangeable magnesium are capable of releasing magnesium from non-exchangeable positions on magnesium-containing clay minerals (Barber, 1995).

Because of differences in weathering and parent materials, magnesium contents of soils vary widely (Barber, 1995). Total magnesium ranges from 100 to about 100,000 mg kg^{-1}, although about three quarter of the measured Mg concentrations in mineral layers are within 500 and 10,000 mg kg^{-1} (Figure I 2-37). The Mg concentration usually increases with increasing clay content.

Total magnesium in the organic layer shows less variability. Three quarters of the values vary from 500 and 4000 mg kg^{-1}. As with potassium and calcium, the magnesium concentration in the organic layer is strongly affected by the Mg content of the underlying mineral soil (r = 0.65). However, accumulations of Mg in organic layers, to such an extent that the organic layer concentration exceeds the concentration in the mineral surface layer, are less common than with K and Ca. They occur in 21% of the plots, most of which have low (< 1000 mg kg^{-1}) mineral Mg concentrations.

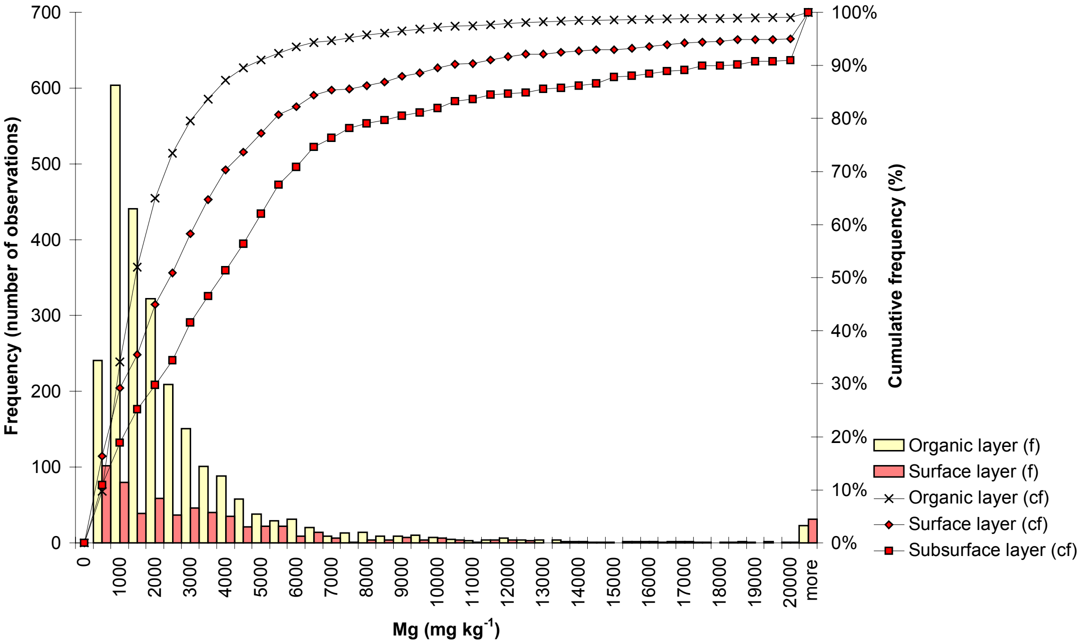


Figure I 2-37. **Frequency (f) and cumulative frequency (cf) distribution of magnesium concentrations in organic and mineral layers.**

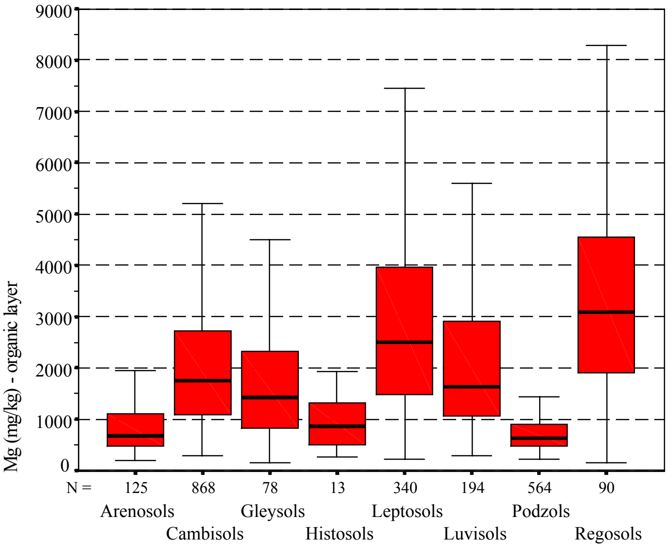


Figure I 2-38. **Distribution of magnesium concentration values in the organic layer of major soil types.**

Magnesium is essential to photosynthesis. The symptoms of magnesium deficiency often appear first on older leaves. Although most forest soils contain ample magnesium for good tree growth, deficiencies have been noted in young tree stands growing on sandy soils (Pritchett and Fisher, 1987). In the past decades, Mg deficiency has become a widespread phenomenon in acid forest soils exposed to high loads of acid deposition because of the depletion of exchangeable Mg (Ulrich, 1995). Podzols, Arenosols and Histosols are more likely to develop Mg deficiency than other soil types, as evidenced by their generally low Mg concentrations (< 1000 mg kg^{-1}) in the organic layer (Figure I 2-38). More than 75% of the Cambisols, Luvisols, Leptosols and Regosols have Mg concentrations in the organic layer that exceed 1000 mg kg^{-1}.

2.5.4.4 Influence of the Mineral Fraction

An appreciable portion of macronutrients, such as K, Ca and Mg, present in soils are trapped in the crystalline structure of minerals. These elements are released through mineral weathering. The chemical composition of a mineral plays a role in supplying nutrients, particularly in relation to the mineral's solubility and rate of solution (Barber, 1995). In highly weathered soils, the minerals remaining in the soil have very low solubilities and therefore constitute a poor source of nutrients.

Figure I 2-39 shows that weatherability of parent material influences the nutrient content of the forest floor material. Organic layers accumulate more Ca and Mg on soils derived from easily weatherable parent material. The average Ca concentration of organic layers of soils derived from very fast weathering carbonate rocks is more than 30,000 mg kg^{-1}, whereas organic layers overlying parent materials with an intermediate and slow weathering rate, have an average Ca concentration of 10,980 and 9860 mg kg^{-1}, respectively. A similar, though less clear trend is observed in the organic layer concentrations of Mg. Organic layers overlying carbonate rocks contain an average of 4275 mg kg^{-1} Mg, which is almost two times the average Mg concentration of organic layers of soils derived from slow weathering parent materials. The differences between average K concentrations of the weathering class clusters is almost negligible: 2680, 3000 and 3120 mg kg^{-1} K for slow, intermediate and very fast weathering materials, respectively. This observation can be explained by two processes that may act simultaneously:

- an increased plant uptake, and subsequent return by litter fall, of Ca and Mg in soils containing high amounts of these nutrients; and
- an increased biological activity in nutrient rich soils, resulting in the incorporation of mineral materials, rich in Ca and Mg, in the organic layer.

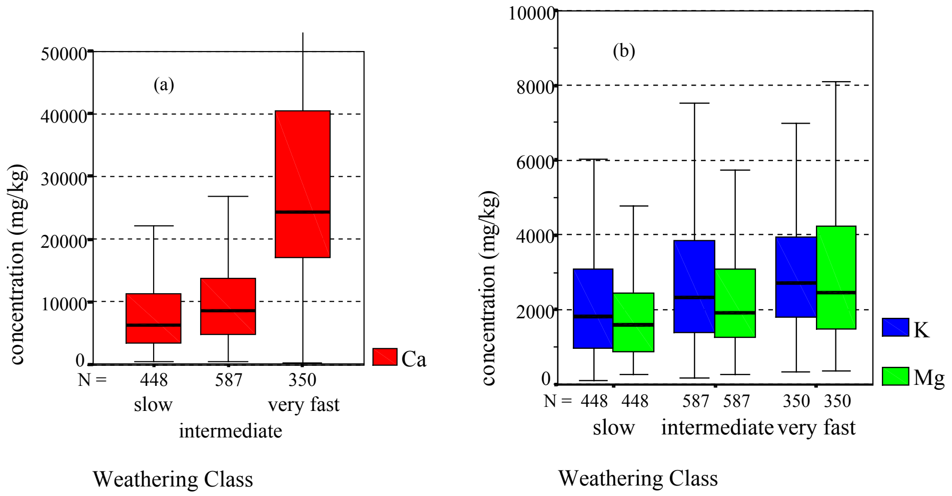


Figure I 2-39. Calcium (a), potassium and magnesium (b) concentration of organic layers of soils derived from slow, intermediate and very fast weathering parent materials.

Minerals constituting the sand and silt fraction of the mineral soil material are usually poorer in macronutrients than clay minerals. As a result, an increase in nutrient content of mineral layers is observed with increasing clay content (Figure I 2-40). The increase is significant for K, but is most pronounced for Ca and Mg concentrations. Median values of Ca and Mg concentrations in mineral surface layers for medium fine, fine or very fine are more than tenfold the median values for sandy materials, which is approximately 300 mg kg^{-1}.

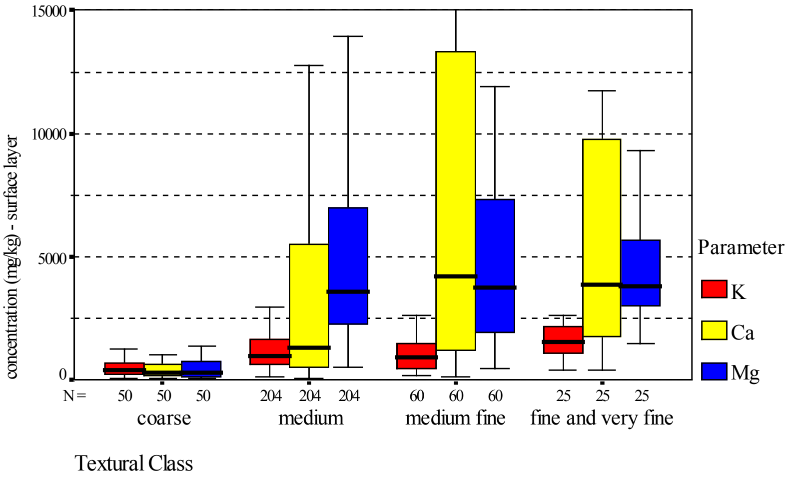


Figure I 2-40. Influence of texture on the macro-nutrient content (K, Ca and Mg) in mineral surface layers.

2.5.4.5 Relative concentrations of potassium, calcium and magnesium

The availability of potassium, calcium and magnesium for plant uptake is determined by many factors apart from their 'total' concentrations. One of the influencing factors is the degree of competition between cations for absorption. When several cations are present in available form, absorption of one ion may be influenced by the level of a second ion (Barber, 1995). For example, conditions which have been described as Mg deficiency are not always associated with extremely low Mg concentrations, but may result from the presence of relatively large quantities of other cations, especially Ca and K. Plant growth may be reduced when available Mg greatly exceeds Ca. The tendency for Mg deficiency increases with increasing content of available K (Heald, 1965).

The chemical composition of the soil organic layer varies widely and is in constant flux as micro-organisms break the organic matter down. Due to the presence of mineral materials, geological factors also affect the nutrient composition of the organic layer. Cationic nutrients are mainly held on cation exchange sites and are rapidly released from forest litter. Potassium is absorbed by tree roots in greater amounts than any other cation. Because it is rapidly cycled in forest ecosystems, its soil concentration is generally lower than that of calcium. Potassium is held less tightly than divalent calcium or magnesium, and magnesium is held less tightly than calcium. Calcium is the dominant exchangeable cation in most soils. The presence of Ca increases the uptake of many other cations (Barber, 1995). Exchangeable magnesium is usually the second most abundant cationic nutrient. Ideally, the exchangeable Ca concentration should be approximately two times that of Mg, which in turn should be double the concentration of K. This reflects the variation in the degree of dissociation of the three cations in soils (Barber, 1995).

Table I 2-18. Average relative concentrations (in %) of Ca, Mg and K in organic layers of major humus types.

Humus Type	Ca	Mg	K	Total
Peat	50	21	29	100
Mor	62	15	24	100
Moder	62	16	21	100
Mull	69	14	17	100

The average relative concentrations of the dominant cations in the organic layer are Ca: 64%, Mg: 15%, and K: 21%. The degree of decomposition mostly influences the relative concentration of Ca and K. Humus types rich in undecomposed materials, such as peat, have less Ca and more K compared to the strongly decomposed mull layers (Table I 2-18).

During mineralisation of organic materials, potassium is released in soil solution, where it is readily available for plant uptake and leaching processes. Fast decomposition results in a quick removal of K from the organic layer. Frequently observed humus types (moder, mor and mull) can often be differentiated by the fraction of K in the total cationic nutrient content of the organic layer. As a result of a generally slow decomposition rate, mor layers usually contain significant amounts of K. Highly decomposed organic layers may have higher nutrient concentrations, but are relatively low in K, because this element has been preferentially leached out. The majority (71%) of the mull layers has a K concentration, which is at least 4 times smaller than the sum of Ca and Mg (Figure I 2-41).

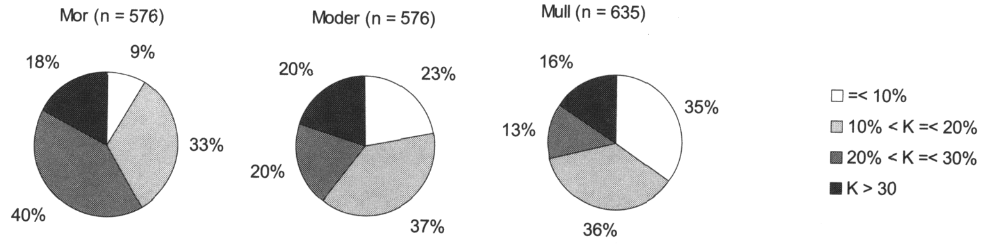


Figure I 2-41. Relative concentrations of K (as a fraction of the sum of Ca, Mg and K) in major humus types (n = number of observations).

Plant uptake of Ca and Mg is less dependent of organic matter decomposition and these elements are also more strongly retained by negatively charged surfaces. In contrast with potassium, their relative concentrations are not so much determined by the degree of organic matter decomposition. Organic layers with unusually low relative concentrations of Mg and particularly Ca are more equally spread between different humus types (Figure **I** 2-42).

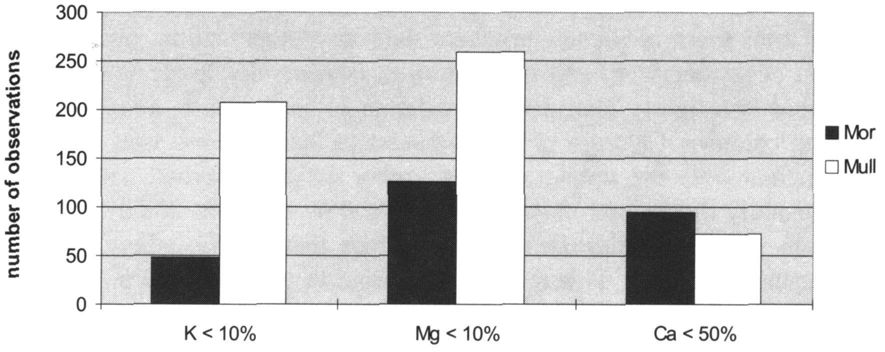


Figure I 2-42. Relative frequency of occurrence of unusually low relative concentrations of K, Mg and Ca in mull and mor humus types (K < **10%** occurs in 22% of the **plots, Mg** < 10% in 30% of the **plots, Ca <** ***50%*** in 18% of the plots).

It should be mentioned that the above comments on the relative concentrations of K, Ca and Mg are based on measured values that may have a high analytically caused variation and need to be confirmed by other studies, e.g. correlative studies between chemical composition of leaves/needles and soil.

2.6 Calcium Carbonate

Inorganic carbon occurs in soils commonly as carbonate minerals, calcite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$] and magnesian calcites ($Ca_{1-x}Mg_xCO_3$). Other less common forms are aragonite ($CaCO_3$) and siderite ($FeCO_3$). All of these minerals have a moderate solubility in H_2O, which allows them to weather readily (Doner and Lynn, 1989).

Carbonates within the top 20 cm of mineral soil are reported in about 14% of the plots. Carbonate in soils can be of primary (inherited from parent material) or secondary (pedogenic) origin. Secondary carbonates are usually aggregates of silt- and clay-sized calcite crystals, while large crystals of calcite or dolomite are of primary origin (Tee Boon Goh et al., 1993). When secondary carbonates precipitate as coatings in the soil matrix, it may clog pores and restrict penetration of roots. Generally, the coarser the particle size of the soil constituents, the less carbonates are required to form a cemented layer.

The highest reported carbonate contents of mineral surface and subsurface layers are 928 and 976 g kg^{-1}, respectively. Carbonates may make up more than 90% of the soil mass in calcretes, i.e. subsurface horizons cemented by calcite accumulation (Allen and Hajek, 1989). About one third of the calcareous soils contains at least 200 g kg^{-1} carbonates in both surface and subsurface layers. This proofs that certain trees can grow in conditions where the mineral soil consists mainly, up to 90% and more, of carbonate minerals. The carbonate content of calcareous soils usually increases with depth (Figure I 2-43): 44% of the surface layers of calcareous soils have 20 g kg^{-1} carbonates or less, but only 27% of the subsurface layers.

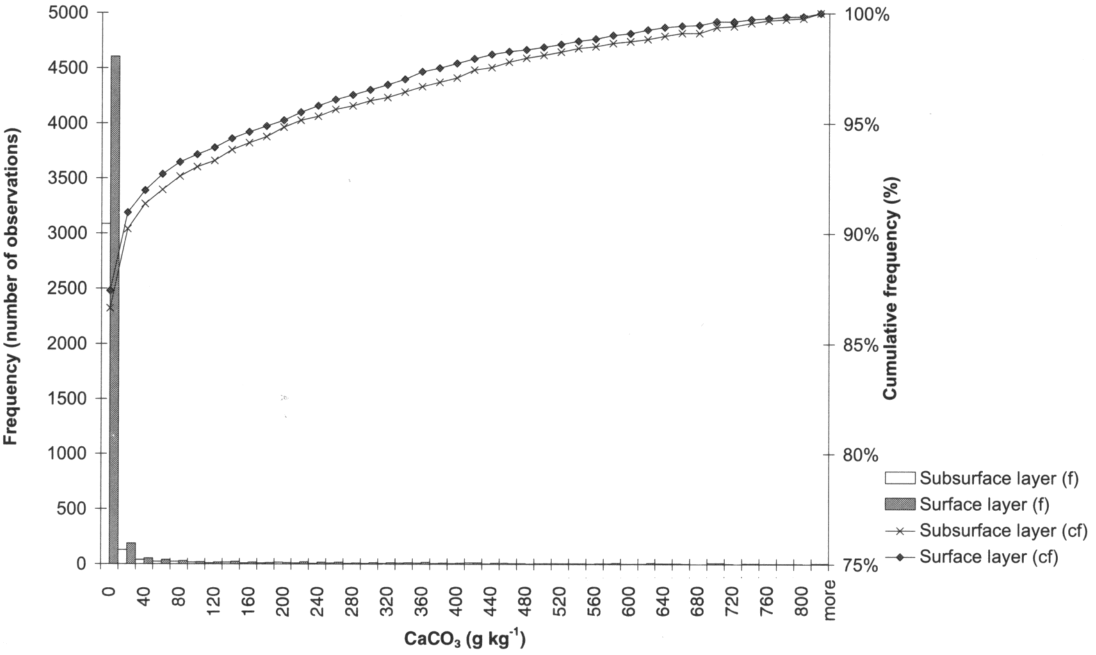


Figure I 2-43. Frequency *(f)* and cumulative frequency (cf) distribution of calcium carbonate concentrations in mineral layers.

The occurrence of carbonates in soils depends primarily on the nature of the parent material. The majority (77%) of the calcareous soils, having carbonates within the upper 20 cm of the soil, have carbonate rocks as parent material. The persistence and distribution of carbonates further depend on the leaching conditions. In dry climates, carbonates remain in the soil; secondary carbonates may accumulate near the surface. Most calcareous soils formed on carbonate-free parent materials, i.e. having secondary carbonates, are found in southern or continental Europe. About half of the calcareous plots occur in the Mediterranean region, partly because carbonate rocks are a common rock type in this region and partly because climatic conditions prevent the removal of carbonates from the topsoil. The same area covers only 15% of the non-calcareous soils.

If other factors are constant, increased rainfall means removal of carbonates from upper layers and redeposition in deeper layers or removal from the soil. All topsoils of the plots in high-leaching areas, such as the Boreal, temperate Boreal and the northern Mountain regions, are carbonate-free. In environments with great effective leaching, residual profiles over limestone are acid with an abrupt contact between parent rock and soil. Most of the plots on carbonate rocks that are leached free of carbonates, are located in northern Europe,

The average carbonate content of calcareous soils differs between climatic regions (Figure I 2-44). Carbonate contents usually exceed 200 g kg^{-1} in the Mediterranean region, but are mostly less than 100 g kg^{-1} in the moister Atlantic regions. All plots, except 2, with more than 50% (500 g kg^{-1}) carbonates in their mineral surface layer are located in three climatic regions: Mediterranean (higher), Mediterranean (lower) and Mountainous (south).

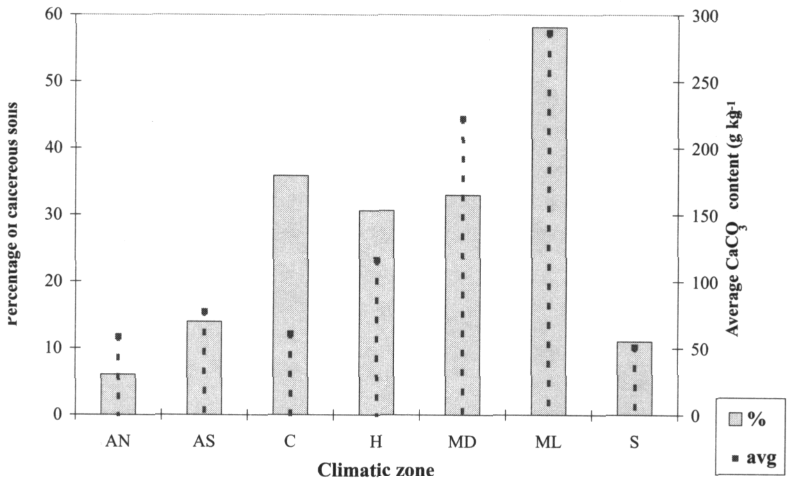


Figure I 2-44. Occurrence and distribution of carbonates in different climatic regions.

Soil carbonates constitute an important buffering power against acidification. In the presence of insoluble carbonates, the pH is buffered between pH 8.0 and 6.8 (De Coninck and Van Ranst, 1993). Addition of acids in calcareous soils will lead to a pH decrease, only after the carbonate reserve has been depleted. Soils with high carbonate content are very tolerant to acid deposition. Unfortunately, calcareous soils represent only 10% of the plots located in the region that receives a high or medium atmospheric deposition load (Figure 12-45). Moreover, 22% of the calcareous soils in this region is already leached free of carbonates in the surface layer, having carbonates only in their subsurface layers. Buffering against deposited acids must be provided by soil constituents different from carbonates in the majority of forest soils in the high deposition region. Southern Europe, having a lower load of acidity, on the other hand, is much better armed against acidification processes. About half of the soil plots in this area has enough carbonates (> 200 g kg^{-1}) to buffer acid input almost indefinitely.

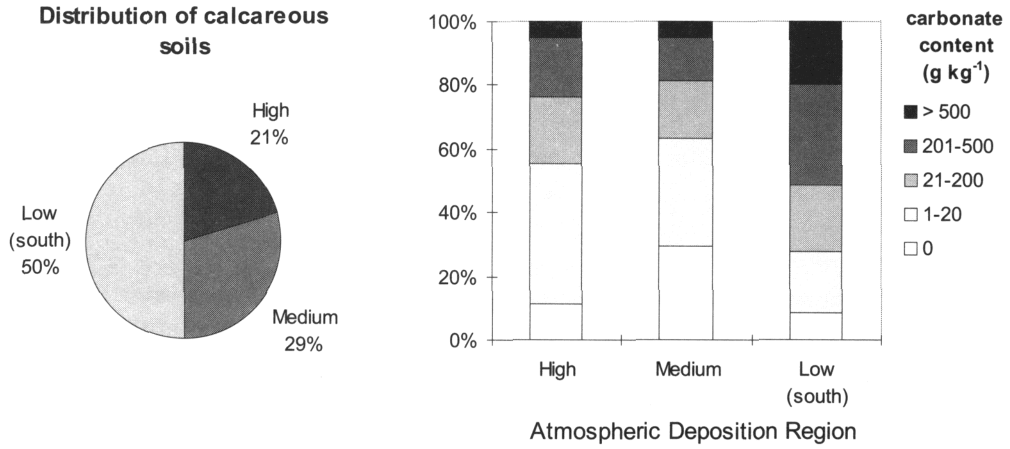


Figure I 2-45. Distribution of calcareous soils (= soils with carbonates in at least one sublayer within 20 cm depth) over atmospheric deposition regions and their carbonate content in the mineral surface layer.

2.7 Cation Exchange Properties

Negatively charged colloids, such as clay minerals and organic compounds, can absorb cations and retain them in an exchangeable form. Exchangeable cations normally associated with negatively charged colloids are Al^{+3}, Ca^{+2}, Mg^{+2}, H^+, K, Na^+ and NH_4^+ (Bain and Smith, 1987). However, heavy metal cations also take part in exchange reactions with negatively charged surfaces (Jones and Jarvis, 1981).

Negative charges resulting of atomic substitution in the lattice of soil minerals are known as permanent charge, and are independent of conditions such as pH and ion activity. When the negative charges result of hydrolysis reactions on broken edges of the lattices and the surfaces of oxides, hydroxides, hydrous oxides and organic matter, they are dependant of pH and ionic strength (Hendershot et al., 1993).

Ion exchange reactions in soils are important as a source of nutrients for plant growth (Hall, 1987). This particularly applies to exchangeable Ca, Mg and K. Ion exchange processes also play a role in the immobilisation of undesirable cations such as heavy metals and organic pesticides.

2.7.1 Cation Exchange Capacity

The availability of information on cation exchange capacity (CEC) is illustrated in Table I 2-19.

Table 12-19. Cation exchange capacity (optional parameter) - data availability (see **also** Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	0	0	100	0	0	0	0	0	0	0	0	0	41	0	100	0	0	100	0	0	0	0	0	893
Min. Layer	100	32	100	97	0	0	0	0	0	95	0	100	46	99	100	100	99	92	72	100	0	0	100	2817
Analysis	N	R	N	N	X	X	X	X	X	R	X	R	N	N	R	R	N	N	R	N	X	X	R	8%

The extent to which the negatively charged colloids can retain cations in the soil is expressed by its CEC. In situations where agricultural practices have significantly changed the soil pH or Ca concentration, CEC is commonly measured using the ammonium acetate method buffered at pH 7. Studies of soils with pH-variable charge properties should not employ buffered methods for 'potential' CEC determination, but methods that simulate field conditions of pH and ionic strength (Hendershot and Duquette, 1986). Unbuffered 'effective'

CEC methods, such as the 0.1M $BaCl_2$ method, that determine the CEC at soil pH, are recommended in research on acid forest soils (Hendershot et al., 1993).

The CEC varies among the different kinds of negatively charged colloids in the soil, mainly clay and organic matter. The CEC of clay minerals is mainly determined by the extent of isomorphous substitution of cations in the lattice by cations of lower charge (Hall, 1987). The functional groups on humic materials are responsible for the high CEC values and metal-complexing properties of soil organic matter. The CEC depends on dissociation of H from -COOH and -OH groups and is markedly pH-dependent, possibly increasing several times from pH 3 to 10 (Oades, 1989). The cation exchange capacity of organic matter can be up to thirty times as great as'mineral colloids. The CEC of the soil is a function of the content and nature of charged colloids, mineral and organic, in the soil. It may vary from 0.1 to 100 cmol(+) kg^{-1} soil (Figure I 2-46). Because soil organic matter usually increases towards the soil surface, the CEC of surface layers is somewhat higher than that of subsurface layers. Exactly 80% of the reported CEC values of subsurface layers are within 1.1 and 21.4 cmol(+) kg^{-1} soil, whereas 10- and 90-percentile values of surface layers are 1.9 and 28.4 cmol(+) kg^{-1} soil, respectively.

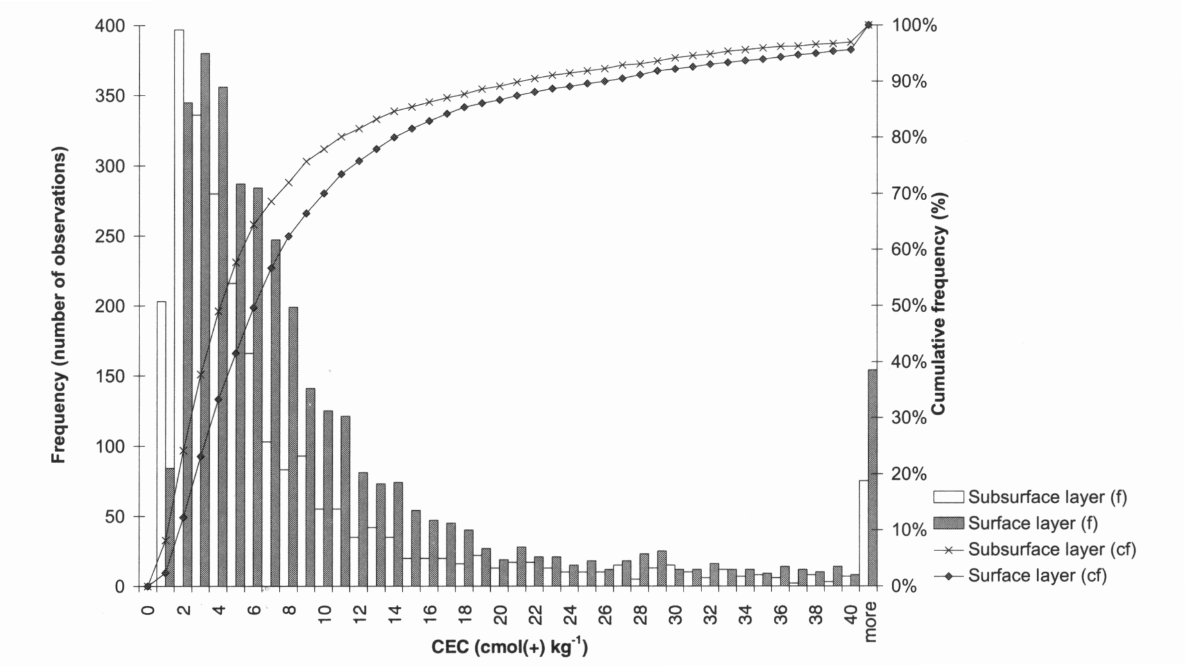


Figure I 2-46. Frequency (f) and cumulative frequency (cf) distribution of CEC values of mineral layers.

CEC is often used in soil classification systems to differentiate nutrient holding capacities between soil types. In general, soils in a recent stage of weathering have high CEC values, because their clay minerals are dominantly 2:1 minerals. Oxides and hydroxides of iron and aluminium and 1:1 clay minerals, which have low CEC values, dominate in soils in an advanced stage of weathering. For example, the distinction between Luvisols and Lixisols is based on the difference in cation exchange capacity. In Europe, strongly weathered soils are not common. Forest soils in a recent stage of development are usually characterised by relatively high CEC values (Figure I 2-47). Half of the Leptosols has a CEC value of more than 20 cmol(+) kg^{-1} soil in their subsurface horizon. Cambisols and Luvisols are somewhat further in the soil evolution sequence and have a median CEC value in the same layer of approximately 5 cmol(+) kg^{-1} soil. Values are even lower for soil types characteristically low in clay, such as Podzols and Arenosols.

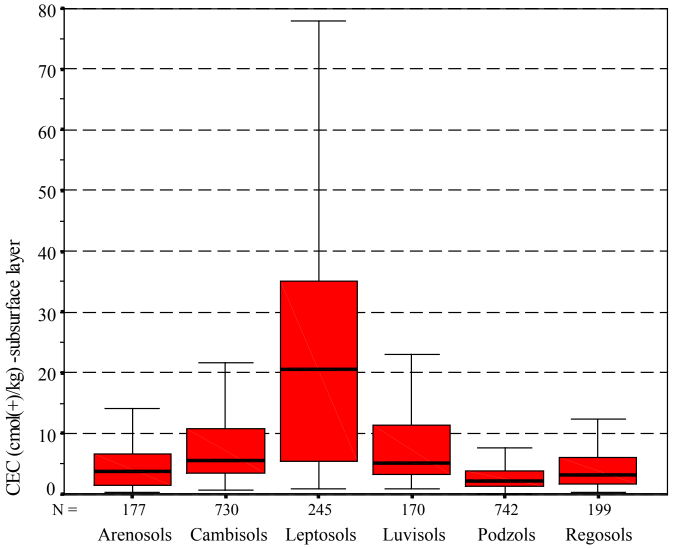


Figure I 2-47. Distribution of mineral subsurface CEC values for the major soil types.

Soil texture largely determines CEC in deeper, organic matter poor, soil horizons. Figure I 2-48 shows that subsurface layers with a fine or very fine texture mostly have a CEC above 10 cmol(+) kg^{-1} soil, whereas the majority of coarse textured subsurface layers have a CEC below this value. The CEC of medium and medium fine textured soils vary within a wide range.

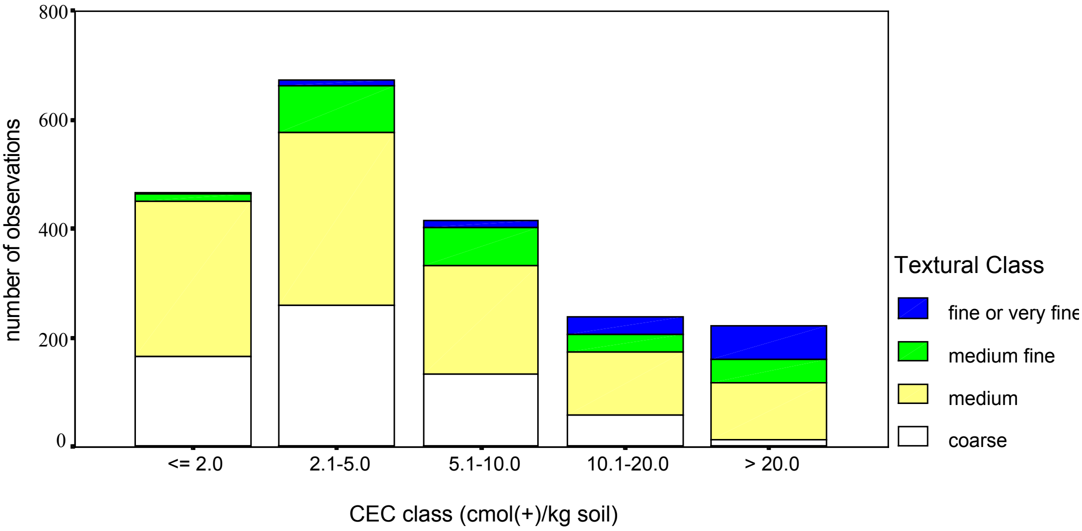


Figure I 2-48. Effect of soil texture on CEC values in the subsurface mineral layer.

In soils low in clay, the majority of the cation exchange sites are due to organic colloids. Figure I 2-49a illustrates the effect of pH on CEC of coarse textured mineral layers, where organic exchange sites dominate. The CEC of sandy surface layers, rich in organic matter (50 g kg^{-1} < Org. C ≤ 100 g kg^{-1}), remains low at pH values below 5.0, but increases manifold with decreasing acidity above pH 5.0. Although the potential effect of a pH change on the CEC may be more pronounced than the effect of organic matter content (Oades, 1989), the latter has more practical consequences, because high pH rarely occurs in coarse textured forest soils. Figure I 2-49b shows that the average CEC of acid (3.2 < pH ≤ 4.0) soils also increases several times with increasing Org. C content, but the number of sandy soils in this pH range is much larger than the number of soils with pH above pH 5.0.

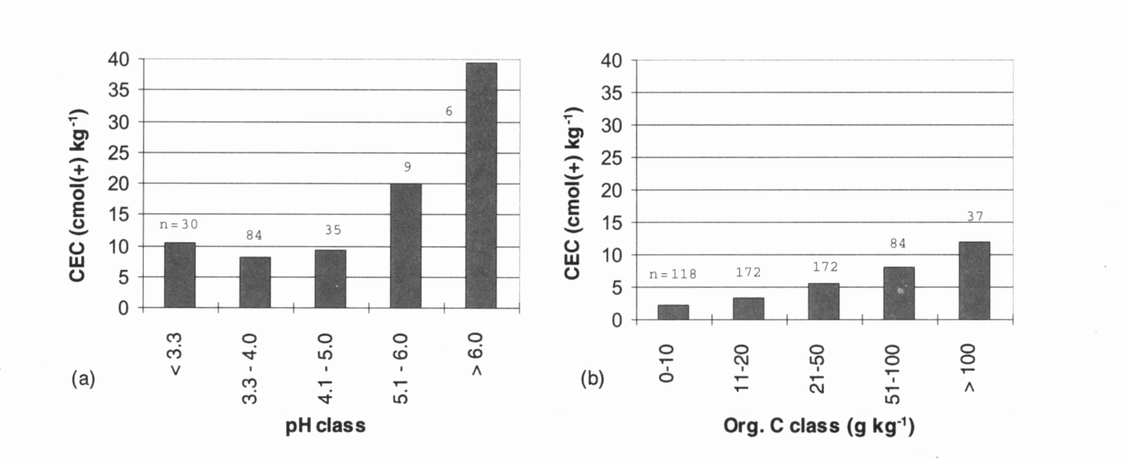


Figure I 2-49. **Effect of pH (a) and organic carbon content (b) on average CEC values of coarse textured mineral surface layers;** (a) organic carbon **is** between 50 and 100 mg kg^{-1}; (b) pH is between **3.2** and 4.0; n = number of observations.

2.7.2 Exchangeable Basic Cations

The availability of information on the sum of exchangeable basic cations (BCE) is illustrated in Table 12-20.

Table 12-20. **Sum of exchangeable basic cations (optional parameter) - data availability** (see also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	0	0	100	0	0	0	0	0	0	0	0	0	41	0	100	0	0	100	0	0	0	0	0	893
Min. Layer	100	32	100	97	0	0	0	0	0	95	0	100	46	99	100	100	99	92	72	100	0	0	100	2817
Analysis	N	R	N	N	X	X	X	X	X	R	X	R	N	R	R	R	N	N	R	R	X	X	R	3%

Calcium is the dominant exchangeable basic cation in most soils. Exchangeable magnesium is almost always present in smaller quantities than calcium, though on serpentine-derived soils, magnesium may be the dominant exchangeable cation (Barber, 1995). Potassium usually comes in third place but may be exceeded by the amount of exchangeable sodium in neutral and alkaline soils. The BCE may be as high as 100 cmol(+) kg^{-1} soil in clayey soils, having mostly smectitic clays, but **is** generally (about 90% of the plots) less than 20 cmol(+) kg^{-1} soil in subsurface and 25 cmol(+) kg^{-1} soil in surface layers (Figure I 2-51). Because many forest soils are acid, having a cation exchange complex with dominantly acid cations, BCE values are often very low; more than 50% of the forest soils have a BCE of less than 1 cmol(+) kg^{-1} soil in the subsurface layer.

Soil buffering processes against acidification result in the removal of base cations from exchange sites on humic compounds and clay minerals. Base cation loss does not necessarily result in diminished biomass growth. In fact, the opposite, i.e. a simultaneous tree growth increase and base cation loss, has been recently observed in Scandinavian countries (Olsson, 1994). The most probable explanation for this observation is a successful forest management with the support from atmospheric nitrogen deposition. In areas with relatively low N deposition, the decrease in base cation pools may not yet affect production, because they are still in excess in comparison to other growth limiting factors such as N (Ulrich, 1995), especially when there is also a relatively large input of basic cations from the atmosphere. In areas receiving high inputs of both N and **S,** such as the Netherlands and parts of Germany, deficiencies of basic cations are very relevant due to their replacement with e.g. Al and NH_4 on the exchange complex (Roelofs et al., 1985, de Vries and Leeters, 1995).

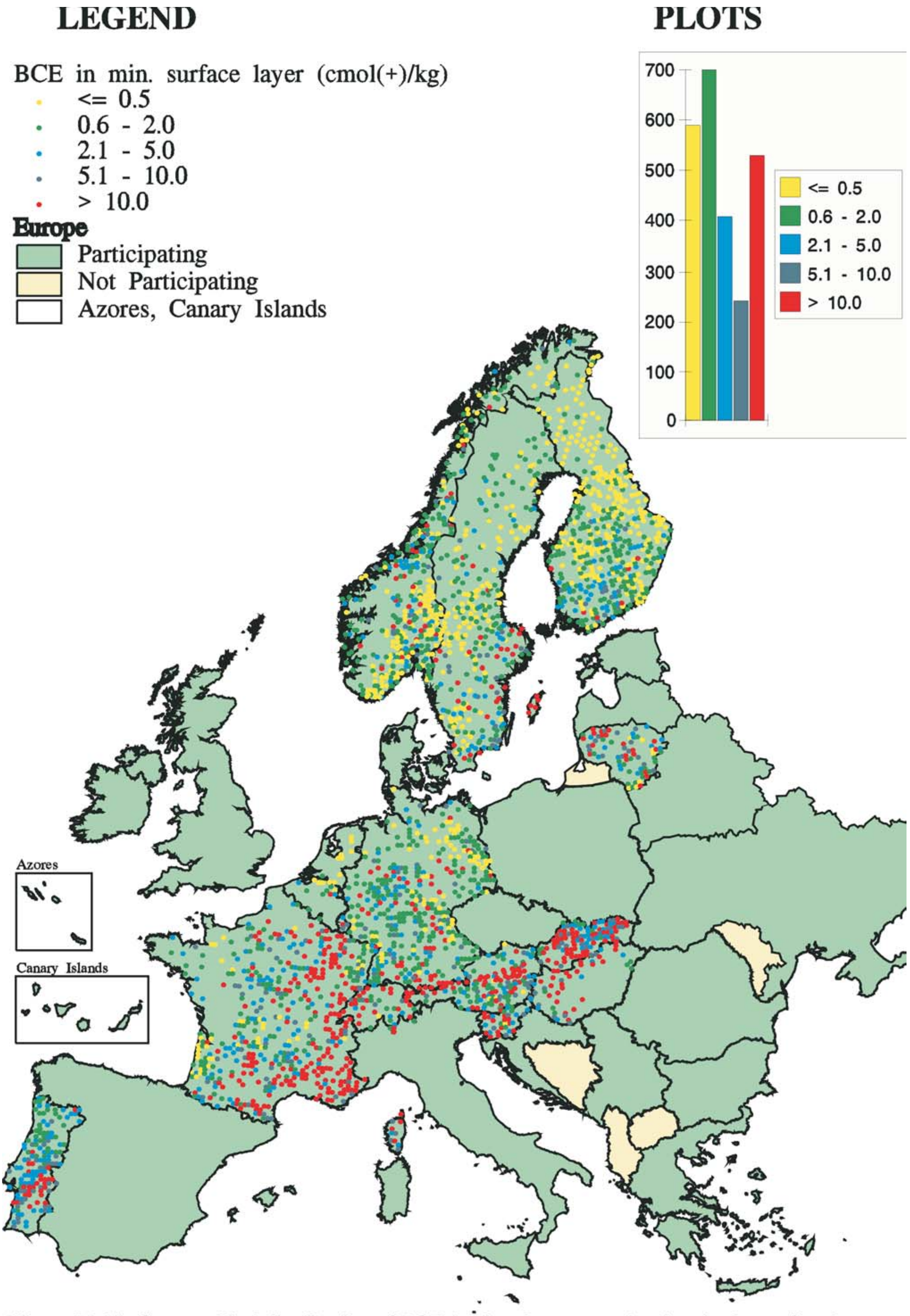


Figure I 2-50. Geographical distribution of BCE (optional parameter) values in the surface layer. The Relative Interlaboratory Variation (V) of BCE values is estimated at 3%.

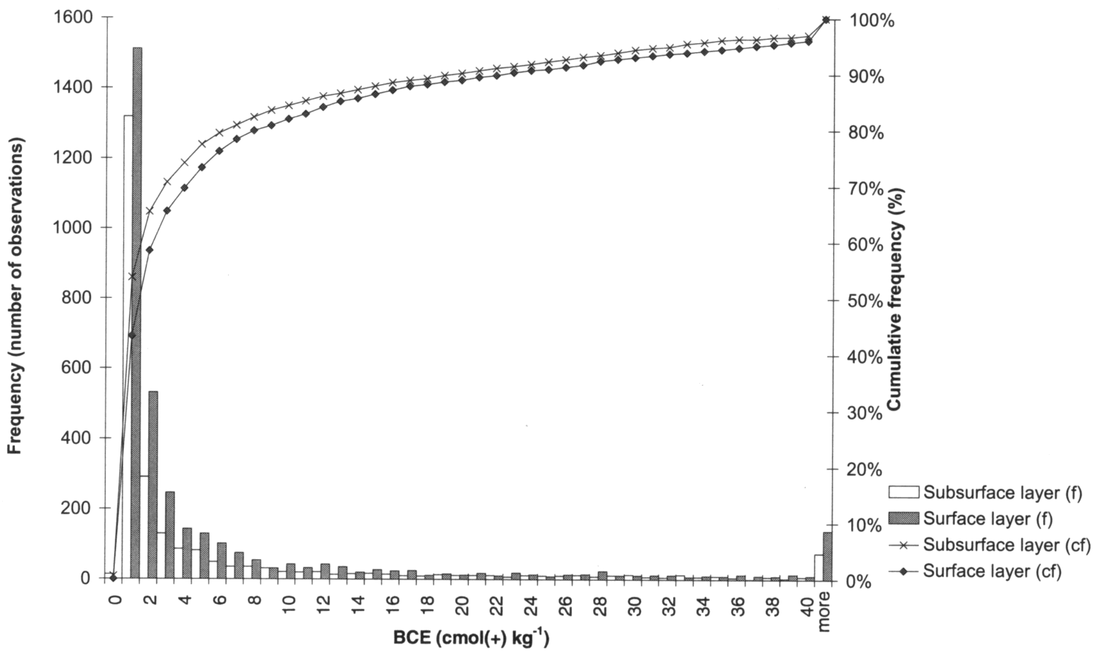


Figure I 2-51. Frequency (f) and cumulative frequency (cf) distribution of BCE values of mineral layers.

However, as leaching of acid soils proceeds, the proportion of exchangeable aluminium and hydrogen ions on clay and humus increases, and the proportion of exchangeable calcium, magnesium and potassium decreases. This not only reduces the availability of these important nutrients, but it also produces soil solutions high in aluminium that may stunt roots or impair their physiological functioning. Especially Al and to a lesser extend Fe and Mn ions in soil solution are the major cause of biological harm due to acidity (e.g. Sverdrup and Warfvinge, 1993). The sum of basic cations is a measure for the buffering capacity of carbonate-free soils, where cation exchange is the main buffering process. Figure I 2-50 shows an overall north-south decrease of surface layer BCE values, locating the most sensitive soils to acidification in northern Europe.

The loss of base cations is somewhat counteracted by the deposition of Ca^{+2} and Mg^{+2}. In acidified forest soils with low CEC and base saturation, the Ca^{+2} deposition adds significantly to the Ca^{+2} turnover within the ecosystem (Matzner and Murach, 1996).

2.7.3 Exchangeable Acid Cations and Exchangeable Acidity

The availability of information on the sum of exchangeable acid cations (ACE) and on exchangeable acidity (AcExc) is illustrated in Table I 2-21.

Table I 2-21. Sum of exchangeable acid cations and exchangeable acidity (optional parameters) - data availability (see also Figure I 2-1 for interpretation).

ACE	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	0	0	100	0	0	0	0	0	0	0	0	0	0	0	100	0	0	100	0	0	0	0	0	452
Min. Layer	100	0	100	97	0	0	0	0	0	0	0	0	0	99	100	100	0	92	72	0	0	0	100	1736
Analysis	N	X	N	N	X	X	X	X	X	X	X	X	X	R	R	R	X	N	R	X	X	X	R	31%

AcExc	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	0	0	0	0	0	0	0	0	0	0	0	0	41	0	100	100	0	0	0	0	0	0	0	985
Min. Layer	93	32	0	0	0	0	0	0	0	95	0	100	46	0	100	100	99	0	0	100	0	0	100	2171
Analysis	N	R	X	N	X	X	X	X	X	R	X	R	N	X	R	R	N	X	X	R	X	X	R	18%

In addition to basic cations (Ca, Mg, K and Na), there is also an amount of acid cations that can be displaced from the exchange complex of a soil. The amount of this acidity is largely a function of soil pH and the exchange capacity. In most soils, the AcExc is composed of (i) exchangeable H^+, (ii) exchangeable Al as either Al^{3+} or partially neutralised Al-OH compounds such as $AlOH^{2+}$ or $Al(OH)_2^+$, and (iii) weak organic acids (Hendershot et al., 1993). Many experiments have shown the toxic effect of Al^{+3} and H^+ ions on root growth and their antagonistic effects on cation uptake (Ulrich, 1995). Acid forest soils contain large amounts of hydrogen and aluminium in exchangeable form. The ACE largely consists of exchangeable Al compounds and protons, but considerable amounts of exchangeable Fe may be important in some very acid forest soils.

Neutral and alkaline soils have an exchange complex fully saturated with basic cations. More than 10% of the forest soils have ACE or AcExc values equal to 0; these soils are mostly calcareous soils. Acid cations occupy the majority of exchange sites in acid soils. Acid soils rich in negatively charged colloids may have ACE or AcExc values of more than 50 cmol(+) kg^{-1} soil, but the majority of forest soils has values varying from 0.5 to 5 cmol(+) kg^{-1} soil, with slightly higher values in the mineral surface layer (Figure 12-52).

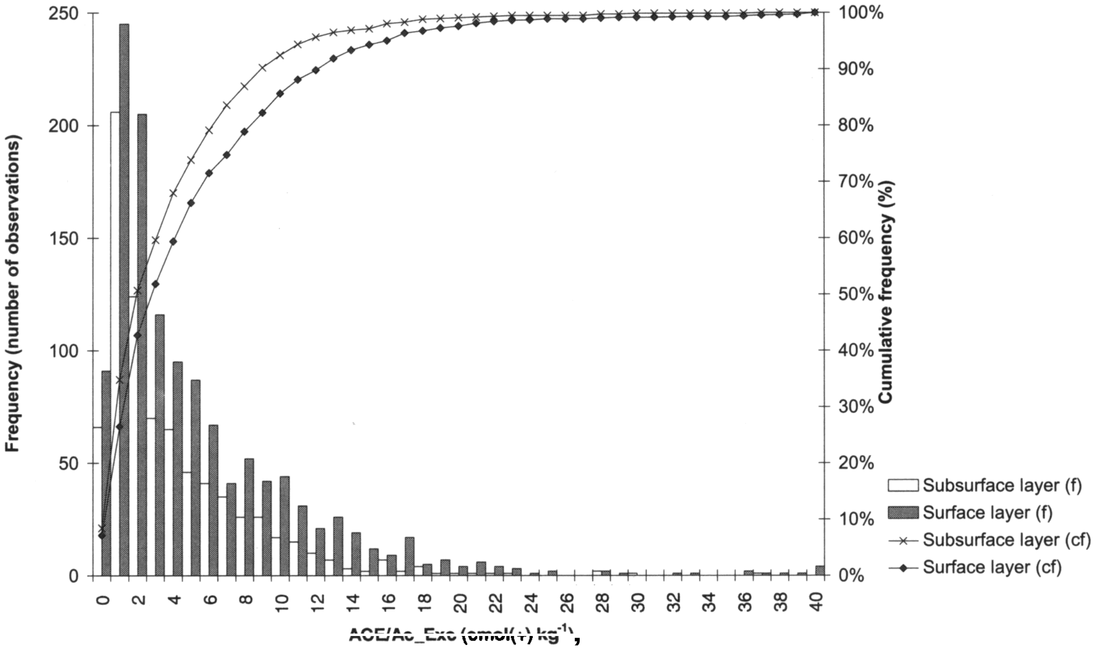


Figure I 2-52. Frequency (f) and cumulative frequency (cf) distribution of ACE and AcExc values of mineral layers.

2.7.4 Base Saturation

The availability of information on base saturation is illustrated in Table I 2-22.

Table I 2-22. Base saturation (optional parameter) - data availability (see also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	0	0	100	0	0	0	0	0	0	0	0	0	41	0	100	0	0	100	0	0	0	0	0	893
Min. Layer	100	32	100	100	0	0	0	0	0	95	0	100	46	99	100	100	99	92	72	100	0	0	100	2828
Analysis	N	R	N	N	X	X	X	X	X	R	X	R	N	N	R	R	N	N	R	N	X	X	R	4%

Many forest soils possess a very low degree of base saturation. About 25% of the forest soils in Europe has a mineral topsoil in which basic cations occupy only 15% or less of the cation exchange sites (Figure 12-53). At base saturation < 15%, protons and acid cations, mainly aluminium, are released in the soil solution, resulting in a continuous acid stress to roots and soil organisms (Ulrich, 1995). Similar to pH, the frequency distribution of base saturation values is bimodal, showing a second peak at the saturated end of the value range. In neutral and alkaline soils, the exchange complex is completely saturated with basic cations.

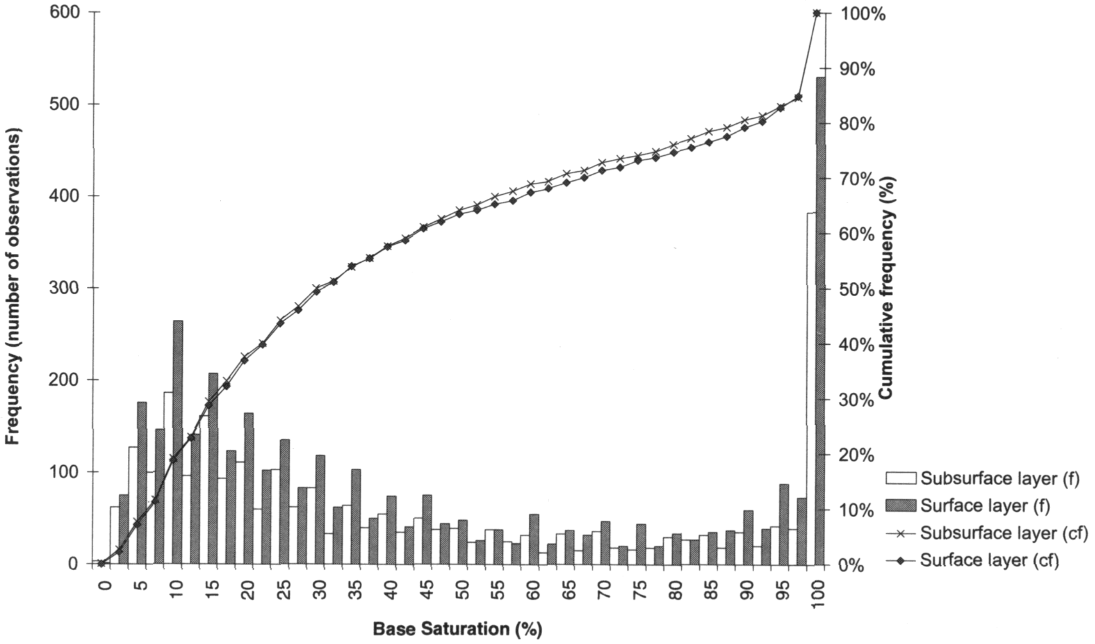


Figure I 2-53. **Frequency (f) and cumulative frequency (cf) distribution of base saturation values of mineral layers.**

Table I 2-23. **Percentile values of base saturation in subsurface layers of soils with Calcic, Leptic, Spodic and Albic properties as compared to the overall distribution.**

Plots grouped by soil properties	**Percentile values (base saturation in %)**				
	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile
Calcic	99	100	100	100	100
Leptic	25	77	100	100	100
Spodic	5	10	19	34	51
Albic	3	7	18	36	61
all soils	7	13	31	78	100

Base saturation varies greatly among soil types (Table I 2-23). All soils with Calcic properties are fully base saturated. Soils with Leptic properties have a distribution of base saturation values inclining towards higher values than in the overall distribution. Spodic and Albic properties occur in soils generally low in basic cations.

Under natural conditions, base saturation is influenced by climate, by the material from which the soil was formed and by the vegetation it supports. Leaching of basic cations from exchange sites is a natural process in most European topsoils. Soil buffering processes following acid deposition accelerate natural acidification processes. Aluminium ions released into the soil solution during H^+ buffering processes compete with other cations for the occupation of exchange sites. With its small diameter and high charge, Al^{+3} gradually supersedes the basic cations, causing a decrease of base saturation. The buffering capacity against acidification is largely determined by the composition of mineral and organic colloids and by the kind of exchangeable cations (Ulrich, 1981). Figure I 2-54 illustrates that differences in acid deposition cannot be indicated as the major factor in determining the observed spatial distribution of base saturation values in the surface layer of European forest soils. Northern Europe is the region with the lowest deposition load, but reports the highest proportion (21%) of extremely low base saturation values (BS ≤ 10%).The observation that the Mediterranean region, generally receiving a higher load of atmospheric acids, reports no base saturation values in the 0 to 10% range, must be attributed to other factors, such as differences in parent material, climate, and vegetation.

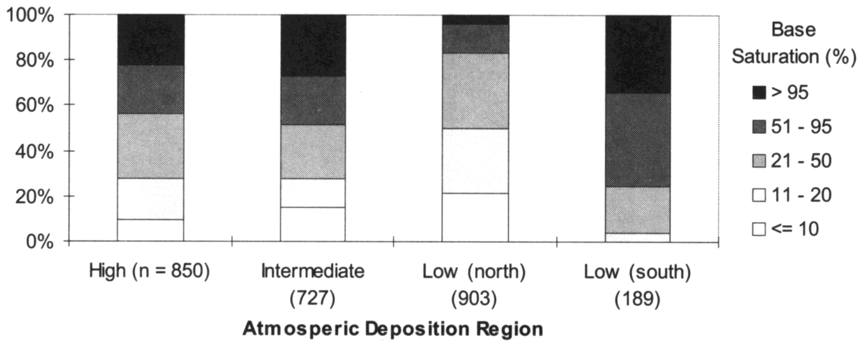


Figure I 2-54. Base saturation of the mineral surface layer in different atmospheric deposition regions (n = number of observations).

Soils formed from limestone or basic igneous rock are more base saturated than soils formed from sandstone or acid igneous rocks in the same climatic zone. More than 90% of the soils derived from carbonate rocks in Europe are fully base saturated in the layer between 10 and 20 or 30 cm (Figure I 2-55). More than 30% of the plots on crystalline rocks, sedimentary rocks or loose sandy sediments have soils with a base saturation of 20% or less. The proportion of strongly desaturated soils gradually decreases according to the following sequence: loamy sediments (23%), clayey sediments (22%) soils derived from volcanic rocks (11%).

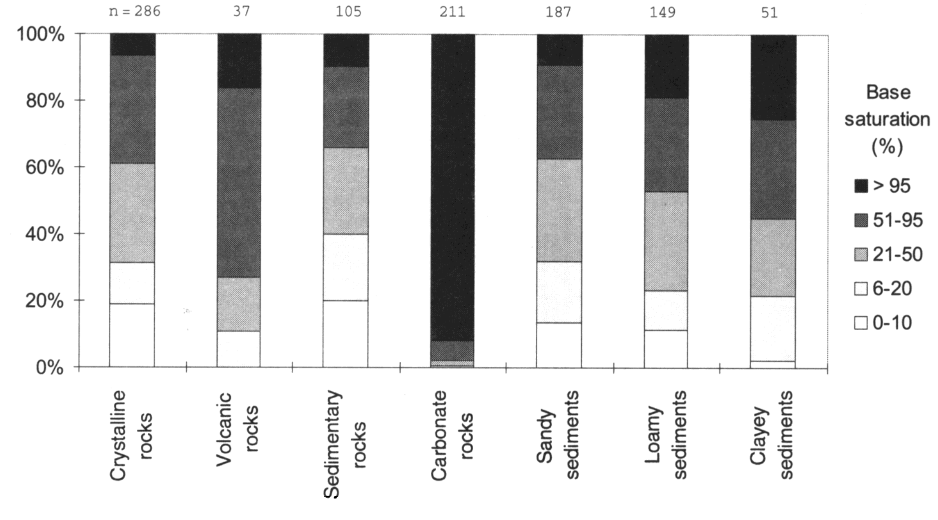


Figure I 2-55. Influence of parent material on base saturation in the mineral subsurface layer (n= number of observations).

Soils in dry regions normally have a higher base saturation than those in humid regions. The effect of climate on base saturation is demonstrated in Figure 12-56. The base saturation in the mineral surface layer of non-calcareous forest soils increases from an average of 26% in the Boreal region to averages of 79% in the lower Mediterranean region and 80% in the Continental region. Both a north-south and a west-east gradient are observed, following the climatic change from a precipitation surplus in soils in north-western Europe to an evapotranspiration deficit in eastern Europe and in the Mediterranean area.

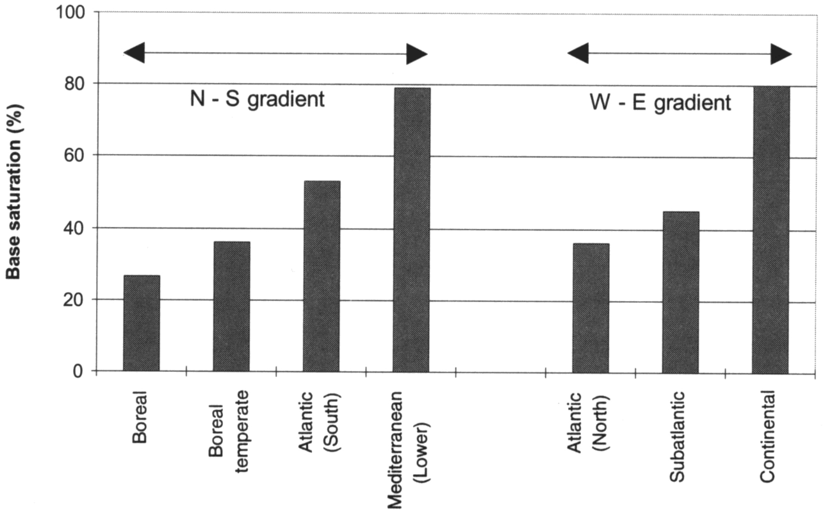


Figure I 2-56. Influence of climate on the average base saturation in the mineral surface layer of non-calcareous soils.

As a general rule, the pH and fertility level of a given soil increase with an increase in base saturation. Soil acidity is strongly correlated with base saturation. Linear correlation coefficients of 0.76 and 0.72 were determined for mineral surface and subsurface layers, respectively. Soil mineral layers, having pH values above 6.0, are fully base saturated. Figure I 2-57 shows that base saturated soils can also have a much lower pH; one third of the mineral surface layers with a base saturation above 90% has a pH below 5. Values around pH 4.2 - 4.4 appear to be critical. The majority (97%) of the soils, having a pH value above this range, has exchange sites that are dominantly saturated with basic cations (base saturation above 50%). Acid cations, however, dominate in soil layers having pH values of 4.2 or less; 86% of these acid soils have a base saturation of less than 50%.

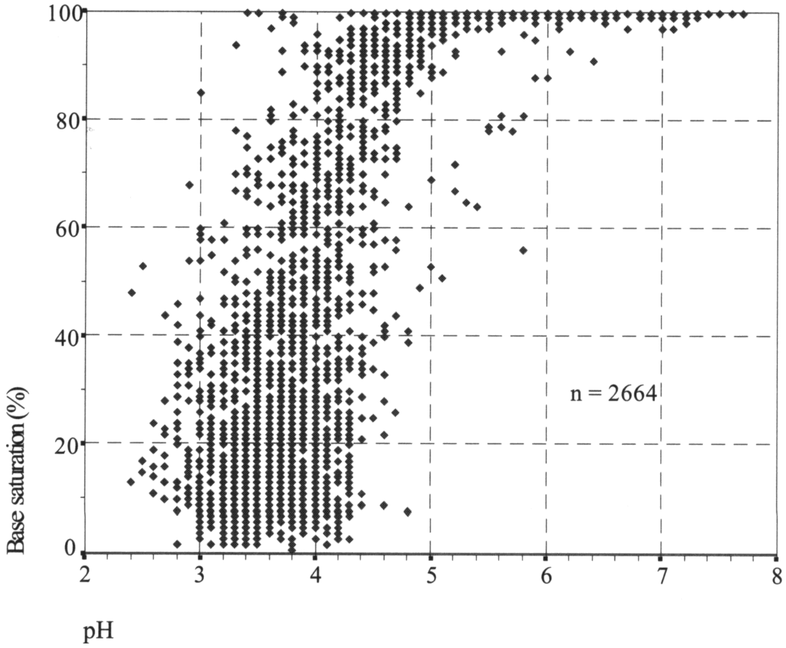


Figure I 2-57. Relationship between pH and base saturation in mineral surface layers (n = number of observations).

Nutrient availability for forest trees is usually poor in soils with acid (pH < 3.5) and/or strongly leached (base saturation < 20%) conditions. Such conditions occur in 42% of the plots for which both parameters are available. Table I 2-24 illustrates this proportion strongly varies among European countries; most of the acid and/or strongly leached soils are found in N- and NW-Europe, whereas nutrient availability conditions are more favourable in S- and E-Europe. The proportion of plots with unfavourable conditions is also relatively small in countries with a large number of plots in mountainous areas, such as Norway, Austria and Switzerland.

Table I 2-24. Occurrence of plots with acid topsoil conditions, i.e. base saturation (optional parameter) of 20% or less, or pH value below 3.5, in countries where both parameters are measured (n = number of plots; % = percentage of plots for which data is available).

	FR	BE	NL	DL	PO	LX	SW	AU	FI	SR	NO	CH	HU	LI	SL	all plots
n	98	8	11	247	8	0	254	40	239	28	152	15	1	13	9	1123
%	19%	80%	100%	61%	5%	0%	78%	31%	54%	25%	41%	35%	2%	18%	27%	42%

The high nutrient content of base saturated soils favours biological activity. Burrowing animals transport organic materials, accumulated in the litter layer, in the underlying mineral soil, thereby breaking them down mechanically. This results in a thin litter layer and a fast decomposition rate. Decomposition is, however, slowed down at molecular level, due to the strong bonding between organic molecules and clay minerals through the dominant Ca and Mg ions in base saturated soils. As a result, nutrient-rich soils have an organic matter distribution that differs from nutrient-poor soils. Nutrient-rich soils usually have a thin organic layer and a high organic carbon content in the mineral top soil (Figure I 2-58). The majority (67%) of forest soils having more than 95% base saturation has 50 g kg^{-1} organic carbon or more in their mineral surface layer, whereas this concentration is exceeded in only 29% of the surface layers having less than 20% base saturation.

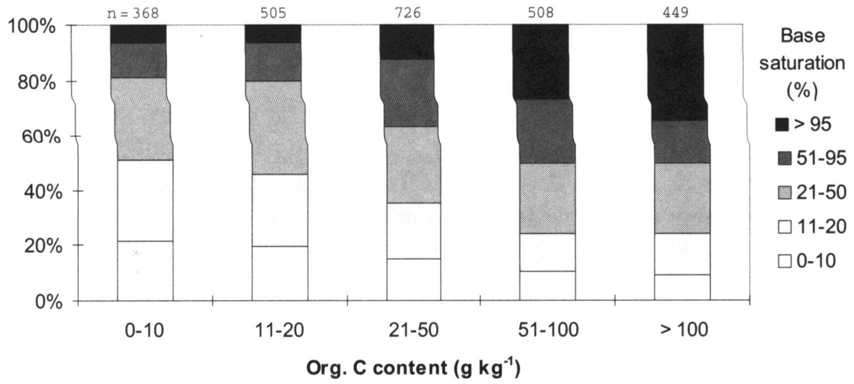


Figure I 2-58. Distribution of base saturation values in mineral surface layers with varying organic carbon concentration (n = number of observations).

2.8 Sodium

The availability of information on sodium is illustrated in Table I 2-25.

Table I 2-25. Sodium concentration (optional parameter) - data availability (see also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	0	0	100	32	0	100	0	100	0	95	0	0	0	0	100	100	0	100	0	0	0	0	0	929
Min. Layer	0	32	100	1	0	0	0	100	0	90	0	0	0	0	0	100	0	92	0	0	0	0	0	352
Analysis	X	R	N	N	X	N	X	R	X	R	X	X	X	X	N	R	X	N	X	X	X	X	X	30%

In most soils, a large part of the total sodium is present in rather insoluble silicate minerals. However, in saline soils or sodic soils, large amounts are present in soluble forms, where it is generally the dominant exchangeable cation (Pratt, 1965; Barber, 1995). Total sodium in mineral soil varies from a few mg kg^{-1} to about 5000 mg kg^{-1}, but is usually less than 300 mg kg^{-1} (Figure I 2-59). The sodium concentration of organic layers is mostly between 50 and 300 mg kg^{-1}. It is usually slightly higher than the concentration of the mineral surface layer, except when weathering processes are able to liberate more sodium in the soil than required by the plants.

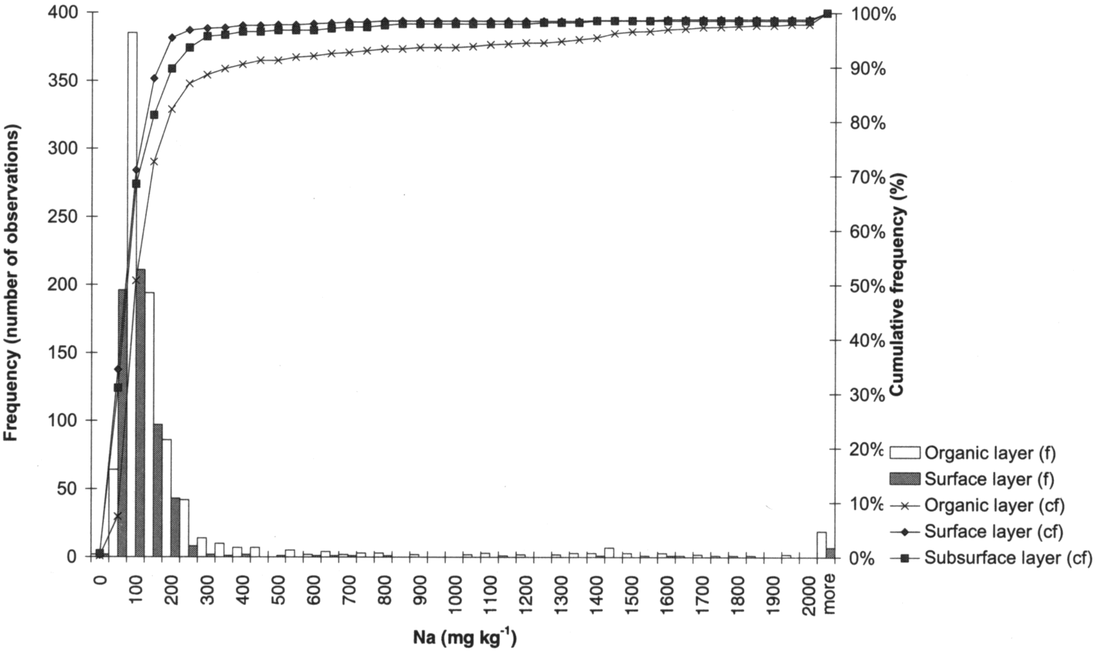


Figure I 2-59. Frequency (f) and cumulative frequency (cf) distribution of sodium concentrations in organic and mineral layers.

Since Na is not an essential element, there is generally little concern about its availability to plants in the low range of amounts. However, Na plays a part in plant nutrition in that it may partially substitute for K. It has a depressing effect on growth of plants when present in large amounts in exchangeable or soluble forms (Pratt, 1965).

2.9 Aluminium

The availability of information on aluminium is illustrated in Table 12-26.

Table I 2-26. Aluminium concentration (optional parameter) - data availability (see **also Figure I 2-1 for interpretation**).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	0	0	100	99	0	100	0	0	0	95	0	0	0	100	100	100	0	100	98	0	0	0	0	1327
Min. Layer	0	32	100	27	0	0	0	0	0	90	0	0	0	0	0	100	0	92	0	0	0	0	0	434
Analysis	X	R	N	N	X	N	X	X	X	R	X	X	X	N	N	R	X	R	R	X	X	X	X	13%

Aluminium is a major component of almost all common inorganic soil particles (exceptions are quartz, chert and ferro-manganiferous concretions). The most common primary and secondary minerals are alumino-silicates. Aluminium occurs also in several other forms in soils (McLean, 1965). It is frequently found as gibbsite, which is precipitated $Al(OH)_3$.

Total aluminium concentration is useful as a basis for characterising a soil with respect to type of parent material and weathering. It varies from less than 1000 mg kg^{-1} in strongly leached sands to about 100,000 mg kg^{-1} in soils with a high content of weatherable alumino-silicates (Figure I 2-60). Average aluminium concentrations of mineral layers are 10,000 to 25,000 mg kg^{-1}. In organic layers, the aluminium concentration gives an indication of the content of mineral soil material, since aluminium is largely present in inorganic form. For the same reason, organic layer concentrations are usually lower than mineral contents. More than 80% of the reported values for organic layers are less than 10,000 mg kg^{-1}.

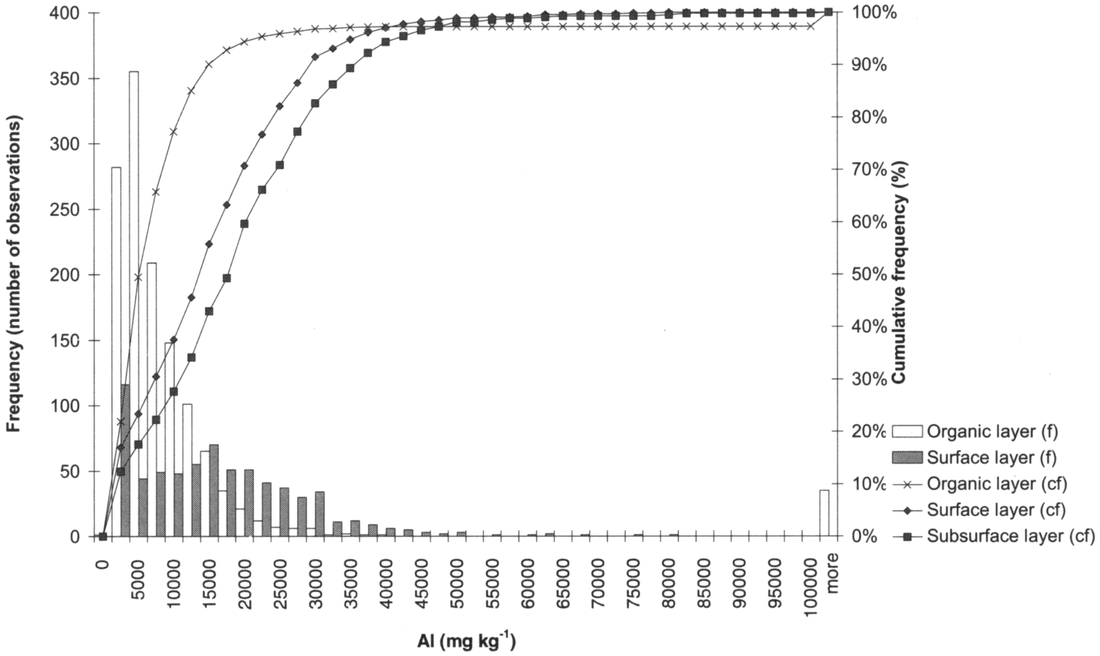


Figure I 2-60. Frequency (f) and cumulative frequency (cf) distribution of aluminium concentrations in organic and mineral layers.

Dissolution of aluminium from the solid phase is the dominant mechanism of proton buffering in many forest soils of northern Europe (Ulrich, 1981; Berggren and Mulder, 1995). Reactive forms, such as amorphous aluminium hydroxides and partly hydroxylated Al bound on organic matter, are present in many soils, but constitute only a fraction of the aluminium extracted in strongly acid solutions. The buffering action is situated around pH *5* and results in the release of hydrated Al ions into the soil solution (De Coninck and Van Ranst, 1993), where they may reach toxic concentrations.

In strongly acid solutions, aluminium occurs as the trivalent cation complex, with each Al^{3+} surrounded by 6 water molecules. Soluble aluminium may reach toxic levels in acid soils. Toxicity symptoms related to increased levels of soil aluminium are (i) reduced root penetration, and (ii) an increased susceptibility to drought. Appreciable amounts of soluble aluminium are generally present at pH (H_2O) values below *5.2* in soils having amorphous aluminium compounds that can release aluminium into solution. As the pH increases, the water molecules gradually lose H^+ ions, forming first di- or monovalent hydroxy-A1 cations, and later the Al hydroxide $Al(OH)_3$ is precipitated (McLean, 1965). Above pH *5.2,* little soluble aluminium tends to be present (Barber, 1995).

2.10 Heavy Metals

The heavy metals which, by definition, are elements having a density greater than five in their elemental form, comprise some 38 elements. However, the term usually refers to twelve metals that are used and discharged by industry, i.e. Cd, Cr, Co, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sn and Zn. The discussion is often centred on those metals that may represent potential hazards to plants, animals or men; these are Cd, Cu, Hg, Ni, Pb and Zn (Jones and Jarvis, 1981).

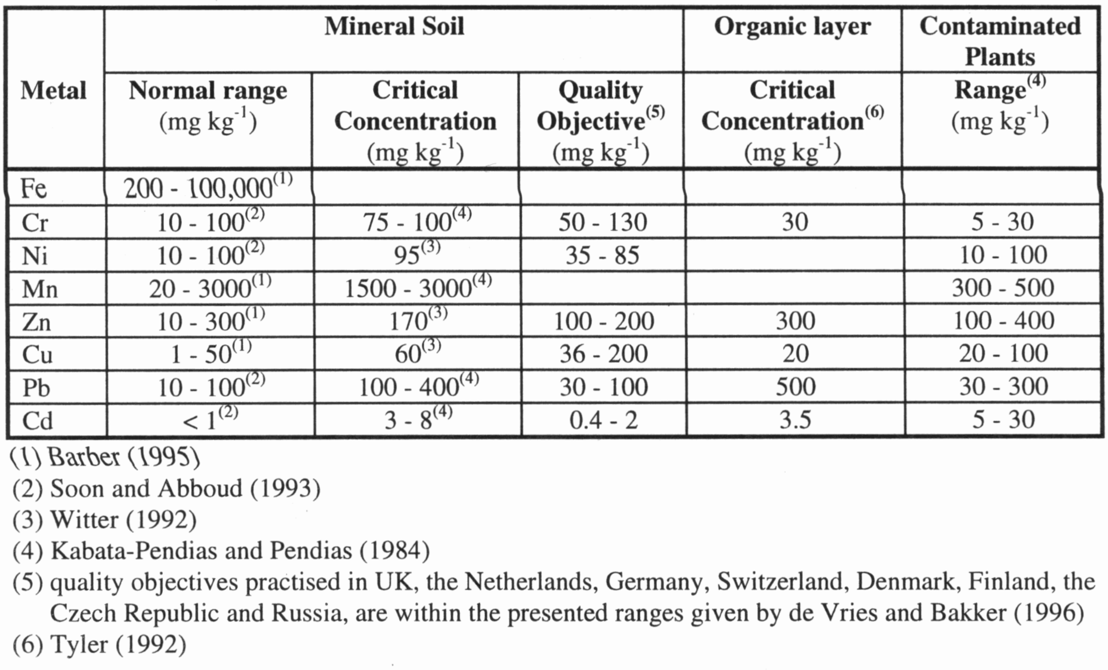
Heavy metals are widely distributed in the environment, in soils, in plants and animals. The concentrations of individual metals in living tissue are ordinarily very low and must be maintained within narrow limits to permit optimum biological performance of most organisms. Some heavy metals are essential in trace amounts, such as Cu, Fe, Mn and Zn for plants and, in addition, Cr and Ni for animals. Although beneficial in small amounts, these elements become harmful when the available forms are present in the soil in large quantities. Cadmium, lead and mercury have not been shown to be essential for either plants or animals. Deficiencies of metals have been frequently reported, but of increasing concern are the possible adverse effects of high concentrations of heavy metals on plants and animals and, in turn, on human health (Jones and Jarvis, 1981).

Although plant availability is also a concern, total element concentrations are required to quantify the accumulation of nutrients and pollutants in soils for evaluation of nutrient reserve and the degree of contamination (Soon and Abboud, 1993). Because correlations have been established between heavy metal contents in soil and concentration levels in plants **(Ross,** 1994c), total contents in humus layers and topsoil can be used as indicator for toxicity assessments (Andreae, 1996).

Source and Retention of Heavy Metals in Soils

Heavy metals are present in all uncontaminated soils as the result of weathering from their parent materials. Background or normal concentrations (Table 12-27) of one or more of these elements may be significantly increased by human interference (Jones and Jarvis, 1981). The bio-availablity of a metal is dependent, not only on total concentration, but also on the form in which it is present in the soil and on the composition of the soil matrix. So-called ‘toxic’ values (Kabata-Pendias and Pendias, 1984) are tentative because tolerances may strongly differ between plant species, but are useful for their signal function. Critical values given by Tyler (1992) for Swedish humus layers and by Witter (1992) for mineral soils are derived from so-called Lowest Observation Effect Concentration (LOEC) data in field and laboratory studies of soil microbiota. When available, critical concentrations were used as limit values of the upper heavy metal concentration classes (Annex D). The number of plots where critical values are exceeded are given in the following sections.

Table 12-27. Normal concentrations of heavy metals in mineral soils, critical concentrations for microbiota in mineral and organic layers, quality objectives for mineral soils, and metal concentrations in contaminated plants.



Metal	Mineral Soil			Organic layer	Contaminated Plants
	Normal range (mg kg^{-1})	Critical Concentration (mg kg^{-1})	Quality Objective(5) (mg kg^{-1})	Critical Concentration(6) (mg kg^{-1})	Range(4) (mg kg^{-1})
Fe	200 - 100,000(1)				
Cr	10 - 100(2)	75 - 100(4)	50 - 130	30	5 - 30
Ni	10 - 100(2)	95(3)	35 - 85		10 - 100
Mn	20 - 3000(1)	1500 - 3000(4)			300 - 500
Zn	10 - 300(1)	170(3)	100 - 200	300	100 - 400
Cu	1 - 50(1)	60(3)	36 - 200	20	20 - 100
Pb	10 - 100(2)	100 - 400(4)	30 - 100	500	30 - 300
Cd	< 1(2)	3 - 8(4)	0.4 - 2	3.5	5 - 30

(1) Barber (1995)
(2) Soon and Abboud (1993)
(3) Witter (1992)
(4) Kabata-Pendias and Pendias (1984)
(5) quality objectives practised in UK, the Netherlands, Germany, Switzerland, Denmark, Finland, the Czech Republic and Russia, are within the presented ranges given by de Vries and Bakker (1996)
(6) Tyler (1992)

Critical concentrations of Cr, Ni, Mn and Zn in the mineral soil are within the "normal" range of these elements. In fact, toxic ranges and critical values indicate that toxicity symptoms may occur in a situation where soil conditions favour plant uptake. Whether toxic amounts are taken up by the plant depends, however, on many factors, including some that are not related to soil. Environmental quality objectives for heavy metal contents in soil to assure multifunctional use, practised in different European countries, were summarised by de Vries and Bakker (1996). National quality objectives of Cr, Zn, and Cu, are similar to the critical concentration, those of Ni, Pb and Cd are lower.

The availability of elements, including potentially toxic elements, to plants and ecosystems depends on the nature of the parent rock and its ease of weathering. For example, sandstones and certain types of acid plutonic rocks are composed of minerals that weather with difficulty and generally contribute small amounts of elements through weathering. Trace element contents in soils overlying acid parent materials are usually well below average soil contents (Figure I 2-61). Several easily weathered minerals from basic igneous and metamorphic rocks, including olivine, hornblende and augite, contribute significant quantities of trace elements to soils. This may explain the higher than average concentrations of Ni and Cu in soils developed on metamorphic rocks.

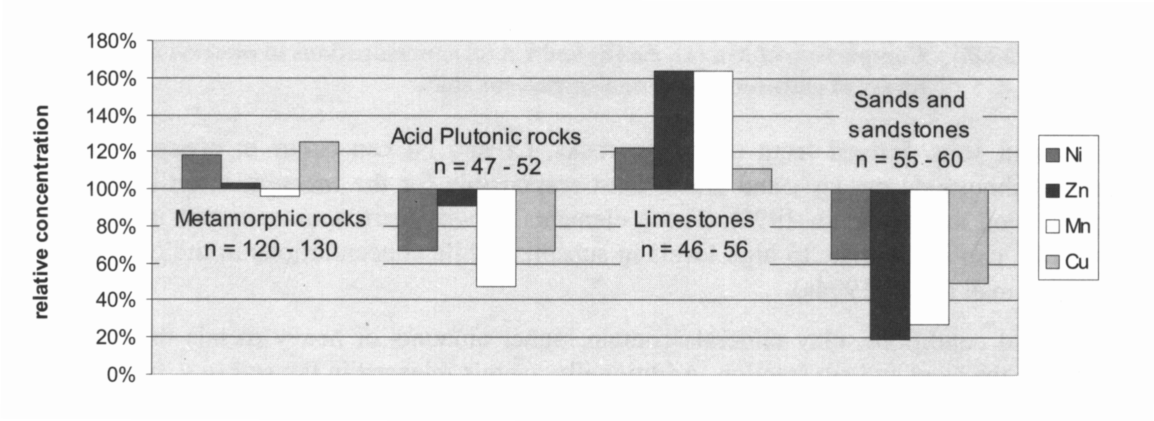


Figure I 2-61. Impact of parent material on trace metal concentrations in the mineral subsurface layer (average values in mg kg^{-1}, corresponding to 100%, are Ni: 27, Zn: 58, Mn: 638, Cu: 18; n = number of observations).

When heavy metals are associated with minerals that are digested by aqua regia, such as carbonates, usually large amounts are measured. Moreover, carbonate minerals are able to adsorb certain heavy metals, such as Zn (Jurinak and Bauer, 1956), Mn (McBride, 1979) and Cd (McBride, 1980). These elements are often present as trace elements in limestones. Figure 12-62 shows the concentration of these trace elements in the soil may be strongly influenced by carbonates. The relationship is most obvious for cadmium; a concentration of 1 mg Cd kg^{-1} is rarely measured in carbonate-free soils, but is exceeded in 65% of the calcareous subsurface layers. However, due to the pronounced effect of pH on heavy metal (particularly Cd) retention, this correlation may be largely indirect.

Most forest soils contain sufficient primary and secondary minerals as components of the parent material to insure an adequate cycle of cations through normal weathering processes. Deficiencies and toxicities of trace elements can frequently be related to contents of these elements in the parent material (Brady and Weil, 1996). Soils overlying sandy deposits or sandstone are most likely to show micronutrient deficiencies. Average concentrations of Cu, Zn and Mn are 50% or less of the average value for all soils (Figure 12-61).

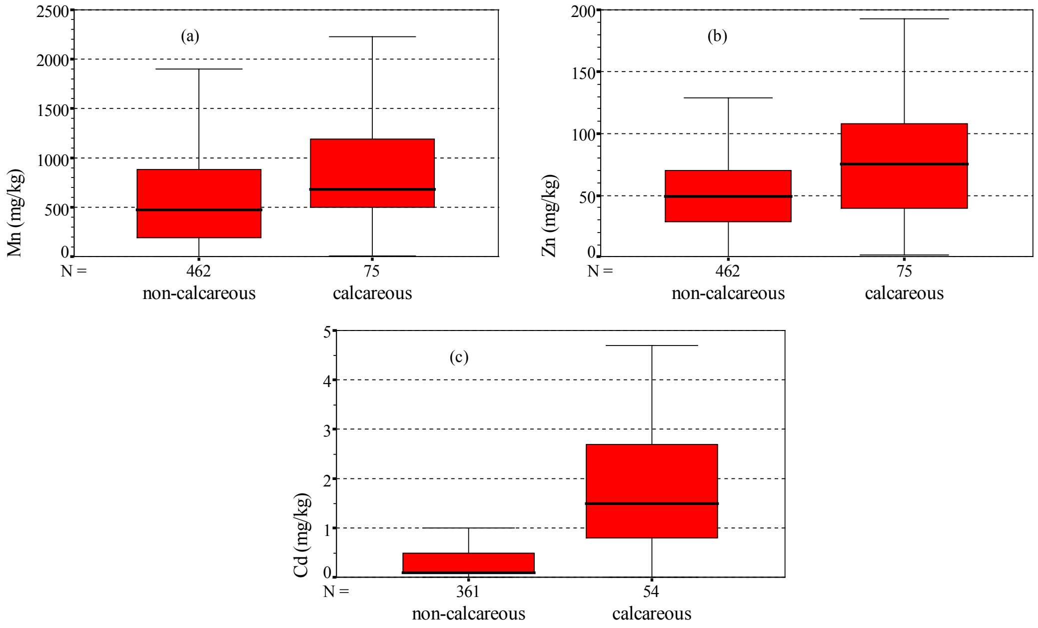


Figure I 2-62. Comparison of Mn (a), Zn (b) and Cd (c) concentrations in mineral subsurface layers of calcareous and non-calcareous soils.

In certain soils derived from ultrabasic rocks, Cr and Ni can occur in concentrations of several thousands mg kg^{-1}, and are at least responsible for the inherent infertility of these soils (Soon and Abboud, 1993). These elements, whose main source in soil is the parent material, can accumulate to high levels in subsoils, while concentrations in the organic litter remain small (Ross, 1994a).

In natural conditions, clay minerals contain higher amounts of heavy metals than minerals found in the sand and silt fraction. Additionally, metals released in the soil (e.g. by pollution) will be stronger retained in clayey soils, due to the capacity of clay mineral surfaces to absorb cations. Concentrations of some heavy metals in the mineral soil are directly related to clay content. Figure I 2-63 shows that, although the variation may be high, average concentrations of Cr, Ni, Cu and Zn in subsurface layers of coarse textured soils are only 46 to 64% of the overall average concentrations in these layers.

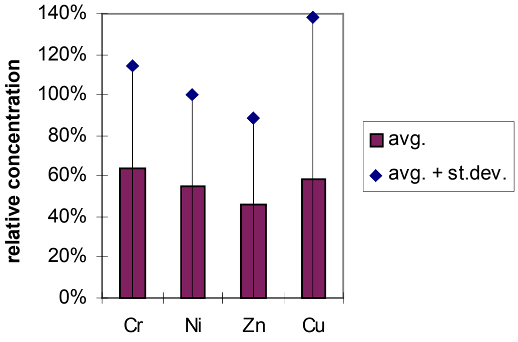


Figure I 2-63. Average concentrations of Cr, Ni, Cu and Zn in the mineral subsurface layer of coarse textured soils as compared to overall average concentrations (= 100%).

Significant linear relationships were found between several metal concentrations on the one hand and organic carbon content, pH and CEC on the other hand (Table I 2-28). CEC is well correlated with concentrations of heavy metals that are mostly present in exchangeable form, such as cadmium, zinc and lead. Correlation coefficients are higher in the surface than in the subsurface layer. Parent material is usually not a significant contributor to total soil concentrations of cadmium and lead. The major source of these elements in the topsoil is probably air pollution, but retention in the soil is determined by the presence of organic and mineral cation exchange sites.

In the organic layer, organic carbon content is usually negatively correlated with metal concentrations. Incorporation of mineral materials in the litter layer, decreasing the Org. C content, results in higher concentrations of particularly Fe, Cr and Ni. Significant amounts of these elements are usually present in free oxide or hydroxide form in the soil. Zinc, cadmium and especially lead concentrations in the mineral soil appear to be strongly associated with organic matter.

Another major factor controlling metal content in soils is acidity. More metals are retained on exchange sites at high pH. The best positive relationships are found with Mn, Zn and Cd, because these elements can be specifically adsorbed by carbonates in alkaline soils.

Table I 2-28. Two-tailed correlation matrix of heavy metal concentrations and CEC, organic carbon, and pH in (1) organic, (2) mineral surface, and (3) subsurface layers (r values above 0.25, significant at 0.05 level, are given; those above 0.50 are in bold).

Metal	CEC		Org. C.			pH		
	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
Fe			-0.41			0.27		
Cr			-0.30					
Ni			-0.28					
Mn	0.25	0.32					0.32	
Zn	**0.52**	0.39		0.33		0.28	0.36	0.29
Cu								
Pb	**0.59**	0.48		**0.63**	**0.55**		0.26	0.33
Cd	**0.53**	0.45		0.46	0.40	0.35	0.49	0.43

The main anthropogenic sources of heavy metals are: (i) urban industrial aerosols; (ii) liquid and solid wastes from animals and man; (iii) mining wastes; or (iv) industrial and agricultural chemicals. Large quantities of cadmium are applied to agricultural soils in phosphate fertilisers (Ross, 1994a). Forest soils adjacent to agricultural lands may receive significant amounts of cadmium via this route. Industrial processes involving metal smelting and/or refining often result in large aerial inputs of heavy metals to neighbouring soils and vegetation, causing acute local problems in the vicinity of emission sources (Jones and Jarvis, 1981). For example, lead concentrations in soils located near mines can attain 5000 mg kg^{-1}, bringing about toxicity indications in plants (Aubert and Pinta, 1977).

Although the degree of contamination via the atmospheric route decreases rapidly with distance from the source and is dependent upon wind speed and direction, chronic and regional or even global perturbations of metal cycles have been found to result from long-range air transport and deposition. Another source of aerial contamination is the Pb that is emitted from the combustion of petrol containing tetraethyl lead; this contributes substantially to the content of Pb in soils in urban areas and in those adjacent to major roads. Zinc and Cd may also be added to soils adjacent to roads, the source being tyres and lubricant oils. Fly ash residues from coal combustion may contribute locally to annual atmospheric inputs of Cd, Mn and Ni. Addition to the soil and subsequent transfer from soil to plant is for most heavy metals the major route of entry into the living tissue of plants, animals and men (Jones and Jarvis, 1981).

Atmospheric deposition has changed heavy metal chemistry of organic layers in European forest soils (Figure 12-64). Increased levels of lead and zinc are often observed in the central European area, where atmospheric deposition is highest. Heavy metal deposition may be expected to be correlated with acidic deposition in the sense that acid and heavy metal pollution both usually emanate from industrial areas (de Vries and Bakker, 1996). The majority of lead (93%) and zinc (73%) concentrations of 80 mg kg^{-1} and more in the organic layer are found in the region with the highest deposition load, while this region covers less than half of the observation plots where these elements are measured.

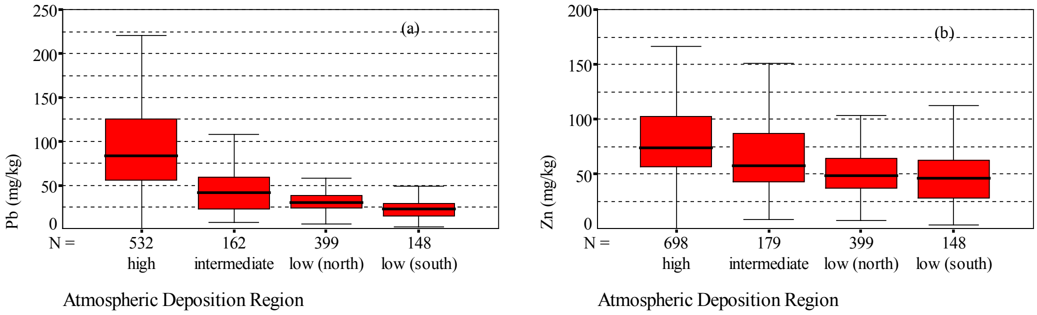


Figure I 2-64. Distribution of Pb (a) and Zn (b) concentrations in the organic layer among atmospheric deposition regions.

Forests represent a potentially larger sink than grassland, snow and water surfaces due to their larger surface area and the roughness aspect (Andreae, 1996). Processes such as wet and dry deposition, canopy leaching, throughfall, stem flow and litter fall all ultimately result in the addition of heavy metals to the soil surface (Martin and Bullock, 1994). The litter layer is the repository for metals accumulated in leaves prior to shedding (Ross, 1994c). The soil compartment, particularly litter and surface organic horizons, shows the highest concentrations of metals in forest ecosystems. The concentrations of metals in fallen leafs usually increase over time on the forest floor as metal ions exchange onto the cation exchange sites of the decaying litter (Ross, 1994c).

2.10.1 Iron

The availability of information on iron is illustrated in Table I 2-29.

Table I 2-29. Iron concentration (optional parameter) - data availability (see also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	0	0	100	72	0	100	0	0	0	95	0	0	0	100	100	100	0	100	98	99	69	0	0	1354
Min. Layer	0	32	100	1	0	0	0	0	0	95	0	0	0	100	0	100	0	92	0	0	0	0	0	458
Analysis	X	R	N	N	X	N	X	X	X	R	X	X	X	N	N	R	X	N	R	R	R	X	X	10%

Iron is present in soils in higher concentrations than any other nutrient. Iron minerals, such as goethite, hematite and lepidocrocite are commonly found in soils, and iron is a major constituent of many silicate minerals. However, amorphous iron as $Fe(OH)_3$ is probably the most significant mineral form in supplying iron for plant uptake (Jones and Jarvis, 1981). Aqua regia dissolves the iron oxides, but may leave most of the iron in silicates in place.

Iron in mineral soil layers varies from no more than 100 to almost 100,000 mg kg^{-1} (Figure I 2-65). The majority, about 80%, of the reported Fe concentrations in mineral layers is between 5000 and 40,000 mg kg^{-1}. The Fe concentration of organic layers is usually less than 10,000 mg kg^{-1}, but may occasionally be as high as 50,000 mg kg^{-1} in organic layers rich in mineral materials.

Iron forms stable complexes with organic compounds that occur in both the soils' solid phase and as soluble organic compounds. Plant roots absorb iron from these Fe^{3+} chelates. The plant root releases a reductant that reduces Fe^{3+} in the chelate. After reduction, Fe^{2+} is released into solution and absorbed by the root. Because iron reduction is pH-dependent, iron stress is more often observed in high-pH soils. The highest Fe-concentrations are found in mineral soils with a pH between 4.0 and 6.0, having a moderate to high organic matter content (Figure I 2-66). In low-pH soils Fe is easily reduced and leached out to the subsoil or the groundwater. Soils with high pH tend to be relatively low in Fe due to the presence of carbonates.

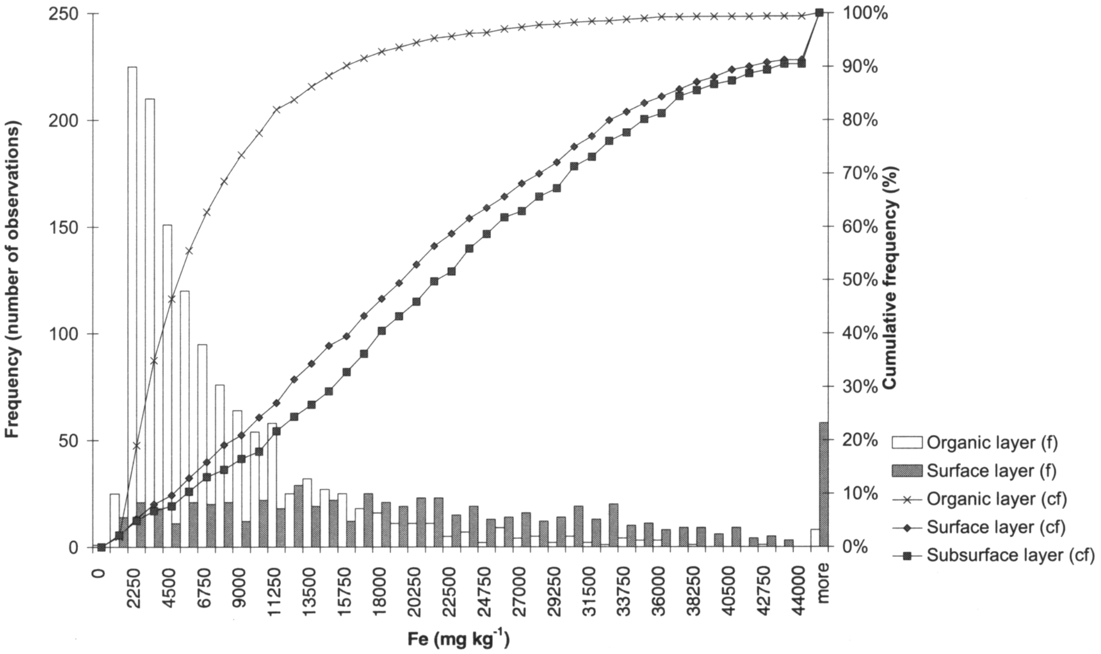


Figure I 2-65. Frequency (f) and cumulative frequency (cf) distribution of iron concentrations in organic and mineral layers.

Excessive soluble concentrations of Fe, largely in the ferrous state, are most common in highly acid soils or soils having poor aeration. In such cases, plants growing in the soil develop toxicity symptoms (Olson, 1965).

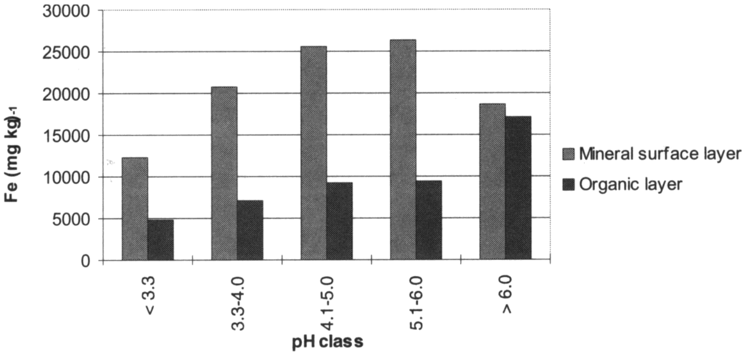


Figure I 2-66. Average iron concentrations in organic and mineral surface layers for different pH classes.

In spite of the large amounts of iron in the soil and the low quantities needed for plant growth, iron deficiencies occur because little of the element is in an available form. Deficiencies of iron are mostly problems of nurseries and poorly sited plantations on calcareous soils (Stone, 1968, in Pritchett and Fisher, 1987). Symptoms of deficiency in angiosperms are characterised by green midrib and veins with lighter green, yellow or white interveinal tissue. In conifers, deficiency appears as uniformly pale green or yellowish-green new foliage (Pritchett and Fisher, 1987).

Manganese and copper compete with iron for absorption. There are also indications that high level of calcium inhibits iron uptake, which may be one reason why iron deficiencies occur on high-calcium soils. High levels of phosphorus have also been shown to reduce iron uptake (Barber, 1995).

Organic layers with few mineral materials are very low in Fe (Figure 12-67). Because most iron is in mineral form, there is a negative correlation between Fe concentration and Org. C content in the organic layer (Table 12-28).

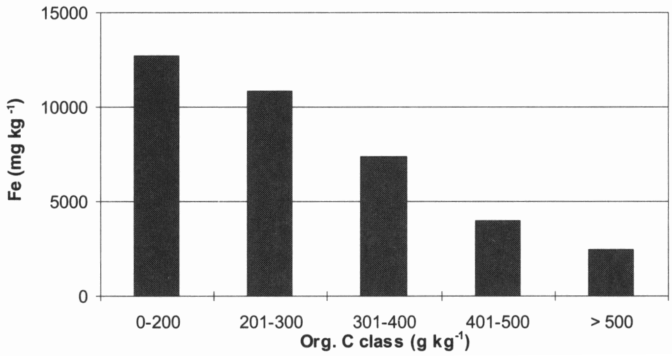


Figure I 2-67. Average iron concentrations in the organic layer for different organic C classes.

Basic species of free Fe, i.e. hydroxides and oxides, can act as a buffer against soil acidification (Ulrich, 1981) in two ways (De Coninck and Van Ranst, 1993): (1) in very acid soils, having pH values below 3.5, H^+ ions are taken up to form hydrated Fe; and (2) when Fe^{+3} compounds are reduced to the more soluble Fe^{+2} form, H^+ ions are also removed from the solution. However, the opposite takes place during oxidation.

2.10.2 Chromium

The availability of information on chromium is illustrated in Table 12-30.

Table I 2-30. Chromium concentration (optional parameter) - data availability (see also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	0	0	100	37	0	100	0	0	0	95	0	0	0	100	100	0	0	100	0	99	0	0	0	1010
Min. Layer	0	0	100	27	0	0	0	0	0	95	0	0	0	100	0	0	0	92	0	0	0	0	0	444
Analysis	X	X	N	N	X	N	X	X	X	R	X	X	X	N	N	X	X	N	X	R	X	X	X	23%

Chromium is believed to be present mostly as chromite, a mixed oxide of Cr^{3+} and Fe^{2+}. Cr^{3+} has an ionic radius between that of Fe^{3+} and Al^{3+} and thus precipitates readily in iron and aluminium oxides (Soon and Abboud, 1993). The chemistry of Cr in well-aerated soils resembles that of Fe. The concentration of Cr^{3+} is controlled by chromic oxides or hydroxides, these being very stable and insoluble (Jones and Jarvis, 1981).

Soil contents are close to those of parent rocks and range between 1 and more than 500 mg kg^{-1} (Figure 12-68). The so-called 'toxic' level of 75 mg kg^{-1} (Kabata-Pendias and Pendias, 1984) is exceeded in mineral surface layers of 21 plots, or 5% of the plots for which soil Cr concentrations are reported (Table I 2-31). Since most of these high Cr containing layers occur in relatively 'young' soils (14 Cambisols and 3 Leptosols), raised contents seem to be usually inherited from the soil parent material.

Nine percent of the reported Cr amounts for organic layers exceed the critical value of 30 mg kg^{-1}, given by Tyler (1992) (Table 12-31). Organic layer concentrations of more than 100 mg kg^{-1} are measured in 9 plots.

Table I **2-31.** Exceedence - number (n) and percentage (%) of plots - of critical chromium concentrations (optional parameter) for organic (org) and mineral (min) surface layers.

	NL	DL	UK	PO	AU	FI	CH	LI	all plots
org > 30	0	21	7	40	4	14	0	0	**86**
mg kg^{-1}	0%	14%	10%	27%	3%	3%	0%	0%	**9%**
min > 75	0	5	n.d.	14	2	n.d.	0	n.d.	**21**
mg kg^{-1}	0%	5%	n.d.	9%	2%	n.d.	0%	n.d.	**5%**

n.d. = not determined

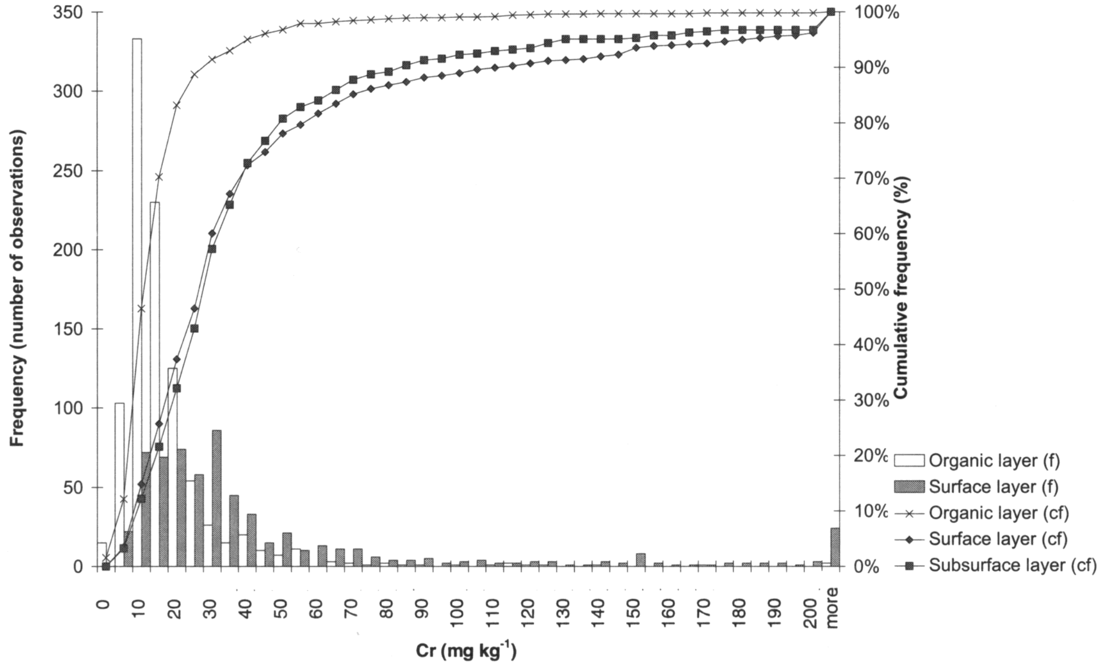


Figure I **2-68.** Frequency **(f)** and cumulative frequency (cf) distribution of chromium concentrations in organic and mineral layers.

Within the soil profile, chromium accumulates in humus rich horizons, but positive relationships have also been observed with pH and clay content. Although no linear relationship between Cr concentration and pH is found (Table I 2-28), the average Cr concentration of mineral surface layers having a pH between 5.1 and 6.0 is four times higher than that of very acid topsoils (pH ≤ 3.2). In spite of higher concentrations in the mineral layers of medium pH soils, concentrations in the organic layer of these soils remain low (Figure 12-69). This may indicate that Cr in these soils is largely in unavailable form.

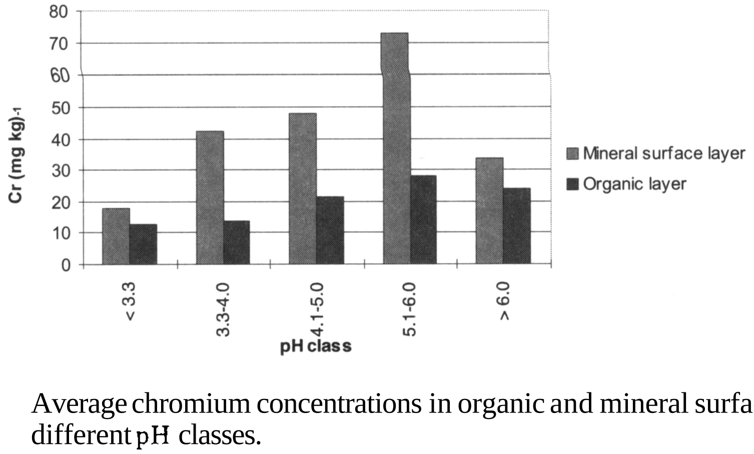


Figure I **2-69.** Average chromium concentrations in organic and mineral surface layers for different pH classes.

Due to higher solubility at low pH, risk of chromium toxicity is highest in acid soils, especially if they are poor in phosphorus (Aubert and Pinta, 1977). Deficiency of chromium is very uncommon.

Because Cr is taken up by trees in very small amounts, its concentration in the organic layer is mainly determined by the presence of mineral materials. Highly organic humus layers have an average Cr concentration of 5 mg kg^{-1}; this value increases significantly with increasing mineral material content (Figure I 2-70).

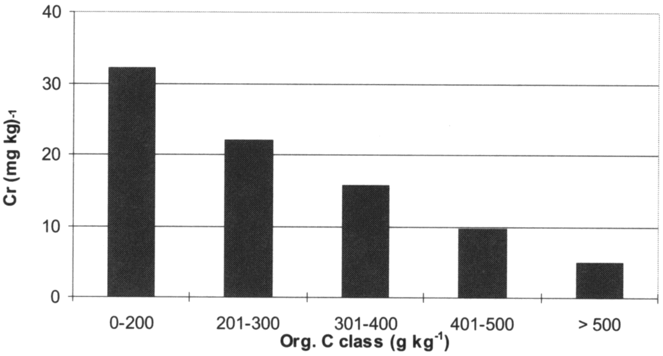


Figure I 2-70. Average chromium concentrations in the organic layer for different organic C content classes.

2.10.3 Nickel

The availability of information on nickel is illustrated in Table 12-32.

Table I 2-32. Nickel concentration (optional parameter) - data availability (see also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	0	0	100	37	0	100	0	0	0	95	0	0	0	100	100	0	0	100	0	99	0	0	0	1010
Min. Layer	0	0	100	27	0	0	0	0	0	95	0	0	0	100	0	0	0	92	0	0	0	0	0	444
Analysis	X	X	N	N	X	N	X	X	X	R	X	X	X	N	N	X	X	N	X	R	X	X	X	16%

Soil total nickel concentrations vary within wide limits. These variations can often be related to the rock type on which the soils are formed. Nickel concentrations are highest in ultrabasic rocks and in the products of their metamorphism (Aubert and Pinta, 1977). Nickel is present as a constituent of silicate clay minerals derived from these parent materials (Soon and Abboud, 1993).

Nickel concentrations in mineral soil layers are below 50 mg kg^{-1} in almost 90% of the plots for which they have been reported (Figure 12-71). The critical Ni concentration of 95 mg kg^{-1}, suggested by Witter (1992), rarely occurs in European forest soils (Table 12-33). The three soils, for which surface layer Ni concentration exceeds this amount, are Cambisols. The increased Ni concentration is probably associated with the mineralogical composition of the parent rocks of these soils.

Organic layer concentrations of nickel are usually well below levels measured in the mineral soil, although they may exceed those in the underlying mineral layer in very acid soils. Among the plots for which organic layer concentrations have been reported, 55% contains 10 mg kg^{-1} Ni or less, and only 2% has more than 35 mg kg^{-1} Ni (Table I 2-33).

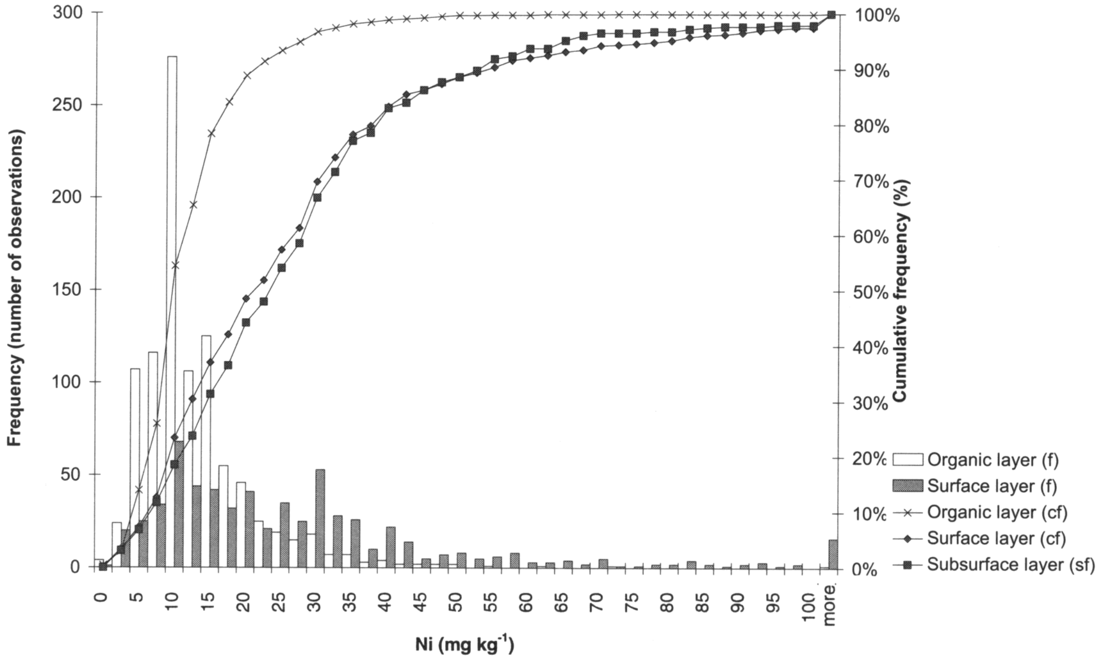


Figure I 2-71. **Frequency (f) and cumulative frequency (cf) distribution of nickel concentrations in organic and mineral layers.**

Table I 2-33. **Exceedence - number (n) and percentage (%) of plots - of limit concentrations of nickel (optional parameter) in organic (org) and mineral (min) surface layers.**

	NL	DL	UK	PO	AU	FI	CH	LI	all plots
org > 35	0	3	1	11	3	2	0	0	**20**
mg kg^{-1}	0%	2%	1%	7%	2%	0%	0%	0%	**2%**
min > 95	0	1	n.d.	2	0	n.d.	0	n.d.	**3**
mg kg^{-1}	0%	1%	n.d.	1%	0%	n.d.	0%	n.d.	**1%**

n.d. = not determined

The distribution of nickel in the soil profile follows that of organic matter and clay. Soil acidity also plays a significant role in soil nickel accumulations: average aqua regia extracted Ni is 10 mg kg^{-1} in very acid soils, but as high as 40 mg kg^{-1} in mineral surface layers having a pH between 5.1 and 6.0. There may also be an accumulation of nickel in certain horizons very rich in iron or aluminium sesquioxides. This is confirmed by highly significant linear correlation coefficients between Ni and Fe (0.40), respectively Al (0.42) concentrations of mineral layers.

Some cases of nickel toxicity have been found in podzolic and hydromorphic soils derived from basic rocks (Aubert and Pinta, 1977). However, there are many instances of complete vegetation cover on highly nickeliferous soils. Nickel toxicity can be ameliorated by increasing the concentration of Ca^{2+} and Mg^{2+} ions in the soil solution (Proctor and Baker, 1994). Nickel is likely to be at non-toxic concentrations in soil solutions with a pH exceeding 6.0 in well-aerated soils.

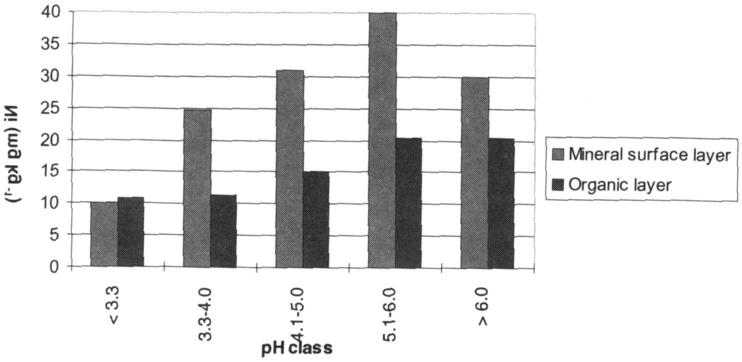


Figure 12-72. **Average nickel concentrations in organic and mineral surface layers for different pH classes.**

2.10.4 Manganese

The availability of information on manganese is illustrated in Table 12-34.

Table I 2-34. **Manganese concentration (optional parameter) - data availability** (see also **Figure** I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	0	0	100	81	0	100	0	0	0	95	0	100	0	100	100	100	0	100	98	99	69	0	0	1397
Min. Layer	0	0	100	27	0	0	0	0	0	95	0	0	0	100	0	100	0	92	0	0	0	0	0	555
Analysis	X	X	N	N	X	N	X	X	X	R	X	R	X	N	N	R	X	N	R	R	R	X	X	4%

Total soil manganese may be divided into mineral manganese, organically complexed manganese, exchangeable manganese and solution manganese. The equilibrium between these forms is greatly influenced by soil pH and redox conditions. Soil manganese exists in three oxidation states - Mn^{2+}, Mn^{3+} and Mn^{4+}. Manganese absorbed by plant roots **is** primarily as Mn^{2+}, which is the most soluble form. Divalent manganese also forms complexes with soluble and insoluble organic compounds. Exchangeable manganese essentially exists as Mn^{2+}. In well aerated soils Mn^{2+} is readily oxidised to Mn^{4+} and precipitated as an oxide. The most common manganese minerals in soils are oxides, occurring in iron-manganese concretions or as coatings on other minerals.

Manganese concentrations in mineral soil layers vary between 2 and 6000 mg kg^{-1}, but the majority of the reported values (± 80%) is lower than 1000 mg kg^{-1} (Figure 12-73). Kabata-Pendias and Pendias (1984) proposed 1500 mg kg^{-1} as the threshold value at which manganese toxicity symptoms may occur. In 44 plots 'toxic' values (> 1500 mg kg^{-1}) were measured in the mineral surface layer (Table 12-35). The highest Mn amounts in mineral soil layers are found in soil groupings associated with a recent weathering stage, such as Cambisols (21 plots) and Leptosols (16).

Compared to most other heavy metals, manganese is required by plants in relatively large amounts, in ***so*** much that the concentration in the organic layer usually exceeds the concentration in the mineral soil. Most observations are made in the range from 100 to 2000 mg Mn kg^{-1}, although **7%** of the reported values for organic layers exceeds 3000 mg kg^{-1} (Table I 2-35) and values of more than 10,000 mg kg^{-1} have been reported in 30 German plots.

Table I **2-35.** Exceedence - number (n) and percentage (%) of plots - of limit concentrations of manganese (optional parameter) in organic (org) and mineral (min) surface **layers.**

	NL	DL	UK	PO	LX	AU	FI	SR	CH	HU	LI	CR	all plots
org > 1500	0	58	3	6	0	4	6	12	0	7	0	0	**96**
mg kg^{-1}	0%	18%	4%	4%	0%	3%	1%	11%	0%	18%	0%	0%	**7%**
min > 3000	0	4	n.d.	15	n.d.	5	n.d.	20	0	n.d.	n.d.	n.d.	**44**
mg kg^{-1}	0%	4%	n.d.	10%	n.d.	4%	n.d.	18%	0%	n.d.	n.d.	n.d.	**8%**

n.d. = not determined

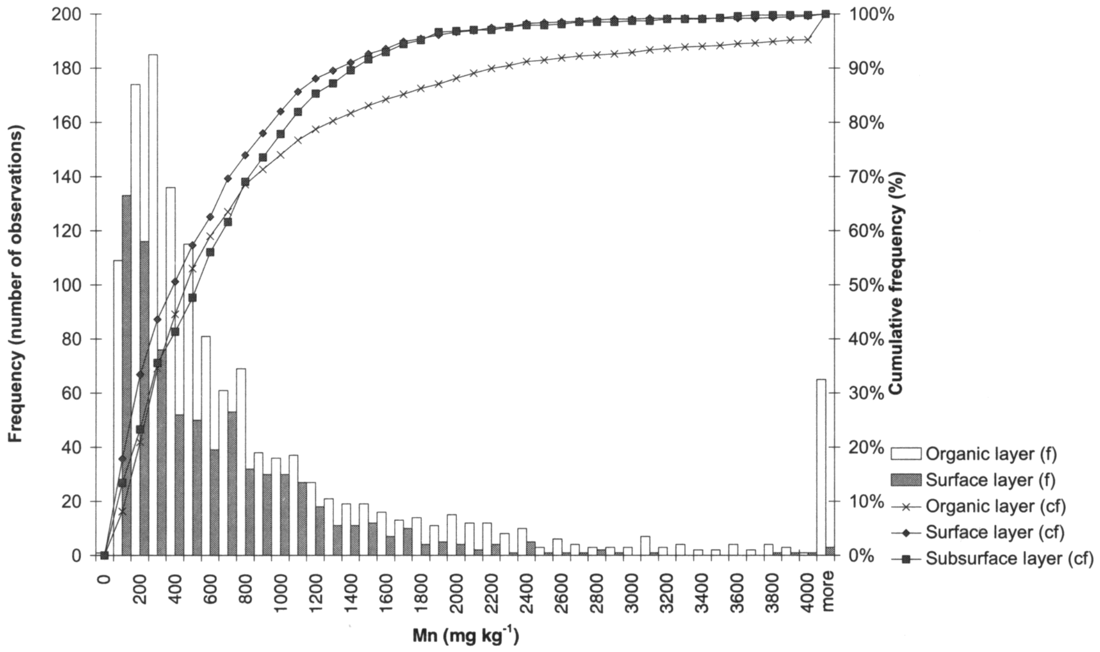


Figure I **2-73.** Frequency **(f)** and cumulative frequency (cf) distribution of manganese concentrations in organic and mineral layers.

Uptake of manganese increases from pH 4 to pH 6, but above pH 6, oxidation of Mn^{2+} reduces uptake rate (Barber, 1995). The concentration of Mn^{2+} in solution in neutral soils is largely controlled by Mn oxides but it is very sensitive to changes in pH, soil water content and microbial activity (Jones and Jarvis, 1981). In soils with an alkaline pH, where manganese is immobilised as insoluble oxides, the Mn concentration of the organic layer barely reaches the level measured in the underlying mineral soil (Figure 12-74). In very acid soils the difference between the concentration in the organic and mineral layers is far greater than in less acid soils.

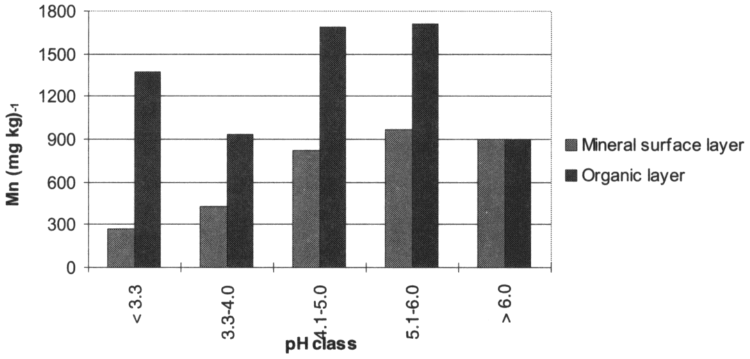


Figure I **2-74.** Average manganese concentrations in organic and mineral surface layers for different pH classes.

Manganese deficiency occurs principally in soils with an alkaline pH or on calcareous rocks, where manganese is immobilised as insoluble oxides. Deficiency may also occur in strongly acidic and very permeable soils where the acidity favours manganese leaching. The range between deficiency and toxicity is not large for acid sensitive tree species. Toxicity for forest trees is most often observed in acidified soils (Hüttl, 1985b; Schone, 1992). This toxicity probably results from the destruction of organic complexes on which manganese is fixed and can be corrected by enriching the soil with organic matter and by raising the soil pH (Aubert and Pinta, 1977).

2.10.5 Zinc

The availability of information on zinc is illustrated in Table 12-36.

Table I 2-36. **Zinc concentration (optional parameter) - data availability** ***(see*** also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	0	0	100	99	0	100	0	0	0	95	0	0	0	100	100	100	0	100	0	99	69	0	0	1423
Min. Layer	0	0	100	27	0	0	0	0	0	95	0	0	0	100	0	100	0	92	0	0	0	0	0	555
Analysis	X	X	N	N	X	N	X	X	X	R	X	X	X	N	N	R	X	N	X	R	R	X	X	23%

Zinc is present in the soil in only the divalent form. Relatively insoluble mineral forms account for more than 90% of the zinc in soils. Zinc that may become available for plant uptake is present as Zn^{2+} in solution, exchangeable zinc, organically complexed zinc in solution and in the soil solid phase. These forms of Zn are extracted by aqua regia and other strong acids.

Zinc concentrations in organic and mineral soil layers are usually lower than 100 mg kg^{-1}, although values of more than 400 mg kg^{-1} have been reported (Figure 12-75). Contaminated plants usually accumulate more than 100 mg kg^{-1} Zn (Table 12-28). National environmental quality objectives for zinc concentration in mineral soils, practised in Europe, range between 100 and 200 mg kg^{-1} (de Vries and Bakker, 1996). The critical level for zinc proposed by Witter (1992), 170 mg kg^{-1}, is exceeded in the mineral surface layer of 16 plots, which corresponds to 3% of the plots for which Zn concentrations in the mineral soil are reported (Table 12-37). Again Cambisols (9) and Leptosols (3) are the soil types which are most likely to display high Zn amounts. The lower 'toxic' limit suggested by Kabata-Pendias and Pendias (1984) of 70 mg kg^{-1}, at which toxicity symptoms may occur under soil conditions favouring plant uptake, is exceeded in the mineral surface layer of 187 plots (34%). This observation suggests that this 'toxic' limit may need to be re-examined.

Tyler (1992) found that 300 mg kg^{-1} is a critical Zn concentration for humus layers in Swedish forest soils. If this value is compared with the reported values for organic layers in the survey, exceedences are observed in only 9 out of 1423 plots (Table 12-37).

Table I 2-37. **Exceedence - number (n) and percentage** (%) **of plots - of critical zinc concentrations (optional parameter) for organic (org) and mineral (min) surface layers.**

	AU	CH	CR	DL	FI	LI	NL	PO	SR	UK	all plots
org > 300	1	0	0	5	0	1	0	0	2	0	**9**
mg kg^{-1}	1%	0%	0%	1%	0%	1%	0%	0%	2%	0%	**1%**
min > 170	9	0	n.d.	0	n.d.	n.d.	0	0	7	n.d.	**16**
mg kg^{-1}	7%	0%	n.d.	0%	n.d.	n.d.	0%	0%	6%	n.d.	**3%**

n.d. = not determined

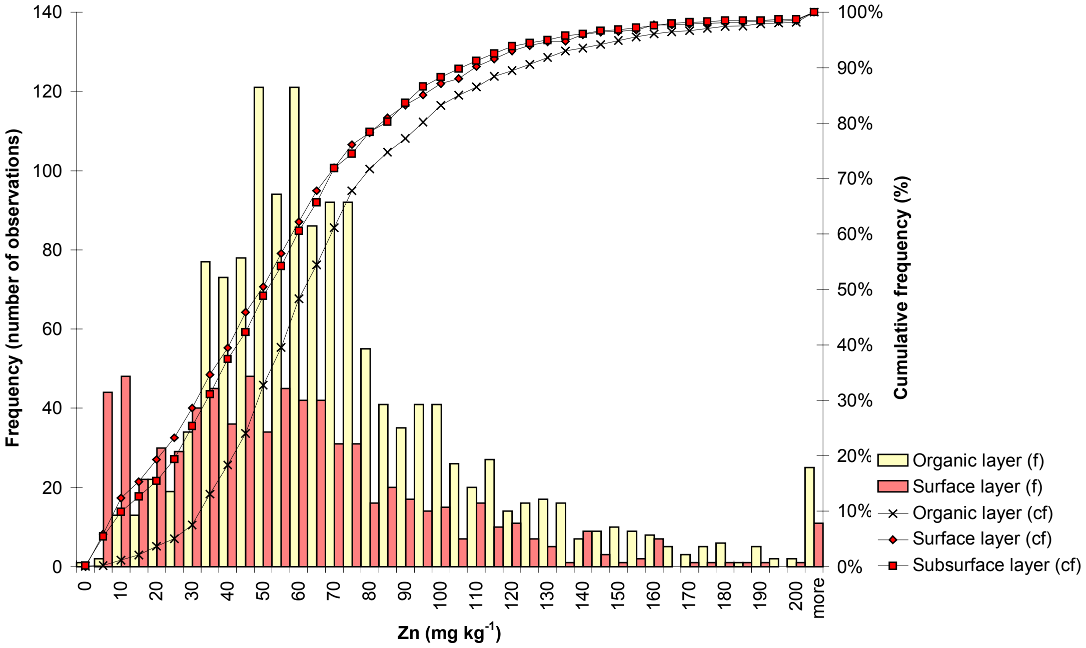


Figure I 2-75. Frequency (f) and cumulative frequency (cf) distribution of zinc concentrations in organic and mineral layers.

The adsorption of zinc is increased by increased cation exchange capacity (Figure I 2-76), pH and the presence of calcium carbonate (see also Figure I 2-62). Exchange sites for zinc ions may be provided by organic matter or clay particles, but these soil constituents tend to strongly hold onto the zinc. At low CEC values, aqua regia extractable zinc is restricted to a narrow range of 0 to about 25 mg kg^{-1}. With increasing CEC, an increasingly wide range of Zn concentrations is reported.

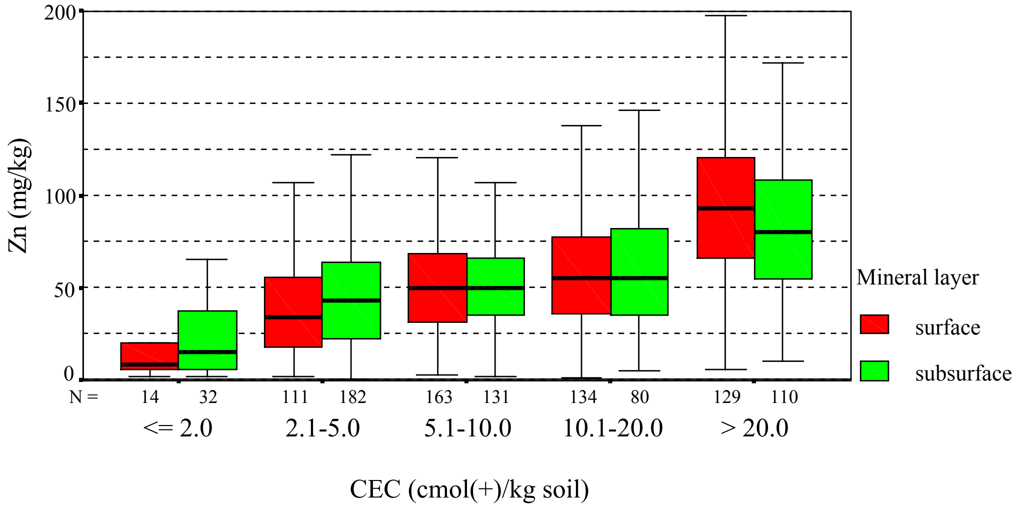


Figure I 2-76. Distribution of zinc concentrations in the mineral soil for different CEC classes.

Exchangeable zinc decreases as soil pH increases. At high pH levels more zinc is adsorbed onto positions from which it is not readily displaceable. Organic matter forms co-ordination complexes with zinc, which is the most important source of soluble zinc in high-pH soils. Average zinc concentrations in the organic layer mostly slightly exceed concentrations in the mineral soil, except in soils having pH above 6.0 (Figure I 2-77). Zinc uptake is also affected by the presence of other cations. Alkaline-earth cations, such as Mg and Ca, seem to inhibit zinc uptake non-competitively, while copper strongly competes with zinc for uptake by roots (Barber, 1995).

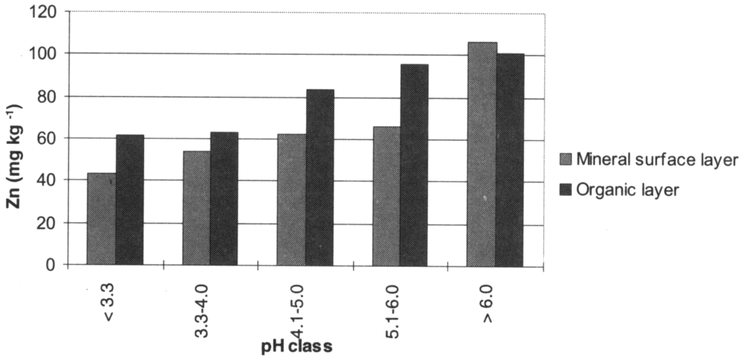


Figure I 2-77. Average zinc concentrations in organic and mineral surface layers for different pH classes.

2.10.6 Copper

The availability of information on copper is illustrated in Table 12-38.

Table I 2-38. Copper concentration (optional parameter) - data availability (see also Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	0	0	100	99	0	100	0	0	0	95	0	0	0	100	100	100	0	100	0	99	0	0	0	1363
Min. Layer	0	0	100	27	0	0	0	0	0	95	0	0	0	100	0	100	0	92	0	0	0	0	0	555
Analysis	X	X	N	N	X	N	X	X	X	R	X	X	X	N	N	R	X	N	X	R	X	X	X	9%

Exchangeable plus solution copper mostly represent a very small fraction of total copper concentration in soils. Specifically adsorbed copper appears to constitute the major copper reserve that buffers the copper concentration in the soil solution. Organic matter is the primary constituent specifically adsorbing copper. Soil pH has a large effect on specific adsorption: more copper is adsorbed as pH increases. The residual copper, present in oxides and other minerals, usually constitutes about 50% of total copper, but is of little significance for plant uptake. The most common mineral form of copper is the sulphide, such as chalcopyrite, $CuFeS_2$. Under oxidising conditions, the copper is oxidised to the divalent form as the mineral is released by weathering. Copper can also be substituted for Mn, Fe and Mg in various minerals (Barber, 1995).

Approximately 10 mg kg^{-1} of dry weight of plants is Cu (Barber, 1995). Contaminated plants usually contain more than 20 mg kg^{-1} Cu (Kabata-Pendias and Pendias, 1984). More than 90% of the soils for which mineral layer concentrations are reported contain a total of 1 to 50 mg kg^{-1} of copper (Figure 12-78). The copper concentration of soils where Cu deficiency may occur is 1 to 3 mg kg^{-1} (Barber, 1995). About 10% of the mineral surface layers of European forest soils contains 3 mg kg^{-1} Cu or less.

Copper deficiency occurs in relatively few soils, probably because of the low requirements of most plants (Barber, 1995). Soils showing copper deficiency are usually organic or sandy soils in regions with high rainfall and can often be associated with parent rocks poor in copper. Highly weathered soils and calcareous sands have also been reported to be deficient in copper (Pritchett and Fisher, 1987). Symptoms are generally noted as distortion of the terminal and leading lateral shoots, often followed by defoliation and dieback.

There appears to be a relatively narrow range over which copper concentration is satisfactory for plant growth. In soils where excessive Cu has accumulated, total Cu concentration is 200 mg kg^{-1} or more (Fiskell, 1965). Witter (1992) and Kabata-Pendias and Pendias (1984) suggested 60 mg kg^{-1} as the threshold value at which toxicity symptoms may occur. This critical value is exceeded in the mineral surface layer of only 11 plots for which Cu concentrations were reported (Table I 2-39). Excessive copper availability leads to stunted root systems (Fiskell, 1965). Copper toxicity is corrected by increasing the organic matter content and by increasing the pH through liming (Aubert and Pinta, 1977).

The range of values over which Cu concentrations varies is narrower in organic layers than in mineral layers. Copper concentrations in organic layers of either less than 4 mg kg^{-1} or more than 32 mg kg^{-1} occur in 5% of the plots. However, concentrations in organic layers of 100 mg Cu kg^{-1} and more have been reported for 1 Finnish, 3 German and 3 Slovakian plots. Exceedence of the critical concentration for organic layers of 20 mg Cu kg^{-1}, proposed by Tyler (1992), is quite common (Table 12-39). Nineteen percent of the reported organic layer Cu concentrations are above this critical value. Particularly in the Slovak Republic, Germany and the Netherlands a high proportion of soils with elevated Cu concentrations in the organic layer are found.

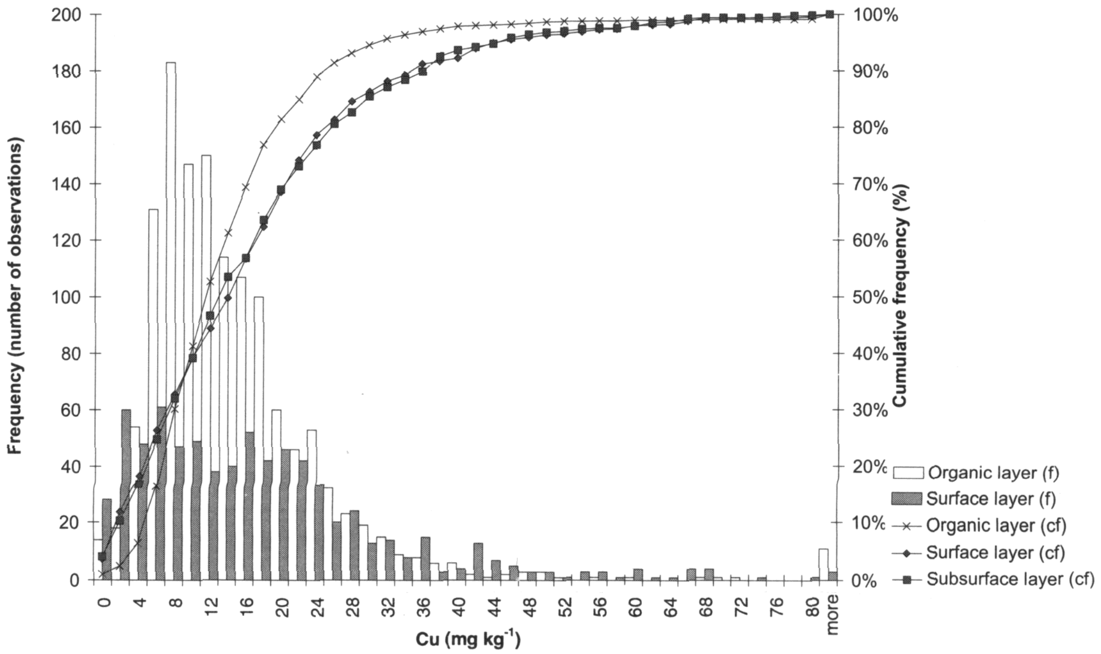


Figure I 2-78. Frequency (f) and cumulative frequency (cf) distribution of copper concentrations in organic and mineral layers.

Table I 2-39. Exceedence - number (n) and percentage (%) of plots - of critical copper concentrations (optional parameter) for organic (org) and mineral (min) surface layers.

	NL	DL	UK	PO	AU	FI	SR	CH	LI	all plots
org > 20	3	122	13	33	14	27	42	1	0	**255**
mg kg^{-1}	27%	32%	19%	22%	11%	6%	38%	13%	0%	**19%**
min > 60	1	1	n.d.	7	1	n.d.	1	0	n.d.	**11**
mg kg^{-1}	9%	1%	n.d.	5%	1%	n.d.	1%	0%	n.d.	**2%**

n.d. = not determined

In general the element accumulates in upper clayey horizons. Soil acidity seems to have little effect on Cu concentrations in the mineral soil (Figure 12-79). Experiments have shown that the soil is able to maintain an adequate level of copper even when free Cu^{2+} is reduced by increasing soil pH (Barber, 1995). This is confirmed by similar average Cu concentrations in organic layers of various pH.

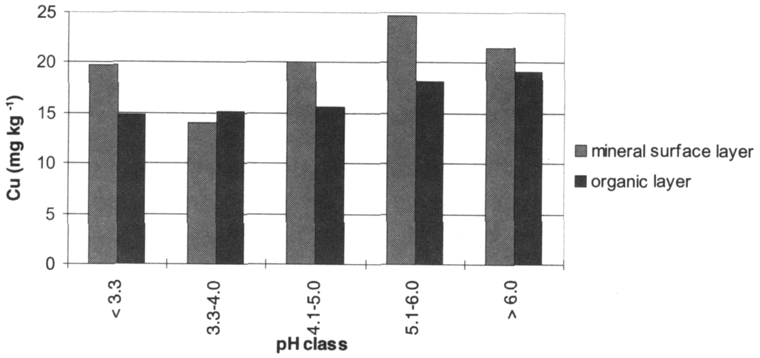


Figure I 2-79. Average copper concentrations in organic and mineral surface layers for different pH classes.

The formation of insoluble compounds between copper and fulvic acids at pH 2.5-3.5 is a possible cause for copper deficiency in acid peaty soils (Aubert and Pinta, 1977). Laboratory experiments of free Cu^{2+} in solution versus soil pH suggest that pH should have a considerable effect on copper uptake (Cottenie and Verloo, 1984; Masscheleyn et al., 1996). Other experiments have shown that soil pH does not greatly affect copper uptake in practice, i.e. that the soil is able to maintain an adequate level of copper even when free Cu^{2+} is reduced by increasing soil pH (Barber, 1995).

2.10.7 Lead

The availability of information on lead is illustrated in Table 12-40.

Table I 2-40. Lead concentration (optional parameter) - data availability (see **also** Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	0	0	0	99	0	100	0	0	0	95	0	0	0	100	100	0	0	100	0	99	0	0	0	1241
Min. Layer	0	0	0	27	0	0	0	0	0	95	0	0	0	100	0	0	0	92	0	0	0	0	0	433
Analysis	X	X	X	N	X	N	X	X	X	R	X	X	X	N	N	X	X	N	X	R	X	X	X	38%

Lead extractable with diluted acids, so-called plant-available lead, constitutes only a small fraction of total lead in soils. Soil lead is largely unavailable to plants, as evidenced by the small increases in lead content of plants following soil applications of the element (Brady and Weil, 1996). Total lead concentrations are often slightly higher than those of parent rocks. Soil lead concentrations usually decrease from the forest floor downward. Median lead concentration values decrease from 41 mg kg^{-1} in organic layers, to 32 mg kg^{-1} in mineral surface and 24 mg kg^{-1} in subsurface layers (Figure 12-80). Accumulation of lead in upper soil horizons indicates little downward movement.

A 'toxic' amount of 100 mg kg^{-1}, proposed by Kabata-Pendias and Pendias (1984), has been reported in the surface layer of 23 plots (Table I 2-41), and in the subsurface layer of 11 plots. Very high metal concentrations are infrequently measured in soil types associated with low microelement concentrations, such as Podzols. This appears to be less valid for lead accumulations in soil, because Podzols (4 plots) occur in the list of soil types of plots with an unusually high Pb concentration in the mineral topsoil. Observations of lead accumulating at the soil surface, independently of soil type, support the theory that atmospheric deposition is the major source of lead in forest soils.

The lead concentration in the organic layer is usually higher than in the underlying mineral soil, but the critical limit of 500 mg kg^{-1}, given by Tyler (1992), is rarely exceeded (Table I 2-41). Lead concentrations of more than 500 mg kg^{-1} have been measured in the organic layer of only 7 plots.

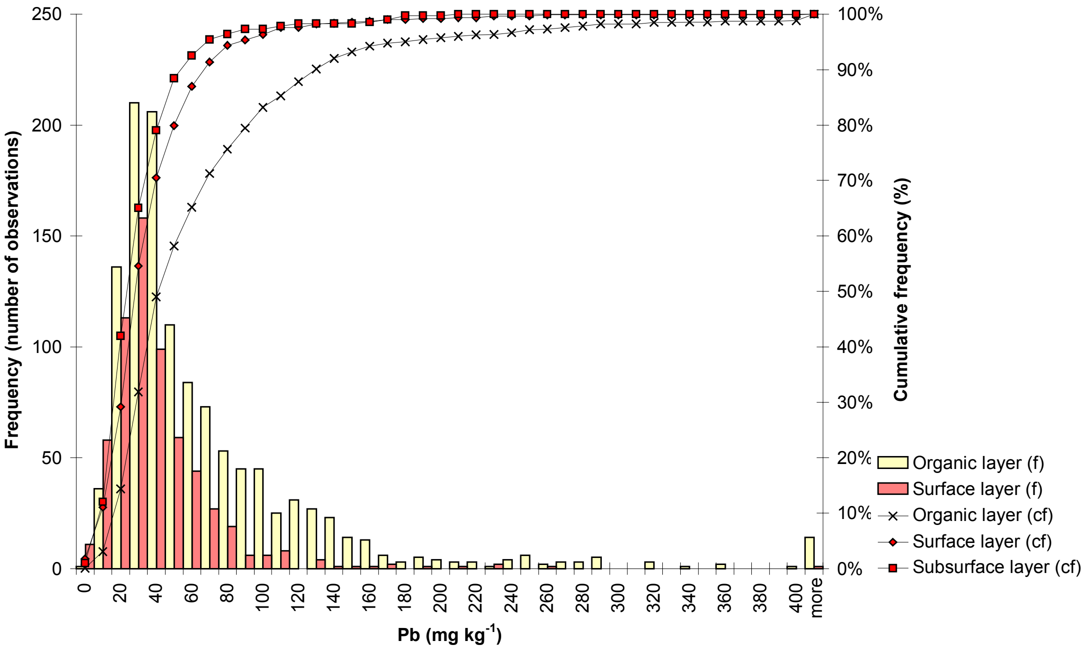


Figure I 2-80. **Frequency (f) and cumulative frequency (cf) distribution of lead concentrations in organic and mineral layers.**

Table I 2-41. **Exceedence - number (n) and percentage (%) of plots - of critical lead concentrations (optional parameter) for organic (org) and mineral (min) surface layers.**

	DL	UK	PO	AU	FI	CH	LI	all plots
org > 500	6	1	0	0	0	0	0	**7**
mg kg^{-1}	2%	1%	0%	0%	0%	0%	0%	**1%**
min > 100	3	n.d.	0	19	n.d.	1	n.d.	**23**
mg kg^{-1}	3%	n.d.	0%	15%	n.d.	2%	n.d.	**5%**

n.d. = not determined

Retention of lead in the soil is largely determined by the CEC of the material and its organic matter content (Figure I 2-81).

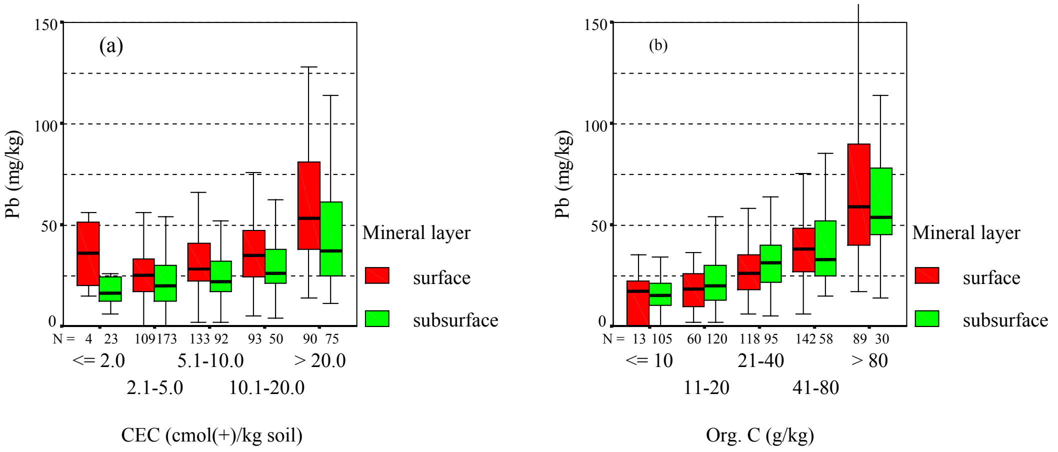


Figure I 2-81. **Variation of lead concentrations related to CEC (a) and organic C content (b).**

Lead concentrations in the organic layer are usually higher than those in mineral soil, except in neutral or alkaline soils (Figure I 2-82). The largest difference between organic layer and mineral layer concentrations are observed on very acid soils, indicating a higher bio-availability of lead in acid conditions.

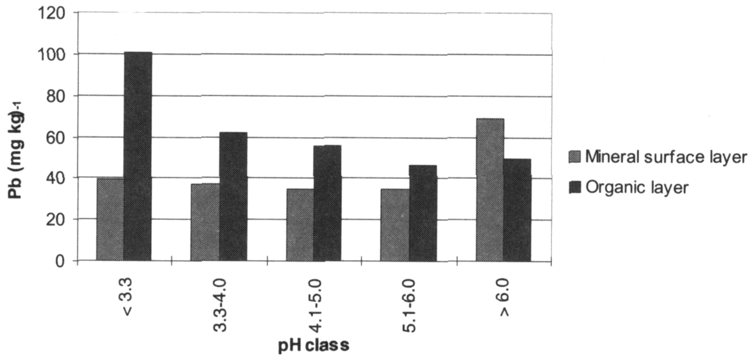


Figure I 2-82. **Average lead concentrations in organic and mineral surface layers for different pH classes.**

2.10.8 Cadmium

The availability of information on cadmium is illustrated in Table **I** 2-42.

Table I 2-42. **Cadmium concentration (optional parameter) - data availability** (see **also** Figure I 2-1 for interpretation).

	FR	BE	NL	DL	IT	UK	IR	DK	EL	PO	ES	LX	SW	AU	FI	SR	NO	CH	HU	LI	CR	CZ	SL	# Total
Org. Layer	0	0	0	97	0	100	0	0	0	95	0	0	0	100	100	0	0	100	0	99	0	0	0	1235
Min. Layer	0	0	0	27	0	0	0	0	0	95	0	0	0	100	0	0	0	92	0	0	0	0	0	433
Analysis	X	X	X	N	X	N	X	X	X	R	X	X	X	N	N	X	X	N	X	R	X	X	X	45%

Cadmium does not appear to enter into the crystal lattice of layer silicates. Among the heavy metals, only Cd, which is less strongly absorbed, tends to occur in significant proportions in the exchangeable form in soils (Soon and Abboud, 1993). Organic and mineral soil layers display similar cadmium concentrations, which are usually less than 1 mg kg^{-1}, but may occasionally be as high as 5 or 6 mg kg^{-1} (Figure 12-83). A cadmium amount of 3 mg kg^{-1} in the mineral soil may cause toxic effects in plants (Kabata-Pendias and Pendias, 1984), but is only occasionally measured in European forest soils. In 16 soils, of which 9 are Leptosols, the Cd concentration of the mineral surface layer exceeds this 'toxic' amount (Table **I** 2-43).

Among the 1235 reported organic layer cadmium concentrations 75% are below 1.0 mg kg^{-1}, and only **7** reported values exceed the critical concentration of 3.5 mg kg^{-1}, proposed by Tyler (1992) (Table I 2-43).

Table I 2-43. **Exceedence - number (n) and percentage** (%) **of plots - of limit concentrations of cadmium (optional parameter) in organic (org) and mineral (min) surface layers.**

	DL	UK	PO	AU	FI	CH	LI	all plots
org > 3.5	2	4	0	1	0	0	0	**7**
mg kg^{-1}	1%	6%	0%	1%	0%	0%	0%	**1%**
min > 3.0	0	n.d.	3	6	n.d.	7	n.d.	**16**
mg kg^{-1}	0%	n.d.	2%	5%	n.d.	16%	n.d.	**4%**

n.d. = not determined

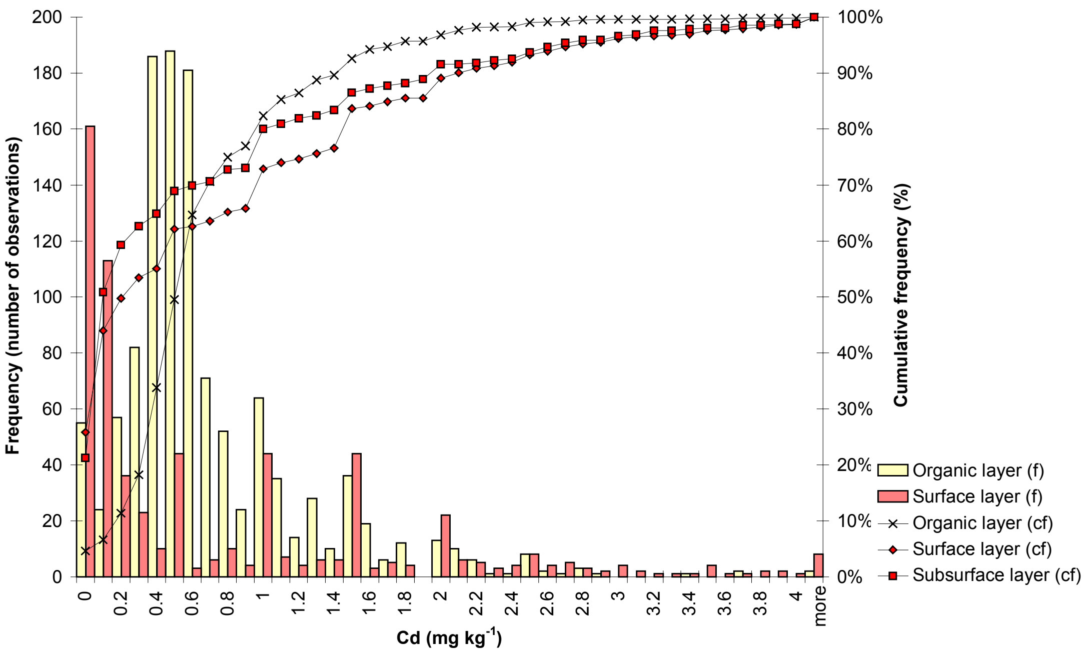


Figure I 2-83. Frequency (f) and cumulative frequency (cf) distribution of cadmium concentrations in organic and mineral layers.

Cadmium is mostly associated with organic matter in the mineral soil. Average concentrations in surface layers poor in organic materials are about ten times smaller than the average concentrations in soils high in organic matter (Figure I 2-84b).

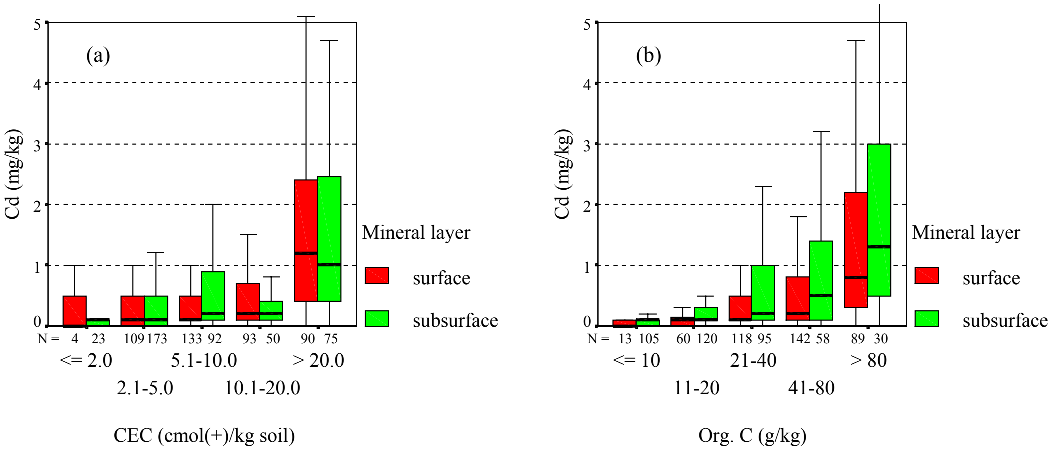


Figure I 2-84. Variation of cadmium concentrations related to CEC (a) and organic C content (b).

The highest concentrations, up to 5 mg kg^{-1} and more, are found in calcareous soils with a high cation exchange capacity (> 20 cmol(+) kg^{-1}). Cadmium is poorly retained in soils with a low exchange capacity (Figure I 2-84a). In only 10% of mineral surface layers with a CEC of 10 cmol(+) kg^{-1} or less, Cd concentration exceeds 1 mg kg^{-1}. Linear correlation coefficients between Cd concentration and CEC of 0.53 and 0.45 in the mineral surface layer and in the subsurface layer, respectively, indicate that cadmium in the soil is largely in exchangeable form.

Cadmium ions adsorbed on organic and mineral exchange sites may be leached from the soil in acid conditions. Although the cadmium concentration in mineral soil increases with increasing pH, the same trend is only partially followed in the overlying organic layer (Figure

12-85). This may indicate a stronger retention in high-pH soils, where Cd concentrations in the organic are usually lower than in the mineral soil.

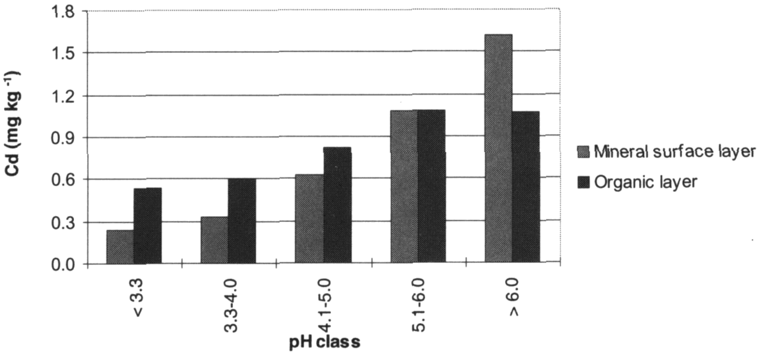


Figure I 2-85. **Average cadmium concentrations in the organic and mineral surface layer for different pH classes.**

3. EVALUATION OF SOIL QUALITIES

3.1 Concept of Data Evaluation

In this chapter the soil condition data are used to evaluate the ecological quality of the observation plots in function of their:

- nutrient availability (nitrogen, phosphorus, basic cations);
- sensitivity to soil acidification;
- heavy metal availability (focus on Zn, Pb, Cd).

For each of these soil qualities indicator values were calculated and classified in qualitative terms; for example general terms such as ‘high’ and ‘low’ but also ‘risk for toxicity’ or ‘risk for deficiency’ are used. Because none of the above qualities was directly measured, they were derived from a combination of individual parameter values by means of a rating system. The rating system is based on simple arithmetic principles, combining measured parameters and derived stress parameters.

Measured parameter results were ranked and grouped in 5 classes (1 = very low; 2 = low; 3 = medium; 4 = high; 5 = very high), based on their frequency distribution, while taking into account ecologically relevant limit values (see also section 1.4.1 and annex D). Most measured parameters express total concentrations of a certain element in the soil and give on their own little or no information about the availability of the element. However, in combination with other measured parameters, ecological soil quality indications can be obtained.

Stress Parameters were derived from measured parameters and were attributed a rating value. Rating values were defined in function of the effect the stress parameter has on the availability of the concerned nutrient or contaminant (Table I 3-1).

Table I 3-1. Stress parameters used in the determination of ecological indicator values.

Stress Parameter	Reference Data	Rating Value	Qualitative Description
C/N ratio	≤ 16	5	very narrow
	17 - 24	4	narrow
	25 - 30	3	intermediate
	31 - 40	2	wide
	> 40	1	very wide
C/P ratio	≤ 200	5	very narrow
	201 - 400	4	narrow
	401 - 600	3	intermediate
	601 - 800	2	wide
	> 800	1	very wide
Climatic Zone	South Atlantic	5	the rating values reflect differences in decomposition rate of plant residues as determined by climate
	Mediterranean	4	
	North Atlantic, Subatlantic, Continental	3	
	Temperate Boreal, Mountainous (South)	2	
	Boreal, Mountainous (North)	1	
pH class	element-dependent rating values are attributed to pH ($CaCl_2$) intervals, relative to element mobility (Table I 3-5 and 3-8)	variable range	

The rating system, which is inspired by a concept used by Block et al. (1996), applies a simple arithmetic key. The class and rating values of the parameters that determine the soil quality indicator are summed or multiplied, resulting in an ecologically interpretable indicator value (Figure I 3-1). Thus, the range of each indicator value is determined by the ranges of underlying class and rating values. The indicator values have a relative value, and allow direct comparison between plots. They are classified in qualitative terms (see sections 3.2 to 3.5). The used rating system has the advantage that the chemical data are not evaluated for their absolute measured values, which show a very high variability, but for their ecological value.

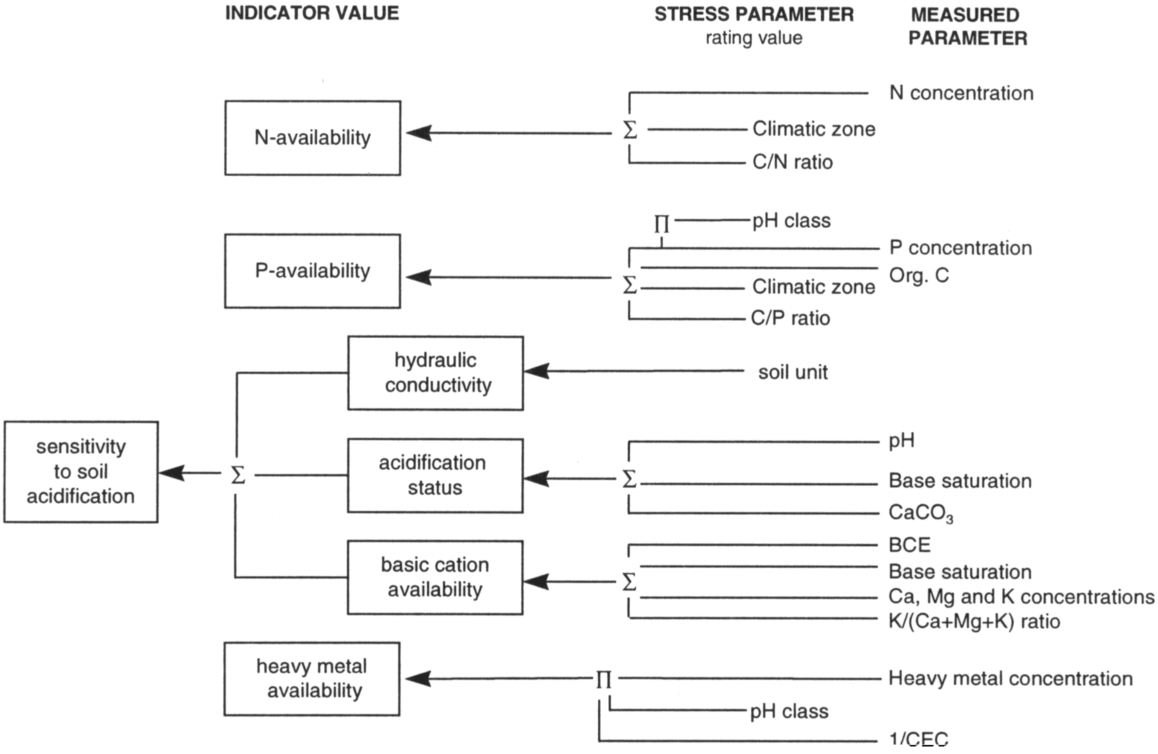


Figure I 3-1. Schematic presentation of the data evaluation concept, using measured parameters and stress parameters to obtain indicator values ('Σ' indicates summation, 'Π' multiplication).

It should be noted that the proposed evaluation procedure does not take into account all influencing factors. With improving knowledge and data availability, both the rating system and the arithmetic key could be amended in order to evaluate soil quality in a more realistic way.

Mineral soil parameters (pH, BCE, CEC, base saturation, $CaCO_3$, C/N) are weighted according to depth and thickness in such a way that the sum of the weighting factors of the individual mineral layers until 20 cm (or 30 cm) equals 2 (Table I 3-2). Surface layers received a higher weight than subsurface layers, because it is assumed that root density decreases with depth. Buffering processes against acid deposition also take place mostly in the upper part of the soil.

Table I 3-2. Depth weighting factors.

Layer	Weighting Factor
O or H	1
M05 (0-5 cm)	2/3
M51 (5-1 cm)	2/3
M01 (0-10 cm)	4/3
M12 (10-20 cm) or M13 (10-30 cm)	2/3
M02 or M03	2

3.2 Nutrient Availability

Plant nutrient availability in soil depends greatly on the amount and nature of the nutrients in the soil solution and their association with nutrients adsorbed by or contained within the solid phase of the soil. The reaction of nutrients with soil surfaces is affected by the nature of the inorganic and organic materials that make up the soil particles (Barber, 1995).

Nutrient deficiencies are uncommon in undisturbed forests, because of the conservative nature of nutrient cycling, deep-rooting habits of most trees, and the apparent capacity of mycorrhizal roots to extract some minimally available nutrients from soils (Pritchett and Fisher, 1987). However, the intensification of forest management and the increase in plantation forest, particularly of exotic species, have resulted in increasingly higher demands on chemical fertility levels in forest soils.

The calculated indicator values, assessing nutrient availability, have only a relative indicative value, but can be used for comparison between plots. Classification of the obtained indicator values in qualitative terms is based on their frequency distribution. Class limit values correspond approximately to the 10-, 30-, 70- and 90-percentile values (Table I 3-3).

Table I 3-3. Percentile values (in %) used in the interpretation of indicator values for nutrient availability.

Qualitative Availability Class	Percentile values used for class intervals
very low	*0 - 10*
low	*10 - 30*
medium	*30 - 70*
high	*70 - 90*
very high	*90 - 100*

3.2.1 Nitrogen Availability

Nitrogen in forest soils is found largely in organic forms in the humus layer and the surface mineral layer. Nitrogen availability for forest growth is determined by the rate of decomposition of plant residues and not so much by the underlying pool size (Waring and Schlesinger, 1985). Decomposition rates are strongly influenced by the carbon to nitrogen ratio of the organic residue (Barber, 1995). During mineralisation of organic litter, the C/N ratio decreases with time. This results from the gaseous loss of carbon dioxide, while the nitrogen remains bound in organic combination. When low-nitrogen residues are added to the soil, nitrogen is immobilised during decomposition and transformed into relatively stable nitrogen forms. If the C/N ratio is low, on the other hand, nitrogen is released, as micro-organisms decompose the residues.

The slow rate of decomposition in forest soils of cool climate areas sometimes results in nitrogen deficiencies (Weetman and Webber, 1972). Microbial activity increases exponentially with increasing temperature. The overall decomposition rate is also influenced by soil moisture. Most forests grow in temperate conditions, where soil moisture does not usually limit microbial activity (Waring and Schlesinger, 1985). However, when precipitation is not evenly distributed throughout the year, soil moisture can limit decomposition during the dry season.

The indicator value for N-availability (I_N) is calculated as follows:

$$I, = N_c + R_{CN} + R_{CZ}$$

where:

N_c = ***cumulative class value of the nitrogen concentration in the mineral layers (range 0 to 10);***
$R_{C/N}$ = ***cumulative rating value of the C/N ratio in the organic and mineral layers (range 1 to 15);***
R_{CZ} = ***rating value associated to the climatic zone (range 1 to 5);***

Although pH has an effect on the availability of nitrogen (Pritchett and Fisher, 1987), it is highly variable and therefore not considered in the determination of I_N..

When mineral layers are involved, the class values of the individual layers until a depth of 20 cm (or 30 cm in case of M13 and M03 layers) are weighed before summation. As a result of the

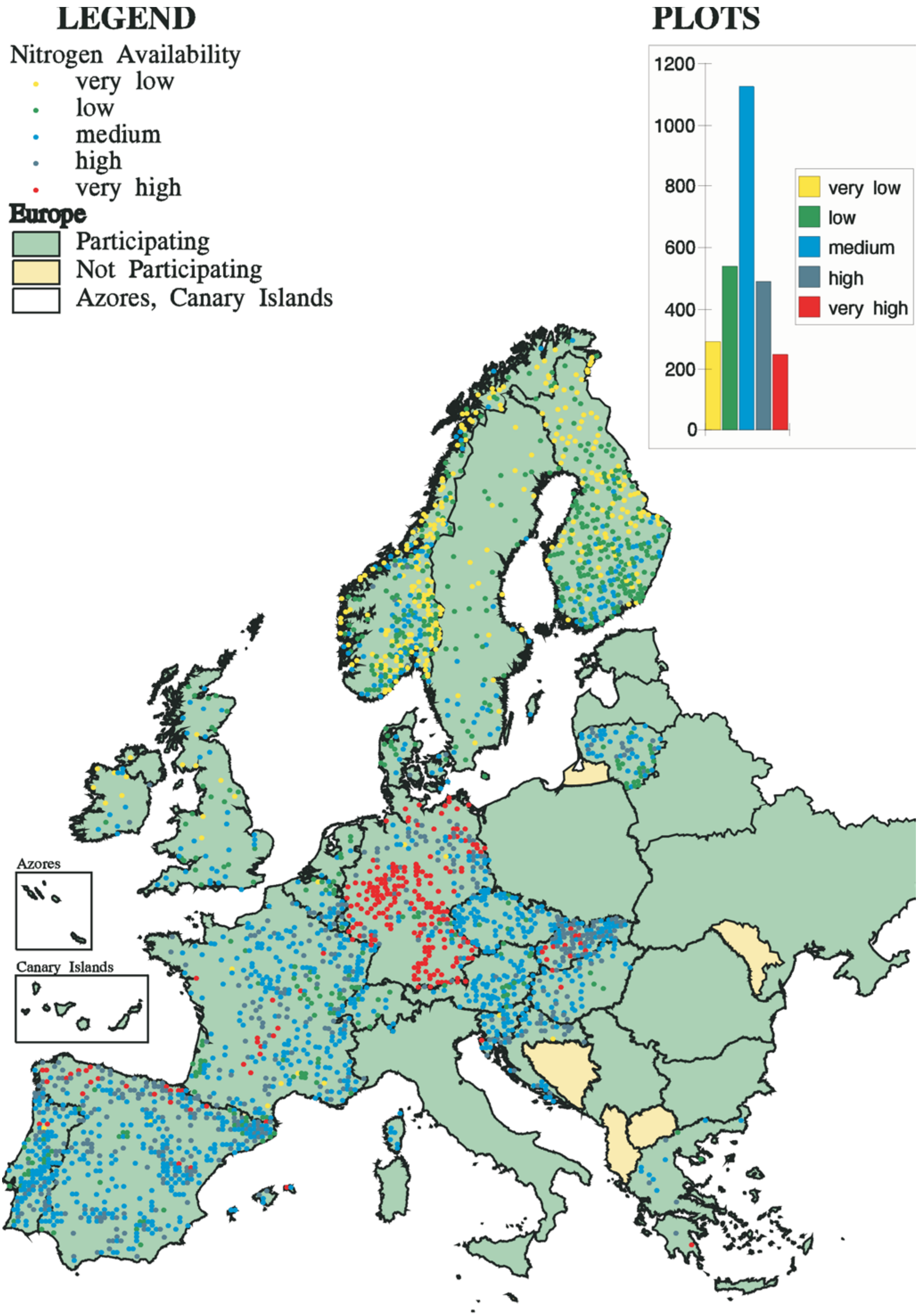


Figure I 3-2. Nitrogen availability.

summation, the range of class values may be a multiple of the original class value range (1 to 5), when parameter results of more than one layer are considered. For example, N_c, is calculated as:

$$N_c = \sum_i w_i \cdot (N_c)_i$$

where:

$(N_c)_i$ = *class value of the nitrogen concentration in layer i;*
w_i = *weighting factor of layer i (Table I 3-2).*

Histosols consisting only of an organic layer, without mineral layers, receive class value 0 for mineral layer parameters. Since mineral surface and subsurface layers are considered in the calculation, the resulting N_c may range between 0 and 10. When the organic layer is also considered (e.g. in the calculation of $R_{C/N}$), a class value range of 1 to 15 is obtained.

The range of calculated nitrogen availability indicator values was subdivided into 5 classes (Table I 3-4).

Table I 3-4. Class distribution of nitrogen availability: range of indicator values (I_N), number (n) and percentage of observations.

Nitrogen Availability Class	I_N	n	observations (%)
very low	≤ 12.0	293	11
low	12.1 - 17.5	538	20
medium	17.6 - 23.0	1129	42
high	23.1 - 26.5	489	18
very high	> 26.5	248	9

The assessed nitrogen availability indicator values show a distinct spatial trend. Figure I 3-2 shows a low availability in Scandinavian countries and on the British Isles. In the rest of Europe, very low nitrogen availability is expected to occur rarely. A concentration of plots with high or very high N availability is found in Germany, the Slovak Republic, and northern Spain.

Because humus type has not been used in the assessment of N availability, it can be used to verify the validity of the indicator value (Figure I 3-3). It is generally known that humus type is related to the nutrient conditions in the soil. The majority of plots with peaty organic layers is expected to have a very low availability of nitrogen. Nitrogen supply may be low or very low in approximately one half of the soils with mor humus, whereas soils with moder or mull humus are expected to have an adequate N supply.

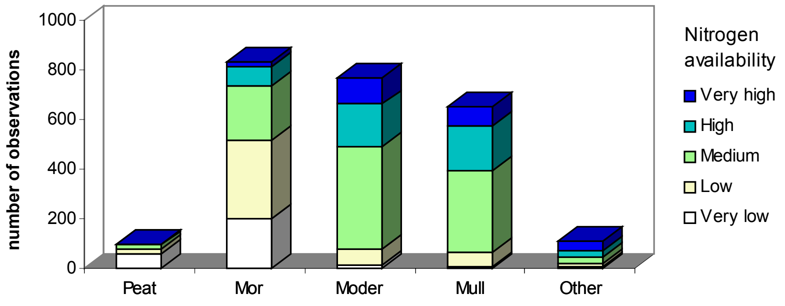


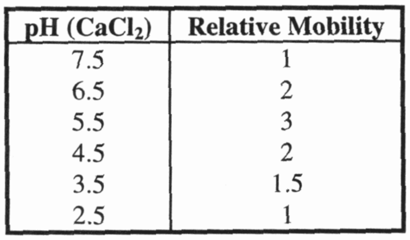
Figure I 3-3. Class distribution of nitrogen availability for plots grouped by humus types.

3.2.2 Phosphorus Availability

Similar to nitrogen, the availability of phosphorus is much more determined by the rate of decomposition of organic material than by the total pool size of P in the soil (Waring and Schlesinger, 1985). The decomposition rate can be assessed based on climatic conditions and on the C/P ratio. The C/P ratio decreases during decomposition of organic material (Staaf and Berg, 1982, in Waring and Schlesinger, 1985). During the growth of micro-organisms, which metabolise the organic *C* contained in litter, P is retained in microbial tissue while C is respired as CO_2. The biomass of bacteria and fungi does not contain a large percentage of the nutrient pool in soils, but the growth of these organisms frequently immobilises P that might otherwise be made available from decomposition. When microbial activity slows down and the microbial populations die, available P is released.

The availability of phosphorus to trees is influenced by soil acidity and its effect on the solubility of iron, aluminium and manganese, which form insoluble precipitation products with phosphorus in very acid soils. In less acid soils, phosphorus solubility is reduced in the presence of large amounts of calcium, which reacts with phosphorus to form calcium phosphate. The relative effect of soil acidity on the availability of phosphorus is expressed by a pH-dependent rating value (Table I 3-5). Since pH does not influence solution calcium activity in non-calcareous soils, the activity of calcium was assumed at a constant arbitrary level, consistent with values found for soil solutions (Barber, 1995).

Table I 3-5. Relative mobility of phosphorus as a function of soil pH ($CaCl_2$).
Adapted from Barber, 1995.



pH ($CaCl_2$)	Relative Mobility
7.5	1
6.5	2
5.5	3
4.5	2
3.5	1.5
2.5	1

Phosphorus concentration data are mostly available for organic layers, much less for mineral layers. However, since phosphorus is usually associated with organic matter, the organic carbon content of the mineral layers can be used to indirectly assess the P reserve in the mineral soil.

The indicator value for P-availability *(I_P)* is calculated as follows:

$$I, = P_c . R_{pH} + R_{C/P} + R_{CZ} + Org.C_c$$

where:

P_c = ***class value of the phosphorus concentration in the organic layer (range 1 to 5);***
$R_{C/P}$ = ***rating value of the C/P ratio in the organic layer (range 1 to 5);***
R_{CZ} = ***rating value associated to the climatic zone (range 1 to 5);***
R_{pH} = ***pH-dependent rating value for relative element availability (range 1 to 3).***
$Org.C_c$ = ***cumulative class value of the organic carbon concentration in mineral layers (range 0 to 10)***

The pH-dependent relative mobility is directly used as rating value in the evaluation of heavy metal availability. An arbitrary rating value of 1 is assumed at pH 7.5. Linear interpolation is used to obtain the rating value corresponding to a pH value in between two listed pH values. Above pH 7.5, a rating value of 1 is maintained. By multiplying the pH rating value with the P concentration class in the determination of ***I_P***, soil acidity is given a weight which is relative to its effect on the P mobility.

The range of calculated phosphorus availability indicator values was subdivided into 5 classes (Table I 3-6).

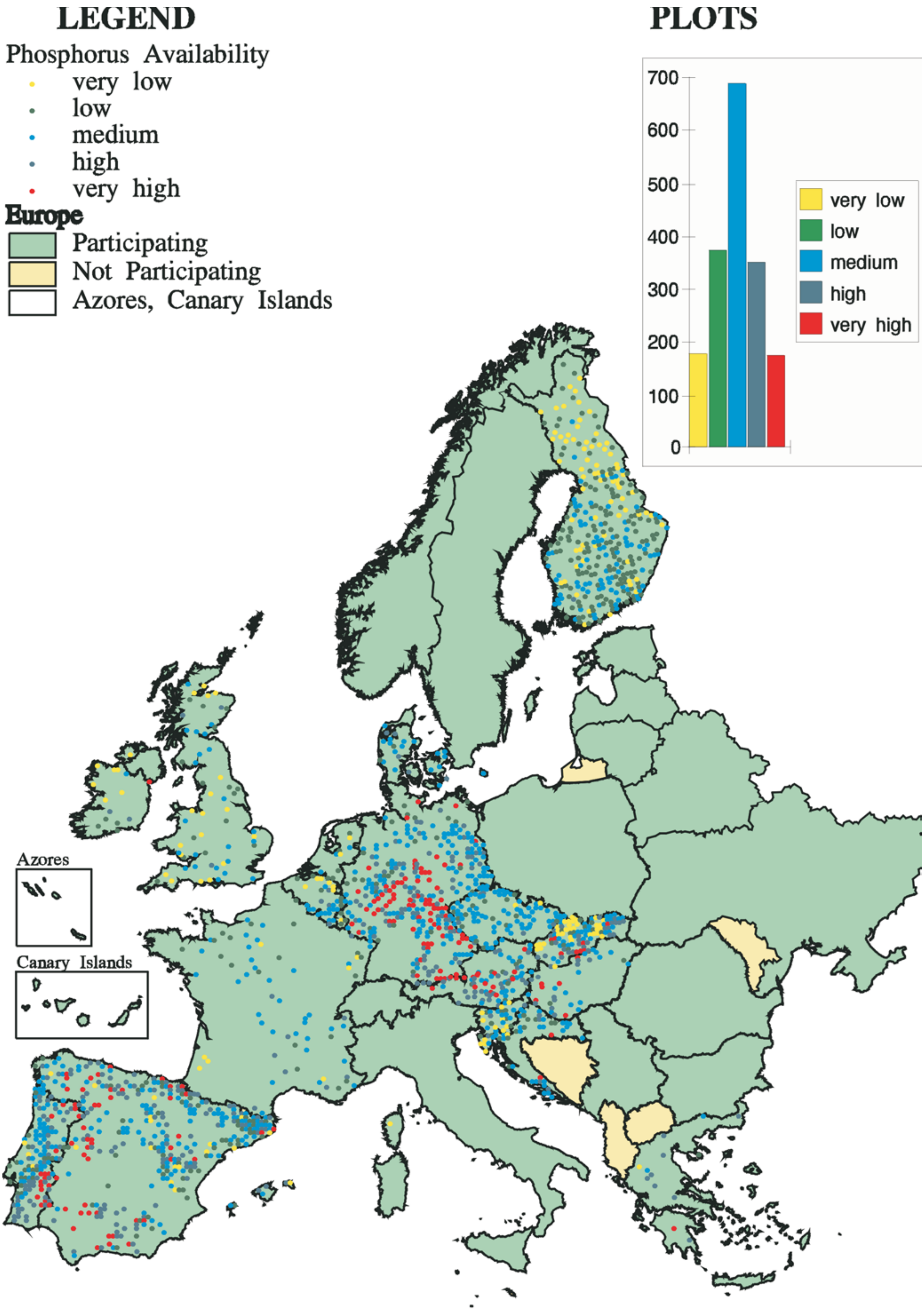


Figure I 3-4. Phosphorus availability.

Table I 3-6. Class distribution of phosphorus availability: range of indicator values (I_P), number (n) and percentage of observations.

Phosphorus Availability Class	I_P	n	observations (%)
very low	≤ 8.2	180	10%
low	8.3 - 10.8	374	21%
medium	10.9 - 14.6	688	39%
high	14.7 - 18.8	351	20%
very high	> 18.8	177	10%

Data unavailability for one of the required parameters prevented the calculation of phosphorus availability indicator values for the plots of 5 countries (CH, IT, LI, NO, SW). Although the spatial trend is not as obvious as with nitrogen availability,

Figure I 3-4 shows a general increase in expected P availability from north to south in Europe. The use of analysis methods that cause an incomplete analysis of P, may partly explain the clusters of plots classified as very low in P in the Slovak Republic, Slovenia and Croatia. Although Croatian and Slovak laboratories applied reference methods for the analysis of P, this hypothesis is confirmed by the relatively low intercalibration results for both standard samples. Measured P values are often low in these countries, resulting in relatively high C/P ratios. In the other countries, soils where phosphorus deficiency may occur, are usually poor in organic matter, either strongly acid or neutral, and have organic layers with a C/P ratio exceeding 500.

When plots are grouped by humus type, significant differences in estimated P availability become apparent (Figure I 3-5). Low availability is expected to occur two to three times more frequently in plots having peat or mor humus than in plots with mull or moder humus.

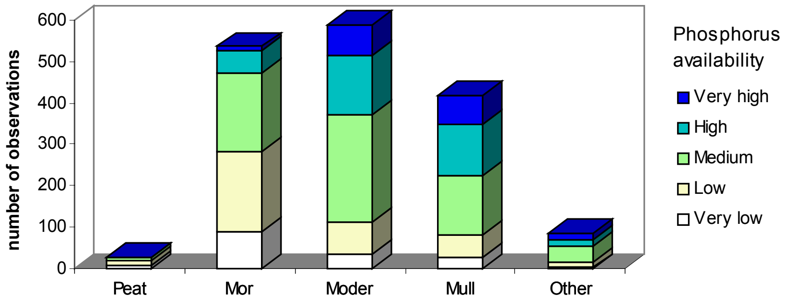


Figure I 3-5. Class distribution of phosphorus availability for plots grouped by humus types.

3.2.3 Basic Cation Availability

Calcium, magnesium and potassium are used by trees in large amounts. They are normally found in soils in sufficient quantities, but may be deficient in leached acid soils.

The indicator value for basic cation availability *(I_{BC})* is calculated as follows:

$$I_{BC} = BCE_c + BS_c + \frac{1}{3}\cdot\left(Ca_c + Mg_c + K_c\right)$$

where:

BCE_c = *cumulative class value of the sum of exchangeable basic cations in mineral layers (range 0 to 10);*

BS_c = *cumulative class value of the base saturation in mineral layers (range 0 to 10);*

Ca_c, Mg_c, K_c = *class value of the concentration of Ca, Mg and K in the organic layer (range 1 to 5).*

Concentrations of the major nutrient elements in the organic layer, instead of total amounts, are used in the assessment of basic cation availability, because of the high spatial variability of organic layer weight data *(OrgLay),* which affects the reliability of the calculated nutrient reserve values.

The sum of basic cations (BCE) and the base saturation express the capacity of the mineral soil layers to retain basic exchangeable cations. BCE indicates the number of cation exchange sites, both organic and mineral, that are occupied by cationic nutrients; it is largely dependent of the cation exchange capacity. The base saturation provides a measure of the competition with acid cations for these exchange sites and expresses the difficulty plants experience to take up nutrient cations.

The range of calculated basic cation availability indicator values was subdivided into 5 classes (Table I 3-7).

Table I 3-7. Class distribution of basic cation availability: range of indicator values (I_{BC}), number (n) and percentage of observations.

Basic Cation Availability Class	I_{BC}	n	observations (%)
very low	≤ 7.5	196	11
low	7.6 - 10.0	335	19
medium	10.1 - 17.5	699	40
high	17.6 - 23.5	332	19
very high	> 23.5	167	10

The availability of basic cations shows a north-south gradient similar to the spatial distribution of N and P indicator values (Figure I 3-7), but is also strongly affected by soil type. The majority of plots classified as very low in basic cations have soil types typically poor in nutrients, such as Podzols (60%) and Dystric or Gleyic Cambisols (20%). Plots classified as having a very high availability of basic cations are mostly associated with calcareous parent materials. The most frequently observed soil types at these plots are Rendzic and Eutric Leptosols (49%) and Calcaric, Chromic and Eutric Cambisols (28%). Podzols are not represented in the highest availability class.

The estimated indicator value for basic cation availability is related to soil texture (Figure I 3-6). The majority of soils with fine and very fine texture are well supplied of nutrient cations. The proportion of plots with a poor nutrient supply increases with increasing sand content.

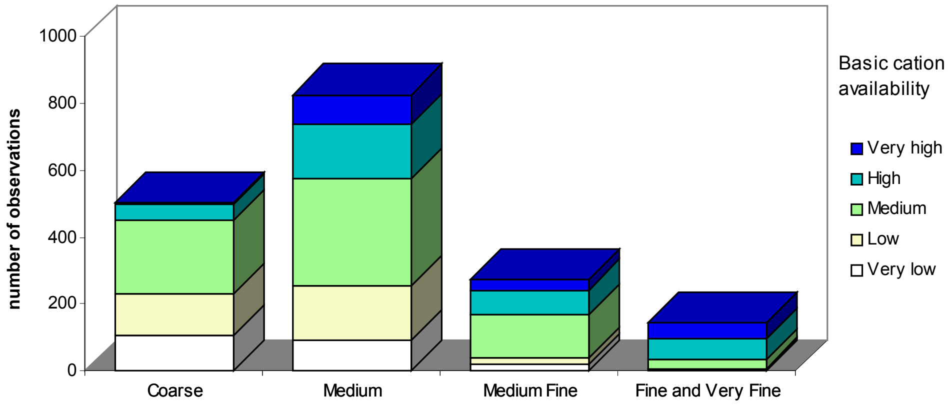


Figure I 3-6. Class distribution of basic cation availability for plots grouped by texture.

The relationship between humus type and nutrient availability is also valid for nutrient cations. Figure I 3-8 shows that half of the mor humus layers occurs on soils with a low or very low basic cation availability, whereas only 6% of the plots with mor layers is classified as having a high or

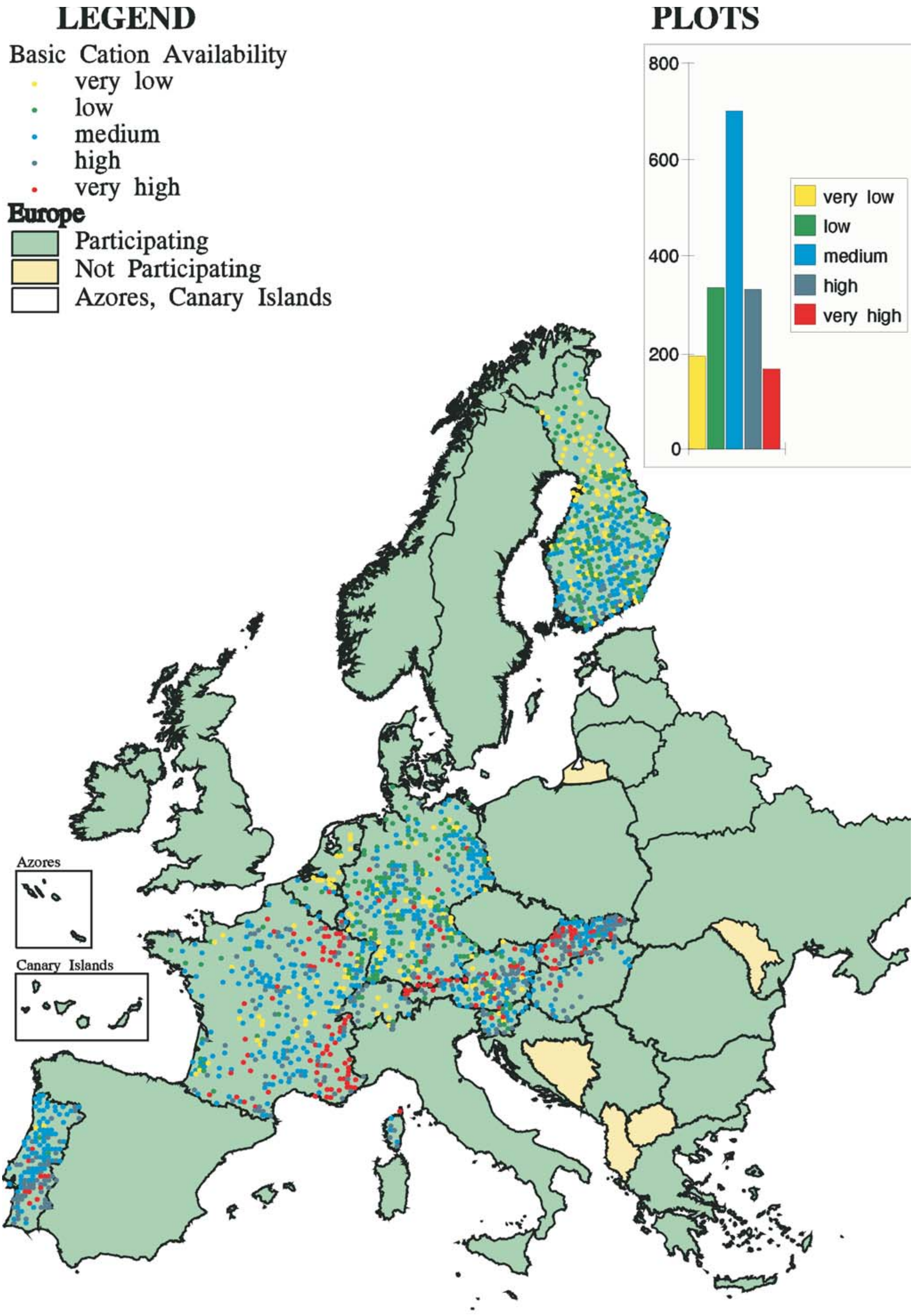


Figure I 3-7. Basic cation availability (derived from optional parameter results).

very high basic cation availability. The proportion of the classes 'high' and 'very high' increases gradually according to the mor-moder-mull sequence, covering 27% and 53% of the plots having respectively moder and mull humus.

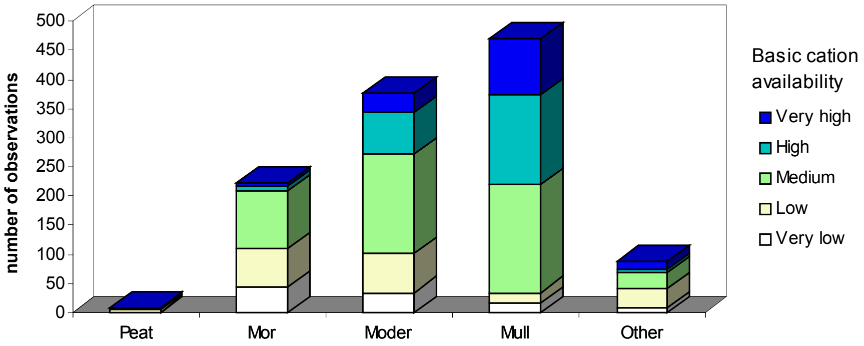


Figure I 3-8. Class distribution of basic cation availability for plots grouped by humus type.

3.3 Soil Acidification

3.3.1 Acidification Status

Soil acidification comprises several chemical soil processes that cannot be measured by single parameters. Soil acidity is determined by the nature of the acid-base reactions taking place in the soil. Soil pH is a measure for the acid-base equilibrium, and largely controls the weathering intensity and the depletion of nutrients. Strongly acidified soils have a low pH in the organic and surface mineral layer. However, it is not the only criterion to evaluate soil acidification status, because acid input can have effects on a soil without changing its pH. Carbonates, if present, are the first constituents to react when acids are added to the soil. The $CaCO_3$ concentration is a measure of the total reserve of carbonates, that may buffer acid input. In the absence of carbonates, removal of basic cations from the exchange complex is a common process associated with acidification. A progressive acid input results in a lowering of the base saturation. Thus, base saturation expresses the elasticity of a soil to further react against ongoing acid input. During this reaction basic cations are replaced by acid cations. Acid cations, present on the exchange complex, are in equilibrium with acid cations in solution, where they may reach toxic concentrations.

The assessment of the acidification status of a soil considers soil pH, base saturation and the presence of carbonates as a source for acid neutralisation. The indicator value for acidification status (I_{AS}) is calculated as follows:

$$I_{AS} = pH_c + BS_c + \left(CaCO_3\right)_c$$

where:

pH_c = *cumulative class value of the pH in the organic and mineral surface layer (range 1 to 10);*
BS_c = *class value of the base saturation in the mineral surface layer (range 0 to 5);*
$(CaCO_3)_c$ = *class value of the $CaCO_3$ concentration in the mineral surface layer (range 0 to 5).*

The range of calculated acidification status indicator values was subdivided into 5 classes (

Table I 3-8).

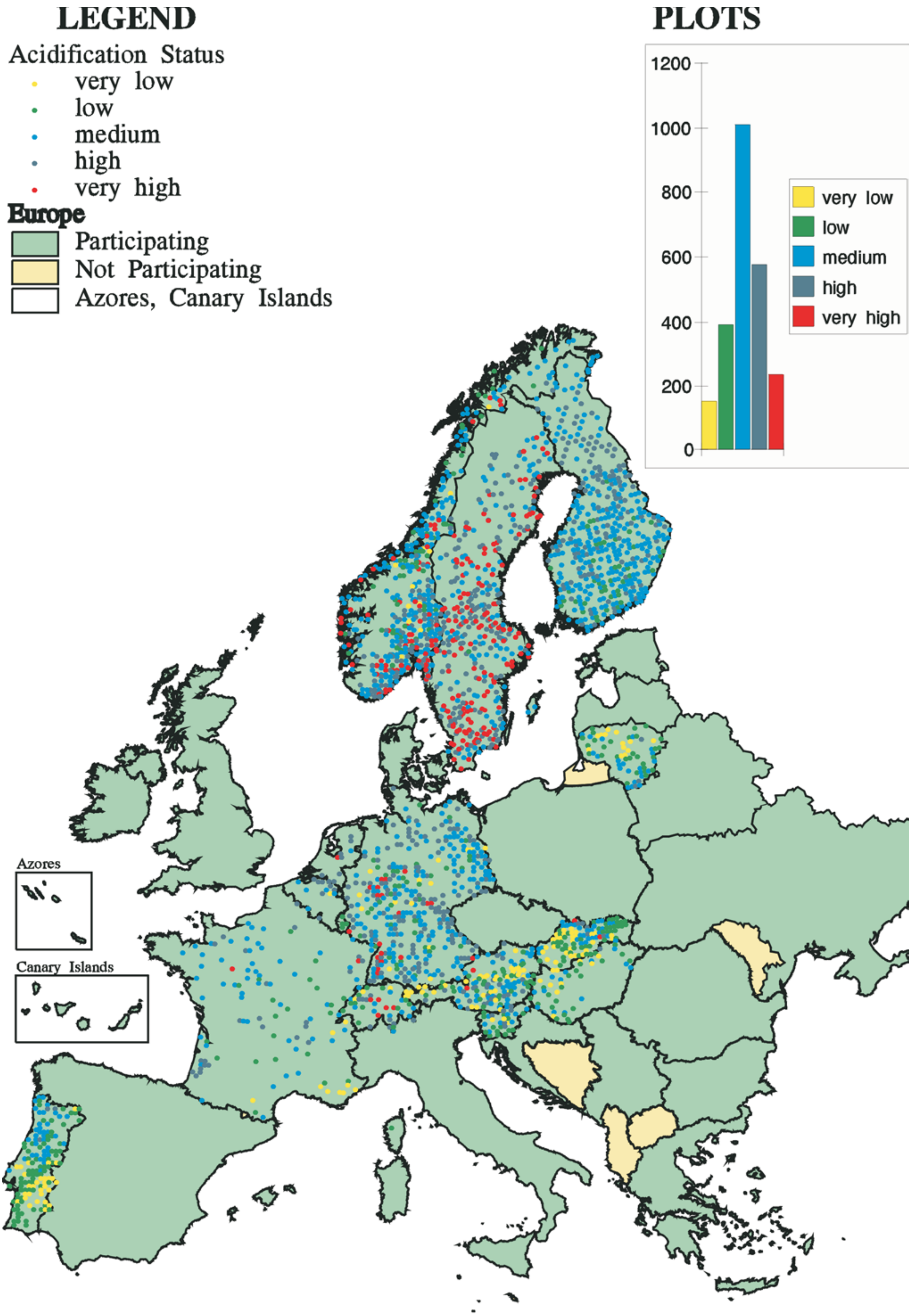


Figure I 3-9. Soil acidification status (derived from optional parameter results).

Table I 3-8. Class distribution of acidification status: range of indicator values (I_{AS}), number (n) and percentage of observations.

Acidification Status Class	I_{AS}	n	observations (%)
very low	> 12	157	7
low	10 - 12	394	17
medium	7 - 9	1011	42
high	4 - 6	578	24
very high	≤ 4	239	10

The acidification status has been assessed for plots of 15 countries (AU, BE, CH, DL, FI, FR, HU, LI, LX, NL, NO, PO, SL, SR, SW); 23% of the plots are attributed a low or very low acidification status, 34% a high or very high acidification status. The spatial distribution of the classified indicator values (Figure I 3-9) shows a NW-SE gradient. Countries with a continental or Mediterranean climate, such as Portugal, Slovenia, Hungary, the Slovak Republic and Lithuania have more than 50% of their plots classified in the ‘low’ and ‘very low’ acidification status classes. Sweden, the Netherlands and Belgium have 50% or more of their plots in the classes ‘high’ or ‘very high’. The large number of Swedish plots in the higher classes may be associated with the use of a buffered solution of relatively high concentration for the determination of cation exchange properties.

Arenosols and Podzols are often found among the highly acidified soils, but organic soils are best represented; 86% of the Histosols are attributed a ‘high’ or ‘very high’ acidification status class. More than 80% of the Fluvisols, Lixisols and calcareous soils, such as Rendzic Leptosols and Calcaric Cambisols, are found at the opposite end of the acidification status classification. Because some calcareous soils have strongly leached surface layers, they may not be attributed a low acidification status, although their subsurface layers may be fully base saturated.

Figure I 3-10 illustrates the association of humus type and acidification status. With increasing acidification the proportion of mull humus type decreases dramatically, whereas the proportion of mor humus type increases. The dominant humus type of the most strongly acidified soils is peat. The assessment of acidification status is in agreement with the observation that thick accumulations of litter on the soil surface in peat or mor layers mostly occur under acid conditions.

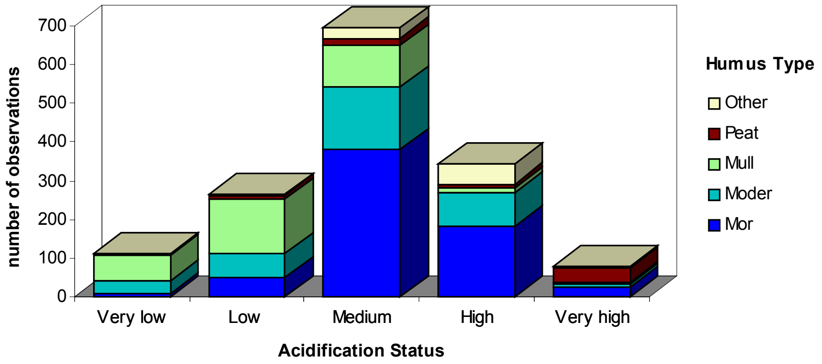


Figure I 3-10. Distribution of humus types in different acidification status classes.

3.3.2 Hydraulic Conductivity

During soil acidification processes nutrients are released into the soil solution. The degree to which these nutrients are removed from the rooting zone is largely determined by the hydraulic soil properties and the chemical filtering capacity of the subsoil. The CEC is a measure for the filtering capacity of the subsoil, while the speed at which nutrients are drained from the soil by percolating water is described by the hydraulic conductivity. Soil drainage is function of pore size, which in turn is influenced by particle size distribution and structure. The FAO soil classification name provides indirect information on one or more of the involved parameters. As such, soil unit can be used for a qualitative assessment of hydraulic conductivity (Table I 3-9).

Table I 3-9. Assessment of hydraulic conductivity from the attribute Soil Unit.

Indicator Value	Qualitative Description	Soil Groupings and Units
-5	fast	Arenosols, Leptosols, Podzols
5	slow	Vertisols, Gleysols, Planosols, Histosols and all Vertic and Stagnic subgroups
0	medium	all other soils

Soils with a sandy texture, such as Arenosols and most Podzols, and shallow soils overlying hard rock surfaces generally have a high infiltration capacity. Nutrients released during acid buffering are quickly drained from these soils, making them more sensitive to acidification. A slow internal drainage can result from a shallow water table, as in Gleysols and most Histosols, or from relatively impermeable horizons throughout the soil profile (Vertisols) or in the subsoil (Planosols, Stagnic subgroups). These soils are capable of retaining the released nutrients within the rooting zone, where they remain available for buffering processes against acidification.

The indicator value for hydraulic conductivity, I_{HC}, is introduced in the assessment of the sensitivity to soil acidification as a surcharge of **5** for slowly draining soils and a reduction with the same value for soils with a high hydraulic conductivity.

3.3.3 Sensitivity to Soil Acidification

The sensitivity to acidification of a soil is determined by its buffering capacity against added acids. The processes involved in soil acidification result in a loss of acid neutralising capacity. The sensitivity to soil acidification is assessed by summation of the indicator values for basic cation availability, acidification status and hydraulic conductivity:

$$I_{SA} = I_{AS} + I_{BC} + I_{HC}$$

The obtained indicator value is a measure for the susceptibility of the soil for acidification by acid input, but it disregards most biotic, climatic and forest management factors that may influence the nutrient concentration of the soil. It evaluates the soil's capability to neutralise added acids through replacement of basic cations from exchange sites, through dissolution of carbonates, if present, through release of basic cations by organic matter mineralisation or through mineral weathering,

The parameters involved in the determination of I_{SA} are:

- $CaCO_3$: dissolution of carbonates efficiently neutralises acids added; the carbonate content is a measure of the reserve of soil constituents capable of immediately neutralising acids;
- pH gives an indication of the kind of buffer processes taking place in the soil; a low pH generally indicates the lack of soil constituents that may act as buffers against acid input;
- BCE is a measure for the total reserve of basic cations that may be replaced during buffering processes;
- base saturation is an indication for the kind of buffer reaction taking place in the soil; at low base saturation, the soil passes from the cation buffer range to the Al buffer range, which may cause toxic levels of Al and Mn in the soil solution (Ulrich, 1995);
- the sum of total contents of Ca, Mg and K in the organic layer, is a measure for the total reserve of basic cations in the organic layer; they may be released from organic matter through mineralisation, or from mineral constituents in the organic layer through weathering;

- hydraulic conductivity interferes with the soil's sensitivity to acidification insofar that highly permeable soils easily leach basic cations from the upper soil horizons, making them unavailable for H^+ buffering.

Indicator values for sensitivity to soil acidification have been calculated for all plots for which I_{BC}, I_{AS} and I_{HC} values are available, i.e. 1425 plots in 12 different countries. Classes were determined using the 10-, 30-, 70- and 90-percentile indicator values as class limits (Table I 3-10).

Table I 3-10. Class distribution of sensitivity to soil acidification: range of indicator values (I_{SA}), number (n) and percentage of observations.

Sensitivity to Soil Acidification Class	I_{SA}	n	observations (%)
very low	> 33.5	141	10
low	24.8 - 33.5	281	20
medium	13.8 - 24.7	560	39
high	8.8 - 13.7	298	21
very high	≤ 8.7	145	10

Table I 3-11 shows that the highest proportion of acid sensitive plots are found in the Netherlands, Finland and Belgium, whereas in Luxembourg, the Slovak Republic, Hungary, Slovenia, Portugal, Switzerland and Austria the majority of the studied forest soils is resistant to acidification.

Table I 3-11. Classification of national plots according to their sensitivity to soil acidification (derived from optional parameter results; n = number of observations).

Country	Class Distribution (in %)					n
	Very low	Low	Medium	High	Very high	
Austria	25	25	30	12	8	130
Belgium	10	0	40	10	40	10
Finland	0	6	36	38	20	442
France	11	20	45	19	5	94
Germany	6	13	51	23	6	369
Hungary	25	36	36	2	0	44
Luxembourg	25	50	25	0	0	4
Netherlands	0	0	9	18	73	11
Portugal	12	45	42	1	0	146
Slovak Republic	34	37	27	2	0	110
Slovenia	12	45	33	9	0	33
Switzerland	3	50	25	3	19	32

Shallow and leached acid soil types are usually associated with a low acid neutralising capacity. Two third of the Podzols are classified as having a 'high' or 'very high' sensitivity, although these classes represent only 30% of the plots. Other acid sensitive soil types are Cambic Arenosols and Lithic Leptosols. Calcareous and nutrient-rich soil types are found at the opposite end of the classification. More than 80% of the Calcaric, Eutric and Chromic Cambisols, Eutric and Rendzic Leptosols, Lixisols, Gleysols (except Dystric and Umbric subgroups) and Fluvisols are attributed a 'low' or 'very low' sensitivity to acidification. In general, clayey calcareous soils score the highest I_{SA} values, acid sandy soils the lowest.

Soils that are classified as highly sensitive to acidification are usually derived from coarse textured or nutrient-poor parent materials, such as sands, sandstones and acid crystalline rocks (Figure I 3-12). Most soils derived from clays, limestones, volcanic or basic metamorphic rocks, on the other hand, are able to buffer a high input of acids.

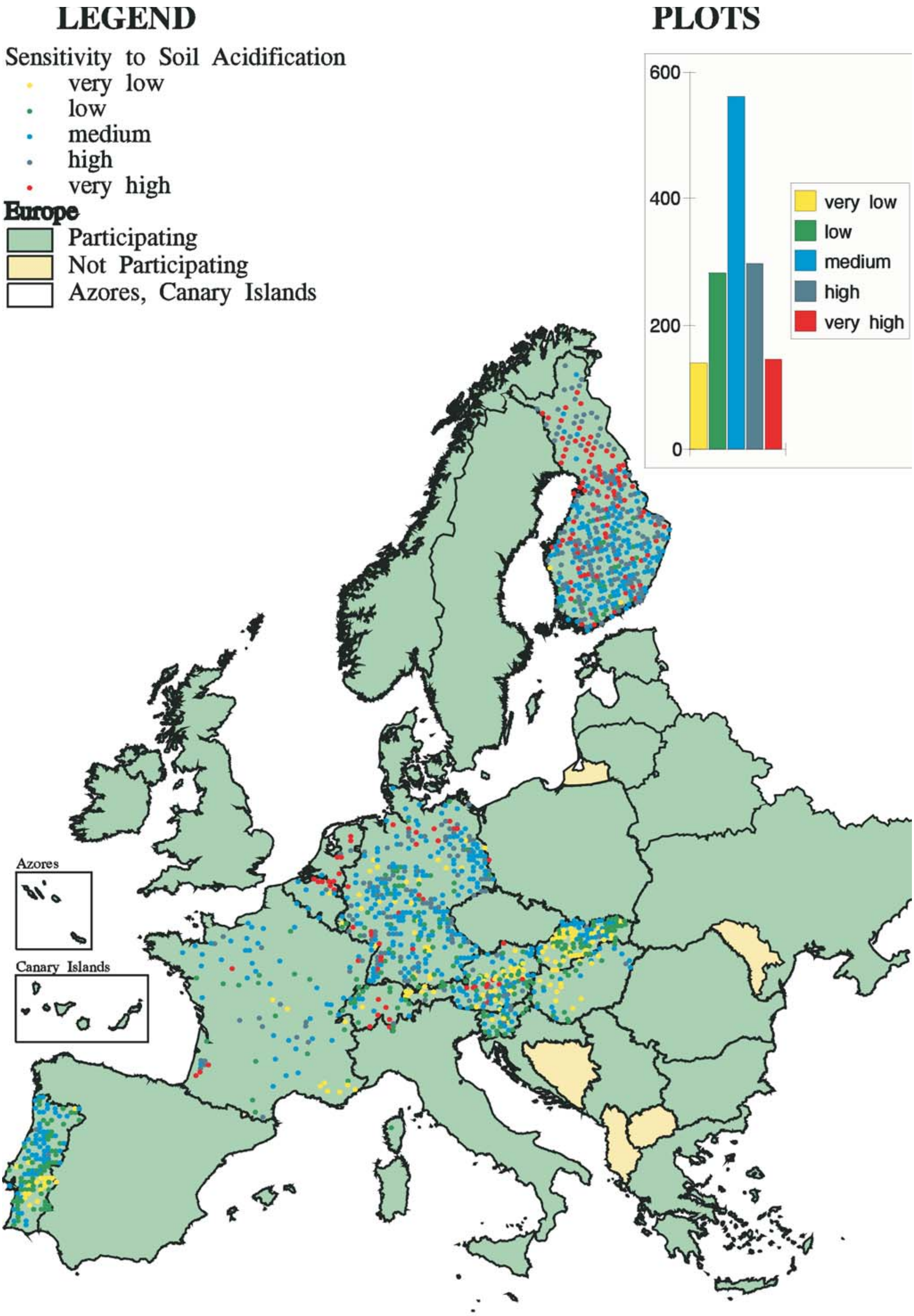


Figure I 3-11. Sensitivity to soil acidification (derived from optional parameter results).

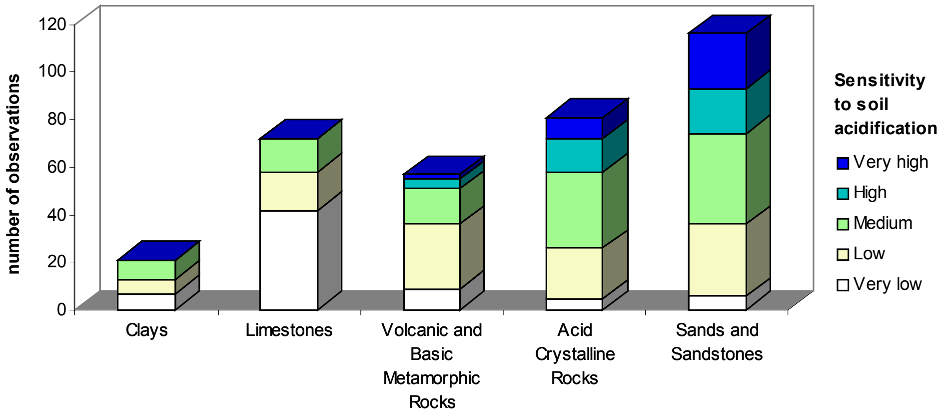


Figure I 3-12. Relationship between nature of parent material and sensitivity to soil acidification (data on parent material are unavailable for Slovenian and Finnish plots).

Table I 3-12 illustrates that an increasing sensitivity to acidification is accompanied by a decrease in pH and base saturation. Very resistant soils to acidification are characterised by a high reserve of exchangeable basic cations and insignificant amounts of acid cations. Very sensitive soils are distinguished from less sensitive soils not by extremely low pH values, but more by a very low base saturation and a lack of exchangeable basic cations.

Table I 3-12. Comparison of average soil conditions in the mineral surface layer at plots grouped according to their expected sensitivity to soil acidification.

	Sensitivity to Soil Acidification Class				
	Very low	**Low**	**Medium**	**High**	**Very high**
pH ($CaCl_2$)	5.8	4.5	3.7	3.6	3.6
Sum of basic cations (cmol(+) kg^{-1})	36.5	12.8	2.4	0.7	0.4
Sum of acid cations (cmol(+) kg^{-1})	0.4	2.6	3.8	3.6	3.1
Base saturation (%)	98	78	35	18	10

3.4 Heavy Metal Availability

The massive number of influential factors and their interaction in soil is a major problem when evaluating the heavy metal load in soils (Ross, 1994b). Although total element concentrations give an indication of the total load of the concerned element in the soil, they generally provide little information about the risk of plant-toxicity or, in case of low amounts, the possibility of deficiency. Relatively small proportions of metals added to forest ecosystems are taken up and recycled through the biomass (Ross, 1994c). Whether metals are plant-available depends on the form of the metal and on the plant species. Equally important is the potential mobility of metals in the soil, since this determines their transfer to hydrological systems such as groundwater and surface waters. Factors controlling metal mobility also control to a large extend its bio-availability (Cottenie and Verloo, 1984).

Numerous studies have described forest ecosystems contaminated by aerial deposition of heavy metals, mainly zinc, lead and cadmium. The soil concentration of these elements appear to be dependent of soil properties, such as pH and CEC. The following discussion focuses on the assessment of the availability of these three heavy metals (Zn, Pb and Cd), in function of the prevailing soil conditions.

Behaviour of Heavy Metals in Soils

One of the most important factors controlling metal solubility in soils is acidity **(Ross,** 1994b). In general, the solubility and availability of heavy metals increase with increasing acidity (Martin and Bullock, 1994). Besides its direct effect, pH also has an indirect influence on the adsorption equilibria, the stability of organo-mineral complexes and the redox potential, which all modify the solubility relationships.

The possible transfer of an element from the solid to the liquid phase of the soil can be studied by determining its mobility in function of pH. Experimentally, this is carried out by equilibrating a soil suspension at decreasing pH-values (Cottenie and Verloo, 1984; Masscheleyn et al., 1996; Tack et al., 1996). In a controlled laboratory environment usually good relationships are found between the mobile metal fraction and pH (H_2O). With decreasing pH, changes in the solubility of Cd and Zn occur in the pH range 5.5 - 6.0, for Pb in the 4.0 - 4.5 pH range (Martin and Bullock, 1994).

Table 13-13 summarises the approximate relative mobility of some heavy metals in relation to pH, assuming that pH ($CaCl_2$) is 0.5 units lower than pH (H_2O). It is also assumed that the relationships found in a laboratory environment for contaminated materials are also valid for forest soils. The solubility increase with acidification of Zn and Cd is exponential.

Several metals, such as Pb, occur in soils in more than one oxidation state. The effect of redox is potentially much greater than that of acidity in determining the activity of these elements in soil. However, at any given redox state, decreasing the pH will result in increased solubility **(Ross,** 1994b). Many trace metals are relatively more mobile under oxidising conditions and are retained strongly under reducing conditions. Because of the important temporal variability of the soil redox potential, it is difficult to distinguish between different redox conditions in the evaluation of heavy metal availability. It is therefore preferred to consider the worst case scenario in view of metal toxicity, i.e. for oxidising conditions in the case of Zn, Pb and Cd.

Table I 3-13. Relative mobility of Zn, Pb and Cd as a function of soil pH ($CaCl_2$). Based on experimental data from Cottenie and Verloo, 1984 and Masscheleyn et al., 1996.

pH ($CaCl_2$)	**Relative Mobility**		
	Zn	**Pb**	**Cd**
7.5	1	1	1
6.5	1	1	1
5.5	1.5	1	2
4.5	2	1	5
3.5	5	1.5	10
2.5	10	2	25

Cation exchange is the principal filtering mechanism for heavy metals added to soils (Leeper, 1978). Heavy metals mostly find specific adsorption sites in the soil, where they are retained very strongly (Greenland and Hayes, 1981). By substituting its common cations with metals, the topsoil chemically immobilises the added metals, thereby protecting plants against direct toxic effects. The exchange capacity is largely determined by the amount and type of clay and organic matter. Concentrations of Zn, Pb and Cd in the mineral soil are well correlated with CEC (see also Table 2-7), confirming cation exchange as the major mechanism in the immobilisation of these elements. Martin and Bullock (1994) showed that plant extractable forms of Zn and Cd are primarily present in cationic form, whilst in the case of the relatively immobile Pb there is an equal or higher proportion of organic complexes in the extracts. The CEC of the surface layer is a measure for the soil's capacity to retain these elements on cation exchange sites. Due to the high CEC of humic substances, capable of immobilising Pb both in cationic form and in organic complexes, CEC may be indirectly used to assess also Pb availability.

The indicator value (I_{HM}) for “plant-available” amounts of individual heavy metals is determined as follows:

$$I_{HM} = \frac{M \cdot R_{pH}}{CEC_c}$$

where:

M = ***heavy metal (Zn, Pb, Cd) concentration in the organic layer;***
R_{pH} = ***pH-dependent rating value for relative metal availability;***
CEC_c = ***class value of CEC of the surface layer (range 1 to 5) (when measured CEC values were unavailable, class values were attributed according to texture class: CEC class 2 to texture class 1, 3 to texture class 2, 4 to texture class 3, and 5 to texture classes 4 and 5).***

Heavy metal concentrations (in mg kg^{-1}) in the organic layer are essential in the risk assessment of heavy metal contamination. An estimation of plant availability is indirectly derived from a pH-dependent stress parameter and the CEC class of the surface mineral layer. Relative availability factors do not apply to class values of metal concentrations, because the latter have irregular intervals. Therefore, total concentrations are used in the evaluation procedure, instead of class values.

The effect of pH on element availability is assessed similarly to the procedure used for the estimation of P availability, except that measured metal concentrations are used, instead of class values. By using multiplication as the operator and measured concentration values in the calculation, the indicator value approaches nil in the absence of the considered metal (concentration near zero), independently of prevailing soil conditions.

Deficiency and Toxicity

Several trace metals are essential micronutrients for plant and animal growth. For example, zinc promotes protein synthesis and seed maturation. It interferes in the formation of growth hormones and in the reproduction process of certain plants (Brady and Weil, 1996). There are essentially no micronutrient deficiencies in natural forests, growing on undisturbed soils. This is largely due to the small quantities of micronutrients required by forest stands, to the efficient nutrient cycling of natural forest ecosystems and to the kind of natural selection of tree species taking place in native stands (Pritchett and Fisher, 1987). Even in forest plantations or disturbed stands, micronutrient deficiencies are not common.

In soil ecosystems, metal toxicity is usually defined as a poisonous effect on a living organism. The margin between adequacy and toxicity of heavy metals can be narrow, often as little as a factor of 2 when expressed in mg kg^{-1} dry biomass (Ross, 1994a).

The I_{HM} class intervals for the interpretation of heavy metal availability were determined based on a predefined key of relative class frequencies (Table I 3-14).

Table I 3-14. Class distribution of the availability of zinc, lead and cadmium: range of indicator values (I_{HM}), number (n) and percentage (%) of observations.

Heavy Metal Availability Class	**Zn**			**Pb**			**Cd**		
	I_{HM}	n	%	I_{HM}	n	%	I_{HM}	n	%
risk for deficiency	≤ 34.7	70	5						
low	34.8-95.5	352	25	≤ 21.0	373	30	≤ 1.8	383	31
medium	95.6-221.0	566	40	21.1-57.5	485	40	1.9-5.2	471	39
high	221.1-625.0	349	25	57.6-303.3	307	25	5.3-16.0	305	25
risk for toxicity	> 625.0	70	5	> 303.3	61	5	> 16.0	61	5

3.4.1 Zinc Availability

Zinc deficiencies are sometimes reported in forest plantations. Marked chlorosis or bronzing of young leaves, **loss** of older leaves from leading shoots and dieback of terminal shoots are common in ’deficient broadleaves (Pritchett and Fisher, 1987). In conifers, extreme shortening of branches, needles and needle spacing in the upper crown, together with general yellowing of foliage, loss of all but the first- and second-year needles, and dieback, are symptoms of Zn deficiency (Stoate, 1950, in Pritchett and Fisher, 1987).

However rare, some cases of toxicity have been observed in acid soils in relatively dry areas. At low pH, zinc adsorption is low and the element may be mobilised. Liming eliminates zinc toxicity (Aubert and Pinta, 1977).

Soils are capable of fixing relatively large quantities of zinc if the soil pH is above 6.5 and drainage is good. Zinc concentrations measured in the mineral layers are positively correlated with pH and CEC, indicating accumulation of zinc under high pH and high CEC conditions. The inventory results also suggest that mineral weathering may contribute significantly to zinc concentrations in soils derived from limestones. The association of zinc and carbonates generally causes higher Zn concentrations in the litter layer of calcareous soils; 86% contain more zinc than the median value (61 mg kg^{-1}). Nevertheless, because soil conditions in calcareous soils favour immobilisation of zinc, toxicity is probably non-existent.

Zinc availability is assessed for the plots of 10 countries (AU, CH, CR, DL, FI, LI, NL, PO, SR, UK).

Figure I 3-13 shows concentrations of plots with a high expected Zn availability in northern Germany, the Netherlands, Lithuania, the United Kingdom and northern Portugal. Although Zn concentrations are generally lower in Finland, soil conditions favouring metal mobility are responsible for the occurrence of plots with high Zn availability, scattered throughout the country. **A** large number of plots where Zn deficiency may occur, are located in the Slovak Republic and southern Portugal.

Toxicity symptoms are most likely to occur in very acid soils with a low CEC, having a Zn concentration above the median value (Table I 3-15). Podzols (24 plots), Dystric and Gleyic Cambisols (21), and Arenosols (15) cover 86% of the soil types, classified in the ‘risk for toxicity’ class, whereas the same soil types represent only 23% of the ‘risk for deficiency’ class. These soil types cover 61% of all plots for which Zn availability is assessed. A risk for deficiency is assessed either on soils low in zinc, or on high-pH soils with medium zinc concentrations. Common soil types, found at plots with an increased risk for zinc deficiency, are Eutric and Calcaric Cambisols (26 plots) and Rendzic Leptosols (9)

Table I 3-15. Soil conditions at plots with increased risk of Zn deficiency and toxicity.

	Risk for Deficiency n = 70			Risk for Toxicity n = 70		
	avg.	max.	min.	avg.	max.	min.
Zn content (mg kg^{-1}) of organic layer	50	112	1	110	460	34
CEC (cmol(+) kg^{-1}) of mineral surface layer	23.1	105.8	2.8	4.0	13.1	0.8
pH $CaCl_2$ of organic layer	5.0	6.8	3.7	3.1	4.3	2.6

3.4.2 Lead Availability

Soil lead is largely unavailable to plants. It is strongly retained by organic matter. There may be down-profile movement associated with dissolved organic matter (Ross, 1994c). Mineral weathering may contribute locally to the soil lead content, but the main source of lead in most European forest soils is atmospheric deposition, as evidenced by the distinct accumulation in litter layers and the spatial gradients in Europe.

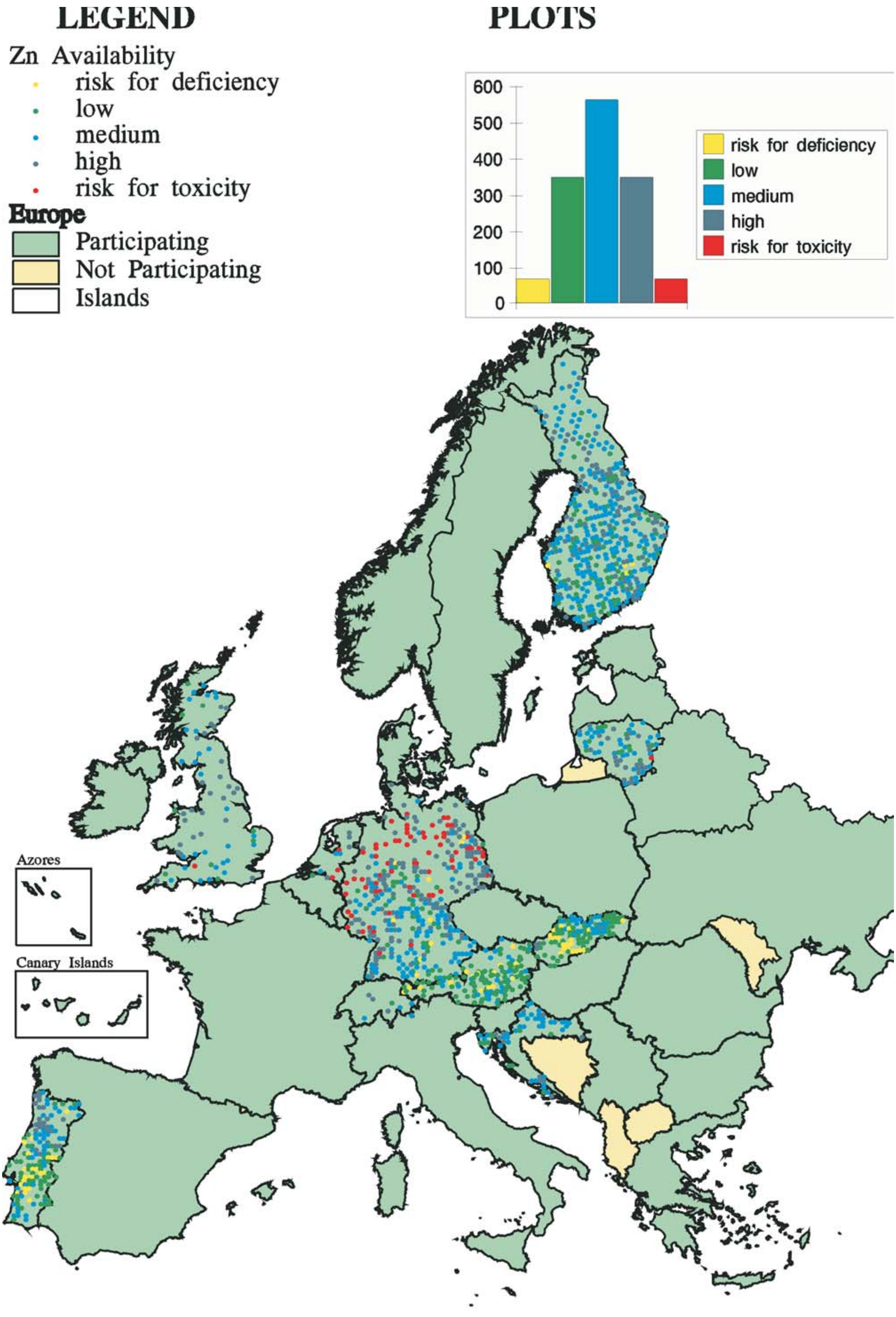


Figure I 3-13. Zinc availability (derived from optional parameter results).

Data availability limitations restrict the assessment of Pb availability to 7 countries (AU, CH, DL, FI, LI, PO, UK). Figure I 3-15 illustrates the association of strongly industrialised areas in Germany, England and Wales, with a risk for toxic amounts of plant available lead. All plots, classified in the highest availability class, are located in the region in Europe receiving a high or moderately high deposition load (Figure I 3-14).

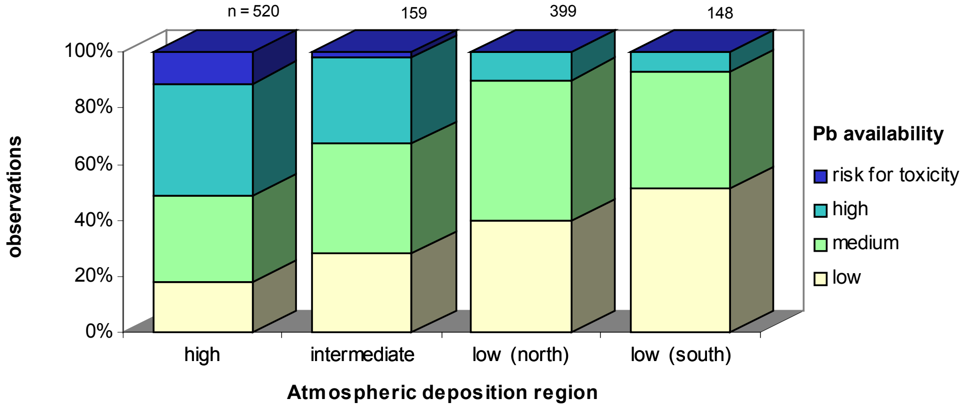


Figure I 3-14. Expected lead availability in different deposition regions.

Adverse effects on soil biological processes were measured in Swedish forest soils with mor layers containing 500 mg Pb per kg humus or more (Tyler, 1992). The coincidence of lead accumulation in the organic layer and conditions that favour its mobility in the soil, i.e. low pH and low CEC, determine the risk for plant uptake of toxic amounts (Table I 3-16). A low lead availability is assessed in soils with very low Pb concentrations in the organic layer, or having high pH and/or CEC values.

Table I 3-16. Soil conditions at plots with increased risk of Pb toxicity as compared to plots with a low Pb availability.

	Risk for Toxicity n = 61			Low Availability n = 373		
	avg.	max.	min.	avg.	max.	min.
Pb content (mg kg^{-1}) of organic layer	320	2114	81	29	102	0
CEC (cmol(+) kg^{-1}) of mineral surface layer	5.1	14.6	1.2	12.2	105.8	1.6
pH $CaCl_2$ of organic layer	3.2	4.5	2.5	4.3	6.8	2.9

Thus, nutrient-poor acid soils are most vulnerable to lead pollution. Dystric and Gleyic Cambisols (22 plots), Podzols (16), and Arenosols (11) cover 80% of the soil types found at plots, classified in the highest lead availability class. The same soil types represent also 54% of the plots with a low expected lead availability, which is not much less than the fraction (64%) of these soil types in the overall distribution. Although soil conditions at these plots are usually favourable for metal mobilisation, plant uptake may be very low when only small amounts of lead have accumulated in the litter layer.

3.4.3 Cadmium Availability

In neutral and alkaline soils the exchange reactions between cadmium and negatively charged surfaces are partly irreversible, i.e. the metal remains unavailable to plants (Jones and Jarvis, 1981). At low pH, adsorption decreases and the reaction becomes largely reversible, mobilising cadmium.

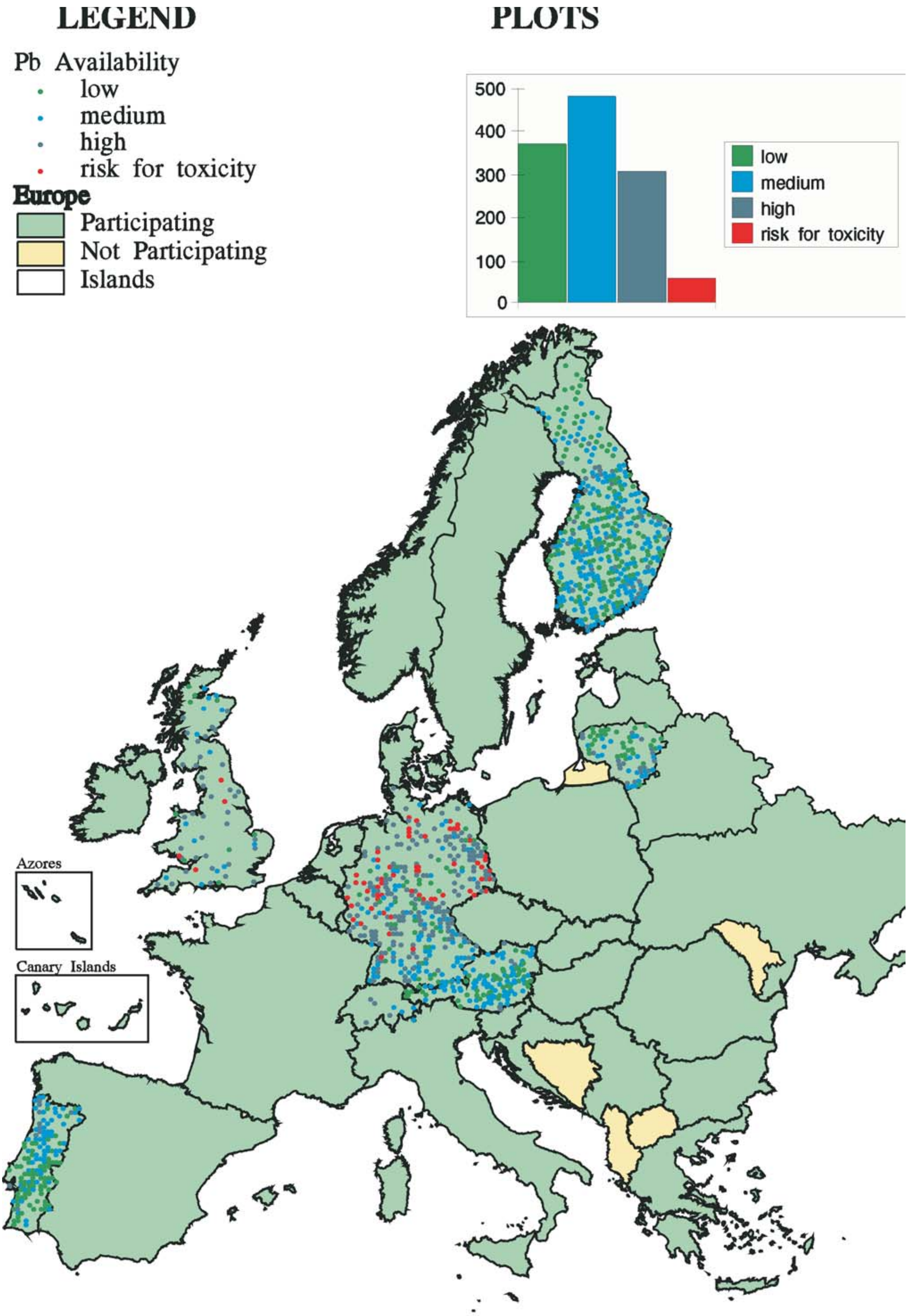


Figure I 3-14. Lead availability (derived from optional parameter results).

Cadmium availability is assessed for the plots of the same **7** countries as in the previous section. Plots where plant available cadmium may reach toxic levels are found in Lithuania, the United Kingdom, Germany and Portugal (Figure I 3-16). In Bavaria (Germany), southern Portugal, Finland and Austria, cadmium levels are expected to be well below toxic levels at most plots.

Tyler **(1992)** stated that, for Swedish forest soils, measurable adverse effects on soil biological processes are likely to occur at a Cd concentration in the humus layer of 3.5 mg kg^{-1}. Toxicity symptoms may occur at lower concentrations, if soil conditions favour Cd mobility, i.e. (i) a very low pH and (ii) a low CEC (Table 13-17). On the other hand, calcareous soils with organic layer Cd contents up to 3.4 mg kg^{-1} have been classified as having a low Cd availability. Cadmium is adsorbed or precipitated by carbonates in these soils.

Table I 3-17. Soil conditions at plots with increased risk of Cd toxicity as compared to plots with a low Cd availability.

	Risk for Toxicity n = 61			**Low Availability** n = 383		
	avg.	max.	min.	avg.	max.	min.
Cd content (mg kg^{-1}) of organic layer	1.7	6.6	0.4	0.6	3.4	0.0
CEC (cmol(+) kg^{-1}) of mineral surface layer	4.1	13.1	1.1	15.1	122.8	1.0
pH $CaCl_2$ of organic layer	3.3	4.4	2.6	4.3	6.8	2.2

Almost half of the soils with an increased risk for cadmium toxicity are Podzols **(27** plots). All other soil types, except Anthrosols (2 plots), are under-represented in the highest availability class, as compared to the overall distribution. The majority (83%) of the calcareous soil types (subgroups of Leptosols, Cambisols, Luvisols, Gleysols, Fluvisols and Regosols) was attributed a 'low Cd availability' class, in spite of generally higher Cd concentrations.

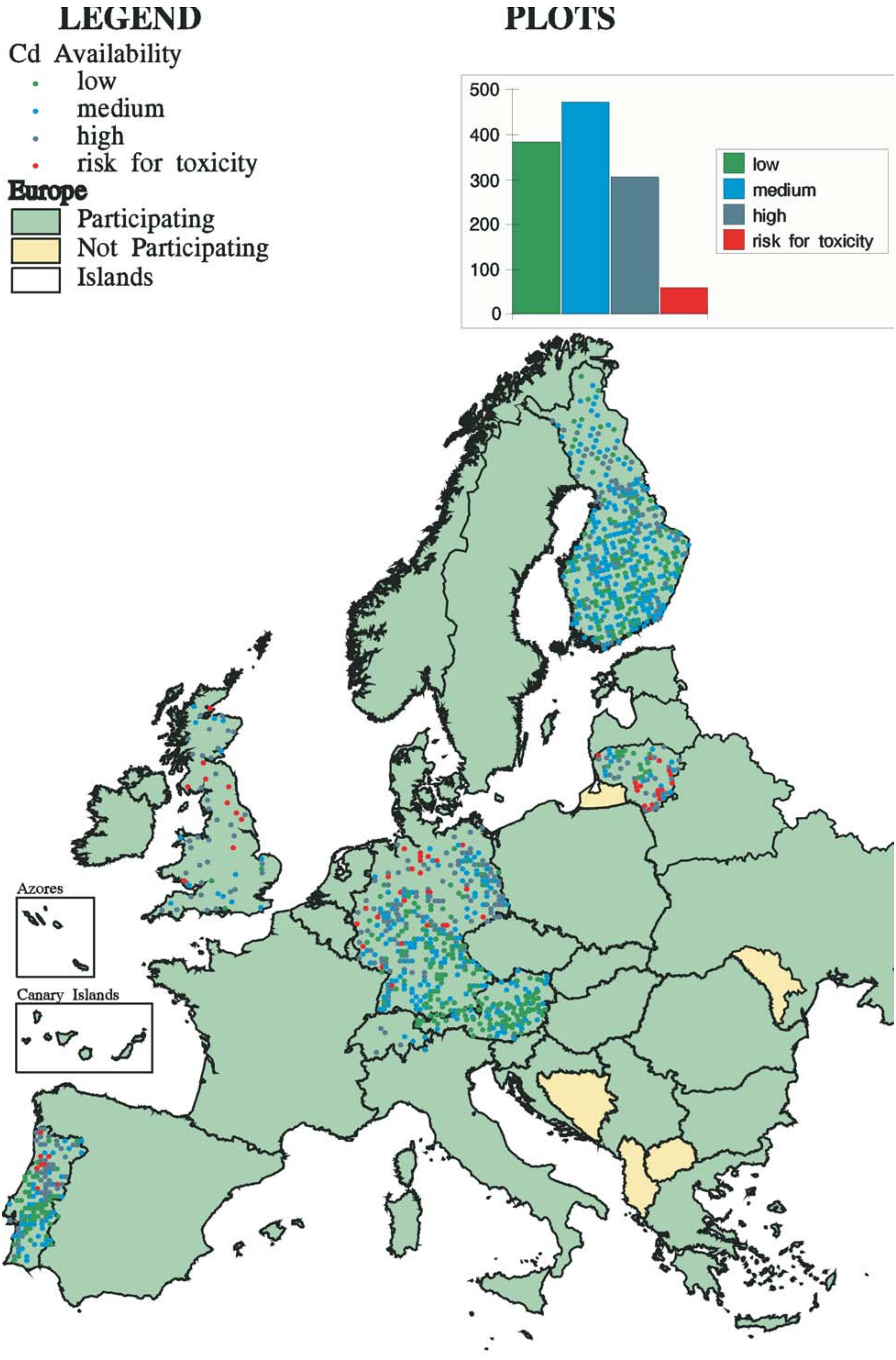


Figure I 3-16. Cadmium availability (derived from optional parameter results).

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PARTII.

NATIONAL INVENTORIES

1. NATIONAL SURVEY METHODS

1.1 General Information

The national reports of the forest soil condition inventories usually provide an extensive description of the applied survey methods. Information on general aspects of the national inventories, such as forested area, period of observation, date of data submission, etc., is summarised in Table II 1-1.

Table II 1-1. General information on national soil inventories.

Country	Submission date MMM-YY	Forested area km^2	Area covered km^2	Soil plots	Observation period	Plot selection
Austria	Sep-94	38,800	38,800	131	1987 - 1989	16x16 km
Belgium (Fl)	Apr-94	1,149	1,149	10	1993	16x16 km
Belgium (W)	Jan-96	5,306	4,285	21	1994 - 1995	16x16 km
Croatia	Feb-96	20,610	12,500	87	1992 - 1994	16x16 km
Czech Rep.	Jan-96	26,420	26,420	100	1995	16x16 km
Denmark	Apr-95	4,930		25	1994	16x16 km
Estonia	Dec-96	20,200	20,200	91	1990 - 1994	16x16 km
Finland	Jan-96	200,590	200,590	442	(i) 1986 - 1989 (ii) 1995	16x16 (<65°N); 32x24 (>65°N)
France	Feb-96	140,020	131,000	517	1993 - 1994	16x16 km
Germany	Dec-95	106,960	106,960	416	1987 - 1993	16x16 km
Greece	Dec-95	25,120	acid soils	15	1993 - 1994	16x16 km
Hungary	Feb-96	17,192	17,192	67	1994	16x16 km
Ireland	Jan-95	4,980	3,640	22	1995	16x16 km
Italy	Jan-96	86,750	32,000	20	1994	16x16 km
Latvia	Dec-98	28,817	28,817	306	1991	16x16 km, 8x8 km
Lithuania	Jan-96	18,231	18,231	70	1992 - 1993	8x8 km
Luxembourg	Dec-95	890	890	4	1994	16x16 km
Netherlands	Dec-95	3,110	2,810	11	1995	16x16 km
Norway	Dec-95	119,000	119,000	441	1988 - 1992	9x9 km
Poland	Jan-97	86,000		122	1995	2 or 3 points per region
Portugal	Jan-96	30,860	30,860	157	1995	16x16 km
Romania	Jul-96	63,000	63,000	242	1993 - 1995	16x16 km
Slovak. Rep.	Oct-95	18,850	18,850	111	1993	16x16 km
Slovenia	Mar-96	10,710		34	1994 - 1995	16x16 km
Spain	Jan-96	117,920	117,920	464	1993 - 1995	16x16 km
Sweden	Sep-95	230,000		(i) 1174 (ii) 75	(i) 1985 - 1988 (ii) 1995	16x16 km
Switzerland	Dec-95	11,860		48	1993	16x16 km
Ukraine	?	61,510	6,797	36	1996	16x16 km
United Kingdom	Jan-95	23,900	23,900	67	1993 - 1994	16x16 km

The measured surface area of forests and the number of sample plots allow the calculation of the actual plot density (Figure II 1-1). A few countries, such as Italy and Greece, reported data for a subset of the 16x16 km sample plots. As a result, plot density in these countries are lower than the expected density based on the forest area. Because Finland applied a 32x24 km grid above latitude 65°N, a relatively low average density is obtained for the entire country.

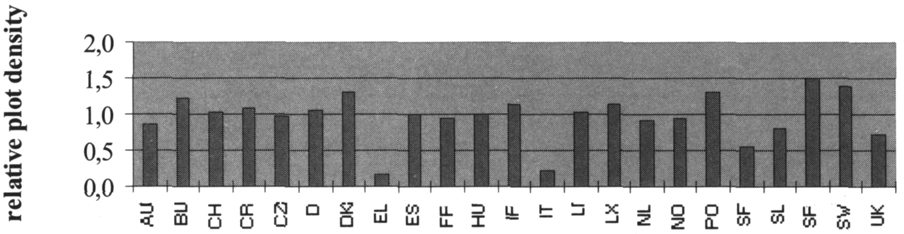

Figure II 1-1. Density of observation plots in the transnational database, relative to the theoretical plot density of 1 plot for every 16x16=256 km^2 of forest area.

The plot locations of the soil condition inventory in Austria, Finland, Norway and Sweden do not coincide with the 16x16 km grid intersections. These countries have initiated a national soil survey before the start of the transnational programme, using a different, usually denser, grid system. For the European database, only data of those plots that are located nearest to the16x16 km grid intersections, were retained. In this way, a plot density that is similar to the predetermined level I density is simulated.

1.2 Pedological Characterisation of Sampling Plots

The pedological characterisation is optional for the study plots of the large-scale inventory (level **I**). When it is carried out, it consists of one or more detailed profile descriptions, made before starting soil measurements. It provides background information on the concerned soil in order to improve the interpretation of other data collected at the plot location. Soil classification according to the FAO system (FAO, 1988) requires information on several items that are observed during a profile description.

It was recommended to carry out profile descriptions according to the FAO-guidelines for soil description (FAO, 1990) on a location that is representative for the actual sampling area. In most countries the observation plots were pedologically characterised, although some used national guidelines (Table II 1-2).

Table II 1-2. National soil sampling methodologies.

Country	Pedological characterisation	Sampling depths	Mineral layer sampling	No. of samples in composite
Austria	National	M01/M12	1 profile pit	12
Belgium (Fl)	National	M05/M51/M12	bores	36
Belgium (W)	National	M01/M12	bores	10
Croatia	ICP	M01/M12	bores	20
Czech Rep.	ICP	M01/M12	bores	5
Denmark	ICP	M05/M51/M12	bores	16
Estonia	ICP, National	variable	1 profile pit	3
Finland	ICP	M05/M52 (86-89) M05/M51/M12 (1995)	small pits	5
France	ICP	M01/M12	profile pit	2
Germany	National	M05/M51/M13	pit + bores	8
Greece	ICP	M01/M12	1 profile pit	2
Hungary	National	M05/M51/M12	pits or sampling tubes	3
Ireland	ICP	horizons	1 profile pit	
Italy	no	M01/M12	bores	5
Latvia	no	organic layer at 2-5 cm depth	not taken	
Lithuania	ICP	M05/M51/M12	bores	20
Luxembourg	National (Belgian)	M05/M51/M12	bores	30
Netherlands	no	M01/M12	bores	20
Norway	National	horizons	pit + bores	variable
Poland	ICP	M05/M51/M12	other	9
Portugal	ICP	M05/M51/M12	bores	16
Romania	ICP	M05/M51/M12	1 profile pit	3
Slovak. Rep.	no	M01/M12	1 profile pit	20
Slovenia	ICP	M05/M51/M12	bores	3
Spain	ICP	M01/M12 (1993) M05/M51/M12 (94-95)	1 profile pit	4
Sweden	ICP	horizons (85-88); M01/M12 (1995)	1 profile pit	
Switzerland	ICP	M05/M51/M12	profile pit	1
Ukraine	National	M05/M51/M12	profile pit	4-6
United Kingdom	ICP	M05/M51/M12	4 profile pits	7

1.3 Methodology for Soil Sampling

Soil sampling is one of the more difficult and more important aspects in the determination of chemical soil status. No amount of care in preparation and analysis can overcome the problems of careless or inappropriate sampling in the field (Bates, 1993). Although there is usually a gradual transition between soil classification units in the field, a high spatial variability resulting in marked local variations, should be kept in mind when sampling soils. The actual sampling area should be as homogeneous as possible, and the several sources of variation within the plot should be sampled if valid inferences are to be made about the sampled soil (Petersen and Calvin, 1986). It is recommended to select a sampling area in a part of the plot, that may be considered as representative in terms of ground vegetation, forest floor and slope conditions.

The organic layer, which is undoubtedly the most distinctive feature of forest soils, is sampled separately. Soil sampling for atmospheric deposition, where a contaminant impinges as a gas, dust, or is deposited in rain, necessitates assessing the superficial layer (Crépin and Johnson, 1993). Care must be taken to avoid unnecessary dilution with non-impacted, deeper soil. The organic layer includes all organic matter, including litter and decomposing organic matter, resting on the mineral soil surface. **A** distinction is made between H-horizons, which are saturated with water for prolonged periods, and 0-horizons, which are mostly not water saturated (FAO, 1990).

Usually, three layers or strata of the forest floor are designated by forest soil scientists, although they do not appear on all soils. They are (Pritchett and Fisher, 1987): (1) the L layer consisting of unaltered dead remains of plants and animals, (2) the F layer immediately below the litter consisting of fragmented, partly decomposed organic materials, and (3) the H layer which consists of well decomposed, amorphous organic matter. In the large-scale forest soil survey, no distinction was made between these different organic layers. If sampled and analysed separately, the obtained results were averaged for submission to FSCC.

After removal of the litter, the mineral soil is sampled by genetic horizons or by layers with predetermined depths. The method using predetermined depth layers is preferred, because it facilitates comparison between soils. If sampling is done by fixed depth, results are reported for the following layers :

- 0 to 10 cm (M01); it was advised to sample 0 to *5* cm (M05) and *5* to 10 cm (M51) separately;
- 10 to 20 cm (M12).

Sampling methods may differ from reference methods in national surveys that commenced before the start of the transnational programme. For example, Germany reported results on the 10 to 30 cm layer (M13). The database further contains 11 plots with data for M02 (0-20 cm) layers, and 3 plots with M03 (0-30 cm) layers.

If samples are taken according to horizons, depth and thickness of the horizons are also recorded **as** observed during profile description.

Samples are taken from augerings at different locations in or near the plot area, or from one or more profile pits. For every sampled layer or horizon, one representative composite sample or several separate samples are collected; the number of subsamples collected is reported. The reported number of subsamples per composite varies between 1 and 36 (Table II 1-2). Pritchett and Fisher (1987) found that a composite of 12 to 15 subsamples usually forms an adequate sample for operational purposes. In the composite depth sampling method the whole soil core is homogenised and a subsample is taken for laboratory analysis.

1.4 Sample Preparation

Macroscopic roots, stones and gravel are manually removed at the sample location. In the laboratory, the samples are air-dried at a temperature usually not higher than 40°C (Table II 1-3). After drying organic samples are usually milled. Mineral soil samples are ground and sieved through a 2 mm sieve. The fraction < 2 mm ("air-dried fine earth") is homogenised and constitutes the sample that is subjected to the laboratory analyses. The calculation of the results of soil analysis is done on basis of "oven-dry" soil.

Table II 1-3. Sample preparation and storage.

Country	Temper. during drying °C	Humid. during drying %	Grinding of mineral samples	Removal of coarse material	Storage medium	Temper. during storage °C	Humid. during storage %	Preser-vative
Austria	45	40-80	agate mortar & pestle	2mm (stainless)	cardboard	18-22	40-60	no
Belgium (Fl)	40		mechanical grinder (steel)	2mm (stainless)	plastic boxes	room t°		no
Belgium (W)	16-24		mortar & pestle, mechanical	2mm (stainless)	plastic bags	16-24		no
Croatia	18-22	50-65	mechanical (porcelain)	2mm(stainless)	cardboard	18-22	50-65	no
Czech Rep.	20-23		agate mortar	2mm (stainless)	plastic	20-23		no
Denmark			mortar & pestle, mechanical	2mm (stainless)	cardboard			no
Estonia	18-25	60-80	mechanical (aluminium)	other	paper bag	15-22	60-80	no
Finland	40-60		mill	2mm	plastic bags in carboard	18	room cond.	no
France	25-35		porcelain mortar & pestle	2mm (stainless)	plastic boxes	30-40	variable	no
Germany	60		mill	2mm	polyethylene bottles	room t°		no
Greece	20-35	50-80	agate mortar & pestle	2mm (stainless)	cardboard			no
Hungary	15-30	50-60	agate mortar & pestle, mechanical (iron)	2mm(stainless)	plastic	15-20	50-60	no
Ireland	15-25	40-43	not ground	2mm (stainless)	cardboard	4		no
Italy	18-30	50-70	mechanical grinder (stainless steel)	2mm (stainless)	plastic bag	18-24	50-70	no
Latvia	25-30	90-95		2mm (stainless)		not stored		
Lithuania	20-25	40-70	mechanical (ceramic, stainless steel)	2mm (stainless)	cardboard	10-25	40-70	no
Luxembourg	105 (min) 60 (org)	2-5	steel roller	2mm (stainless)	glass	10-15		no
Netherlands	40-50	0-10	mechanical (manganese)	2mm(stainless)	plastic boxes	20-25		no
Norway	38-40	30-45	not ground	2mm(stainless)	cardboard	12-16		no
Poland	40		agate mortar & pestle	2mm (nylon)	plastic bag	18-22		no
Portugal	30-40		wood block	2mm (stainless)	plastic boxes			no
Romania	20-25		agate mortar & pestle	2mm (stainless)	plastic bag	20-25		no
Slovak. Rep.	19-28	50-80	agate mortar & pestle	2mm (stainless)	paper bag	19-28	50-80	no
Slovenia	20-25	room cond.	stainless grinder / cheramic mortar	2mm (stainless)	plastic	20-25	room cond.	no
Spain	20-30		mechanical grinder / stainless steel	2mm (stainless)	glass	20-25		no
Sweden	30-40		wood block	2mm (stainless)	cardboard	5-30		no
Switzerland	60		mechanical grinder (hardened steel)	2mm (stainless)	plastic	15-25	40-60	no
Ukraine	15-45	70-90	agate mortar & pestle	2mm (aluminium)	cardboard	10-25	70-80	no
United Kingdom	room T.	variable	mortar & pestle	2mm	poly-ethylene	< 20		no

1.5 Storage of Soil Samples

It was advised to store the soil samples in a soil bank for eventual reanalysis in the future. The nutrient content, in particular ammonium-N and P, may change if samples are stored for a prolonged period at temperatures above 40°C or below freezing (Bates, 1993). Storage conditions within this temperature range and at a reasonably low humidity will have little or no influence on the nutrient contents of soil samples.

All participating laboratories store the inventory samples for future use (Table II 1-3). The soil material is kept without preservative, shielded from incident light, under conditions that are usually similar to room conditions.

1.6 Soil Analysis

The soil analysis methods applied in the national inventories are described in Annex A.

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2. NATIONAL SOIL CONDITION REPORTS

2.1 AUSTRIA

M. Englisch, F. Mutsch

The Austrian Forest Soil Monitoring System consists of 514 sample plots arranged in a systematic grid of 8.7 x 8.7 km. This data base was used for the evaluation of the Austrian forest soils (Federal Forest Research Centre, 1992); 131 of these plots are situated near the European I6 x I6 km grid and are subject to the European Forest Soil Condition Report.

Sampling and Analysis

The soils were sampled in the period 1987-1989 at 3 profiles per observation plot. Three or more samples of the ectorganic layer, collected with a steel frame, were bulked to form a representative humus sample. Mineral soil material was sampled at predefined depths (0-10 cm, 10-20 cm, 20-30 cm, 30-50 cm) from all **4** faces of the profile pits and mixed to get a composite sample.

Apart from all mandatory and optional parameters, also texture and total sulphur content were determined. The methods used were either reference methods or national methods similar to reference methods. Total N was determined by the Kjeldahl method; for the acid digestion a 5+1 $HNO_3/HClO_4$ mixture instead of aqua regia was used.

The laboratory participated in national and international ring tests in order to check the analytical methods and the quality of the analytical results. Standard soils were always analysed together with the soil samples.

Data Processing

All data were stored in a relational ORACLE data base. For statistical analysis 2 main clusters were formed: 35 % of all Austrian forest soils are carbonate influenced, 65 % are free from carbonates. For these **2** populations descriptive statistics (10-percentile, median, 90-percentile, minimum, maximum, average and standard deviation) were obtained in order to describe the distributions of the chemical analysis results with regard to ecological parameters. Similar statistical interpretations were also done for groups of soil types and growth areas.

Information Regarding Forest Soil Condition

Level of Acidity

The geochemical and climatic diversity of the Austrian landscape results in a wide range of soil conditions. The pH ($CaCl_2$) ranges between 2.7 and 8.0. The exchangeable base supply of the mineral soil (0-50 cm) varies between 25 (median for Leptic Podzols) and 1200 kmol(+)ha^{-1} (Eutric Cambisols on limestones).

The 35 % of carbonate influenced soils cover mainly the Limestone Alps and the northern forelands, and are resistant against acidification.

The remaining 65 % of non-calcareous soils were classified as very acid: 83 % have a pH of ≤ 4.2 in the upper soil. The CEC is usually low (median of subsoil layers < 5 cmol(+) kg^{-1}); the lowest values are observed in Dystric Cambisols and Podzols. Base saturation (BS) varies within a wide range: 39 % of all plots are well saturated (BS > 18 % in all depth layers). In 49 % of the plots, however, base saturation is ≤ 12 % in at least one depth layer; in 23 % of the plots BS is ≤ 6 %. These poor soils include Podzols on acid bedrock located at high altitudes, naturally developed and with healthy forest communities, that are well adapted to these soil conditions. Thus, acidity itself is not a criterion for soil degradation. More likely, degraded soils and active acidification processes are found among the 12 % of very acid Cambisols, where site conditions and profile development are obviously not in accordance with the high level of acidification.

Nutrient Status and Nutrient Balance

While the total contents of P and with some exceptions of K are sufficient (minimum values not below 0.1-0.2 g kg^{-1}), the Ca- and especially the Mg-supply seems to be poor on some very acid soils (minimum values below 1 g kg^{-1}). Using limit values for N-supply (< 4 t ha^{-1}) and for C/N-ratio (> 25), N-deficiency was estimated to affect about 3 % of the forested area in Austria.

Presence of Toxic Elements

An important and widespread toxic element is Pb. For agricultural soils the limiting value is 100 mg kg^{-1}. This value is exceeded in at least one depth layer on 26 % of all sample plots, but direct toxicity could not be proved. The average amounts of immitted Pb on forest soils till 1990 ranged from about 10 to 100 kg ha?.

Discussion on Investigated Relationships

The 10-percentile value of the C/N ratio is 21 for the humus layer and 13 for the mineral soil (0-10 cm). The 90-percentile values are 33 (humus layer) and 25 (0-10 cm), respectively. The 10-percentile value of the C/P ratio of carbonate free soils is 240 in the humus layer and 50 in the 0-10 cm layer. The 90-percentile values are 550 and 250, respectively. On carbonate influenced soils these ratios are about 10 to 25 % wider. Correlations exist between humus forms and the stock of N- and C-supply (average contents):

Mull	N: 0.23 t ha^{-1}	C: 5.0 t ha^{-1}
Moder	N: 0.62 t ha^{-1}	C: 16.3 t ha^{-1}
Mor	N: 1.54 t ha^{-1}	C: 42.8 t ha^{-1}

Between the so-called total contents of K, Ca and Mg on the one hand and their exchangeable contents on the other, significant correlations were found.

Floristic data, which were obtained by a vegetation survey at the monitoring plots, were compared with soil characteristics, using ecological indicator values of individual plant species. Indicator values for soil reaction, averaged over the plot, are strongly related to base saturation. Correlations between mean indicator values for acidity and soil pH are of exponential character. The actual nutrient status of soils is well characterised by the nitrogen indicator value of plants.

A relationship was found between the contents of Pb and Cd in the mineral soil and the altitude (aspect) of the sample plots: Pb- and Cd-contents increase significantly with increasing altitude and can be put down to the fact of long range transport. Whereas on calcareous soils Pb and Cd are accumulated, on acid soils mainly Cd but also Pb are washed out. In the course of long distance transport not only Pb and Cd but undoubtedly many other noxious components, such as acids and organic pollutants, are deposited in great amounts at the exposed high-altitude sites of the Alps. Apart from being a weather divide, the Alps seem to act as a sink for air pollutants.

Measures to Restore Damaged Forest Soils

On soils where site conditions and the profile development are obviously not in accordance with the high level of acidification, anthropogenic acidification processes can be assumed. They are caused by historical land-use (e.g. forest litter utilisation) and/or acid deposition. To restore such degraded forest soils, fertilisation and/or liming could be recommended (melioration fertilisation). In connection with silvicultural measures (mixed stands, deep rooting trees), good results may be obtained.

References

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2.2 BELARUS

R. Shvubovich

Forests cover approximately 70,000 km^2 of land *or* one third of the country. Permanent monitoring plots were installed at 415 forest sites in a 16x16 km grid.

Sampling and Analysis

Soil samples from 81 monitoring plots have been collected, but the modernisation of the laboratory equipment, necessary to perform the analyses according to the reference methods, causes a delay of the soil analysis activities. Soil analysis results on mandatory parameters for a selection of the permanent monitoring plots will be available in 1998. Submission of additional information on parent material, soil texture and coarse fragments content is also foreseen.

A report summary on the forest soil condition in Belarus has not been received at the time of completion of this report.

2.3 BELGIUM

2.3.1 Flemish Region

P. Roskams

Ten plots of the transnational forest vitality grid in the Flemish Region (16x16 km) were sampled during the Level I soil condition inventory in 1993.

Sampling and Analysis

The organic layer and 3 depth layers of the mineral soil (0-5 cm, 5-10 cm and 10-20 cm) at each observation plot were sampled according to a fixed procedure, resulting in 4 mixed samples per plot. Each mixed sample consisted of 36 subsamples, collected in the 4 quadrants of the plot. L, F and H layers were sampled together. Prior to the sampling a pedological characterisation by augering was carried out.

All mandatory analyses were performed on the samples. Optional analyses included exchangeable cations and exchangeable acidity.

Chemical analyses were carried out according to the reference methods of the ICP Forests soil submanual, except for total nitrogen, for which Kjeldahl digestion was used.

Data Processing

All data were stored in a database. Basic statistics were calculated and the results were compared to literature references.

Information Regarding Forest Soil Condition

Acidity

The pH ($CaCl_2$) values in the plots range from 2.9 to 5.6 in the mineral layers and from 3.1 to 6.8 in the organic layer. Nine plots out of ten have acidic soils, with pH below 4 in organic and mineral layers. In general, the lower pH values are found in surface mineral layers (0-5 cm): in 8 out of 10 plots the pH ($CaCl_2$) of the surface mineral layer is below 3.5.

Cation exchange capacity and base saturation in the mineral layers vary considerably but are in general low to moderate. Median values for effective CEC are 6.3 cmol kg^{-1} in the 0-5 cm layer, 3.7 cmol kg^{-1} in the 5-10 cm layer and 3.5 cmol kg^{-1} in the 10-20 cm layer. Acid soils are found in most of the plots and are characterised by a dominance of aluminium on the exchange complex, occupying up to 84 % of the CEC.

Base saturation values lower than 20 % in at least 2 mineral depth layers are found in 7 plots. Very low base saturation values (< 5 %) are found in 3 plots.

These results can be partly explained by the nutrient poor parent material and the coarse soil texture in many plots; they indicate a high sensitivity to soil acidification. Since this is the first soil condition inventory in these plots, no conclusions can be drawn on soil changes. Other studies (e.g. Ronse et al., 1988), however indicated that a significant acidification occurred in the upper layers of Podzols and Regosols under forests during the last decades.

Nutrient Status

In 7 out of 10 plots the C/N ratio of the organic layer (average = 27) is smaller than the C/N ratio of the subsurface mineral layer (average = 32). However, a literature review revealed that the C/N ratio of organic layers is usually higher than the ratio in underlying mineral layers. Lower C/N ratios in the organic layer may be the result of atmospheric nitrogen deposition, but there are no data available to check *this* in the plots studied. Tree species have an important influence on the C/N ratio, with the higher ratios being found under conifers and the lower under broadleaved tree species.

In general C/N and C/P ratios increase with decreasing humus quality. The same applies to the pools of carbon and nitrogen in the organic layer (Table II 2-1).

Table II 2-1. Average chemical properties of various humus types in level I plots (n = number of observations).

Humus type	n	C/N	C/P	C ($t\ ha^{-1}$)	N ($kg\ ha^{-1}$)
Mor	7	30	753	31.4	1034
Moder/mor-moder	2	24	601	8.2	345
Mull	1	17	163	0.8	50

In the acid soils total concentrations of potassium, calcium and especially magnesium are low, e.g. median values for the concentrations in the organic layer of Podzols are 515 mg kg^{-1} for K, 1873 mg kg^{-1} for Ca and 316 mg kg^{-1} for Mg.

Similar to carbon and nitrogen, the average pool of macronutrients in mor layers is higher than in moder and mull layers, due to the low microbial activity and the slow decomposition of the organic matter.

Measures to Restore Damaged Forest Soils

In the Flemish Region melioration fertilisation and liming in forests have been carried out only on a very limited scale. Under certain circumstances liming and/or melioration fertilisation could be recommended to restore degraded forest soils. Positive results are expected from silvicultural measures in the framework of regional forest policy, e.g. mixed stands and use of secondary and deep rooting tree species.

References

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2.3.2 Walloon Region

V. Dumn

Twenty-one plots, of which 19 are currently covered by trees, have been sampled. The trees at the two remaining plots were felled by wind during storms.

Sampling and Analysis

Soil samples were taken from the organic layer and from bores of the 0-10 and 10-20 cm mineral layers. At each level 10 samples formed one composite sample. In the laboratory, the samples were dried at room temperature, mechanically ground and sieved to separate the fine earth fraction. All mandatory parameters were determined using reference analysis methods. Total element contents **(P,** K, Ca, Mg) were measured in the organic layer of the different plots after extraction with aqua regia.

Results

At the Walloon region scale, the level I network has a density which is too low to develop assumptions on the reasons of degradation of our forests. However, some comments may be made on the results obtained for the 21 plots of the 16x16 km network in parallel with the knowledge acquired through different studies of the Ardennes forest.

There is a certain homogeneity in different parameters (climate, soil texture, soil drainage).

The pH ($CaCl_2$) values measured in the different spruce plots are generally very low (Table II 2-2). Norway spruce is largely used on poor soils of the Belgian Ardennes. In beech stands pH ($CaCl_2$) is also very low.

Because aqua regia is not often used in Wallony, reference threshold values are unavailable. The determination of 'risk soils' is generally based on the contents of exchangeable elements of the soil. In spite of the differences observed between plots, the analysis of the organic layer alone is not very discriminating in evidencing soils in risk situation. Differences in foliar composition between species on the same soil suggest that the absorption capacity for certain elements varies among tree species. For example, for one of the studies carried out in the Ardennes, foliar content of Mg of oaks was 1.5 to 2 times higher than the Mg content of beech leaves, and only beech trees suffered from yellowing.

In a study in progress, total Mg content in the organic top layer of the soil ranged between 300-500 mg kg^{-1} in Norway spruce stands and 800-1000 mg kg^{-1} in beech stands. Those soils are considered in a risk situation and the sanitary situation of the trees is sometimes severely degraded.

Values observed in the European network range from very low values under Norway spruce (Table II 2-2) to the highest values under oak. One plot (n° 106) presents much higher values than the others, probably because of the acceleration of the decomposition of the organic matter due to increased light intensity after windfall. The effect of a clear cut on the decomposition of organic matter is also shown by the Norway spruce plot nr. 121. In this plot, values of P, K, Ca and Mg in the soil are above the mean values of the other Norway spruce plots.

There is a relation between total Mg content in the organic top layer of the soil (1994 samplings) and the foliar discoloration observed in 1995. Discoloration is non-existent when concentrations of Mg in soils are high. When soil contents are low, discoloration may be marked.

The nutrient content in the organic top layer (sampling in 1994) is not always linked with contents measured in foliage (sampling in 1995). A positive relation exists for K (r = 0.58**) and Ca (r = 0.65**) but there is no significant correlation for P (r = 0.12) or Mg (r = 0.42). Looking at the results of analysis of the 16x16 km network, Mg nutrition seems rarely optimal. This is general in the Ardennes.

Table II 2-2. Comparison of pH ($CaCl_2$) and elements extracted with aqua regia in soils under stands of different species

main species **(number of trees)**	*Picea abies* *(24)*	*Picea abies (16)* *Pinus sylv. (7)*	*Pinus sylvestris* *(24)*	*Pinus sylv. (17)* *Q. petraea* *F. sylvatica*	*open, before:* *Picea abies (12)* *Q. robur (10)*	*Q. robur* *+petreae* *(24)*
number of plots	7	1	1	1	1	2
pH						
layer **O**	**3.0**	**3.2**	**3.7**	**3.7**	**4.7**	**4.5**
layer 0-10 cm	**3.2**	**3.3**	**3.9**	**3.3**	**4.4**	**4.0**
layer **10-20 cm**	**3.6**	**3.8**	**4.1**	**3.8**	**4.6**	**4.1**
Layer O						
total Mg (mg kg^{-1})	**453**	**711**	**2377**	**884**	**5668**	**4773**
total Ca (mg kg^{-1})	**1967**	**4839**	**1260**	**4982**	**4650**	**3951**
total K (mg kg^{-1})	**857**	**1777**	**1845**	**1480**	**4388**	**3260**
total P (mg kg^{-1})	**1005**	**1331**	**837**	**938**	**1005**	**912**

main species **(number of trees)**	*Q. robur (18)* *F. sylvatica* *(6)*	*Q. petreae(12)* *F. sylvatica.* *(11)*	*F. sylvatica (17-20)* *Q. robur +petreae* *C. betulus*	*F. sylvatica* *(24)*	*Q. petreae (7)* *C. betulus (8)* *Betula sp. (7)*	*Fr. excelsior (6)* *T. cordata (4)* *Th. species (4)*
number of plots	1	1	3	1	1	1
pH						
layer O	**3.8**	**3.6**	**3.6**	**3.7**	**4.0**	**4.5**
layer 0-10 cm	**3.6**	**3.5**	**3.3**	**3.5**	**3.7**	**4.1**
layer **10-20 cm**	**4.2**	**4.2**	**4.0**	**3.4**	**4.0**	**4.3**
Layer O						
total Mg (mg kg^{-1})	**1056**	**952**	**754**	**1250**	**3295**	**1100**
total Ca (mg kg^{-1})	**4899**	**2731**	**3253**	**3404**	**1890**	**6706**
total K (mg kg^{-1})	**1615**	**1656**	**1345**	**1628**	**2437**	**1770**
total P (mg kg^{-1})	**1077**	**4113**	**1353**	**1049**	**939**	**524**

Q: Quercus; F Fagus; C: Carpinus; Fr: Fraxinus; T: Tilia; Th: Thuya

Compared to other Norway spruce stands in the Ardennes, the K contents in the 7 monospecific spruce plots of the level I network are particularly low. Because a different extractant ($HF+HClO_4$) was used for the other stands, we should be careful when comparing results. In most of the Walloon forests, productivity is not reduced by Ca, which is better retained in soil than K.

The C/K ratio in the organic top layer gives an indication of the rate of organic matter decomposition. In the two peaty soils of the network, K has been largely removed from the organic layer, resulting in a very high C/K ratio. In the three mull layers, which mostly consist of young debris, the C/K ratio is similar to that of fresh litter.

In many soils of the Ardennes, the majority of the nutrients are provided through decomposition of organic matter. In spite of a low C/P ratio, the risk of a degradation of the sanitary situation is not excluded.

The C/K and C/P ratios evolve quite similarly (r = 0.90**). According to Evers (1967), nutritional disorders can be expected in pure or mixed Norway spruce stands for C/P and C/K ratios respectively above 350-450 and 400-500. These values are exceeded for seven plots for the ratio C/P, all of which are conifer stands. Nearly all Norway spruce plots are concerned. The C/K ratio is above 500 in 5 Norway spruce plots. Nevertheless, it is important to underline that extractants are different (extraction with HCl 30% for Evers). It is possible that the aqua regia method underestimates total concentrations of P and especially K.

Measures against Damaged Forest Soils

The ongoing acidification (by atmospheric input of acids) may progressively reduce the diversity of trees and the number of microfauna and microflora species, especially species that are less tolerant to acidity. In such cases, restoration of the soil's nutritive function can be realised by adequate fertilisation. Several projects are studying the chemical composition of forest soils of different regions, managed with different types and quantities of fertilisers. The association of certain species appears also as a promising way to ameliorate tree nutrition but its efficiency has still to be demonstrated.

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2.4 BULGARIA

E. Pavlova

The soil survey in Bulgaria was carried out at the plots of the large-scale (16x16 km) grid, where crown assessment, foliar analysis and other monitoring activities have also been implemented.

Methods

Soil condition was characterised by chemical analysis of samples taken from fixed depth layers (0-5, 5-10 and 10-20 cm) of the mineral soil. The organic layer was analysed by separate horizons (01, 02, 03). Organic layer results were reported as mean values for the whole organic layer. A detailed profile description was carried out at every sample plot. The organic layer and the 0-5 cm layer of the mineral soil were analysed in 3 or more repetitions in the course of several successive years. The reported results are averages for the whole period of investigation.

Results

Level of Acidity

A great variety of pH conditions is observed. Soil acidity ranges between slightly alkaline to very acid. The soils in the western part of the Rhodopi mountains are among the most acid, having pH (H_2O) values between 4.2 and 4.4, in some cases up to pH 3.8-3.9. A correlation was found between soil acidity and altitude above sea level. Higher soil acidity is registered at higher altitudes. At 1000-1200 m, due to higher precipitation values and the presence of acidic silicate rocks, the forest soils are poor in bases and highly acid. Temporal changes in soil pH could not be studied at a regional scale due to a lack of data from the past. Instead, soil acidification was assessed by changes of other parameters that characterise soil acidity. The results show increasing concentrations of exchangeable Al in the upper layers of most soils, which may be due to the acid destruction of clay minerals. The amount of exchangeable acidity decreases in depth. This acidification may be explained by a low supply of bases from organic matter decomposition and parent rock weathering, as well as by acid deposition from the atmosphere.

The cation exchange properties of soils at higher altitudes and their level of acidity, characterise these soils as poor in reactive colloids, with a low buffer capacity and a high sensitivity to atmospheric pollution.

Nutrient Status

The studied forest soils are in general well supplied with nitrogen. There is a great variety in P and K contents, depending on the parent material. A general conclusion can be drawn that most soils are well supplied with K, whereas the content of P is low. The widespread Cambisols are particularly poor in bases.

Presence of Toxic Elements

The evaluation of heavy metal concentrations in soils was made on the basis of national norms, which are a function of pH. Further, an anomaly coefficient, based on heavy metal concentrations in the upper soil layer and in the C-horizon, was used to determine the degree of contamination. The results show higher Zn concentrations, as compared to the national norms, in 86% of the samples taken from the mountains in south-west Bulgaria, and in 66% of the samples taken from the central part of the Balkan ridge. The main reason was not aerosol pollution but a higher acidity of the parent rock Increased Pb contents in some soils were proved to be of anthropogenic origin.

Discussion on Investigated Relationships

In spite of the great variety in forest conditions in Bulgaria, a relationship with the soil condition could be established in the Sredna Gora mountain region. Changes in chlorophyl content were registered only in stands with increased soil concentrations of Zn and Pb. A higher level of defoliation was registered in those *Pinus nigra* and ***Quercus*** *sessiliflora* stands, where soils are slightly acid and Zn content is high.

Literature

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2.5 CROATIA

N. Komlenovic, P. Rastovski and B. Vrbek

The large-scale forest soil condition inventory in Croatia covers approximately 12,500 km^2 and is represented by 87 observation plots of the 16x16 km grid.

Sampling and Analysis

Twenty sampling sites were located at regular intervals along the 4 lengths of a square area formed by 4 sample trees. At each sampling site the organic layer was sampled separately. Mineral soil samples from the 0-10 and 10-20 cm depth layers were taken from bores. Next, the samples of the different sites were mixed to form representative composite samples of each layer.

Soil analyses were carried out by the Forest Research Institute at Jastrebarsko in the period from 1993 to 1995. Reference methods were used for the determination of pH and the extraction of P, K, Ca, Mg, Fe, Mn and Zn from the organic layer. Organic Carbon (Tjurin method) and total nitrogen (Kjeldahl method) were determined by wet oxidation.

Data Processing

The statistical analysis of the soil condition results, applied to individual geographical regions, is still in progress. The following single and multi-dimensional statistical methods are used: variance analysis, multiple regression and factor analysis.

Information on Forest Soil Condition

Due to the very dissected and diverse geomorphology, a wide range of taxonomic units is observed among Croatian forest soils. According to the available information for the 16x16 km plots, six main pedosystematic units are recognised, which are further divided into subunits. The soils at 44 observation plots were classified as Cambisols. Other soil types are Luvisols (17), Leptosols (11), Gleysols (9), Planosols (5) and Podzoluvisols (1).

Soil nutrient contents and acidity levels vary within a wide range (Table II 2-3) and mostly depend on the nature of the parent rock and other ecological circumstances.

Table II 2-3. Nutrient contents and pH of the surface mineral layer of Croatian forest soils.

Soil Unit	pH	Nutrient Content	Frequency
Eutric Gleysols	6.2-7.5	high	9
Mollic Leptosols	4.4-6.4	medium high	5
Rendziic Leptosols	6.4-7.1	medium-medium high	6
Eutric Cambisols	6.5-6.6	high	4
Dystric Cambisols	4.5-5.5	low-medium low	12
Chromic Cambisols	5.6-6.4	medium low-low	26
Ferralic Cambisols	5.2-6.6	low	2
Eutric Planosols	6.4	high	1
Dystric Planosols	4.8-5.8	low-medium low	4
Dystric Podzoluvisols	3.8	low-medium low	1
Haplic Luvisols	4.3-5.2	low	9
Stagnic Luvisols	4.4	medium-low-low	1
Gleyic Luvisols	4.1-5.1	medium low-low	7

For several locations, contents of some heavy metals (Pb, Cu and Zn) and sulphur are available. Lead concentrations in the humus layer exceed the value of 100 mg kg^{-1} in plots located at high altitude. Most lead values range between 35 and 85 mg kg^{-1}, those of copper and zinc are usually lower.

The average Pb concentration in the surface layer of the mineral soil of twenty-eight beech stands in north and west Croatia is 55 mg kg^{-1}. Decreased pH-values and high lead, copper and zinc concentrations have been noted in the beech trunk base area at the majority of these plots. Elevated amounts of these metals are particularly notable in western Croatia, where they increase with increasing altitude. Beech defoliation follows the same pattern. However, this may not be directly linked to increased soil acidity and heavy metal accumulation, because also the site conditions for beech growth become less suitable with increasing altitude (Komlenovic and Rastovski, 1995).

In the vicinity of power plants and coal-consumers, besides sulphur, increased lead contents in the surface layer of the mineral soil have been established.

In the assessment of the impact of atmospheric acid deposition, the buffer capacity of different soil typological units, is of great significance. The buffer capacity is dependent of the amounts of humus and clay in the topsoil.

Measures to Restore Damaged Forest Soils

Because the effect of "ploughing" during logging procedures, which causes compaction and other structural soil damage, forest management in the lowland regions using heavy mechanisation is disputable.

The accumulation of pollutants (heavy metals and others), transported by underground streams or deposited after flooding is another form of soil damage observed along the major river systems (Sava, Drava, Mura) (Komlenovic et al., 1992).

Changes in the underground and flood water regime due to agricultural and hydro-technical management have had an extremely negative impact on the status of lowland forests.

The biggest problem in maintaining the function of the forest soil in karst areas is the increased soil erosion hazard following karst vegetation fire. Considering the soil units and their erodibility, afforestation and fire protection measures have received priority in karst areas. To prevent large-scale soil loss, remedial actions are indispensable, primarily in areas susceptible to erosion.

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2.6 CZECH Republic

K. Škarecká, P. Fubidnek

Introduction

Forest soil condition observations have been made in the Czech Republic since the 1950s, when the first symptoms of health damage of forest stands, presumably caused by acid deposition, began to occur. A process of gradual degradation of forest soils was evident, particularly an increase in soil acidity, which was partly neutralised by broadcast liming of young forest stands in selected forest regions. In the early 1990s, the Czech Republic adopted the ICP methodology for sampling and analysis of soils. Observation plots of a national and transnational network are now regularly monitored at 5-year intervals In 1995, mandatory and optional soil analyses were performed on soil samples of 100 level I plots of the 16x16 km grid and 8 level II plots.

Methodology

At each observation plot, 5 sampling sites were located at regular space intervals in the direction of the slope (sloping terrain) or from north to south (flat terrain). The organic litter (L), fermentation (F) and humus layer (H) were sampled separately at every site, using a square 25x25 cm frame. The 5 samples of each layer were then bulked. Using the weight of the individual layers, analysis results were recomputed for the whole organic layer.

From the same sampling sites, mineral soil samples were taken from the prescribed 0-10 and 10-20 cm soil depth layers, which were also bulked to form composite samples.

All mandatory and optional parameters were determined on the composite samples of the organic L and F+H layers, and the 0-10 and 10-20 cm mineral layers. Reference analysis methods were used, except for the determination of organic carbon and nitrogen, for which wet oxidation methods were used.

Some results

Soil Types

Dystric Cambisols, the most frequently observed soil type, is represented by 28.7 % of the monitoring plots (Figure II 2-1). Cambic Podzols (13.9 %), Dystric Planosols (12.0 %), Gleyic Cambisols (11.1 %), Cambic Arenosols (7.4 %) and Gleyic Podzoluvisols (5.6 %) are also important; 21.3 % of the plots is occupied by other soil types, such as Haplic Greyzems and Terric Histosols.

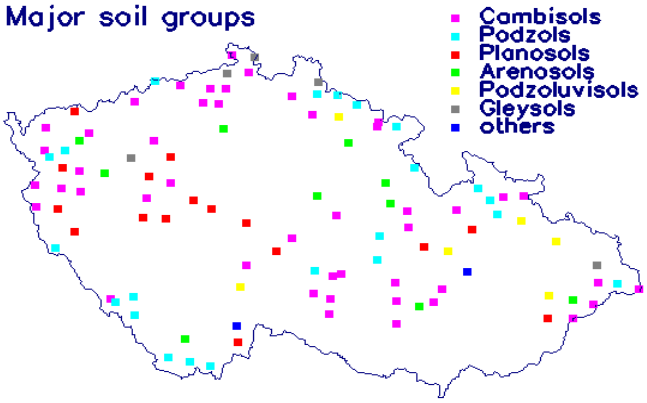

Figure II 2-1. FAO Major Soil Groups observed at the plots of the Czech Republic.

Soil Reaction

Values of pH ($CaCl_2$) of the L layer range from 3.2 to 5.4, but at most of the plots it is between 3.4 and 5.2. The F+H layer is more acid; pH values are usually between 2.9 and 3.5. In the mineral soil, pH gradually increases with depth. The pH interval with the highest number of observations is pH 3.1 - 3.7 in the 0-10 cm layer and pH 3.4 - 4.0 in the 10-20 cm layer.

In the 1986-1995 period, a pH increase in the organic layer has been observed, caused by the extensive liming programme of the 1980s. In comparison with the L layer, the effect of liming is slightly delayed in the F+H layer. Since 1991, when the liming programme ceased, pH has decreased again. The effect of liming is less evident in mineral layers. Values of pH in the 0-10 cm layer of the mineral soil have remained stable around pH 3.4 since 1986.

Carbon and Nitrogen Metabolism

The C/N ratio of organic layers is lower than 25 at most plots. The mean value of this ratio in the L layer is 19.2, and 21.9 in the F+H layer, which are values favouring the decomposition of organic matter. The influence of soil type on the C/N ratio seems of low importance.

The average C/P ratio in the L layer is 379, in the F+H layer it is 330, which can be considered as normal values. Carbon and nitrogen concentrations are affected by stand, site and climatic conditions, as well as by the immission load of a given area. The content of carbon and nitrogen in organic layers decreases with increasing altitude but their ratio is not influenced. An accumulation of organic matter is observed in the region receiving a high load of acid deposition. In the same region, the amount of nitrogen available to plants is reduced, but not the total soil nitrogen content.

Soil Sulphur Content

The highest sulphur concentrations are found in the mountainous regions in northern Bohemia. In some areas, above all in central and southern Bohemia, concentrations of sulphur in organic layers increased with 500 mg kg^{-1} in comparison with the year 1991. In the early 1990s sulphur emission significantly decreased after it culminated in the late 1980s. It is expected that the effect of this decrease in emission will manifest itself within 5 years in the L layer and much later in the H horizon.

Soil Lead Content

The amount of lead in the organic L layer ranges between 0.8 and 295.0 mg kg^{-1}. Concentrations of lead in the F+H layer are higher, with an average value of 153 mg kg^{-1}. The highest lead concentrations are found in mountainous regions in southern Bohemia and Moravia, in particular at the plot located near the uranium mining area. In comparison with 1991, lead concentrations in the F+H layer increased at approximately 50 % of the plots from less than 100 mg kg^{-1} to a level between 100 and 200 mg kg^{-1} (Figure II 2-2). The average increase is 25 mg kg^{-1}.

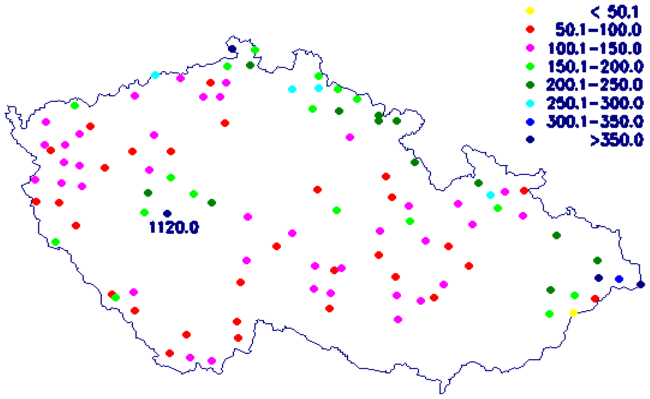

Figure II 2-2. Measured concentration (in mg kg^{-1}) of lead in the organic F+H layer in 1995 at the observation plots of the Czech Republic.

Soil Arsenic Content

The concentration of arsenic is mostly lower than 5 mg kg^{-1}, in the L layer, although accumulations of more than 15 mg kg^{-1} arsenic are found at 6 % of the plots. Arsenic levels are usually higher in the F+H layer. Differences are observed among the various soil types: Cambisols and Podzols have higher concentration of arsenic in the F+H layer. At 10 % of the plots the concentration in the F+H layer exceeds 50 mg kg^{-1}.

Cadmium and Zinc in Soil and Mosses

Cadmium and zinc, unlike the other heavy metal elements, are more concentrated in the L layer than in the F+H layer. Still higher concentrations are found in mosses, such as *Dicranum scoparium* and *Hypnum cupressiforme*. Accumulation of cadmium and zinc are most evident in Cambisols and Podzols.

A relationship between metal concentration and altitude was not found. Also the investigated relationship between crown defoliation patterns in the period 1986-1995 and soil type did not yield significant differences (Figure II 2-3).

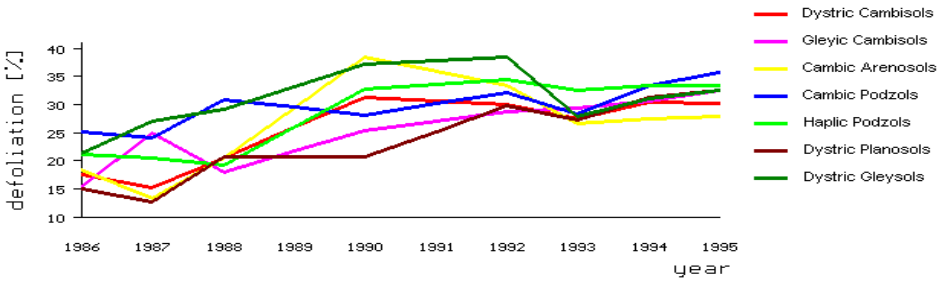

Figure II 2-3. Relationship between FAO soil unit and defoliation.

Conclusions

The pedological observations since 1986 indicate that:

- most observed forest soils belong to the category of acid to extremely acid soils, situated in the Al-Fe buffer range;
- soil nutrient supply, except nitrogen, is generally low, particularly the calcium supply;
- the cation exchange capacity of mineral soils is low and the adsorption complex is mostly saturated with acid cations;
- the load of sulphur and heavy metals, especially lead, is high;
- the positive effect of liming on soil reaction, base saturation and in general on the buffering capacity of forest soils is confirmed.

2.7 DENMARK

M. Olsson, J. Bille Hansen

The Danish forest condition is annually surveyed at 54 plots, situated at the intersection points of a 7x7 km network. The soil was sampled and analysed at a subset of 25 forest plots more or less corresponding to the 16x16 km ICP network.

Sampling and Analysis

Fieldwork was performed in the spring of 1994. Each sampled plot measured 50x50 m. The organic layer, and 6 mineral layers were sampled separately at 0-5, 5-10, 10-20, 20-50, 50-75 and 75-100 cm soil depth. A composite sample for each layer consisted of 16 sub-samples taken with auger, at positions evenly spaced along the diagonal of the square test site. Until a depth of 20 cm, volumetric samples were taken for the determination of bulk density. Within the test site one profile was dug and fully described (FAO, 1977).

Organic layer weight was determined by measuring organic layer thickness multiplied by arbitrarily attributed bulk densities of 0.12 g/cm^3 and 0.14 g/cm^3 for deciduous litter and coniferous litter, respectively. Stony material was removed (> 2 mm). All samples were dried at a temperature not higher than 40°C. In addition to all mandatory parameters, exchangeable acidity and Al were measured from a 1M KCl extract. Mandatory parameters were determined with reference methods, except total nitrogen, for which the Kjeldahl method was used. Aqua regia extracted P, K, Ca, Mg and Na were measured in both organic and mineral layers. The particle size distribution of mineral samples was determined using 6 fine earth fractions.

Discussion

The soils of the level I plots were classified (FAO, 1990) as Podzols (18), Luvisols (4), Cambisol (1), Alisol (1) and Gleysol (1). The plots are located in two major geomorphological units. In the western part of Jutland there are the Saale glacial landscape and the Weichsel glacial outwash plains, while in the eastern part of Jutland and on Zeeland the deposits are derived from Weichsel till which is mostly clayey and in many areas, especially in the south-east, also calcareous.

The sandy and clayey soils in the western part of Denmark have been strongly leached and consequently pH values are rather low, ranging from approximately 3.5 in the uppermost layers to 4.5 at a depth of one meter. The mor layer on these soils is often more than 10 cm thick, up to 25 cm at some places. The rate of organic matter decomposition is very slow in these acid soils.

In the eastern part of Denmark there is a distinct difference between the sandy soils in the north-east and the clayey soils in the south-east. The former are similar to the soils in the western part of the country, but in the southern part soils developed from a clayey and often calcareous till, which in many places still contains calcium carbonate within a depth of one meter.

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2.8 ESTONIA

E. Asi, R. Sepp

The total area of forest land in Estonia is about 2.0 million ha or 47.7% of the dry land of the Republic of Estonia. In the framework of the Estonian level I soil condition survey, soils were sampled at 91 forest monitoring plots, representing the three most important tree species ***(Picea abies, Pinus sylvestris, Betula pendula).***

Investigations of Forest Soils in Estonia

The entire Estonian territory is covered by large-scale (1:10,000) soil maps. The mapping of forest soils was carried out between 1976 and 1988 and is based on the national genetic soil classification system which consists of 92 units. Forest soils cover 62 genetic mapping units that can be clustered in 5 major soil groups (Table II 2-4).

Table II 2-4. Distribution of forest soils in Estonia and among the monitoring plots over the 5 major soil groups of the Estonian Soil Classification System (number of observations/percentage).

Soil Group	number of soil units		number of plots
	in Estonia	among plots	
Dry and Moderately Humid soils	19/31	8/27	31/34
Gleyed soils	19/31	8/27	18/20
Gley soils	10/16	6/20	19/21
Peaty soils	5/8	2/6	10/11
Forest Bog soils	9/14	6/20	13/15
Total	**62/100**	**30/100**	**91/100**

During the large-scale soil mapping approximately 600 soil pits (exposing also the parent material) were morphologically described, sampled and analysed by genetic horizons, which resulted in an extensive database of morphological, physical and chemical parameters. The analysis results have been statistically analysed by soil unit and genetic horizon (RPI EPP, 1983; 1985a; 1985b; 1988; 1989).

Sampling and Analysis

The fieldwork of the soil survey was done between 1990 and 1994. Morpho-genetic horizons were sampled in triplicate at different profile pits in each plot. Sample preparation in the laboratory included drying at room conditions, grinding and sieving.

The used analysis methods differ from the reference methods, because the instruments that are required to perform the recommended methods are unavailable and financial means are inadequate to acquire the necessary equipment. Soil acidity is measured in a 1M KCl solution. Organic carbon and total nitrogen contents are determined by wet digestion; the carbonate content is determined using a calcimeter. Total contents of P, K, Ca and Mg of organic layer samples are obtained after dry ashing at 400-450°C and dissolution in HCl. The analysis results of mineral samples were recalculated to discrete layers (M01 and M12).

Data Processing

The parameter results of the monitoring plots were compared to the arithmetic mean values in the soil database (RPI EPP, 1983; 1985a; 1985b; 1988; 1989), which can be considered as reference values. Most survey results are similar to the reference values (reference value ± 2 x standard deviation, in many cases ± 1 x standard deviation).

Forest Soil Condition

The most informative parameters, such as pH, C/N ratio and particle size distribution (particularly the fractions <0.01 mm and between 0.1 and 0.05 mm), are those that characterise soil acidity, nutrient status, intensity of the biological activity and humidity status of the soil. Because the fertility of forest soils is largely determined by the degree of soil development and the chemical status of the topsoil, organic layer results vary between the main soil types (Table II 2-5).

Table II 2-5. Selected parameter results for organic layers of the most representative FAO soil units in Estonia.

Soil unit	thickness (cm)		pH (KCl)		Org. C (g kg^{-1})		N (g kg^{-1})		C/N	
	X*	S_X*	X	S_X	X	S_X	X	S_X	X	S_X
Haplic Podzols	5.4	2.3	2.91	0.23	443	61	11.4	1.4	38.8	10.5
Dystric Podzoluvisols	3.3	1.1	3.16	0.38	394	76	13.1	2.2	30.1	8.3
Stagnic Luvisols	2.1	0.8	3.86	0.60	349	70	14.1	2.5	24.7	6.2
Gleysols	10.8	3.7	3.78	0.33	365	30	17.3	4.7	21.1	4.9

*: X = arithmetic mean; S_X = standard deviation

There are no indications for any significant acidification of forest soils in Estonia during the last decades. Flue gases, emitted from two gigantic thermal power plants in the north-eastern part of Estonia and consisting of approximately 75% $CaCO_3$ are the cause of alkalinisation of forest soils in about 7% of the Estonian territory. Particularly sensitive to alkalinisation are podzolised soils that have a low buffering capacity. Alkalinisation, recognised by an organic layer pH value which is higher than or equal to the pH value of the underlying mineral layer, is found in 5 monitoring plots. It causes a significant decrease in exchangeable aluminium in forest litter. A decrease in acidity in subsurface horizons of some soils in comparison to reference soils is also observed.

The content of the measured heavy metals (Pb, Cd, Zn) in the forest soils of the monitoring plots is very variable. Although the contents of heavy metals clearly decrease with soil depth, the variation of concentrations in the subsoil tends to be higher than in the surface layers. Significant differences in the contents of Pb and Zn, but not in the contents of Cd, are found between the north-eastern and south-western parts of Estonia; contents of Pb and Zn are 31%, respectively 60%, higher in the south-western part. Nevertheless, heavy metal contents in most monitoring plots are within the normal range, although pollution may have increased metal levels locally. Exceptionally high contents are found in two plots, one located near an airfield, the other at a former open mining area of phosphorite.

Simple correlation analysis failed to reveal consistent relationships between contents of heavy metals and pH of organic and mineral layers on the one hand, and defoliation of tree crowns on the other hand.

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2.9 FINLAND

***P.** Tamminen, M. Starr*

An integrated forest soil and tree vitality inventory, based on a systematic network of 3009 permanent plots arranged in clusters, was established in 1986-1987. In southern Finland (< 65°N), the national network consists of 4-plot clusters in a 16x16 km grid, and in northern Finland (> 65°N), of 3-plot clusters in a 32x24 km grid. Of these plots, 442 (not more than one per cluster) were selected for soil sampling; 338 were sampled in the period 1986-1989, another 104 in 1995.

Sampling and Analysis

Samples were taken systematically at a distance of 11 m out along 10 radii from the centre of the plot at angles of 36" intervals (36°, 72" ... 360"). Organic (humus) samples were taken from all ten locations, mineral soil samples from every other location. At the most representative of the 5 mineral soil sampling locations, a profile pit was dug. A profile description was made according to national guidelines.

The fixed depth mineral soil layers (0-5, 5-20 cm in 1986-1989; 0-5, 5-10 and 10-20 cm in 1995) were sampled from small pits at each sampling location and bulked to give a representative sample of each layer for the plot. Fixed volume samples were also taken from at least 3 pits for bulk density determination.

Sample pre-treatment included air drying (all samples), removal of large pieces of wood, cones etc., milling into fine powder (humus layer samples only), and sieving through a 2mm sieve (mineral soil samples only).

pH (H_2O) values for 1986-1989 samples were converted to pH ($CaCl_2$). pH ($CaCl_2$) values of the 1995 samples were determined using the reference method. Reference methods were used for the analysis of organic C and total N in humus samples. Loss on ignition total C-values for mineral layer samples were converted to organic C-values. The Kjeldhal wet digestion and steam distillation method was used for N-determination in mineral layer samples. Total concentrations of P, K, Ca, Mg, Na, Al, Fe, Cr, Ni, Mn, Zn, Cu, Pb and Cd in organic layer samples (1986-1989) are dry combustion values converted to aqua regia values. In 1995, wet digestion in concentrated $HNO_3 + H_2O_2$ was used. Cation exchange properties of the mineral layers were determined according to the reference method, except exchangeable acidity in the 1986-1989 samples, which was titrated to pH 7.0 and then converted to pH 7.8 values.

Data Processing

Internal checks on the soil condition data were made by examining distributions and intercorrelations between variables. The soil condition variables were also correlated with various site, tree stand and tree vitality variables. In addition, the soil data were compared to the results from various data held by the Institute, including fertilisation experiments and Integrated Monitoring results, and previously handled results (Tamminen and Starr, 1990; Starr and Tamminen, 1992).

Forest Soil Condition

Acidic conditions occur in the organic layer (mor and peaty mor) and upper mineral soil layer (Table II 2-6). The spatial pattern of pH shows forest floor acidity increasing to the north and mineral soil acidity increasing to the south. This is interpreted as being the result of organic matter accumulation, and nutrient release, uptake and cycling - the intensity of which decreases northwards. The native tree species Scots pine and Norway spruce, which dominate Finnish forests, are adapted to grow over a wide soil pH range. There is no evidence that neutralising soil acidity by applying lime increases stand growth (Derome et al., 1986).

Table II 2-6. Soil pH values by soil layer and cumulative distribution.

Layer	Min	25 %	50 %	75 %	Max	n
Mor	2.9	3.2	3.4	3.7	4.8	400
Peaty mor	3.0	3.3	3.4	3.6	4.8	33
0-10 cm	3.3	3.7	3.9	4.1	4.8	438
10-20 cm	3.6	4.1	4.3	4.5	5.2	435

As for northern coniferous forests in general, the main growth limiting nutrient on forested mineral soils is nitrogen. With the exception of the most fertile sites, both pine and spruce respond to nitrogen fertilisation (Kukkola and Saramaki, 1983) and there is a clear correlation between site quality class (or site index) and the nitrogen content and C/N ratio of the organic layer (Table II 2-7). Of the other nutrients, calcium and magnesium contents of both the organic layer and mineral soil layers correlate best with the fertility class of the site, but neither liming nor ash fertilisation have been shown to increase tree growth (Derome et al., 1986).

Table II 2-7. Soil nitrogen contents and C/N ratio by forest site type.

Variable	Layer	Site type†)				
		1+2	3	4	5+6	mean
N, g kg^{-1} d.m.	Org.	13.8	12.1	10.4	8.7	11.6
	0-10 cm	2.33	1.00	0.69	0.76	1.16
	10-20 cm	1.20	0.74	0.62	0.48	0.78
C/N	Org.	27.5	36.4	42.2	46.6	37.2
	0-10 cm	19.4	23.8	25.7	25.6	23.6
	10-20 cm	18.4	22.0	24.0	23.7	22.0

†) 1 refers to the most fertile and 6 to the least fertile site type (Cajander, 1949).

The area around the Cu-Ni smelter at Harjavalta is the only area in Finland where the deposition of heavy metals constitutes a problem for forest health. The area in which damage is observed has a radius of 10 km. Concentrations of heavy metal in the organic layer are otherwise low (Table II 2-8).

Table II 2-8. Concentrations of heavy metals (mg kg^{-1}, d.m.) in the organic layer by cumulative distribution.

Element	Min	25 %	50 %	75 %	99 %	Max
Cd	0.0	0.3	0.4	0.5	0.9	1.3
Cr	1.1	5.9	8.1	11.0	33.8	43.4
Cu	3.0	5.3	6.6	8.5	28.6	109.6
Ni	0.0	6.0	8.2	11.0	26.2	37.1
Pb	6	25	31	39	74	202
Zn	6	36	47	61	137	185

Forest condition, measured by degree of defoliation, is not related to soil acidity. None of the soil acidity parameters (pH, cation exchange capacity, base saturation, exchangeable acidity and Al) were significantly correlated with the 10 year mean defoliation values. Of the soil parameters, only the C/N ratio of the organic layer in spruce stands correlated (positively) with the 10 year mean of defoliation values, which suggests that defoliation may be partly caused by a shortage of available nitrogen (Malkonen et al., 1990).

Measures to Restore Damaged Forest Soils

In Finland there are 18 ‘vitality fertilisation’ experiments on mineral soils and 11 experiments on peat soils. Five of them are situated near the Harjavalta Cu-Ni smelter in south-west

Finland. Treatments consist of liming and multiple-nutrient fertilisation. These experiments were established in 1991-92 and investigations include the determination of nutrient fluxes and biomass.

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2.10 FRANC€

V. Badeau

In the framework of the European large-scale forest soil condition survey a total of 540 forest soils were sampled and analysed in France; the soil data of 517 plots were made available for the transnational database. These plots cover the wide range of ecological conditions observed in French forests, from dry calcareous soils to moist acidic sites.

Sampling and Analysis

Between 1993 and 1994, France launched the ecological survey of its 16x16 km extensive network (level I). Five regional offices were appointed to complete the inventory of 540 observation plots under the supervision of the French Forest Health Department (Ministry of Agriculture) and the National Forest Office (ONF). For each site (i) general information (date, co-ordinates...), (ii) a description of the physical environment (geology, topography...), (iii) a brief soil description (parent material, humus type...) completed by a more detailed one with more than 60 variables per horizon, (iv) a detailed floristic description, and (v) some simple dendrometric measurements, are available.

Litter (L) and fragmented litter (F) layers were sampled together but were separated from humus (H) layer samples. The mineral soil was sampled from a pit to a depth of 60 cm, where possible, at four fixed depth intervals (0-10, 10-20, 20-40 and 40-60 cm). Mandatory and optional analyses were performed, which resulted in nearly 70 analysis results per sampled soil and a total of 26,000 values for the entire network.

Data Processing

This dataset is the most important ever obtained in France with respect to forest soils. Since the completion of fieldwork and analysis activities, a lot of time has been devoted to encoding, organisation **and** validation of the data, while the data analysis has started only recently.

In a first step, the variability of the results is checked and some simple statistics are computed (frequency, average ...). This allows the detection of parameter results outside the expected ranges. These plausibility tests are also based on relationships between two or more parameters (e.g. pH, $CaCO_3$ concentration and parent material). In a second step, parameter values are divided into classes and presented on maps. Class limits are selected in relation to the frequency distribution of the parameter results or in relation to growth constraint levels. In a third step the variables are cross analysed (simple correlations, analysis of variance or multifactorial analysis) in order to determine relations between soil parameters. Lastly, the relationships between soil and crown condition will be investigated.

Soil Acidity and Nutrient Status

Due to the great variability of soil types in France, pH (H_2O) values show a wide bimodal frequency distribution (Figure II 2-4). Based on the acidity of the upper mineral layer (0-10cm) soils can be divided into 4 classes: calcareous soils (pH>7), neutral soils (5.5<pH<7), acidic soils (4.2<pH<5.5) and very acidic soils (pH<4.2). These classes are defined in relation to observed constraint levels and allow the identification of sites where acidity may affect tree nutrition (Figure II 2-5).

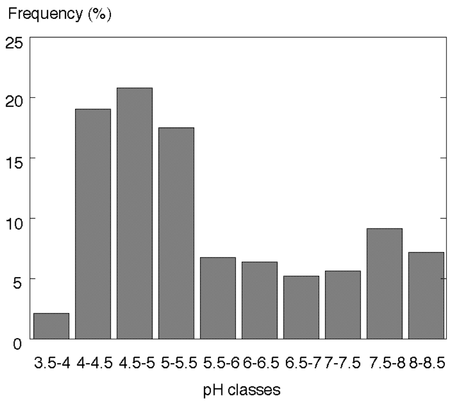

Figure II 2-4. Frequency distribution of pH (H_20) values in the upper mineral soil layer (0-10 cm).

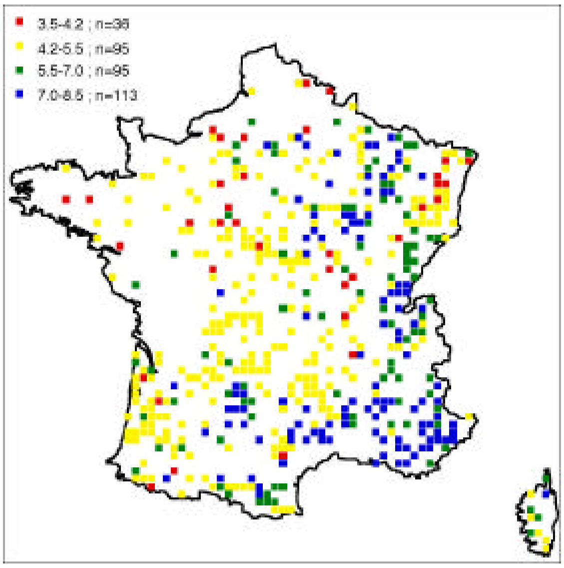

Figure II 2-5. Spatial distribution of pH (H_20) values in the upper mineral layers of the forest soils.

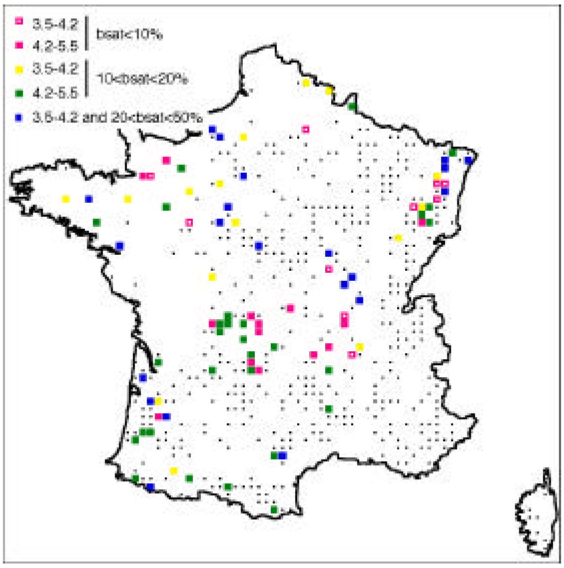

Figure II 2-6. Spatial distribution of forest sites, having an acid upper mineral soil layer (0-10 cm) with low base saturation.

Similar to pH, the observed ranges of nutrient concentration values are very wide and classes were selected in relation to constraint levels. Another approach consists in combining two or more constraint factors, for example level of acidity and base saturation in the upper part of the mineral soil. Table II 2-9 gives the number of sites in each cross-tabulated pH and base saturation class. Figure II 2-6, showing the location of strongly desaturated and acidic soils, confirms the ongoing soil acidification processes in the 'Vosges' mountains (north-east France). Nutrient budgets, studied during the last 10 years, and some historical data suggest that soils with an originally unfavourable chemical status in this region underwent further nutrient depletion in the last decades (Dambrine et al., 1995; Landmann, 1995). Equivalent data are not available for other regions, such as the 'Massif Central' area and Normandy (respectively central and north-west France), where soils are also very acidic and depleted of basic cations.

In the future, the sites of the RENECOFOR network (level II plots) will be regularly sampled and analysed in order to detect possible changes in forest soil conditions.

Table II 2-9. Distribution of soils after cross-tabulation of pH and base saturation values of the 0-10 cm mineral layer (numbers in bold correspond to the plots presented in Figure II 2-6).

	pH Class			
BS class	**3.5 - 4.2**	**4.3 - 5.5**	**5.6 - 7.0**	**7.1 - 8.5**
< 10%	**10**	**14**	0	0
11 - 20%	**15**	**29**	0	0
21 - 50%	**21**	87	0	0
51 - 90%	0	106	0	0
91 - 100%	0	33	90	109

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2.11 GERMANY

W. Riek

The forest soil condition in Germany is represented by 416 soil sample plots, covering a forested area of 106,960 km^2. The soil survey was made between 1987 and 1993.

Sampling and Analysis

According to the federal structure of Germany soil sampling, preparation and analyses were carried out by the German 'Lander' themselves considering the instructions specified in the manual of the German working group (BML, 1990). Since this manual was prepared before the EU regulation No. 926/93 of the Commission came into effect it was not possible to harmonise the methods with those of the EU.

Samples were taken at 10 m from the plot centre in each of the eight principal directions and lumped to form one representative composite sample of the organic layer and up to five composite samples of mineral layers at 0-5, 5-10, 10-30, 30-60 and 60-90 cm depth. In the laboratory, the samples were dried at 60°C, milled and sieved on a 2 mm sieve. Riek and Wolff (1996) compiled the analysis method descriptions of the individual German 'Lander' and evaluated their comparability with the EU reference methods.

Data Processing

The Federal Research Centre for Forestry and Forest Products / Institute for Forest Ecology and Forest Inventory in Eberswalde analysed the soil condition data at national level. Frequency distribution analyses of soil chemical parameters of 416 sample plots in Germany in combination with reference values from literature makes an overview of the German forest soil condition possible. The results may be summarised as follows:

Soil Acidification

One third of the assessed sites show signs of very high up to extremely high acidification and advanced leaching losses of base cations in the soil. There is a risk of acute acid toxicity for fine roots at 13 % of the sites, having a pH-value below 3.0 in the surface layer. Damaged roots can impair the nutrient and water balance of the trees.

Nitrogen Deposition

In spite of the very low pH-values many soils have relatively close C/N-ratios. This discrepancy between acidity (pH) and C/N-ratios is an indication of atmospheric acid respectively nitrogen deposition. As a consequence, imbalances in the nutrient supply of the trees may occur.

Heavy Metal Contamination

The effect of large-scale atmospheric deposition on forest soils is also evident when the heavy metal contents of the litter layers are considered. The average (median) lead content of 134 mg/kg is significantly higher than the maximum values of uncontaminated soils and plants. In view of the low pH-values in the top soils it must be assumed that significant parts of the more mobile heavy metals (zinc, cadmium) are already percolated in the deeper mineral layers and possibly into the groundwater.

Conclusion

In various regions of Germany important functions of forest soils have already reached the limit of their contamination capacity. The main causal factor of this instability is the soil acidification accelerated by the atmospheric deposition of acidifiers. Especially in combination with nitrogen deposition and high heavy metal contents in the organic layers there arises a serious risk In view of the actual data, for a significant part of German forests the sustainable nutrient supply of the trees, the protection of soil organisms against contaminations and the function of the soils for groundwater protection must be regarded endangered. Due to the variety of sites and the differing rates of atmospheric deposition these general statements require specific regional analysis. A more comprehensive analysis of soil chemical data is available within the national soil inventory report (Wolff and Riek, 1996).

In the following figures the percentage cumulative frequency distribution (PCF) of some essential soil parameters are shown. Minimum / maximum values, medians (PCF = 50 %) and any percentiles can be obtained from the graphs. Each individual value is marked by a cross.

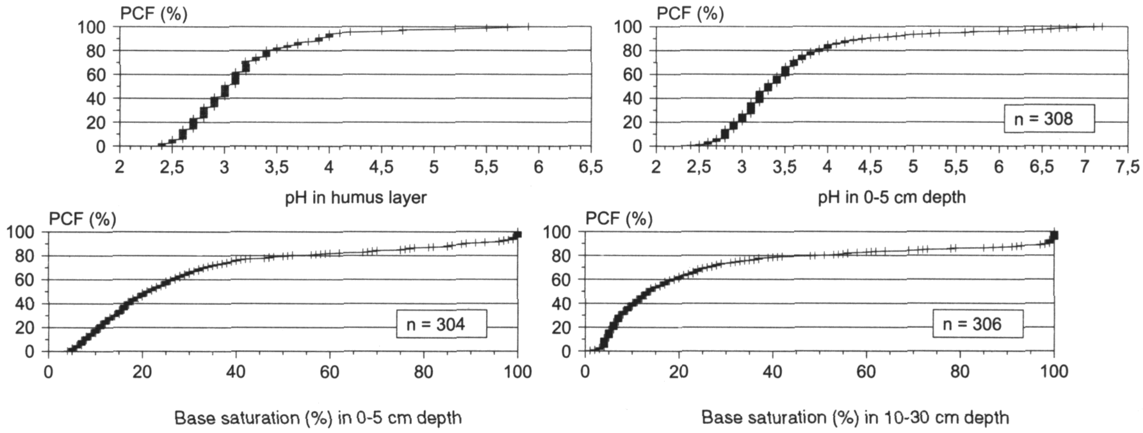

Figure II 2-7. pH and base saturation in mineral soil and humus layer.

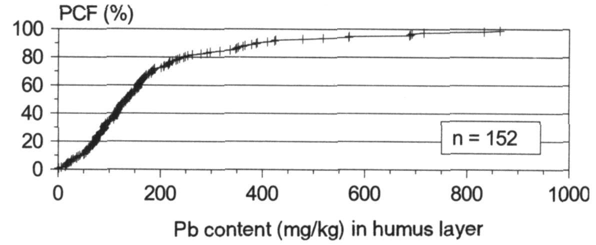

Figure II 2-8. Pb content in humus layer (H-horizon) and reference values.

reference values for Pb (mg kg^{-1})	
lithogenetic soil contents	ca. 5 - 30
content of plants	ca. 0 - 10
content of humus layer incl. Background contamination (Pruess, 1994)	130
critical concentrations for soil invertebrates (Tyler, 1992)	150

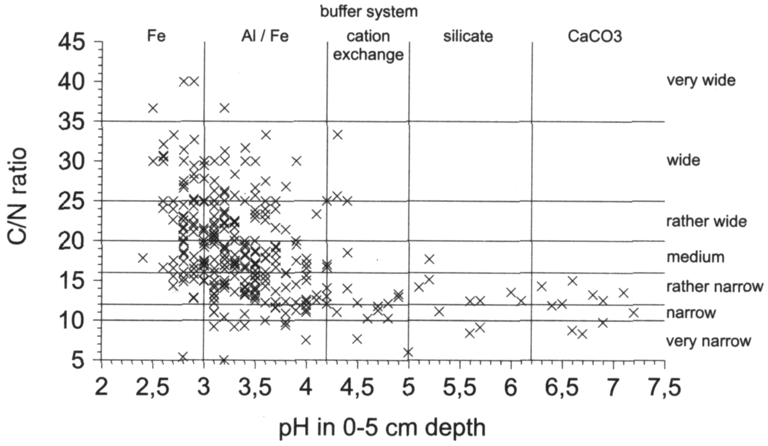

Figure II 2-9. Scatterplot of pH and C/N ratio in 0-5 cm depth.

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2.12 GREECE

G.Nakos

To study the forest soil condition of Greece in relation to possible atmospheric pollution effects, 15 permanent plots (Level I plots) were selected throughout the country with siliceous parent materials, which give rise to acid soils.

Sampling and Analysis

From these selected plots 154 samples of humic layers (if present) and mineral soils to a depth of 20 cm (0-10; 10-20 cm) were collected from four (4) points, one per quadrant of every plot, in the years 1993 and 1994. Humic (in cloth) and mineral (in plastic bags) soil samples were transported to Athens within two weeks after sampling. All samples were air-dried and then passed through a 2 mm sieve. Chemical analysis was carried out in the laboratory of Forest Soils of the Forest Research Institute within 3 to 10 months after sampling and storage of the samples at room temperature. The methods used for the analysis of the samples are shown below:

Property	Method	Remarks
pH	Electronic pH meter	ICP-Manual
Org. C (g kg^{-1})	Wet digestion ($K_2Cr_2O_7$+H_2SO_4)	National
N (g kg^{-1})	Kjeldahl (Conc. H_2SO_4 + catalyst)	"
P (mg kg-1)	Dry ashing (method of $(NH_4)MO_7O_{24}.4H_2O$)	"
Ca (mg kg^{-1})	Wet digestion (Conc. HNO_3 + H_2SO_4)-AAS*	"
Mg (mg kg^{-1})	Wet digestion (Conc. HNO_3 + H_2SO_4)-AAS	"
K (mg kg^{-1})	Wet digestion (Conc. HNO_3 + H_2SO_4)-AAS	"
$CaCO_3$ (mg kg^{-1})	Calcimeter	ICP-Manual

* Atomic Absorption Spectrometry

Results were calculated on the basis of oven dry weight (104°C). Only mandatory parameters were determined in the humic and mineral soil samples (Table II 2-10 and Table II 2-11).

Data Processing

The data of each sampled layer were subjected to an ANOVA test to examine the effect of different types of soil parent material on certain soil chemical properties. Some of the findings were compared with published information on the Greek forest soils (Nakos, 1979; 1984).

Forest Soil Condition

Acidity

In general, humic samples were found to be less acidic than the underlying mineral layers (Table II 2-10 and Table II 2-11). Mineral soils, of both sampling depths, can be grouped as: **very acid** ($5.0 > pH > 4.0$), those derived from granite, gneiss and schists, **moderately acid** ($6.0 > pH > 5.0$), those derived from flysch, peridotite and radiolarite, and **slightly acid** ($7.0 > pH > 6.0$) those derived from hard limestones (Table II 2-11).pH values found here are, in most cases, lower than those given in the literature since a solution of $CaCl_2$ was used in this study instead of H_2O (*Nakos,* 1979; 1984) to prepare the soil suspensions.

Nutrient Status

In the humic layer, soils derived from hard limestones were found to have significantly higher concentrations of Org. C, N, P and Ca compared to humic layers of soils derived from all the other types of parent material. Soils derived from peridotite contained in the humic layer the highest concentrations of Mg (Table II 2-10).

Table II 2-10. Selected chemical properties of humic samples of soils derived from various types of soil parent material.

Soil parent material	pH	C (g kg^{-1})	N (g kg^{-1})	P (mg kg^{-1})	Ca (mg kg^{-1})	Mg (mg kg^{-1})	K (mg kg^{-1})
Granite	6.0	162	8.52	725	7041	1314	2668
Schist	5.0	180	8.64	547	5931	5153	3091
Peridotite	5.3	178	8.39	458	5752	28194	3079
Radiolarite	5.8	106	6.38	875	4416	7243	4063
Hard limestone	6.1	257	13.2	1072	17641	10960	4183

On average. levels of Org. C and total N found here were higher and of total P somewhat lower than those reported for Greek forest soils (Nakos, 1984).

In the mineral soils, significant differences were found in the concentrations of Org. C and total N between soils derived from hard limestones and the remaining categories of soils, except those derived from peridotite (Table II 2-11). In the mineral soils, levels of Org. C and N found here differ from those reported for the **A** horizons of similar soils due to differences in sampling methods (fixed depths vs horizon sampling) (Nakos. 1984). Finally, no comparison can be made between levels of Ca. Mg and K (Table II 2-10), since in the literature these elements are reported to have been extracted with milder reagents (Nakos, 1984).

Table II 2-11. Selected chemical properties of mineral samples of soils derived of various types of soil parent material.

Soil parent material	pH	C (g kg^{-1})	N (g kg^{-1})	pH	C (g kg^{-1})	N (g kg^{-1})
	0-10 cm			10-20 cm		
Granite	4.2	15.4	1.02	4.0	8.42	0.592
Gneiss	4.8	20.0	1.20	4.8	17.1	1.08
Schist	4.9	21.7	1.58	4.8	12.4	0.953
Flysch	5.8	24.5	1.81	5.8	9.79	1.04
Peridotite	5.7	43.9	2.18	5.7	32.2	1.74
Radiolarite	5.7	36.9	2.28	5.4	22.9	1.78
Hard limestone	6.3	70.8	4.49	6.4	38.5	2.73

Discussion

No relationship was found between pH values of the humic and mineral soil samples and the average values of tree defoliation of the years 1993 and 1994 of the plots from which the samples were collected (Table II 2-12).

Table II 2-12 Average pH values in the humic and mineral soil layers and percentage of tree defoliation found (average of years 1993 and 1994) in the observation plots from which samples were taken.

Soil parent material	pH values			Defoliation
	Humic	0-10 cm	10-20 cm	(%)
Granite	6.0	4.2	4.0	22.3
Gneiss	-	4.8	4.8	23.9
Schist	5.0	4.9	4.8	21.4
Flysch	-	5.8	5.8	32.3
Peridotite	5.3	5.7	5.7	8.7
Radiolarite	5.8	5.7	5.4	15.9
Hard limestone	6.1	6.3	6.4	14.7

Relationships established between important soil properties of the Greek forest soils and the various soil-forming parameters, such as the nature of soil parent material. vegetation zone, altitude and physiography have been reported (Nakos, 1979; 1984). It has been found that the nature of soil parent material determines soil texture, level of pH and buffering capacity, whereas bio-climatic zones, found in altidudinal succession, affect pH variations and percent base saturation. Based on these findings the relative sensitivity of the Greek forest soils to atmospheric pollution, especially to acid rain, is expected to be as shown below:

Nature of soil parent material	**Bio-climatic zone** (increasing precipitation with elevation) →		
	Mediterranean (0-600 m)*	Sub-Mediterranean (300-1300 m)	Mountainous (600-1600 m)
Calcareous tertiary deposits	+	+	+
Hard limestone	+	+	+
Basic igneous rocks (peridotite)	+	+	++
Siliceous tertiary deposits	+	++	++
Flysch	+	++	++
Schists	+	++	+++
Gneiss	+	++	+++
Acid igneous rocks (granite)	+	++	+++

* Meters above sea level

+, least sensitive; +++ , most sensitive

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2.13 HUNGARY

A. Szepesi

In the framework of the national forest inventory, site information on Hungarian forests has been collected during the last 25 years. More recently, soil profile descriptions, according to the national methodology, and soil sampling activities have been carried out at 1100 observation plots of a systematic (4x4 km) forest drainage survey. Parallel to this national site survey. a soil condition survey on 67 plots of the pan-European 16x16 km grid was performed following the methodology described in the ICP Manual.

Sampling and Analysis

At each 16x16 km plot a homogenous sampling area was selected; 9 subsamples of each horizon - including litter and humus (H) horizon - were collected in a 2x2 m grid within a 4x4 m square by digging small pits or using special sampling tubes. To reduce the number of samples analysed, 3 subsamples of each horizon were bulked in a systematic way in the field. As a result, 3 parallel composite samples of each horizon were sent to the laboratory **of** the State Forest Service responsible for soil preparation and storage. The analyses were performed by the laboratories of the Forest Research Institute (C, N) and the Soil Science Institute following the methods described in the ICP Manual. All samples arc stored for further analysis in the future.

Data Processing

Site parameters collected at the plots of the national grid (4x4 km) often differ from the parameters described in the ICP Manual. The procedures of the national site survey aim at collecting information indicating site productivity, while the ICP method is focused on a general characterisation of the upper soil layers, and on parameters indicating air pollution effects. Parameters, common for both surveys, were simultaneously analysed with special regard to the deviant methodologies. In other fields, the national dataset complements the data collected only at the pan-European plots.

The statistical analysis of the collected data involved the following steps:

- normality tests and analysis of frequency distributions. Because the results of most parameters are not normally distributed, further analysis was performed in a traditional way;
- determination of correlation coefficients and their significance;
- regression analysis;
- detailed analysis of the derived functions.

To describe the relations between soil condition and forest health, the complete tree vitality dataset of the 1989-1995 period was related to each individual soil parameter, using defoliation, discoloration and crown dieback as key parameters. Where possible, results were compared to national reference values (e.g. pH, CEC).

Forest Soil Condition

At approximately 60% of the plots an alkaline pH is measured in the parent material (Figure II 2-10), indicating the presence of carbonates. At the other end of the pH range, 14% of the mineral surface (A) horizons and 5 % of the subsurface (B) horizons are classified as very acid (pH < 4.5), based on the Hungarian classification. Cation exchange properties were measured in the upper 20 cm. Only 10 % of the non calcareous layers has a base saturation of less than 20 % (sensitive to acidification), whereas 51 % has a base saturation of more than 80 %. Calcium is the dominant exchangeable basic cation, and usually covers 70 to 80% of the sum of basic cations. Samples taken from the alkali soils of the lowlands, representing 15% of the sampled soils, contain at least 15 % exchangeable sodium.

Although an acidification of arable lands was detected about 10-15 years ago, no clear indication of the same phenomenon has yet been observed in forest soils. The survey results show that soil acidity can not be considered as the main problem of forest soils in Hungary. However, at some sites with strongly acidic soil parent materials, the risk of acidification can not be neglected.

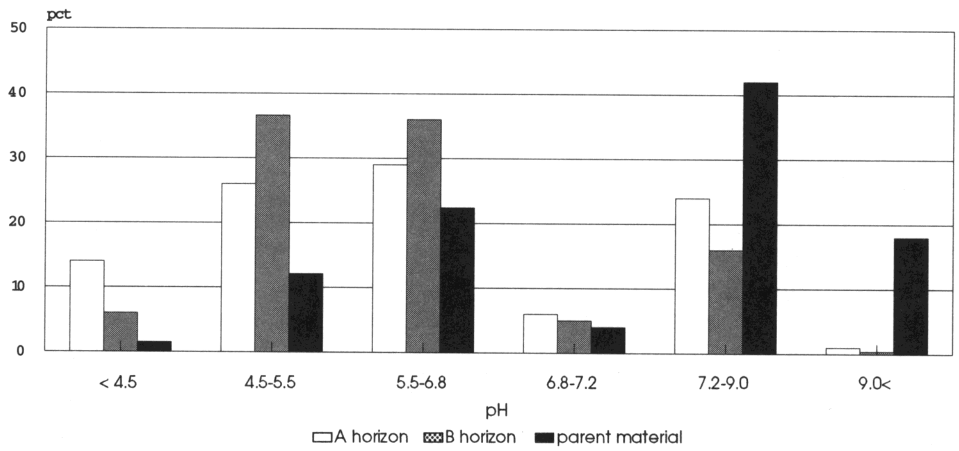

Figure II 2-10. Distribution of the pH (H_2O) values in the major morphogenetic soil horizons.

Observations made during previous forest surveys suggested that nutrient deficiencies may occur on 10 to 20 % of the Hungarian forest soils, more specifically in sandy areas, although the occurrence of deficiency is highly dependent on the specific nutrient demand of different tree species. Partly due to the unavailability of national reference values, nutrient contents measured in the 0-horizon turned out to be impracticable for the characterisation of the nutrient supply in forest soils.

Water availability has always been the main limiting factor to forest growth in Hungary. One fourth of the closed forests are situated in a low rainfall area, where a patchy broadleaf forest (‘forested steppe’) is the natural forest type. Nowadays, closed forest stands are grown there under management conditions.

Positive effects of ground water on forest condition are observed at 22 % of the surveyed soils, most of which are located in the dry lowland areas. Therefore, even moderate descending of the ground water level may endanger one fourth of the forest area.

Investigated Relationships

Relationships between soil condition and several external parameters have been previously investigated on the traditional soil databases. In a recent study, more emphasis was put on an in-depth study of possible relations between soil and tree vitality parameters.

Discoloration is most frequently observed in the low rainfall area, but rarely occurs on sites having ground water within the rooting zone. A similar, but weaker, relationship is found between defoliation and the presence of ground water. Defoliation of *Quercus robur* and *Quercus petreae* is higher in deeper soils, presumably because *oak* roots are unable to follow the descending ground water level. Stands of *Fugus sylvatica*, *Carpinus betulus* and ***Rohinia pseudoacuciu,*** growing on deeper soils, are less defoliated.

The integrated site quality class, which is based on the mean annual increment, is well correlated with discoloration (yellowing is more frequent on weaker sites). Defoliation seems to be independent of site quality class.

A significant correlation between tree vitality parameters and soil chemical parameters of the samples collected according to the ICP Forests methodology could not be found. The analysis of the samples taken by genetic horizons (on the same pan-European plots) showed a better correlation between chemical parameters and defoliation. An increase of defoliation is observed with (i) increasing soil acidity, and (ii) increasing calcium carbonate content in the surface and subsurface layer. No other significant correlation valid for all or major groups of tree species was found yet, but the analysis is continued using multiple regression statistics.

Soil Damage

Nearly 30 % of the actual forest area is a result of the large-scale afforestation of agricultural and waste lands during the last 50 years. The main objectives of the afforestation programme have traditionally been (i) protection of shallow soils (20% of the forest soils) against erosion, and (ii) improvement of high sodium soils (1%). Recently, the descending ground water table, a consequence of consecutive dry years and traditional water management practices such as ditching, is considered as the most important ongoing soil damage. The annual tree vitality assessments, as well as the soil survey, provided indications of a deteriorating forest health. The forest management should recognise water shortage as an increasingly important stress factor, for example by favouring drought tolerant tree species for the afforestation of low rainfall areas.

2.14 IRELAND

R. McCarthy, M. Delaney and J. Hogan

The total forested area of Ireland is approximately 4980 km^2. Of this, 3640 km^2 is semi-privately owned by Coillte, the Irish Forestry Board. The remainder of the forested land is in private ownership. The Coillte Estate is covered in the EU Level I plot network. There are 22 plots in this network, all of which are assessed annually in the Crown Condition Survey. All plots in the network were included in the Forest Soil Condition Inventory.

Sampling and Analysis

Fieldwork for the inventory was conducted from 19/04/95 to 09/06/95. This involved site and soil profile description. and collection of soil samples. Laboratory analysis of samples started on 14/06/95. Because of the close-spaced nature of Irish forests, most trees in the Level I plots are located along forest edges (McCarthy et al., 1995). Samples were collected from one soil pit that was dug as near as possible to the plot, but without disturbing any of the roots of the sample trees. This pit was dug on a site that was representative of the ground conditions in the plot. Soil pits were not dug where the ground was disturbed.

A pedological characterisation of the soil in each pit was made using the FAO-guidelines. Soil samples were collected by genetic horizon. For each horizon, one representative composite sample was collected over the depth of the horizon. Samples were taken to the depth of the parent material or to 80cm, whichever was shallower.

Large stones and rocks were removed from each of the samples which were then placed in separate polythene Ziploc® bags and transported to the laboratory. On arrival at the laboratory, samples were mulched and allowed to air-dry at 15-25°C. Samples were passed through a 2mm stainless steel sieve, but were not ground prior to analysis.

Table II 2-13 summarises the analysis methods used for the mandatory and optional soil chemical parameters in the Forest Soil Condition Survey. A detailed methodology of the National methods and any conversion factors used are outlined by McCarthy et al. (1996). Blanks, laboratory reference control samples, and internationally recognised reference controls [i.e., National Bureau of Standards (NBS), and Community Bureau of Standards (BCR)] were included in all batches of samples, as part of quality control measures in the laboratory.

Table II 2-13. Methods of Analysis

Parameters		Method	Remarks
pH ($CaCl_2$)	Mandatory	pH-electrode	Reference method
Org. C (mineral soils)	Mandatory	Walkley Black	National method
Org. C (organic soils)	Mandatory	Loss on Ignition (LOI)	National method
N	Mandatory	Wet Digestion (H_2O_2)	Reference method
P	Mandatory	Wet Digestion (H_2O_2)	National method
K	Mandatory	Wet Digestion (H_2O_2)	National method
Ca	Mandatory	Wet Digestion (H_2O_2)	National method
Mg	Mandatory	Wet Digestion (H_2O_2)	National method
OrgLay	Mandatory	Volume-dry weight	Reference method
$CaCO_3$	Mandatory	Total Neutralising Value	National method
Ac-Exc	Optional	Titration	Reference method
BCE	Optional	extr:$BaCl_2$	Reference method
ACE	Optional	extr:$BaCl_2$	Reference method

Two subsamples of each soil sample were analysed for the parameters outlined in the table. Analyses were repeated where duplicates deviated from the mean by more than 5% .

After scanning the dataset for any repetitions, means were calculated for each parameter in each horizon. Formulas were then derived for converting the data from genetic horizons to fixed depths.

Results and Discussion

A discussion of the general condition of the soils in the Level I plots, and of the condition of the soils in relation to crown condition and external parameters (i.e. climatic conditions, humus type, soil parent material, soil particle size distribution, vegetation type, altitude etc..) is not presented here, for two reasons. Firstly, historical data regarding the condition of forest soils is extremely limited in Ireland. As a result, there are very few, if any, reference values that the data presented in this report can be compared to. Secondly, the dataset is not yet complete. Data for cation exchange capacity, particle size distribution and soil units are still incomplete or missing for each of the 22 Level I soils. Upon completion, it will be possible to place the soils into one of the Soil Association Classes of Ireland (Gardiner and Radford, 1980), in addition to the mandatory FAO classification of the soils. Limited chemical and physical data are available for all 44 of these Soil Associations in Ireland, which can be compared with the dataset for the Level I Forest Soil Condition Survey upon its completion.

References

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2.15 ITALY

S. Allavena, F. Alianiello

General Information

Of the 220 forest observation plots, covering 37% of the forested area in Italy, 80 plots were selected for the soil condition inventory. Twenty plots, located across the country, have been surveyed in 1995. Data on the 60 remaining sites are processed in the beginning of 1997.

Sampling and Analysis

Soil sampling was carried out in accordance with the recommended methodology described in the ICP manual. Organic layers were sampled separately, the mineral soil was sampled for layers 0-10 and 10-20 cm. Analysis was performed on composite samples comprising of three subsamples. Reference methods were applied for all chemical analyses. All analyses were carried out in duplicate and repeated two times in case differences exceeded 5%. Mean values were submitted for the transnational database. In addition to all mandatory parameters, bulk density of the mineral layers was determined.

Processing of Data

National results were compared with available data regarding Mediterranean and Alpine forests. The main parameters considered in the data evaluation were altitude and dominant tree species.

Forest Soil Condition

Figure II 2-11 shows the results of total carbon, total nitrogen and C/N ratio in the 10-20 cm layer, compared with those of the organic layer at the 20 monitored plots in Italy.

Differences in analytical values can be usually ascribed to altitude, vegetation cover and soil type. For some important parameters a relationship was found with vegetation cover.

Fugus sylvatica sites show the highest mean values of organic carbon concentration, while differences between the other sites are not very high. Nitrogen also shows the highest values in *Fugus sylvatica* sites, while the lowest average value is found in *Quercus cerris* sites.

The C/N ratio decreases regularly with depth, ranging **from** 15.6 to 30.8 in the organic layer and from 8.0 to 30.2 in the lowest mineral layer (10-20 cm). The highest values are found in the *Picea ubies* sites. The C/N ratio at the remaining sites varies within rather narrow limits; the average value is approximately 20 for the organic layer and 12 for the 10-20 cm mineral layer.

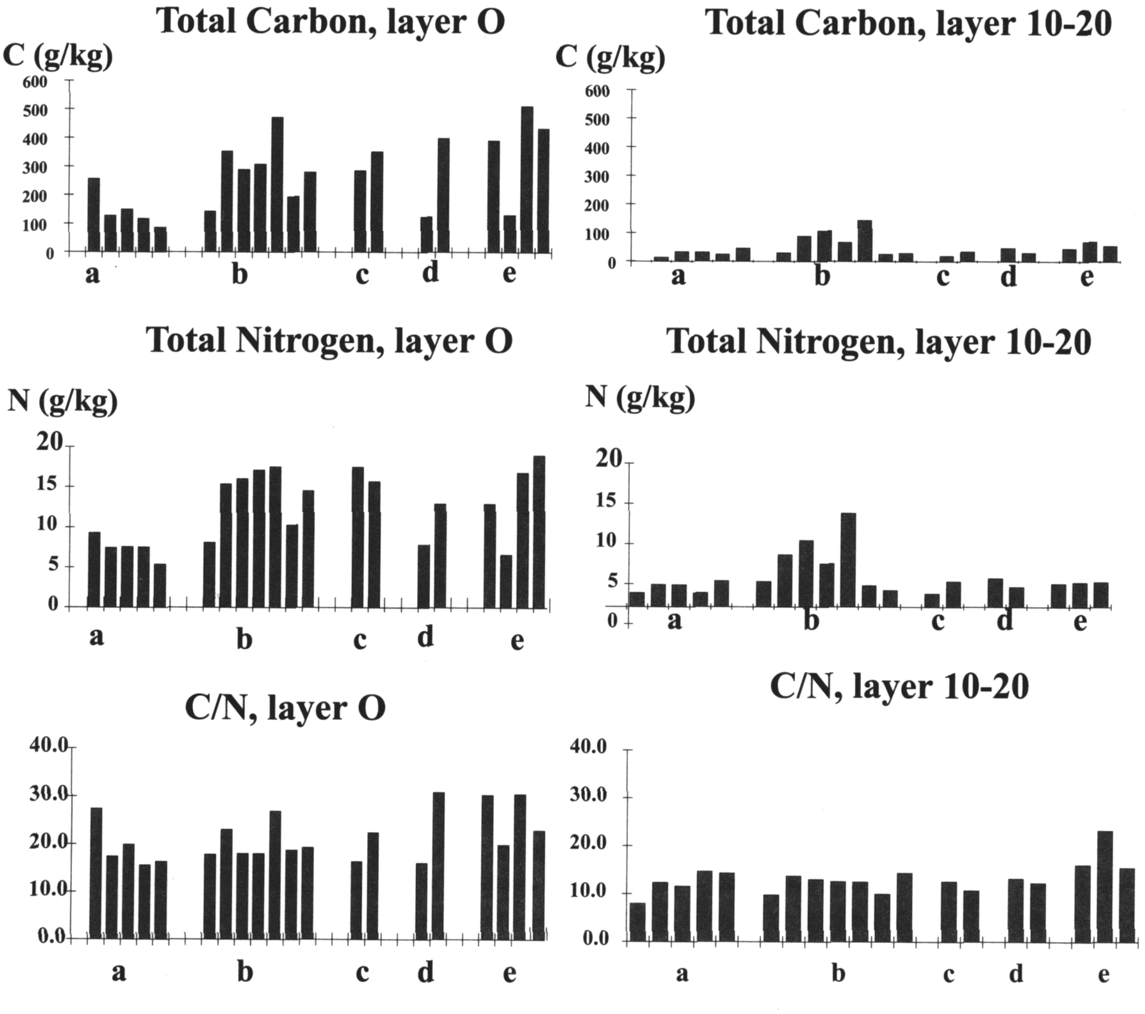

Figure II 2-11. Some results of the Italian forest soil inventory, grouped by vegetation type: a: *Quercus cerris;* **b:** *Fagus sylvatica;* ***c:*** *Quercus robur+Quercus petraea;* **d:** *Quercus ilex;* ***e:*** *Picea abies.*

pH values range from 3.0 to 7.2, the lowest values are found on picea *abies* sites.

Total phosphorus concentration of the O layer ranges from 420 to 1733 mg kg^{-1}; total potassium from 1349 to 8080 mg kg^{-1}; total calcium from 3249 to 27,950 mg kg^{-1}; total magnesium from 569 to 31,512 mg kg^{-1}.

$CaCO_3$ is present only in three soils, its value ranges from 0.4 to 22.9 g kg^{-1}.

Total phosphorus shows the highest values in the sites, while total potassium does not display the same regular pattern: the values seem very high everywhere. There is a confirmation of the fertile environment created by the species ***Fagus** sylvatica*, shown also by the values of nitrogen and carbon content. A more reliable interpretation of such parameters could be made, using values of available phosphorus and potassium.

The weight of the organic layer ranges from 1.2 to 81.6 kg m^{-2}. Very low values are due to the warm Mediterranean climate which result in a very fast mineralisation.

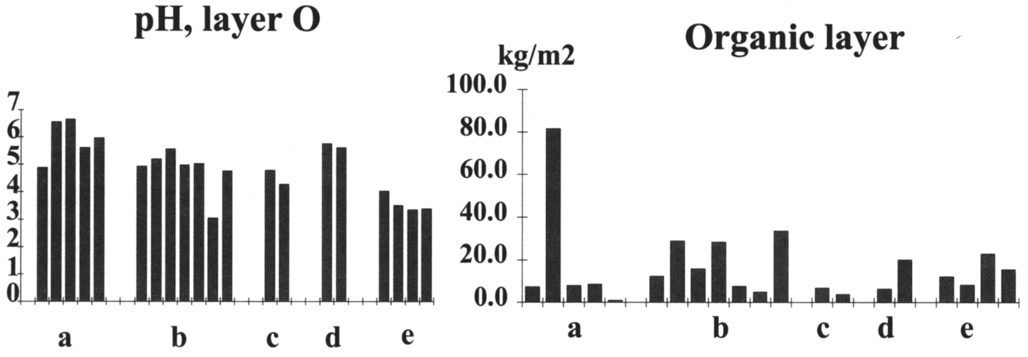

Figure II 2-12. pH and weight of the organic layer.

The collected data provides inadequate information on the chemical forest soil condition in Italy, partly because they cannot be compared with data, previously measured using national analysis methods. It is not possible to find clear indication of pathologies.

2.16 LATVIA

L. Ziedina, M. Laivinš

Sampling and Analysis

The forest condition inventory in Latvia comprises 398 observation plots in a 8x8 km grid. Soil samples from 306 plots, including 75 plots from the transnational 16x16 km grid, were collected in 1991. Each plot is represented by one composite sample that consists of 4 sub-samples taken from the organic surface layer at 2-5 cm depth in the 4 plot sectors.

Samples are analysed for total nitrogen (Kjeldahl method), phosphorus (colorimetry), potassium, calcium, sodium, iron, nickel, chromium, manganese, zinc, scandium, cobalt, arsenic, rubidium, zirconium, molybdenum, silver, antimony, caesium, barium, lanthanum, hafnium, tantalum, gold, thorium, cerium, samarium, europium, terbium, ytterbium and lutetium (neutron activation), and lead, cadmium and bismuth (adsorption spectrophotometry). All analysis methods differ from the reference methods.

Results

The chemical composition of the organic surface layer is related to forest type. The poorest soil nutrient conditions are found in forests having *Pinus sylvestris* as the dominant tree species. Soils of *Picea abies* stands are only slightly richer in nutrients, whereas *Betula* *pendula/pubescens* stands mostly occur on nutrient-rich soils. Also the variation of element concentrations is small in soils of Scots pine forests and greater in soils of Norway spruce and birch forests.

Soils of oligotrophic forest types *(Cladinoso-callunosa, Vacciniosa, Vaccinioso-sphagnosu, Callunosa* turf. mel.) are generally poor in nitrogen, potassium and calcium. The highest soil concentrations of macronutrients are found in eutrophic forest types *(Oxulidosa, Aegopodiosa, Dryopteridosa, Filipendulosa, Mercurialiosa* mel., *Oxulidosa* turf. mel.). Soils of mesotrophic forest types *(Myrtillosa, Hylocomiosa, Myrtilloso-sphagnosa, Caricoso-phragmitosa, Myrtillosa* mel., etc.) have intermediate macronutrient concentrations (Table II **2-14).**

Soil concentrations of most heavy metals (Cr, Ni and Zn) and arsenic (Table II 2-15) show a similar trend; they are low in oligotrophic, but high in eutrophic forest types. The highest soil concentrations of lead are, however, found in mesotrophic forests types. In general, concentrations of nutrients and trace elements increase with increasing soil chemical fertility level, which is reflected by the vegetation type.

Table II 2-14. Concentrations of nitrogen, potassium and calcium (in mg kg^{-1}) in the organic layer of soils of different forest types.

Element		Forest Fertility Type		
		oligotrophic	mesotrophic	eutrophic
N	mean	1.0	1.3	1.5
	(min-max)	(0.8-1.2)	(1.2-1.5)	(1.1-2.3)
K	mean	2300	3380	4450
	(min-max)	(1800-3800)	(2100-8700)	(2600-7100)
Ca	mean	5440	10,600	17,600
	(min-max)	(3000-8600)	(7000-18,200)	(10,000-28,000)

Table II 2-15. Concentrations of heavy metals (Cr, Ni, Zn and Pb) and arsenic (in mg kg^{-1}) in the organic layer of soils of different forest types.

Element		Forest Fertility Type		
		oligotrophic	mesotrophic	eutrophic
Cr	mean	3.6	4.0	7.2
	(min-max)	(3.1-4.3)	(3.2-5.2)	(3.7-12.6)
Ni	mean	3.3	7.1	12.2
	(min-max)	(2.5-3.8)	(4.5-11.0)	(5.0-19.3)
Zn	mean	66.1	87.9	94.5
	(min-max)	(48.1-84.8)	(59.3-154.9)	(44.0-131.4)
Pb	mean	3.5	6.2	3.7
	(min-max)	(1.6-5.1)	(2.5-11.9)	(2.1-5.4)
As	mean	0.6	0.7	0.86
	(min-max)	(0.4-0.83)	(0.47-1.2)	(0.45-2.2)

A higher soil concentration of trace elements in upland areas as compared to lowland areas can be attributed to a higher clay content in the substrate, although differences in atmospheric deposition of pollutants resulting from precipitation differences may also contribute to the observed spatial variability.

2.17 LIECHTENSTEIN

F. Näscher

The ‘Landesforstamt’ of Liechtenstein established in 1994-1995 a country-wide (160 km^2) soil monitoring net, including about 20 forest points. Liechtenstein did not participate in the transnational survey, but it is reasonable to assume that data of neighbouring regions in Switzerland and Austria represent well enough the forest soil condition of Liechtenstein.

2.18 LITHUANIA

M. Vaicys, K. Armolaitis, L. Kubertaviciene and A. Raguotis

The Lithuanian forest soil condition is surveyed at 235 permanent observation plots (POPs) of a regional 8x8 km network, representing 18,000km^2 of forest lands. The soil data on a subset of 74 plots, corresponding to the 16x16 km grid, were submitted for the transnational database.

Sampling and Analysis

Soil samples were collected at the POPs in the period 1992-1993. Sample locations were selected at regular distance intervals (every 2 m) from the plot centre in four directions. Composite samples of the organic layer and the mineral layers at 0-5, 5-10 and 10-20 cm soil depth each consisted of 20 sub-samples. At ten locations, a 0.1 m^2 frame was used to determine forest litter thickness and weight.

In the laboratory, samples were dried at room conditions, ground and passed through a 2 mm sieve. Reference analysis methods were used to determine soil acidity, organic carbon and cation exchange properties. For the determination of total nutrient and heavy metal contents, national methods were applied; wet oxidation and steam distillation (Kjeldahl) for nitrogen dry ashing followed by dissolution in HCl for total cationic nutrients, and extraction with 1M HNO_3 for heavy metal analysis.

Discussion

Scots pine (44%), Norway spruce (29%) and birch (16%) are the dominant tree species in Lithuanian forest stands. Common soil types are Ferric Podzols (31%), Gleyic Luvisols (18%), Gleyic Podzols (17%), Haplic Podzols (11%) and Gleyic Podzoluvisols (8%).

Acidity

The majority of pH ($CaCl_2$) values of litter and upper mineral soil layers ranges between 3.0 and 6.0; the highest number of observations are made in the 4.1-5.0 interval (Table II 2-16). The acidity of mineral layers usually decreases with soil depth, consequently, the 0-5 cm layer is the most acid mineral layer. No relationship was found between pH values of the mineral soil and average defoliation values of Scots pine stands (Table II 2-17).

Table II 2-16. Frequency distribution (%) of pH ($CaCl_2$) values of litter and mineral soil layers in Lithuanian 16x16 km plots.

Layer	pH ($CaCl_2$)				
	3.0-4.0	4.1-5.0	5.1-6.0	6.1-7.0	7.1-8.0
litter	32	38	26	4	0
0-5 cm	38	36	20	3	3
5-10 cm	27	45	21	7	0
10-20 cm	11	57	22	10	0

Table II 2-17. Average tree defoliation (in 1993) observed at POPs (8x8 km) with Scots pine stands, clustered by mean pH ($CaCl_2$) value of the upper 0-20 cm mineral soil.

pH ($CaCl_2$)	POP number (n)	Average defoliation (%)
3.0-3.5	8	25.4±1.9
3.6-4.0	20	27.1±1.1
4.1-4.5	48	25.2±1.3
4.6-6.0	16	25.1±2.0

Nutrient status

The chemical data confirm that organic matter incorporation in the mineral soil is influenced by the type of organic layer. In the sequence Mor-Moder-Mull, the amounts of organic C and total N in the upper mineral soil layer increase, and the C/N ratio decreases (Table II 2-18). As compared to soils with normal wetness conditions, Gleyic soil types contain slightly higher amounts of organic C and have a higher C/N ratio, whereas the amounts of total N are usually lower.

Table II 2-18. Influence of humus type and wetness condition on the average amounts of organic C and total N and their ratio in the 0-20 cm mineral layer (16x16 km plots).

Soils	Mor			Moder			Mull		
	C (g kg^{-1})	N (g kg^{-1})	C/N	C (g kg^{-1})	N (g kg^{-1})	C/N	C (g kg^{-1})	N (g kg^{-1})	C/N
Normal	10	0.7	19	22	2.7	16	36	3.3	14
Gleyic	13	0.6	25	27	2.0	17	41	2.7	15

Presence of potentially toxic elements

Increased amounts of sulphur and heavy metals in forest soils are found in Lithuania's industrial regions. However, when compared to quantities found in uncontaminated and contaminated soils, the 16x16 km plots seem relatively free of heavy metal pollution (Table II 2-19).

Table II 2-19. Amounts of heavy metals (mg kg^{-1}) in the 0-20 cm soil layer (16x16 km).

Metal	Mineral soils		Organic (peat) soils	
	average	range	average	range
Fe	4574	455 - 16855	14155	1525 - 81656
Cr	9.4	2.0 - 41.2	11.6	7.5 - 28.1
Ni	5.8	0.7 - 21.2	8.9	5.0 - 15.6
Mn	146	5 - 545	184	29 - 602
Zn	24	4 - 51	48	21 - 106
Cu	3.7	0.2 - 13.6	12.2	3.8 - 31.2
Pb	13.4	6.0 - 27.2	38.7	27.6 - 51.4
Cd	0.6	0.2 - 1.8	2.2	1.7 - 3.0

Conclusions

A more detailed assessment of chemical changes in forest soils will be possible after a repetition of level I soil sampling and analysis in combination with a more intensive monitoring of forest soils (Level II). Soil changes induced by atmospheric pollution have been revealed by temporal investigations, showing that acidification of sandy podzolic soils (Podzols) in Scots pine stands has decreased pH values with an amount of up to pH 0.7-0.9 during the last three decades, while those of forest brown soils (Cambisols) in *oak* stands with about pH 0.5-0.6 (Vaicys et al., 1995). Unfortunately, soils with a low acid buffering capacity (assessed by the exchangeable cation ratio (Ca^{2+} + Mg^{2+})/Al^{3+} are quite abundant in Lithuania. In certain areas in Lithuania the intensive acidification of forest soils may be associated with atmospheric acids emitted by nearby mineral fertiliser production plants (Armolaitis et al., 1992).

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2.79 LUXEMBOURG

J.-P. Arend, M. Wagner

With only **4** identified sites on the European 16x16 km network on Luxembourg territory, it is not possible to make some valuable general comments. Therefore we include results from 13 other sites of a 8x8 km network which have been surveyed along with the 4 level I plots. On the other hand, it seems important to point out that the statistical error is not well known for the presented analytical data.

Sampling and Analysis

Soil samples were taken near the centres of each of the four satellites within the plot area. Approximately 30 subsamples from bores formed a representative composite sample for every layer: one organic and three mineral layers taken at 0-5, 5-10 and 10-20 cm depth intervals. At arrival in the laboratory, samples were oven-dried (mineral samples at 105°C; organic samples at 60°C), mechanically ground and sieved on a 2 mm sieve.

In addition to the mandatory parameters, total Mn contents of humus samples and cation exchange properties of mineral soil samples were determined. All parameters were analysed using reference methods.

Data Analysis and Evaluation

The soil data were compared with health risk levels for beech and spruce used in the neighbouring Belgian Ardennes. Threshold values were based on exchangeable cations (NH_4Cl, 1%) of the 0-20 cm layer. Conclusions must be taken cautiously because of different extractants used.

Soil Properties

In less than 20 % of the sites, soil depth exceeds 1m20. For most other sites (80 %) depth is less than '80 cm, sometimes not even 40 cm. On Devonian deposits, the soil is under strong influence of the substrate. Soils on Jurassic or Triassic materials are often richer (eolian deposits) than the underlying substrate.

Soil pH ($CaCl_2$) is lower than or equal to 4.2 at sites with undisturbed eolian loam deposits on $li_{4/3}$ and km_3, in sandy soils of li_2 and stony loam soils on E_1 and Sg_3. Exchange acidity is highest (3 $cmol_{(+)}\ kg^{-1}$) for the latter, low for $li_{2/1}$-sands and very low for km_3-soils.

E_1-, Sg_3- and li_2-soils are very poor in K. In addition, li_2-and Sg_3-soils are also poor in Ca and Mg. On the other hand, li_2-soils are poor and E-soils are rich in Mn.

Base saturation is low (BS ± 20 %) for Sg_3-soils, medium (BS = 30 to 50 %) for eolian deposits on li_4 and li_3; sandy soils of li_2 and li_1 and stony loam soils of E_1. For E_2- and km_3-soils base saturation is high ($BS > 80$ %).

It is difficult to make any accurate comment about chemical properties of the organic 0-layer in relation with biological soil activity, since equilibrium conditions are rarely observed (different age classes, species and stand history).

Relations with the State of Health of Forest Stands

Several soil characteristics indicate the difficulty of making an overall estimate of tree nutrition for deep rooting species. However, the standards for the Belgian Ardennes soils seem to be useful for rather shallow rooting species as well as for young natural seedlings or plantations (e.g. beech and spruce).

Table II 2-20. Evaluation of nutrition risks for beech and spruce based on exchangeable cations of the 0-20 cm layer (threshold level for Mn is provisional; x = risk exists; (x) = near risk level).

	Jurassic							**Triassic**				**Lower Devonian**					
Geol. Formation	li_4	li_3	li_2				li_1	km_3		km_1	so_1 E_1a	E_1b	E_1a			Sg_3	
Lithology[1]	m+l	m+l	s				m+l	l		m	s+y	s+p	y			y	
Site number	34	8^2	10^2	35	37	161	67	7^2	101	69	135	195	2^2	163	168	133	166
Deficiency (<)																	
K < 0.10 cmol(+) kg^{-1}	(x)			x	x		x				(x)	(x)	x	(x)	(x)	x	x
Ca < 0.50 cmol(+) kg^{-1}					(x)								x				x
Mg < 0.17 cmol(+) kg^{-1}				x	x		x				(x)					(x)	(x)
Mn < 0.02 cmol(+) kg^{-1}							(x)										
BS < 25 %											x		(x)	(x)		x	x
Excess (>)																	
Mn > 0.30 cmol(+) kg^{-1}	x	(x)				x		x	(x)	(x)	x	x	x	x	x	x	x

[1] m : marl; l : limestone; s : sandstone; y : schist; p : quartzo-phyllite [2] sites of the 16x16km network

K deficiency is diagnosed for 65 % of the sites, half of them being also Mg deficient (li_2- and Devonian soils). Mg deficiency is always accompanied by shortage of one or more other cationic nutrients. Ca and Mn deficiencies are rather rare. Except for li-soils, a risk of Mn excess (toxicity) must be taken into account.

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2.20 NETHERLANDS

G. van Tol, W. de Vries, J. Klap

The forest soil condition in the Netherlands is represented by 11 observation points in the European 16x16 km network. The sampled plots are representative for the sandy soils in the northern, eastern, central and southern parts of the country; the majority of the forests in the Netherlands (80 %) are found on these sandy soils.

Sampling and Analysis

Soil samples were collected from bores at 20 different sampling sites within the plot area. The samples of one organic and two mineral soil layers (0-10 and 10-20 cm depth) taken from each sampling site were mixed to form composite samples, representative for the observation plot.

Preparation of the samples for analysis involved drying at 40-50°C, mechanical grinding and sieving.

All mandatory and most optional parameters were determined for both organic and mineral soil samples. Reference methods were applied for pH and Org. C. The Kjeldahl method was used for the determination of total nitrogen. Contents of P, K, Ca, Mg, Na, Al, Fe, Cr, Ni, Mn, Zn and Cu were obtained by wet digestion in a mixture of concentrated sulphuric and nitric acid. Exchangeable cations were extracted with an unbuffered 0.01M solution of silver thiourea.

Forest Soil Condition

The total number of plots is very small, so no special statistical analysis has been applied. The results of the survey are compared with the results of an earlier soil survey on 150 plots in 1990.

Description

The average data for the 11 plots in the Netherlands are given in Table II 2-21 and II 2-22.

Acidification

The values for pH ($CaCl_2$) in the mineral soil range between 3.1 and 3.8 in the 0-10 cm layer and between 3.5 and 4.1 in the 10-20 cm layer. The mean values per tree species are within the same range. At national level a pH (KCl) value between 3.0 and 3.5 for the 0-30 cm mineral layer is considered critical. The observed pH values are around or just above this critical pH value.

Table II 2-21. Mean values of the soil parameters for acidification (pH, AcExc, BCE, CEC and base saturation), nutrients (P, K, Ca , Mg) and Org. C. in humus and mineral soil layers from 11 plots in the Netherlands.

Parameter	unit	humus layer	0 - 10 cm	10 - 20 cm
pH		3.0	3.4	3.7
AcExc	cmol(+) kg^{-1}	13	2.2	1.4
BCE	cmol(+) kg^{-1}	12	0.29	0.24
CEC	cmol(+) kg^{-1}	25	2.6	1.7
Base Saturation	%	48	10	14
OrgLay	kg m^{-2}	15	-	-
Org. C	g kg^{-1}	348	18	14
N	g kg^{-1}	15	0.83	0.58
P	mg kg^{-1}	557	107	105
K	mg kg^{-1}	641	634	640
Ca	mg kg^{-1}	1927	266	242
Mg	mg kg^{-1}	448	236	255

Table II 2-22. Mean values for the optional soil parameters Na, Al, Fe and heavy metals in humus and mineral soil layers from 11 plots in the Netherlands.

Parameter	unit	humus layer	0 - 10 cm	10 - 20 cm
Na	mg kg^{-1}	31	21	22
Al	mg kg^{-1}	2361	3378	3840
Fe	mg kg^{-1}	2633	2098	1934
Cr	mg kg^{-1}	13	14	15
Ni	mg kg^{-1}	6.8	2.1	2.3
Mn	mg kg^{-1}	114	29	26
Zn	mg kg^{-1}	79	8.1	6.1
Cu	mg kg^{-1}	18	2.7*	1.5*

* value for 10 plots only; values of one plot (no. 125) are extremely high (92.0 and 9.0) and are not included in the mean .

Base saturation is approximately 50 % in the organic layer and 10-15 % in the mineral soil; these values are higher than the values found in a national survey in 1990 (De Vries and Leeters, 1995).

Nutrients

The N content in the 0-10 cm mineral layer varies from 0.3 to 2.4. These results fit reasonably well within the results of a survey of 150 forest stands in 1990 (Leeters et al., 1994), where mean values per tee species range from 1.8 to 2.4 (as % of Org. C.) in the mineral topsoil (0-30 cm).

Generally, the forest soils in the Netherlands have low P values. P content in the 0-10 cm layer ranges from 39 to 170 mg kg^{-1}, with one exceptionally high value of 410 mg kg^{-1}. This high P content is typical for a plantation on former arable land. The values for P content would correspond to levels of 9 to 39 mg P_2O_5/100 g soil, which is well below the critical level of 40 mg P_2O_5/100 g soil for spruce, *oak* and beech (Van den Burg and Schaap, 1995).

Toxic Elements

Values for heavy metals in the humus layer are similar to values found in the national survey in 1990 (De Vries and Leeters, 1995). Especially for Cu and Zn it is known that values in the humus layer are higher than in the mineral soil. Still, these values do not exceed any critical values (e.g. related to micro organisms and decomposition).

Investigated Relationships

Soil Condition Parameters

Average C/N ratios vary from 21 to 23 , both in the humus layer and in the mineral soil. This ratio indicates the rate of mineralisation. Immobilisation of N generally dominates above C/N ratios of 30, whereas mineralisation is usually slow below a C/N ratio of 20. The relatively low C/N ratio (especially in the humus layer) indicates that immobilisation of nitrogen from atmospheric N inputs has occurred for decades. However, retention of N may still occur in these systems. This is in accordance with results of the 1990 survey.

With respect to C/P ratios, information from the literature suggests that P mineralisation is small to negligible above a C/P ratio of 200. In the humus layer this ratio is exceeded manifold (± 700), thus suggesting a very low P release. This may explain the P deficiency.

External Parameters

The N content in the 0-10 cm mineral layer is 0.8 g kg^{-1} on average, but may range from 0.3 to 2.4 g kg^{-1}. The lowest levels are found on poorly developed Arenosols. The highest values (2.4 and 1.4 g kg^{-1}) are found on Umbric Gleysols.

The mean Org. C value in the 0-10 cm layer is 18.1 g kg^{-1}; with again low values in the Arenosols and high values in the Umbric Gleysols. N and Org. C contents decrease with depth in most plots; mean N content in the 10-20 cm layer is 0.6 g kg^{-1}, mean Org. C content is 13.9 g kg^{-1}.

Soil Condition and Forest Damage

All plots are situated on poor sandy soils that are susceptible to acidification and to eutrofication.

Although in several research projects serious imbalances between N and other important nutrients have been established, no direct relations between soil condition and forest condition have been convincingly established so far.

Measures to Restore Damaged Forest Soils

Restoration of a well balanced nutrient status can (temporarily) be achieved by fertilising or liming. Several field experiments have shown a better, more balanced nutrient status after fertilising with the deficient nutrients. Visible improvement of the crown condition, however, was only observed in a few plots and even then not every year. Especially liming, but to a lesser extent also fertilising with phosphate, can affect vegetation and mycoflora (Van Tol 1995).

A special forest protection programme gives financial support for liming and fertilising of forest stands; grants are based on the results of soil and foliar analyses.

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2.21 NORWAY

C. Nellemann

Introduction

Norwegian forests generally receive a much lower atmospheric deposition load than central Europe (Barrett and Berge, 1996). However, in spite of this, extensive die-back of fish and acidification of surface waters have occurred across large areas in southern Norway (Henriksen et al., 1990; Hesthagen et al., 1992). Norwegian forest soils are often shallow and nutrient-poor, and have low weathering rates. The soils are therefore considered vulnerable to a high input of acidifying compounds, which is well reflected in critical load calculations (Posch et al., 1995). Increased concern has also been raised for the potential eutrophication effects of nitrogen (Nihlgård, 1985; Wright et al., 1995).

Methods

Soil samples have been collected from 933 forest plots (each 250 m^2) on a 9x9 km grid in Norway in the period 1988-1991. The forest is mainly coniferous, and is dominated by Norway spruce *(Picea abies)*(378 1 trees), Scots pine *(Pinus sylvestris)*(2927 trees) and birch *(Betula* pendula and *B. pubescens)*(1721 trees).

Outcrops of bedrock and many boulders and rocks often complicate soil sampling procedures. To select a suitable sampling location at a distance of 5 m from the plot centre, compass directions were tried in the following order: N, E, S, W, NW, NE, SE, SW, NW, until a location without hindrances was found.

On each circular sampling location (radius 8.92 m), a soil profile was described to a depth of at least 50 cm (if possible). Samples were taken from the profile pit and composited by morphogenetic horizon with five auger samples, taken within a 2 m radius from the profile pit in order to obtain sufficient sample material for chemical and particle-size analysis. All soils were classified according to the Canadian system.

Samples were dried at 38°C, ground and passed through a 2 mm sieve. Samples were then analysed for pH (both in water and 0.1M $CaCl_2$), total carbon and total N, easily soluble P (by ammonium-lactate extraction), and cation exchange properties (extraction in 1M NH_4NO_3). In addition to determination of exchangeable base cations, the extract was analysed for Al, Fe, Mn, Zn, P and **S.**

The soil chemistry of 56 plots in southeastern Norway, receiving a relatively high deposition load (7-12 kg N ha^{-1} yr^{-1}), is compared with results of 280 plots from the rest of Norway (background area), having a deposition load of less than 7 kg N ha^{-1} yr^{-1}. All data were first tested for normal distribution and variance (Kolmogorov-Smirnov test); and the respective parametric (t-test) or non-parametric tests (Mann-Whitney) were then selected to study population differences. A p-value of less than 0.05 was considered significant. More details on applied methods are given in the research papers referred to in the text. In a general approach, the soil chemistry of different forest strata was investigated based on site indices, tree age, and growing season. Several papers (Thomsen and Nellemann, 1994; Thomsen et al., 1995) discuss the spatial variability of deposition loads, soil chemistry and forest vitality and their interrelations.

Results

The distribution of soil types in spruce plots is 60% Podzols, 20% Brunisols, 12% Gleysols and 6% Regosols (Esser and Nyborg, 1992). For all plots, the distribution is 47% Podzols, 17% Brunisols, 10% Regosols, 8% Gleysols, 16% Organic soils (peat etc.), and 2% other soil types.

Actual sulphur and nitrogen depositions exceed the critical load in 19% of the Norwegian forest soils, according to the MAGIC-model. Upon achievement of the projected emission reduction in 2010, agreed in the 2nd Sulfur protocol, critical loads, particularly of nitrogen, will still be exceeded in 16% of the forest soils. There are relatively strong indications, that the input of sulphur and nitrogen has negatively affected forest soils in southern Norway (Steinnes et al., 1993). The amount of exchangeable base cations, particularly Mg and Ca, are substantially lower in southeastern Norway compared to the rest of Norway, as well as the level of phosphorus (Esser and Nyborg, 1992; Nellemann, 1996) (In the high-deposition areas (SE), critical sulphur loads are exceeded in approximately 32% of the forest soils (MAGIC), compared to 7% in the background areas (SC). Investigations of mycorrhiza have revealed a lower number of mycorrhiza species and smaller amounts of mycorrhiza in the SE compared to background areas (Larsson, 1992). The degree of crown discoloration is 1.5 to 2 times greater on soils with a humus layer pH of 3.75 or less, than in other forests (Nellemann and Esser, 1997).

Table II 2-23). At the same time, humus nitrogen contents tend to be higher in the south-east (Esser and Nyborg, 1992). Nitrogen to magnesium ratios (N/Mg) increase with increasing deposition load, as expressed by exceedances of critical loads in the MAGIC-model (Nellemann and Esser, 1997).

In the high-deposition areas (SE), critical sulphur loads are exceeded in approximately 32% of the forest soils (MAGIC), compared to 7% in the background areas (SC). Investigations of mycorrhiza have revealed a lower number of mycorrhiza species and smaller amounts of mycorrhiza in the SE compared to background areas (Larsson, 1992). The degree of crown

discoloration is 1.5 to 2 times greater on soils with a humus layer pH of 3.75 or less, than in other forests (Nellemann and Esser, 1997).

Table II 2-23. Soil analysis results (mean ± s.e.) of the organic layer of spruce forests in southeastern Norway (high deposition area) compared to results of background areas in south-central and central Norway (SC).

Soil parameter	High deposition area (SE)	Background area (SC)	Mann Whitney test
n	56	280	
pH	4.1 ± 0.1	4.3 ± 0.1	(n.s.)
C (g kg^{-1})	388 ± 14	376 ± 0.7	(n.s.)
Total N (g kg^{-1})	14 ± 1	13 ± 0.2	(n.s.)
Mg ($cmol_{(+)}$ kg^{-1})	2.3 ± 0.2	3.8 ± 0.2	($p < 0.05$)
Ca ($cmol_{(+)}$ kg^{-1})	8.9 ± 0.8	14.1 ± 0.8	($p < 0.05$)
easily soluble P (mg kg^{-1})	10.4 ± 0.8	13.4 ± 0.5	($p < 0.05$)
K	1.4 ± 0.1	1.8 ± 0.1	($p < 0.05$)

Discussion

The dominance of young and shallow soils with relatively low nutrient contents is largely explained by slow weathering due to the cold climate. Natural soil variability is likely to cause bias in the evaluation of the impact of air pollution. However, there are relatively strong indications, such as reduced base saturation values, that the atmospheric input of acidifying compounds accelerates natural soil acidification processes (Dahl, 1988; Løbersli et al., 1990; Mulder et al., 1990; Løbersli, 1991; Frogner, 1991; Steinnes et al., 1993; Nellemann and Esser, 1996). The observed trends of lower base cation contents, associated with an increase in deposition load, cannot be attributed to distribution of soil types or differences in geology alone (Esser and Nyborg, 1992; Steinnes et al., 1993; Nellemann and Frogner, 1994). The patterns correspond to some degree with observations made in other countries, including countries of the Nordic region (Tamm and Hallbacken, 1988; Billett et al., 1990; Eriksson et al., 1992; Gustafsson and Jacks, 1993).

Advanced tree age, low site productivity, and marginal growth conditions at high altitudes and high latitudes appear to account for the high degree of defoliation in many parts of Norway (Thomsen and Nellemann, 1994). However, increased defoliation and reduced increment are observed in areas where critical deposition loads are exceeded, compared to similar forests in background areas (Nellemann and Frogner, 1994; Thomsen et al., 1995). There are thus several indications of air pollution effects, not only on soils and water, but also on forest vitality (Økland and Eilertsen, 1996), although the degree and extent of the induced damage is uncertain. Defoliation in Norway spruce has increased steadily in the past 8 years, and the percentage of spruce trees with discoloured crowns has doubled since 1991. Today, every 4th spruce tree in Norway has more than 10% of the crown classified as discoloured (Støen et al., 1997).

Most Norwegian forests are considered to be deficient or low in available nitrogen. The combined actions of nitrate leaching and increased nitrogen uptake in plants due to input of atmospheric nitrogen is likely to result in increased growth, and hence, accelerated soil acidification. This, in turn, will lead to increased leaching of essential base cations, particularly Mg and Ca. Increased soil acidification is also likely to cause increased toxicity of Al^{3+} to fine roots, and thus affects both nutrient and water uptake (Driscoll et al., 1985; Van Breemen et al., 1983; Mulder et al., 1989; Abrahamsen et al., 1994; Schulze, 1989; Cronan and Grigal, 1995). Hence, increased forest damage resulting from nutrient imbalances and abiotic stress is a possible indirect long-term effect initiated by long-range transported air pollution in Norway. Already, a relatively clear gradient of decreasing contents of exchangeable cations, particularly

Ca and Mg, with increasing deposition load can be seen (Nellemann and Esser, 1996). While part of the observed acidification may be natural, the current deposition scenario is most likely to intensify these patterns in the long-term.

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2.22 POLAND

J. Wojcik

The total forested area of Poland is approximately 86,000 km^2. Soil observations were made during the summer of 1995 at the 122 level II permanent plots. These plots are located in 57 forest regions in Poland (2 or 3 points per region).

Sampling and Analysis

Along the diagonals of the square-shaped plot areas 9 soil pits were made. At each pit, the organic layer and three mineral soil layers (0-5, 5-10 and 10-20 cm) were sampled and lumped to form one composite sample for each layer. Samples were dried at 40°C. Organic layer samples were mechanically ground; mineral samples were crushed by mortar and pestle and sieved to separate the fine earth fraction.

Soil acidity, organic carbon, total nitrogen, carbonates and cation exchange properties and aqua regia extracted amounts of P, K, Ca, Mg, Na, Al, Fe, Mn, Zn, Cu and Pb are analysed for organic and mineral samples, using reference methods.

Data Submission

Completion of soil analysis activities is foreseen at the end of March 1997 after which the data will be digitised and submitted.

2.23 PORTUGAL

J.C. Soveral Dias

The large-scale forest soil condition inventory in Portugal consists of 149 observation points, excluding the Azores.

Sampling and Analysis

Representative soil samples were obtained by bulking subsamples from 16 bores. Organic layers were sampled separately; mineral soil layers were sampled at 0-5, 5-10 and 10-20 cm depth intervals. Sample preparation in the laboratory consisted of drying at a temperature between 30 and 40°C, crushing soil clods on a wood block and sieving on a 2 mm sieve.

All mandatory and optional parameters were measured. Reference methods were applied, except for organic carbon and total nitrogen, which were both determined by wet oxidation. Aqua regia extracted heavy metal contents are available for organic and mineral layers.

Processing of Data

Soil condition data were evaluated by descriptive statistics and by correlation analysis. The soil condition variables were also correlated with the mean defoliation values of the last five years, for each one of the four main tree species *(Quercus ilex* spp. *rotundifolia*, *Quercus suber, Eucalyptus globulus* and *Pinus pinaster),* representing 90% of the Portuguese forest area. Heavy metal concentrations in the soil were also correlated with the soil parent material.

Forest Soil Condition

Acid conditions occur in the majority of organic and mineral layers of the forest soils (Table II 2-24).

Table II 2-24. Soil pH values by soil layer and cumulative distribution.

Layer	Min.	25%	50%	75%	Max.	n
org.	3.0	3.9	4.5	5.0	6.8	148
0 - 5 cm	3.1	3.9	4.5	4.9	7.4	148
5 - 10 cm	3.3	4.1	4.4	4.8	7.5	147
10 - 20 cm	3.7	4.2	4.5	4.7	7.6	144

Stands with Q. *ilex* and *Q. suber* have a significantly ($p < 0.05$) higher pH and a significantly ($p < 0.05$) lower Org. C concentration in the organic layer than P. *pinaster* stands (Table II 2-25). This may be explained by the natural spatial distribution of these species in Portugal: *P. pinaster* grows in the north and centre (with relatively lower temperatures and higher annual precipitation) and Q. *ilex* and *Q. suber* in the south (where climatic conditions and improper soil management in the past favoured soil erosion). *E. globulus* stands have a relatively high Org. C concentration in the organic layer. This seems to result from the quick growth and high biomass production in this species (Madeira, 1995).

Table II 2-25. Mean soil organic carbon and nitrogen concentrations and C/N ratio by vegetation type.

		Vegetation type				
Variable	Layer	*Q. ilex*	*Q. suber*	*E. globulus*	*P. pinaster*	Mean total
Org. C, g kg^{-1}	org.	180	169	236	216	201
	0 - 5 cm	25	27	35	53	39
	5 - 10 cm	17	20	20	39	27
	10 - 20 cm	12	15	18	37	23
N, g kg^{-1}	org.	9.7	6.9	9.2	7.7	8.1
	0 - 5 cm	1.8	1.6	1.8	2.4	2.0
	5 - 10 cm	1.3	1.2	1.3	1.9	1.5
	10 - 20 cm	0.9	1.0	1.3	1.9	1.4
C/N	org.	19.8	29.6	31.9	30.0	28.2
	0 - 5 cm	14.2	17.0	19.9	24.0	19.8
	5 - 10 cm	12.8	16.6	16.2	21.0	17.6
	10 - 20 cm	13.6	15.1	14.5	19.9	16.5

The C/N ratio in the mineral layers also varies with the vegetation type. This results from the higher C/N ratio of the organic residues of *P. pinaster* and ***E.** globulus,* compared with Q. *suber* and *Q. ilex* (Madeira, 1995).

There was no significant ($p > 0.05$) variation in the heavy metal concentration of the mineral soil layers. With the exception of some plots showing Cd, Cr, Mn and/or Ni contamination (believed to be located near some point pollution sources of industrial or mining origin), heavy metal concentrations can be considered normal in non-contaminated soils (Cottenie and Verloo, 1984; there are no reference values for Portuguese forest soils) (Table II 2-26). Comparing the soil heavy metal concentrations with the typical concentrations in the different rocks, as presented by Alloway and Ayres (1993), they reflect quite well the soil's parent material: in fact, soils derived from sandstone or granite have a heavy metal concentration significantly ($p < 0.05$) lower than soils derived from schists.

Table II 2-26. Concentration of heavy metals (mg kg^{-1}) in the organic and mineral (0-5 cm) layers by cumulative distribution (148 plots).

Element	Layer	Min.	25%	50%	75%	99%	Max.
Cd	org.	0	0.5	1.0	1.5	2.5	2.6
	0 - 5 cm	0	0	0.6	1.0	3.5	4.6
Cr	org.	0	6	29	32	362	400
	0 - 5 cm	1	16	40	48	199	391
Cu	org.	2	6	14	20	50	68
	0 - 5 cm	0	4	18	26	68	84
Mn	org.	12	154	802	962	5138	9005
	0 - 5 cm	7	88	493	572	4069	4171
Ni	org.	0	8	18	22	71	233
	0 - 5 cm	0	12	30	38	170	360
Pb	org.	3	15	23	29	65	82
	0 - 5 cm	0	14	25	34	67	68
Zn	org.	4	28	47	62	105	113
	0 - 5 cm	1	10	38	60	107	131

Forest damage, measured by the degree of defoliation is not related to soil acidity. In fact, none of the examined soil acidity parameters (pH, CEC and BS) of the organic and the mineral (0-5 cm) layers were significantly ($p > 0.05$) correlated with the mean defoliation values of the last five years. In the same way, there were no significant ($p > 0.05$) correlations between the degree of defoliation in the different types of vegetation and the Org. C, N, P, K, Ca and Mg concentrations, and the C/N and C/P ratios, with the exception of C/N and C/P ratios of the organic layer in *E. globulus* stands. The observed defoliation may be related to abiotic (drought and forest fires) and biotic factors (fungi and insect attacks).

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2.24 ROMANIA

N. Geambasu, L. Latis, A. Surdu, C. Preda

General Information and Methodology

Soil conditions of Romanian forests, which cover about 63,000 km2 or 26% of the country, were surveyed at 242 plots corresponding to the transnational 16x16 km network The studied plots are situated in coniferous forests (spruce, fir, pine, larch - 24.1%) and in broad-leaved forests (beech, sessile oak, pedunculate oak, cerris oak, frainetto *oak*, lime, ash, elm, carpinus, poplar, willow, acacia - 75.9%).

Sampling and Analysis

Fieldwork started in 1993 and was completed in 1995. Samples were collected from the organic layer and the mineral soil at three fixed depth intervals (0-5, 5-10 and 10-20 cm). Composite samples of individual layers, each consisting of 3 sub-samples, were transported to the laboratory, where they were air-dried, ground and passed through a 2 mm sieve.

Soil analysis included pH ($CaCl_2$) with an electronic pH meter, Org. C by wet digestion in H_2SO_4 and $K_2Cr_2O_7$, and total N (Kjeldahl). Aqua regia extractable P, K, Ca and Mg concentrations were determined for organic layer samples. Heavy metal contents of organic layers were determined for 18 plots.

Soil units were characterised and classified according to FAO (1989) and according to the Romanian soil system (RISA, 1980).

Data Processing

All data are recorded on an IBM computer in the MS-DOS system and stored on magnetic tape. Data processing was done with an application in FOXPRO language. Mean and extreme values for different species groups, soil units and altitudinal classes were calculated. An ANOVA analysis was done using provinces, species groups and their interactions as criteria to stratify the data.

Soil data were interpreted on the basis of the RISA (1980) methodology, of IFRM (1972, 1980,1984) instructions and of recent researches (Latis et al., 1990).

Forest Soil Condition

Soil Parameter Values

Soil acidity

The values of pH in the organic layer of Haplic Luvisols, Albic Luvisols, Eutric Cambisols, Dystric Cambisols, Cambic Podzols and Eutric Fluvisols are between 3.7 and 5.4 (Table II 2-27), showing a decrease from the soils in the hilly region (4.9-5.4) to those in mountainous regions (3.7-4.4). The pH values in the mineral layer (mean value for 0-20 cm) vary, for the same soils, between 2.8 and 7.4. The lowest values are found in Ardeal.

The analysis of variance showed that mean pH values of the 0-5 cm mineral layer differ significantly between provinces and between tree species groups. The lowest mean value is found in Ardeal (pH 3.8), but also the value for Moldova (pH 4.3) suggests ongoing acidification if compared with conditions in Muntenia (pH 4.8). Further stratification based on species shows very well the acidification of the soils in Ardeal and in the Carpathian Mountains. The soils of broad-leaved stands in Ardeal have a mean pH of 3.9, those of coniferous stands a pH of 3.3, which is significantly lower than the mean value found in coniferous stands in Muntenia (pH 4.0).

Table II 2-27. Mean values of pH ($CaCl_2$) in organic and mineral (0-20 cm) soil layers for different provinces and soil units.

Province	Soil layer	Haplic Luvisols	Albic Luvisols	Eutric Cambisols	Dystric Cambisols	Cambic Podzols	Eutric Fluvisols
Ardeal	org.	5.0	4.9	4.8	4.4	3.9	5.1
	min.	4.0	3.7	3.8	3.7	2.8	5.4
Moldova	org.	5.4	5.1	5.0	4.1	3.8	-
	min.	5.2	4.6	4.9	3.6	3.5	6.7
Muntenia	org.	5.1	5.2	5.1	4.4	3.7	5.4
	min.	4.7	4.1	4.5	3.7	4.0	7.4
Total for	org.	5.1	5.0	5.0	4.3	3.8	5.3
the country	min.	4.4	4.0	4.3	3.7	3.7	6.8

Table II 2-28. Mean values of mandatory parameters in organic and mineral (0-20 cm) soil layers for different regions and species groups.

Province	Species groups	layer	pH ($CaCl_2$)	Org. C g kg^{-1}	N g kg^{-1}	P mg kg^{-1}	K mg kg^{-1}	Ca mg kg^{-1}	Mg mg kg^{-1}
Ardeal	Coniferous	org.	3.9	154.1	11.5	791	1153	5975	1656
		min.	3.3	44.6	4.0	-	-	-	-
Moldova	Coniferous	org.	3.8	167.9	12.6	978	1439	4710	1560
		min.	3.4	52.1	4.1	-	-	-	-
Muntenia	Coniferous	org.	4.0	142.6	10.7	820	1212	5322	1400
		min.	4.0	53.4	5.5	-	-	-	-
Total for	*Coniferous*	*org.*	*3.9*	*155.9*	*11.7*	*863*	*1269*	*5364*	*1558*
the country		*min.*	*3.6*	*49.8*	*4.5*	-	-	-	-
Ardeal	Broad-	org.	4.8	148.3	11.2	907	1650	8306	2062
	leaved	min.	3.9	32.6	2.8	-	-	-	-
Moldova	Broad-	org.	5.1	154.9	11.2	1081	1774	11484	2566
	leaved	min.	5.0	29.7	2.3	-	-	-	-
Muntenia	Broad-	org.	4.9	136.6	9.7	853	1853	7388	2452
	leaved	min.	4.6	30.1	2.5	-	-	-	-
Total for	*Broad-*	*org.*	*4.9*	*145.8*	*10.8*	*919*	*1730*	*8582*	*2261*
the country	*leaved*	*min.*	*4.4*	*31.2*	*2.6*	-	-	-	-
Total for	*Coniferous*	*org.*	*4.7*	*148.3*	*11.0*	*907*	*1628*	*7766*	*2094*
the country	*+ broad-leaved*	*min.*	*4.2*	*35.4*	*3.0*	-	-	-	-

Nutrient status

Mean values of organic carbon and nitrogen in the mineral surface layer (Table II 2-28) are low, being between 29.7 and 53.4 g kg^{-1} Org. C and between 2.3 and 5.5 g kg^{-1} N.

Discussion

Indications for an ongoing soil acidification process in the western part of the country, including Ardeal, Banat and Crisana, are obvious. Also the soils of the Eastern Carpathians, in Moldova and Bucovina, and the soils of the Southern Carpathians, in Muntenia and Oltenia, are affected. The acidification process of the soils in the mentioned zones is accompanied by a decrease of the soil organic carbon and nitrogen pool.

Processes of Damage and Deterioration and Possible Causes

The study made by de Vries et al. (1993) showed that critical loads for nitrogen, sulphur and potential acidity are exceeded by more than 100% in almost the whole country including the western part and both sides of the Carpathian Mountains. Air pollution, both transboundary pollution and pollution emanated from the more than 50 internal sources distributed over the country, is probably a major cause for the observed soil acidification, most particularly in the western part of the country.

Measures to restore damaged forest soils

The plots affected by soil acidification are selected for further research in the framework of the Level II monitoring programme. At the same time field experiments with soil amendments and fertilisers are carried out. The use of ameliorative species for soil fertility is a recommended forest management measure. A national monitoring network, denser than the transnational one, is proposed to support future forest management decisions and research activities.

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2.25 SLOVAK Republic

***P.** Pavlenda*

The forest soil condition in the Slovak Republic was monitored at 111 observation points, corresponding to the 16x 16 km network.

Sampling and Analysis

Soil samples were collected from 20 sampling pits, 5 in each of the **4** subplots located along the cardinal directions. Outside the monitoring plot area, one profile pit was pedologically described and characterised. For every plot, composite samples were mixed for the organic layer and two mineral soil layers (0-10 and 10-20 cm). Prior to analysis, the samples were dried at room temperature, crushed by mortar and pestle and sieved.

All mandatory and optional analysis results were obtained with reference methods. 'Total' amounts of K, Ca, Mg, Al, Na, Fe, Mn, Zn and Cu were measured in organic and mineral layer samples.

Discussion

The geochemical and climatic diversity of the landscape has resulted in rather differentiated forest soil conditions in Slovakia.

The altitude ranges between 110 and 1285 m asl. The relative distribution of forest vegetation (climatic-altitudonal) zones is as follows: 1st (oak) zone - 12.6 % , 2nd (oak-beech)- 11.7 %, 3rd (beech-oak) - 24.3 %, 4th (beech) - 17.1 %, 5th (beech-fir) - 21.6 %, 6th (spruce-beech-fir) - 10.8 % and 7th (spruce) - 1.8 %.

Important parent material groups are: consolidated non-calcareous sedimentary rocks (flysch) - 28.9 %, crystalline rocks - 18.9 %, carbonate rocks - 18.0 %, volcanic rocks - 12.6 %, non-consolidated sedimentary materials - 14.4 %.

Most of the soils of the observation plots were classified as Cambisols - 64.9 %. Other important soil groupings are: Leptosols (Rendzic) - 12.6 %, Luvisols - 10.8 % and Podzols - 3.6 %.

The evaluation of soil condition results is restricted by a rather small number of monitoring plots as compared to the strongly different conditions. Relations and differences were investigated using common statistical methods including frequency analysis, analysis of variance and regression analysis. Results were compared with standard values or values known in literature. The evaluation is not yet completed.

Level of acidity is an important parameter in the evaluation of soil properties in relation to forest damage and forest soil degradation. Relatively favourable conditions on many plots are determined by parent material and in the organic horizon by tree species composition of stands as well.

The pH values distribution in classes is shown in Table II 2-29:

Table II 2-29. Distribution of pH values in organic and mineral soil layers.

pH range	O layer	0-10 cm layer	10-20 cm layer
< 3.2	5.4 %	3.6 %	0.9 %
3.2 - 4.0	21.6 %	40.5 %	54.1 %
4.0 - 5.0	39.7 %	32.5 %	20.7 %
5.0 - 6.0	31.5 %	6.3 %	5.4 %
>6.0	1.8 %	17.1 %	18.9 %

The values of exchangeable acidity are usually related to soil type and site conditions. Rather high values were observed in Podzols and Dystric Cambisols on some plots.

The cation exchange capacity is very variable. Extremely low values are found in soils developed on poor non-calcareous eolian sands. Values below 10 $\text{cmol}_{(+)}\,\text{kg}^{-1}$ in 0-10 cm layer were observed on 30% of the plots, values above 50 $\text{cmol}_{(+)}\,\text{kg}^{-1}$ on 14 % of the plots.

Total amounts of lithogeneous nutrients vary within a wide range as a result of different parent materials. For example, extremely low contents were found in quartz-rich eolian sands, whereas a good supply is ensured in soils of volcanic parent material.

The average organic carbon content in the 0-10 cm layer is **55** g kg^{-1}, in the 10-20 cm layer it is 32 g kg^{-1}. Average values of total nitrogen in the 0-10 cm and 10-20 cm layer are 4.1 g kg^{-1} 10-20 cm and 2.8 g kg^{-1}, respectively.

Accumulation of organic matter on the soil surface depends not only on climatic factors but also on the tree species composition of forest stands (thinner organic layer under similar site conditions in beech stands than in spruce stands; rather high amounts of accumulated organic matter on the surface of sandy soils under pine stands etc.).

Contents of most heavy metals correspond to average values of uncontaminated soils. Contents of Cu and Zn in mineral horizons are rather high in some cases. In comparison with results of geochemical surveys, we can state that the high amounts are of lithogeneous origin in most cases (geochemical anomalies), though some plots may be influenced by pollution.

Relations between individual soil condition parameters and between soil condition parameters and external parameters were also investigated. Many parameters, especially those determining the susceptibility to acid deposition, are related to altitude. Values of exchangeable Ca and Mg, base saturation and pH decrease with increasing altitude. Values of exchangeable H and Al and exchangeable acidity increase with increasing altitude. The relations are not strong because of the influence of parent material and other factors. Organic layer parameters depend on the type of parent material and on the tree species composition of forest stands.

Direct relations between soil conditions and forest damage have not been found. Rather strong defoliation and other signs of damage are also observed on sites with carbonaceous soils including sites with broadleaf forest stands that are not expected to be damaged by air pollution. Relations may be explained by very detailed multi-factorial analyses.

Ongoing processes of soil deterioration and acidification are not easy to demonstrate on the base of one survey. Discrepancies between morphological or pedogenetic parameters and some chemical parameters show symptoms of negative changes. High amounts of some heavy metals in the organic layer (outstanding accumulation in comparison to amounts in mineral layer) on three plots in the neighbourhood of metallurgy plants can be explained by industrial pollution.

Liming as a mitigation tool was applied in a region with damaged spruce forests on acid soils, presumably influenced by long-range air pollution. About 10,000 ha of forest have been limed since the beginning of the 1980s with ground lime or dolomitic lime. A common application rate is 2 to 5 t ha^{-1}. Positive results are relatively small because of rather coarse particle size composition of ground lime. New methods of acidity compensation and other measures are now being tested.

2.26 SLOVENIA

The forest soil condition was surveyed at 43 of the 86 16x16 km grid plots in Slovenia, and represent a total area of about 20,000 km^2 forest lands.

Sampling and Analysis

Soil observations were made from September 1994 till November 1995. The Slovenian forest plots were subdivided in four subplots. At each subplot a pedological characterisation was made using the FAO guidelines. The subplot with the most representative site conditions was selected for sampling. Samples of the organic layer and the mineral soil at 0-5, 5-10 and 10-20 cm were bulked from three augerings.

In addition to all mandatory parameters, the total content of several metals and the cation exchange properties (except exchangeable Na) were determined. All analyses were performed using the reference methods, except total contents of P, K, Ca, Mg, Al, Fe, Cr, Mn and Zn, which were extracted in a mixture of concentrated nitric and perchloric acid.

A report summary on the forest soil condition in Slovenia has not been received at the time of completion of this report.

2.27 SPAIN

M. López Arias

The 16x16 km forest inventory in Spain consists of 464 observation plots, representing 11,762,000 km^2 of forested area. The soil condition monitoring activities started in March 1993 and were completed at the end of 1995.

Sampling and Analysis

Soil samples were collected at four representative sample locations, one within each quadrant of the inventory plot, and subsequently bulked to form one representative sample for each sampled layer. The organic layer material, collected from the soil surface with a circular frame, is separated in two samples: (i) fragmented, partly decomposed organic materials (F), and (ii) humified materials **(H).** Two (0-10 and 10-20 cm at 154 plots in 1993) or three (0-5, 5-10 and 10-20 cm at 300 plots in 1994-95) mineral layers were distinguished. The sample locations were pedologically characterised according to FAO guidelines.

At arrival in the laboratory, samples were air-dried, ground and passed through a **2** mm stainless steel sieve to separate the fine earth. Organic carbon, total nitrogen, pH and $CaCO_3$ content were determined using reference methods. Total contents of P, K, Ca and Mg of organic F and H materials were measured after digestion in a concentrated HNO_3+HCl mixture. All analyses were performed twice on the same sample, which was repeated when the difference between the duplicates exceeded 10%.Particle size, coarse fragments content, bulk density and hydraulic conductivity were determined in the laboratory, the latter two parameters on undisturbed samples taken at the most representative of the **4** sampling sites.

Data Processing

The soil data were grouped in appropriate classes based on soil unit, parent material, texture + coarse fragments, bulk density, pH, organic layer weight, organic carbon content or nutrient content. With contingency tables, the distribution of parameter results was studied, using a two-way classification with paired variables (e.g. texture-pH). Univariate analysis of the parameter results was performed to check the frequency distribution against theoretical distributions. Bivariate analysis, using ANOVA for normal distributed parameters and non-parametric tests for other distributions, was applied on paired variables. The level **I** data were compared with results contained in a national database of 1600 soil profiles, using stratification methods based on geographic region and tree species. **A** global classification of the level I soil plots, to which also mean monthly climatic data are attributed, involved statistical tools, such as Principal Component Analysis, Correspondence Factorial Analysis and Multivariate Regression. Further, the relationship between defoliation and the data of the combined soil-climatic data base was investigated, using contingency tables and multivariate analysis.

A report summary on the forest soil condition in Spain has not been received at the time of completion of this report.

2.28 SWEDEN

E. Karltun

The first comprehensive forest soil condition inventory on permanent sampling plots started in 1983 and was completed in 1988. The second inventory started in 1993 and is still running. The design of these inventories are different from the design of the Level **I** inventory. The major part of the results reported here are from the first inventory. The reported data correspond to an objectively selected subsample of the plots from the national design reaching a density similar to the EC 16 x 16 km grid. The total number of plots reported from the first forest soil condition inventory is 1174 and they were sampled in the period between 20/5/1985 and 1/7/1988. The data reported from the second inventory correspond to 75 plots from the national systematic network selected for the tree vitality inventory. They were visited by the soil sampling teams during 1995. Thus, only a subset of the plots in the tree vitality inventory are reported with soil condition data.

Methods

The methods used for collecting and analysing samples in the first inventory are in some aspects deviant from the methods recommended in the ICP Manual. The most important approximations that had to be made are:

- the soil type was converted to the FAO classification by using information in the national database. Some units could not be classified and were not reported;
- the sample layers were approximated since the national system uses sampling by horizons rather than fixed depths in the top soil;
- exchangeable cations were extracted by a 1M NH_4Ac solution buffered to pH 7.00.

This evaluation focuses on geographical differences in soil conditions (i) between regions receiving different amounts of acidifying substances and (ii) along the south-to-north direction. The statistical evaluation made is either estimates of mean values combined with estimates of precision expressed as 95% confidence intervals or linear correlation analysis.

Results

The mean and 95% confidence intervals (CI) for pH ($CaCl_2$) for different soil layers for four regions receiving different deposition loads of acidifying substances in Sweden are presented in Table II 2-30.

Table II 2-30. The mean and 95% confidence interval (CI) for pH-$CaCl_2$ at different soil layers for four regions receiving different deposition loads of acidifying substances in Sweden (1=low, 2=low-intermediate, 3=intermediate-high, 4=high). Data from 1985-1987.

Soil layer	Deposition region							
	1		2		3		4	
	Mean±½CI	n	Mean±½CI	n	Mean±½CI	n	Mean±½CI	n
H	3.69±0.15	103	3.54±0.13	108	3.43±0.23	36	3.12±0.16	9
O	3.45±0.05	298	3.34±0.05	310	3.28±0.08	101	3.09±0.10	45
M05, M01	3.60±0.05	283	3.93±0.10	304	3.88±0.15	82	3.53±0.24	27
M51,M12	4.37±0.07	322	4.34±0.07	370	4.09±0.08	132	3.92±0.13	19

Data shows that the pH is significantly lower in areas receiving high inputs of acidifying substances. Particularly the O layer and the lower mineral soil layer (M51, M12) show decreasing pH values towards higher input of acid. The precision in pH estimates makes it possible to detect significant differences between the regions.

Table II 2-31. Correlation coefficients between pH($CaCl_2$) and base saturation (BS) as independent and latitude as dependent variable (significance levels; * p=0.05-0.01, ** p=0.01-0.001, *** p<0.001). Data from 1985-1987.

Horizon	Soil							
	Cambisols		Haplic Podzols		Haplic Arenosols		All soils	
	pH	BS	pH	BS	pH	BS	pH	BS
O	0.40	0.61^{**}	0.30^{***}	0.49^{***}	0.08	0.19^{*}	0.14^{***}	0.26^{***}
	(19)	(19)	(377)	(166)	(220)	(112)	(754)	(380)
M01,M05	0.26	0.28	0.20^{**}	0.43^{***}	0.13	0.13	-0.27^{***}	-0.16^{**}
	(39)	(39)	(263)	(140)	(217)	(93)	(696)	(326)
M51,M12	0.02	0.07	0.51^{***}	0.28^{***}	0.40^{***}	0.10	0.14^{***}	0.11^{*}
	(60)	(60)	(303)	(168)	(251)	(119)	(878)	(446)

Table II 2-31 shows the correlations between pH and latitude and base saturation **(BS)** and latitude for the O layer and both mineral layers, grouped for three major soil groups. Deposition and forest productivity can be expected to decrease towards the north. Cambisols show non-significant correlations with latitude for pH and BS except for the O layer where there is a significant relationship for base saturation. Haplic Podzols show the highest correlation between pH and latitude at the deepest mineral layer and the same observation can be made for Haplic Arenosols. Whereas Podzols show a high correlation for pH in the lower mineral layer and a weaker correlation in the O layer, the situation for base saturation is the opposite. Base saturation and pH in Arenosols are very weakly correlated with latitude except for pH in the deepest mineral layer.

The mean total amount of N, P, K, Ca and Mg were calculated to obtain an estimate for regional comparison with other European countries (Table II 2-32). The number of samples analysed are quite low which makes the estimated mean rather uncertain as seen by the wide confidence intervals.

Table II 2-32. Nutrient amounts in the organic layer - mean and 95% confidence interval (n=65). Data from 1995.

	N (kg m^{-2})	P (g m^{-2})	K (g m^{-2})	Ca (g m^{-2})	Mg (g m^{-2})
Mean±½CI	0.30±0.092	18.8±5.32	13.0±5.62	117±70.8	21.6±10.4

Conclusions and Possible Remediation Measures

The results of the inventory confirm the earlier made observations of an ongoing soil acidification, especially in the south-west parts of Sweden, caused by anthropogenic emission of acidifying substances. The effect of the acidification is accelerated by an increased export of base cations by tree harvest and increased use of biomass for energy purposes (whole tree harvesting). As shown by the data above, the soil survey is a valuable tool in finding which soil types are most prone to be affected by soil acidification. An extensive program with field experiments evaluating the effects of liming or and/or base cation fertilisation have been conducted in Sweden. Since direct negative effects of acidification on trees have not yet been proved and since liming can cause negative effects on important biological processes in the soil, liming policies in Sweden are still restrictive. Regular woodash recycling is tested as a measure to prevent nutrient losses by increased exports of nutrients by harvest.

2.29 SWITZERLAND

S. Zimmermann

The soil condition in the Swiss forests (11,860 km^2) was monitored in 172 observation plots of a systematic (8x8 km) network The 48 plots that correspond to the transnational network (16x16 km) were surveyed in 1993 and their results were made available for the European database.

Sampling and Analysis

A representative soil sampling location was chosen as close as possible, but outside the tree inventory plot. A pedological characterisation according to Swiss survey guidelines was made, including a soil profile description. The soil was sampled at regular intervals till a maximum depth of 200 cm, depending on soil depth: 0-5, 5-10, 10-20, 20-40, 40-80 and >80 cm. For each layer one composite sample was taken from the profile pit. A separate set of samples were taken according to morpho-genetic horizons. The samples were prepared for analysis by drying them at 60°C until constant weight is reached. The dried samples were then mechanically ground and sieved to separate the fine earth fraction.

Reference methods were used for the analysis of pH, organic C and total N. Carbonates were determined gravimetrically. Heavy metals, Al, Na, P, K, Ca and Mg were extracted from both organic and mineral samples with a 2M HNO_3 acid solution. Exchangeable cations were measured in an unbuffered 1M NH_4Cl soil extract.

Processing of Data

Relations among the variables were examined graphically and by correlation analysis. Scatter diagrams were drawn for all pairs of variables. Pearson product-moment correlation coefficients (r) were computed.

The results from an extended statistical analysis seem to point to a causal relation between the transparency of crowns and the ability of the soil to supply water to the trees. Regression equations were computed from which one might predict transparency. These results are in length discussed in a separate paper (Webster et al., 1996).

Some soil chemical parameters were chosen for a discussion in the frame of this report. These are: soil acidity, cation exchange capacity, base saturation and the C/N and C/P ratios. Table II 2-33 shows how the results of these parameters were classified into discrete groups according to recommendations in the literature (Arbeitskreis Standortskartierung, 1980).

Table II 2-33. Classification of the results for the selected chemical parameters.

cation exchange capacity (cmol(+) kg^{-1})		base saturation (%)		buffer range (pH-value)		C/N-ratio	C/P-ratio	
< 15	very low	< 5	very low	2.8-3.2	Fe	< 10	< 50	very narrow
15-40	low	5-20	low	3.2-3.8	Al/Fe	10-12	50-100	narrow
40-70	moderate	20-50	medium	3.8-4.2	Al	12-16	100-200	narrow to medium
70-120	medium	50-80	high	4.2-5.0	exchange	16-20	200-400	medium
120-240	medium to high	80-100	very high	5.0-6.2	silicate	20-25	400-800	medium to wide
240-480	high			6.2-8.3	carbonate	25-35	800-1200	wide
> 480	very high					> 35	> 1200	very wide

Information Regarding Forest Soil Condition

Soil Type and Altitude

The most widespread soil types are Cambisols (25%) and Podzols (26%), followed by Rendzic Leptosols (15%) and Regosols (13%). Within the Cambisols, the fine earth of more than 50% of the soils contains carbonate. Therefore, 45 to 50% of all the investigated soils are strongly affected by a calcareous parent rock composition.

The soils are situated at altitudes between 300 and 2200 meters. The distribution of the altitudes of the sampling sites shows two maxima, one at 600 to 800 meters and a second at 1200 to 1600 meters. Podzols and skeletal soils are found at higher altitudes whereas Cambisols are situated mainly in the lowlands.

Soil Acidity

The distribution of pH values shows two maxima, one around pH 4, another just above pH 7, corresponding to soil samples with and without carbonate. The defined buffer ranges are all more or less equally occupied (Table II 2-34).

Table II 2-34. Distribution of the soil samples over the different buffer ranges.

buffer range		N	%
pH 2.8-3.2	Fe	13	12
pH 3.2-3.8	Al/Fe	22	20
pH 3.8-4.2	Al	14	13
pH 4.2-5.0	exchange	18	17
pH 5.0-6.2	silicate	15	14
pH 6.2-8.3	carbonate	26	24

Half of the samples in the iron buffer range originate from the humus layer (H-horizons), the other half from the 0-5 cm mineral layer. There is a remarkable increase in pH with increasing soil depth but no extraordinary soil acidification has been observed.

The pH values of the same plots were investigated for the first time in 1983/85. A comparison of these values with the actual pH values revealed no significant change in pH that could not be explained by random spatial variability.

Cation Exchange Capacity

79% of all soil samples show a cation exchange capacity (CEC) of more than 7 $cmol_{(+)}$ kg^{-1}, 35% have a CEC of more than 24 $cmol_{(+)}$ kg^{-1}. Apart from three exceptions, all samples having a low to moderate CEC are from 5-10 cm and 10-20 cm mineral layers and have a low content of organic matter. These samples usually have a low base saturation (< 20%) (Figure II 2-13). As soon as the CEC exceeds 12 $cmol_{(+)}$ kg^{-1}, the base saturation passes the 50% level. Soils with a CEC above 12 $cmol_{(+)}$ kg^{-1} and a base saturation above 50% are in the exchange, the silicate or the carbonate buffer ranges.

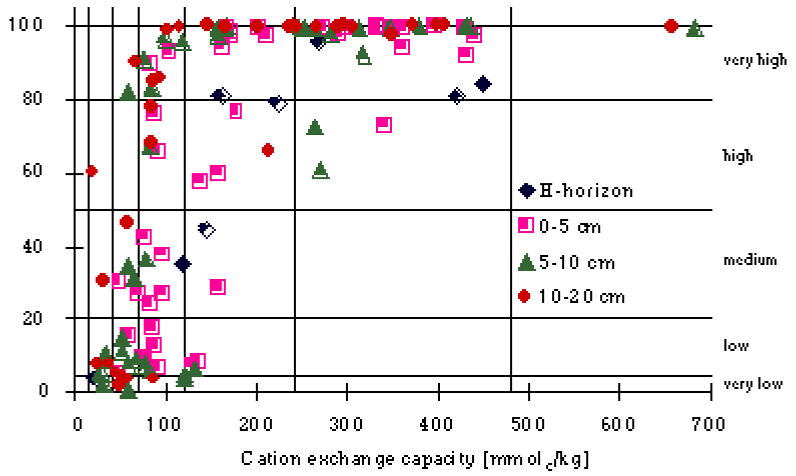

Figure II 2-13. Cation exchange capacity and base saturation of the Swiss soil samples.

C/N and C/P Ratios

According to von Zezschwitz (1980) the microbial decomposition of organic matter is hindered when C/N and C/P ratios exceed values of 20 and 200, respectively. Only the H-horizons and a few samples from the 0-5 cm depth layer show values in this range.

Compared to the threshold values of von Zezschwitz (1980), the C/N ratios are relatively narrower than the C/P ratios. This may be explained by an anthropogenic N input which leads to a narrowing of the C/N ratios (Riek and Wolff, 1995).

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2.30 UKRAINE

I. Buksha

Ukrainian forested lands cover 10 million hectares or about 14.3% of the total territory. The forest composition is approximately 54% coniferous and 46% deciduous. *Pinus* L. (± 35%), *Picea A.* Dietr. (16%) and *Abies* Mill. (3%) are the main forest-forming coniferous species. *Quercus* L. (22%), *Fugus* L. (13%), *Carpinus* L. (2%) are the dominant hardwood species. Softwood genuses are *Betula* L., *Populus* L., *Alnus* Mill. and *Tilia* L. (9%). The primary objective of the Ukrainian national forest monitoring programme is to describe spatial distribution and degree of anthropogenic damage to forests. The crown condition has been monitored since 1989 using the protocol of the ICP Forests programme. The network of plots (grid size 16x16 km) has been established in 14 of the ***24*** administrative regions and in the Crimea republic. In 1996, a soil condition inventory was carried out in the north-eastern part of the country.

Processing of Data

Standard correlation techniques are used for statistical data analysis. The evaluation of the soil condition consists of comparison of measured data with standard and reference values for forest soils. Standard values were determined from results of previous national soil surveys, whereas reference values refer to critical concentrations.

Description of the Forest Soil Condition in Terms of the Investigated Parameters

The results of the investigation show that about 6% of studied soils has a neutral reaction, 47% has a slightly acidic reaction (pH KCl 5.07 - 5.46) and 47% a slightly alkaline reaction (pH KCl 6.30 - 7.35). About 80% of the investigated soils has a medium or high nutrient status. In 10% of investigated soils the Mn content exceeds the critical concentration (more than 1500 mg Mn kg^{-1} soil). Comparison with critical concentrations further revealed high contents of Pb in several samples (more than 20 mg Pb kg^{-1} soil).

Discussion on Investigated Relationships

Relationships between individual soil parameters and between soil parameters and external parameters will be investigated when more field data becomes available. The results of the forest soil condition inventory will be used to determine the forest management in the future

2.31 UNITED KINGDOM

A. Moffat, T. Hutchings and R. C. Boswell

Sixty seven plots from the five most important forestry species (*Picea sitchensis*, *Picea abies*, *Pinus sylvestris*, *Quercus* spp. and *Fugus sylvatica*) were sampled during the UK Level I soil condition survey.

Sampling and Analysis

The soil at each observation plot was sampled mid-way between two adjacent sample trees and beyond each side of the edge by 10% of the distance from the end trees. With a total of 24 trees per plot, six per cardinal direction, 28 sub-sampling positions were produced. At each sub-sampling position, a small pit was dug using a spade. Litter (L) and fermented litter (F) layers were sampled together where present and H layers were sampled separately. Mineral horizons were sampled at 0 to 5, 5 to 10 and 10 to 20 cm. The seven samples of each cardinal direction were bulked. Hence, a plot with conventional L, F and mineral horizons would yield 4 bulk organic and 12 bulk mineral samples.

Mandatory soil analyses were performed on all bulk samples. Mass loss-on-ignition and Kjeldahl digestion followed by steam distillation were used to determine Org. C and N, respectively. Aqua regia extractable P, K, Ca, Mg, Al, Fe, Cr, Ni, Mn, Zn, Cu, Pb and Cd were measured on the organic samples. The average result of the organic sub-layers - L+F+H - and each of the three mineral layer results have been taken up in the European database.

The quality of the analysis results was controlled by periodically running two internal standard samples in each set of analyses and by using commercial standards on a regular basis. The internal standard samples were also sent to three external laboratories to provide analysis results which could be evaluated against the results of the lab that was used in the project.

The UK Soil Database

The survey represents the first rigorous assessment of UK forest soil chemical properties. It is therefore impossible to compare our results with earlier data in order to determine change over time. Nevertheless, the data have been examined by tabulation, correlation and principal components analysis to determine trends, relationships between soil variables, and between soil variables and indices of forest condition for years 1993 to 1996. Table II 2-35 summarises the main soil groups represented in the **UK** forest soil condition database.

Table II 2-35. Representation of the main soil groups in Great Britain and in the UK level I soil condition database.

Soil type (FAO)	Soil type (British class)	Soil type in Great Britain (%)	Soil type under British forest (%)	Soil type under UK Level I sites	
				Number	Per cent
Arenosols	Littoral soils	2	4	3	4
Calcisols	Calcareous soils	4	2	3	4
Cambisols	Brown earths	20	22	14	21
Fluvisols	Ground-water gleys	3	1	1	1
Gleysols	Ground-water gleys	2	4	5	7
Histosols	Peats	25	14	3	4
Leptosols	Skeletal soils	3	2	3	4
Luvisols	Brown earths	9	9	6	9
Planosols	Surface water gleys	27	28	15	22
Podzols	Podzols	5	14	14	21

British forest soils are dominated by Planosols, Cambisols, Podzols and Histosols, due in part to UK land-use policy which has necessitated that afforestation has mostly taken place on the more waterlogged, infertile and acidic soils. Level I plots fairly reflect their distribution except for an under-representation in the Histosol group.

Information Regarding Forest Soil Condition

Nearly all forest plots studied have acidic soils, with pH of both organic and mineral horizons usually below 4. C/N ratios are very stable for each soil depth, and median values range from 35 to 30 for L+F and H horizons to 25-28 for mineral horizons (0-20 cm). Elemental concentrations in organic horizons appear similar to mean values for UK peat soils (McGrath and Loveland, 1992). Concentrations of potentially toxic elements were very small compared to those considered nationally to represent soil contamination (ICRCL, 1987). Across species, significant differences in mineral soil pH, organic carbon and nitrogen contents were obtained between FAO soil groups. There were few consistent significant differences in soil properties in organic horizons between soil groups.

Relationships of Soil Properties and Forest Condition

FAO soil type failed statistically to account for variation in indices of forest condition in all five species, suggesting that soil classification is unhelpful in explaining the range in forest condition measurements.

In the soil organic horizons, simple correlation analysis revealed no consistent relationships between soil properties and indices of forest condition, except between crown density and zinc for *Picea sitchensis.* This relationship has been noted before (Innes, 1993). In mineral horizons, only soil pH (0-5 cm, 5-10 cm) was negatively related to *Pinus sylvestris* diameter at breast height (dbh).

Principal components analysis yielded similar results. For *Quercus* spp., *Fagus sylvatica* and *Pinus sylvestris*, tree condition assessments were almost totally independent of any of the measured soil properties. There was some indication of a link between shoot death extent (sde) and organic carbon and nitrogen in organic horizons under *Picea abies.* In *Picea sitchensis* plots, increase in crown density was associated with increase in pH. The dearth of relationships between soil properties and forest condition supports a previous UK study in 1988 (Innes and Boswell, 1989).

Measures to Restore Damaged Forest Soils

Although soil change has been identified in soils under UK forests from other studies (e.g. Moffat and Boswell, 1990), soil damage or deterioration has yet to be positively identified. Most UK forest soils are young, and still evolving. Hence, there are no perceived needs to address soil restoration in the UK, except for limited fertiliser applications (nitrogen, phosphorus and potassium only) to relieve soil infertility where an economic return on timber production is expected. The issue of forest soil sustainability is being more precisely addressed in the ten UK Level II plots. Because of the lack of relationships between soil and forest condition in the UK, no changes in forest management are considered necessary at present. However, national *Forests and Soil Conservation Guidelines* will be published in 1997. These serve to advise forest managers on how important forest practices can affect soil quality, and on procedures to avoid or minimise damage.

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2.32 YUGOSLAVIA

M. Knezevic

The forest soil condition survey in Yugoslavia is proceeding on 189 observation plots (140 in Serbia and 49 in Montenegro) of a 16x16 km^2 grid. No information on the actual progress of the national soil survey activities was received at the time of completion of this report.

At each observation plot, soil samples are collected from the organic layer and three mineral layers at 0-5, 5-10 and 10-20 cm depth. Organic carbon, total nitrogen, pH and $CaCO_3$ are determined for both organic and mineral soil samples. Total amounts of P, K, Ca, Mg, Zn, Cu, Pb and Cd are measured in the organic layer, cation exchange properties are determined for mineral layers.

CONCLUSIONS AND RECOMMENDATIONS

The annual crown condition assessments at the monitoring plots of the large-scale forest condition inventory (level I) show that the health condition of European forests is declining (UN/ECE-CEC, 1996). Significant large-scale direct effects of atmospheric pollution on tree vitality have not been found so far on the basis of available crown condition data. The concern that the observed loss in forest vitality may be related to soil changes induced by atmospheric pollution, has led to the organisation of a survey of the chemical soil condition at the observation plots of the crown condition inventory.

Conclusions

This first European forest soil condition survey, carried out within the common activities of EU/ICP Forests using harmonised methodologies, has resulted in a considerable increase of knowledge of the condition of forest soils in 23 countries. Considering the objectives of this survey outlined in the introduction, the following conclusions are made.

(1) Intercomparability of data

The Forest Soil Condition database is a valuable source of information for forest ecosystem studies, but a limitation is the comparison among the national datasets. This is due to differences in sampling and analysis methods. The variability of the chemical soil data, resulting from the use of different analysis methods, is illustrated by the variation among the results of two standard samples, simultaneously analysed by most laboratories that participated in the analysis activities of the soil inventory. The big effort in making a common soil manual has resulted in a low variability between the national datasets for the most important soil parameters. Average deviations from the median results of the standard samples are 10% for base saturation, 10% for total N content and 23% for pH. For other parameters, the variation between the different countries can be substantial, e.g. up to 62% for Cr. The use of different sampling procedures, revealed by the highly variable OrgLay (organic layer weight) values reported by neighbouring countries, may also have a significant influence on the parameter results, particularly for organic layers.

(2) Influence of climate and soil characteristics on soil chemistry

The variability of ecological conditions in Europe has resulted in a wide range of chemical soil conditions. In the cold Boreal region in northern Europe, forest soils are usually nutrient-poor and accumulate large amounts of organic matter on the soil surface. Naturally acid organic layers are common but, unless the input of acid is increased, the base saturation is high both in organic and mineral soil layers. Forest soils in the Mediterranean region generally have an adequate nutrient content. Base saturation and pH are often high, especially in soils derived from calcareous parent materials, which are frequently found. Organic litter is rapidly decomposed and incorporated in the mineral soil. Coarse textured soils and soils derived from acid parent materials are often strongly acidified and show poorly decomposed organic layers at the surface. Soils with an adequate reserve of basic cations to buffer acidification processes are usually associated with a higher clay content and show a rapid decomposition of organic litter.

Soil texture, parent material type and climate largely determine the cation exchange properties of forest soils. Cation exchange capacity is usually less than 10 cmol(+) kg^{-1} in mineral subsurface layers of coarse textured soils, but increases with increasing clay content; values of more than 10 cmol(+) kg^{-1} are dominant in fine textured soils. The exchange complex of calcareous soils, which comprise 14% of the European forest soils, is completely saturated with basic cations. On the other hand, basic cations occupy 15% or less of the cation exchange sites of the mineral surface layer of about one quarter of the European forest soils. Average base saturation values of carbonate-free soils increase from north to south, as well as from west to east in Europe, following the climatic gradient of a precipitation surplus in north-western Europe to an evapotranspiration deficit in eastern Europe and the Mediterranean area.

Heavy metal concentrations in the mineral soil are influenced by the mineralogy of the parent material and vary within a wide range. High levels of zinc, cadmium and manganese are often associated with calcareous materials. Soils overlying sandy deposits are relatively low in trace elements. Mineral layer concentrations of potentially toxic metals, such as zinc, lead and cadmium, show significant linear relationships with CEC, organic carbon content and pH.

(3) Effects of atmospheric deposition on soil chemistry

Results show a correlation between soil chemistry and atmospheric deposition of nitrogen, acidity and heavy metals:

- A higher nitrogen content in the organic layer of forest soils is observed in the area receiving a high atmospheric deposition load, as compared to remote areas in Europe. Nitrogen deposition, decreasing the C/N ratio of humus layers, has probably disturbed organic matter and nutrient cycling. Unusually high N contents in the organic layer, indicated by a lower ratio in this layer compared to the mineral layer, were observed in 17 % of the plots.
- Acid topsoil conditions, i.e. base saturation of 20% or less, or pH values below 3.5 are reported in 42% of the plots. Results indicated a relationship between acid deposition and pH, but for base saturation such a direct relationship could not be substantiated. This may be due to the fact that other factors, such as climate and soil type, strongly influence base saturation. Extremely acid topsoil conditions, i.e. having a mineral surface layer pH ($CaCl_2$) value below 3.0, are reported for 80 plots (1.9% of all plots), located almost exclusively in the region receiving a very high atmospheric deposition load. A common characteristic of these soils is a low reserve of basic exchangeable cations (BCE of 2.0 cmol(+) kg^{-1} or less), indicating a low buffering capacity against acidification.
- Atmospheric deposition has resulted in high levels of heavy metals in strongly industrialised areas. Concentrations of certain heavy metals, particularly lead and zinc, in humus layers and topsoils show regional gradients reflecting atmospheric deposition patterns. The majority of plots having an organic layer with high lead or zinc concentrations is found in the region with the highest deposition load. Contaminated soils may accumulate more than 100 mg kg^{-1} of lead in the organic layer and are commonly observed in central Europe. However, critical concentrations of Pb (500 mg kg^{-1}), Zn (300 mg kg^{-1}) and also Cd (3.5 mg kg"), given by Tyler (1992) for humus layers of Swedish forest soils, are exceeded in less than 1% of the plots for which values have been reported. Exceedences of critical organic layer concentrations of Cr (30 mg kg^{-1}) and especially Cu (20 mg kg^{-1}) have been reported more frequently, in 9% and 19% of the plots respectively.

(4) Soil quality assessment

The evaluation of the observation plots in terms of their sensitivity to soil acidification, based on pH, cation exchange properties, nutrient cations and carbonate content, and estimated hydraulic conductivity, indicates acid coarse textured and shallow soils as the most responsive soil types to added acids. Many acid sensitive soils are associated with acid parent materials, such as sands, sandstones and acid crystalline rocks. Because these soil types are very common in northern Europe and in mountaineous regions having soils formed on acid bedrock, these regions are highly vulnerable to acid deposition. Although such soils are less wide-spread in the rest of Europe, short-term negative effects induced by acid deposition are most likely to occur in acid soils with a low buffering capacity in areas receiving a high acid deposition load. Southern European forest soils generally show a high resistance to acidification.

The assessment of nutrient availability, integrating chemical parameters of organic and mineral layers, shows a distinct north-south gradient in the estimated availability of nitrogen, phosphorus and basic cations in European forest soils.

A high heavy metal concentration in the organic layer and soil conditions that determine metal mobility and availability, i.e. low pH and low CEC, were used to identify plots where plant toxicity symptoms caused by lead, zinc or cadmium may occur. In the case of lead, plots with an increased risk for toxicity are found in strongly industrialised areas in Europe. However, unfavourable soil conditions may even result in an increased availability of zinc and cadmium in soils with a relatively low metal content located in remote areas in Europe. In soils, having both a low zinc content and soil properties that limit the availability of this element, a risk of deficiency is assessed.

Recommendations

The Forest Soil Condition Database is a valuable source of information for research activities that may provide a better insight in the cause-effect relationships associated with the observed loss of vitality of European forests. Some recommended future activities are listed below:

- Although a common methodology for sampling and analysis was adopted before the start of the monitoring activities in most countries, differences in national methods exist. The results of the intercalibration exercise emphasise the need for a further improvement of data quality and a critical review of the manual with respect to methods and soil parameters to be determined. More emphasis should be put on the assessment of the pools of organic carbon, nitrogen, exchangeable basic cations and heavy metals in the soil.
- The database can be used to extrapolate soil data to sites where no information is available, applying for example multiple regression techniques to investigate relationships between soil chemical properties and readily available information on climatic region, acid deposition, parent material, soil type, texture class, tree species, humus type, etc. (see also “Ten Years Monitoring of Forest Condition in Europe”). This kind of analysis **is** also needed to substantiate the large-scale impacts of acid deposition on soil chemistry. In this context, a modelled site-specific estimate of atmospheric deposition is needed.
- At national scale, correlative studies generally fail to reveal simple relationships between crown and soil condition parameters. The assessment of soil ecological stress factors may be improved by using a more quantitative simple modelling approach. For example, the database has promising application possibilities to investigate the influence of soil-related stress factors on crown condition (see also “Ten Years Monitoring of Forest Condition in Europe”). Other actual ecological issues, such as the assessment of critical loads and weathering rate, may now also benefit from the soil data available at European scale.
- A repetition of the survey is recommended within a reasonable time schedule (e.g. 10 years) for the following reasons:
  - to monitor the change in soil chemistry, in particular at forest sites that are subjected to high loads of atmospheric deposition;
  - to assess relevant soil parameters and soil layers not considered in the first survey.
- The collected data may significantly contribute to a more accurate determination of critical loads of atmospheric pollutants. Actions are required to reduce unintentional aerial contamination of forest soils. The long-term exposure to pollutants should be reduced below critical loads.

ANNEXES

Annex A. INTERLABORATORY VARIABILITY

A.1. Introduction

Participation in a transnational monitoring programme implicates the adoption of a common methodology. Most countries have long ago established national soil survey programmes, using specific analysis methods. National analysis methods have been tried and tested on soil samples in the past. Changing these methods to a different set of methods would impede data comparison with previously analysed samples, unless parallel analyses, using both national and reference methods, are performed. Unfortunately, parallel analysis often proved to be impracticable for various reasons. For example, several countries reported to have insufficient financial means to acquire the laboratory equipment, required to perform the reference methods. Consequently, the methods applied to analyse the soil samples collected at the inventory plots often deviate from the reference methods. National methods, different from the recommended ones, were also used in countries where soil survey activities were initiated before the start of the European programme. When possible, analyses were repeated using the reference methods.

In order to record the data variability in the transnational database, resulting from the use of different analysis methods, a Second Intercalibration Exercise was organised. Two standard samples, distributed among the laboratories participating in the inventory, were to be analysed together with the samples collected at the inventory plots. The results of two common samples do not allow a complete intercalibration of the transnational database, but the exercise provides valuable information on the extent to which the database user may compare results reported by different countries.

A.2. Second Intercalibration Exercise

Sample location

Standard soil samples were collected from two forest sites in Belgium. The main criterion for the selection of the sample sites was the presence of a thick homogeneous soil horizon. One large bulk sample was collected from a profile pit at each site. Sample A was taken from a Podzolic B horizon enriched in organic matter in a soil on cover sands. Sample B was collected from a Bt horizon of a loess soil.

Sample preparation and distribution

Samples were dried at room temperature and sieved to separate the fine earth fraction (< 2 mm). The bulk sample was first mixed using a sample splitter that divides samples in two equal parts The split parts were then joined and passed through the splitter again. This procedure was repeated 15 times to ensure a completely homogeneous bulk sample. Finally, portions of 100-200 g were weighed out and collected in labelled plastic bags for distribution to the participating laboratories.

Reporting of data

The analysis results were reported on an oven-dry (105°C) basis. For this purpose, the moisture content was determined separately and the analytical results were recalculated. Oven drying involves heating during at least **3** hours at 105°C and subsequent cooling in a desiccator before weighing. In contrast to the First Intercalibration Exercise, it was not required to do repeated measurements on the standard sample. However, if replicate results were available, the laboratories were requested to submit individual values instead of averages.

Reporting forms were provided to avoid errors resulting from the use of variable units. The laboratories were requested to provide a detailed description of the applied analytical procedure, if methods different from the reference methods were used.

A.3. Participating laboratories

The laboratories that participated in the Second Intercalibration Exercise are listed in Table **A-1.** The same laboratories were charged with the analysis of the soil samples taken at the plots of the large scale forest soil condition inventory (level I).

Table A-1. Participating laboratories (countries for which national forest soil condition data were unavailable for the transnational report are printed in italic).

Institute	Address	City	Country	Country code
Forstliche Bundesversuchanstalt	Seckendorff-Gudentweg 8	1131 WIEN	AUSTRIA	AU
Ministry of Forestry	*Chkalov-street 6*	*220039 MINSK*	*BELARUS*	*BL*
Bodemkundige Dienst van België	W. Decroylaan 48	3001 HEVERLEE	BELGIUM (Flanders)	BEf
Faculté des Sciences Agronomiques - Pédologie Forestière IRSIA	Avenue Maréchal Juin 27	5030 GEMBLOUX	BELGIUM (Wallony)	BEw and LX
Higher Forestry Institute *Dpt. Ecology & Environmental Protection*	*Kl. Ochridski str. 10*	*1757 SOFIA*	*BULGARIA*	*BU*
Forest Research Institute	Cvjetno naselje 41	41420 JASTREBARSKO	CROATIA	CR
Forestry and Game Management Research Institute	Jiloviste-Strnady	PRAGUE 516	CZECH REPUBLIC	CZ
Danish Forest and Landscape Research Institute	Hörsholm Kongevej 11	2970 HÖRSHOLM	DENMARK	DK
Estonian Institute of Forestry and Nature Conservation	*Rôômu tee str. 2*	*2400 TARTU*	*ESTONIA*	*ET*
The Finnish Forest Research Institute Dpt. of Forest Ecology	P.O. Box 18	01301 VANTAA	FINLAND	FI
INRA Laboratoire d' Analyses des Sols	Rue de Cambrai 273	62000 ARRAS	FRANCE	FR
Nieders Forstl. Versuchanstalt	Grätzelstr. 2	37079 GOTTINGEN	GERMANY	DL
Forest Research Institute	Terma Alkmanos	11528 ATHENS	GREECE	EL
Forest Management Service	Szechenyi u. 14	1055 BUDAPEST	HUNGARY	HU
Coillte Teoranta Irish Forestry Board Research Division	Sidmonton Place 1-3	BRAY COUNTY WICKLOW	IRELAND	IR
Instituto Sperimentale della Nutrizione Delle Piante	Via Della Navicella 2	00100 ROMA	ITALY	IT
Lithuanian Forest Research Institute Forest Soil Laboratory	Kaunas Distr.	4312 GIRIONYS	LITHUANIA	LI
Staring Centrum	Postbox 125	6700 AC-WAGENINGEN	NETHERLANDS	NL
Norwegian Institute of Land Inventory	Radhuspl. 29, Box 115	1430 AS	NORWAY	NO
Laboratorio Quimico Agricola Rebelo da Silva	Tapada da Ajuda, Apartado 3228	1306 LISBOA	PORTUGAL	PO
Forest Research Institute	Masaryka Street 22	96092 ZVOLEN	SLOVAKIA	SR
Forestry Institute	Vecna Pot 2, p.p.523-X	61000 LJUBLJANA	SLOVENIA	SL
Area de Conservacion Del Medio Natural CIT-INIA	Apartado de Correos 8.111	28080 MADRID	SPAIN	ES
WSL/FNP	Zürcherstrasse 111	8903 BIRMENSDORF	SWITZERLAND	CH
Ecology Laboratory	*Pushkinskaya 86*	*310024 KHARKOV*	*UKRAINE*	*UR*
Environmental Research Branch Forest Research Station	Alice Holt Lodge Farnham	SURREY GU10 4 LH	UNITED KINGDOM	UK

A.4. Description of Soil Analysis Methods

The methods used to analyse the standard samples, which are identical to those applied in the national inventories, vary substantially between laboratories. In the following section, the reference analysis methods of the inventory (UN/ECE, 1994) are framed within the range of methods described in the literature. Special attention is given to the effect of the various analytical procedures on the obtained results. For each parameter or group of parameters, a short description of all methods actually applied by the national laboratories is given. For a detailed method description, we refer to the national reports. In view of the aim to statistically analyse the intercalibration results, an effort is made to introduce a logical method numbering. Results obtained with similar methods are grouped together and as such presented in tables and graphs (see section A.6).

pH

Soil pH is measured in an aqueous matrix such as water or a diluted salt solution. For soils with low electrical conductivity, such as many forest soils, pH measured in water is the closest to the pH of soil solution in the field. The addition of salt does lower the pH by about 0.5 pH units compared to soil pH in water due to the displacement of hydrogen and aluminium ions from the exchange sites (Peech, 1965). The pH decrease, resulting from the addition of salt, is dependent on the concentration of the salt solution. In extremely weathered soils, such as Ferralsols with *Geric* properties **(FAO,** 1988), where the pH is below the zero point charge, the addition of salt to a solution will increase the pH (Bohn et al., 1979).

Method 1 : Reference method. 0.01M $CaCl_2$ (1:5).
The pH of the soil is potentiometrically measured in the supernatant suspension of a 1:5 soil:liquid ($CaCl_2$ 0.01M) mixture. For H and O horizons, use a 1:20 soil:liquid fraction. Take 20 g sample into a 200 ml bottle. Add 100 ml $CaCl_2$ solution and cap the bottle. Shake for *2* hours. Calibrate the pH meter with buffer solutions (pH 7 and pH 4).Before opening the bottles for measurement, shake by hand. Immerse electrode(s) in upper part of the suspension. Read pH when reading has stabilised.
(country codes FR, BEf, BEw, NL, IT, UK, IR, EL, PO, LX, AU, FI, SR, CH, HU, LI, CR, SL, BU)

> country code CZ, UR : The sample is soaked in a 0.01M $CaCl_2$ solution in the ratio 1:5 (V:V) and mixed. The pH is potentiometrically measured in the supernatant suspension.
>
> **Method 1.1** : 0.01M $CaCl_2$ (1:2.5).
>
> country code DK, NO : The pH of the soil is potentiometrically measured in the supernatant suspension of a soilliquid ($CaCl_2$ 0.01M) mixture (1:2.5).

Method 2 : 1M KCl
(country code ET, BL)

> country code DL : The sample is mixed with a 1M KCl solution in the ratio 1:2.5 (V:V). The mixture is stirred *5* times during 4 hours and then the pH is potentiometrically measured in the supernatant suspension.

Organic Carbon

The methods available for the determination of organic carbon (Org. C) operate on one of three principles (Tiessen and Moir, 1993):

- Wet oxidation of Org. C in an acid dichromate solution followed by back titration of the remaining dichromate with ferrous ammonium sulphate and a suitable indicator, or by photometric determination of Cr^{III}.
- Wet oxidation of Org. C in an acid dichromate solution, and collection and determination of the evolved CO_2. If no pre-treatment of calcareous soils is used, carbonates dissolved by the acid medium will be included in the CO_2 determination to give a measure of total C.
- Dry oxidation of Org. C in a furnace, followed by direct determination or collection and determination of the evolved CO_2. At high furnace temperatures, carbonates will also decompose, giving a measure of total C.

Dichromate redox methods suffer from a number of interferences and low Org. C recoveries. In the method described by Walkley and Black (1934) oxidation is incomplete due to the low temperature(≈ 120°C) reached and a correction factor is required. Oxidation can be easily improved by heating on a hot plate or block digester. However, the acid dichromate digestion solution decomposes at temperatures above 150°C, limiting the temperature that can be employed. The reduction of dichromate is also affected by the presence of other redox-active components of the soil (Tiessen and Moir, 1993). The presence of Fe^{2+}, Mn^{2+} and Cl^- causes an overestimation of soil Org. C, since all three are oxidised during the digestion. Higher oxides of Mn, uncommon in free form in soils, cause an underestimation of Org. C. An additional problem is presented by the often low visibility of the colour change during back titration. Despite the difficulties and inaccuracies, the dichromate redox method is widely used because it requires a minimum of equipment and it is suitable for comparative work.

When wet oxidation of Org. C in an acid dichromate is followed by collection and determination of the evolved CO_2, many of the interferences of the titrimetric method are eliminated, and digestion temperatures can be raised above 150°C.

Several options are available for the dry combustion of Org. C in a furnace. The methods using a resistance furnace and collection of evolved CO_2 in NaOH, followed by back titration of the NaOH, suffer from a few inconveniences. When combustion temperatures below 500°C are employed in order to allow the determination of Org. C in the presence of carbonates, some humic materials may resist combustion. The use of a stream of O_2 in the furnace at a temperature of 900°C provides for near complete combustion of Org. C. Addition of MnO_2 and CuO as catalysts converts any evolved CO to CO_2. Samples containing carbonates, however, must be pre-treated with acid, since the high temperature will otherwise give a measure of total C. A problem with combustion at high temperature is the formation of hairline cracks in the ceramic tube of the furnace, causing leaks and low CO_2 recoveries.

Method 1 : Reference method. Dry combustion at temperatures > 900°C.
(country codes FR, BEf, BEw, NL, DL, IT, DK, ES, LX, AU, FI, NO, CH, HU, LI, SL, UR)

Method 2 : Dry combustion at temperatures < 500°C.
The organic matter content is determined by measuring the weight loss after heating the sample to 450°C.

countrv code UK : 5.000 g of sample is oven-dried at 105-110°C for 2 hours, cooled to room temperature in the desiccator and weighed. The sample is then heated to 450 ± 25°C for 6 hours, allowed to cool again in the desiccator and weighed.

Method 3 : Wet oxidation (Walkley and Black).
Oxidation of the organic matter by $K_2Cr_2O_7$ (1 N) in the presence of concentrated H_2SO_4. The excess $K_2Cr_2O_7$ is titrated against $FeSO_4$ (0.5 N) with diphenylamine as indicator.
(country codes IR, PO)

countrv code EL : 0.1 to 0.5 g of sample is mixed with 10 ml $K_2Cr_2O_7$ and 20 ml concentrated H_2SO_4 and left at room temperature for 30 minutes. Then 200 ml H_2O, 10 ml concentrated H_3PO_4, 1 g NaF and 20-30 drops of phenolphthalein indicator is added. Titration with 0.5 N $FeSO_4$ solution.

Method 4 : Wet oxidation (Tjurin).
The organic C is oxidised with a dichromate solution (0.4 N) in the presence of concentrated H_2SO_4. The excess of dichromate is titrated against a 0.2 N ferrous ammonium sulphate solution.
(country code SR)

countrv code CR : 0.1 to 0.5 g of sample is mixed with 10 ml of dichromate solution (1:1 mixture of 0.4 N $K_2Cr_2O_7$ and concentrated H_2SO_4) and 0.1 g Ag_2SO_4. After boiling for 5 minutes and cooling, 2 ml of acid mixture (H_3PO_4:H_2SO_4:H_2O - 3:3:14) and 8 drops of diphenylaminesulphonic acid barium acid redox indicator (0.2 g $C_{24}H_{20}BaN_2O_6S_2$ dissolved in 100 ml distilled water) is added. Titration with 0.1 N Mohr salt solution (39.22 g $FeSO_4(NH_4)_2SO_4.6H_2O$ dissolved in 1000 ml water and 20 ml concentrated H_2SO_4) until the colour of the solution turns green.

countrv code BU : Weigh 0.2 g of organic *or* 0.4 g of mineral soil sample into a 100 ml volumetric flask. Add 75 (organic layers) or 45 (mineral layers) ml mixture solution (40 g dichromate dissolved in 900 ml H_2O, add carefully 1000 ml H_2SO_4 are and make to volume with H_2O to 2000 ml). Place in oven at 125°C for 45 minutes. After cooling make to volume (100 ml) and pipette 25 ml for titration. Add 3 (organic layers) or 2 (mineral layers) ml KI (20%) solution and titrate with 0.2 N $Na_2S_2O_3$ until the brown colour disappears. Add 2 ml starch solution (1 g starch and 250 ml hot water) turning the solution violet. Titrate again with 0.2 N $Na_2S_2O_3$ until the colour turns green.

Method 4.1 : Wet oxidation (Tjurin), colorimetrical measurement.
The organic C is oxidised with a dichromate solution in the presence of concentrated H_2SO_4.

countrv code ET : The final measuring is done colorimetrically.

Method *5* : Wet oxidation (Springer and Klee).
Oxidation of the organic matter by $K_2Cr_2O_7$ in the presence of concentrated H_2SO_4. Oxidation is assisted by heating to maximum 160°C. The excess $K_2Cr_2O_7$ is titrated against $FeSO_4$ or $Na_2S_2O_3$.

country code FR : Organic C in organic layer samples are determined by dry combustion (method 1), mineral soil samples by sulphochromic oxidation. The sample is oxidised in a $K_2Cr_2O_7$ - H_2SO_4 solution heated at 135°C for 30 minutes. Cr^{3+} formed is determined by colorimetry.

country code CZ : To 0.4 g of sample 15 ml of sulphochromic mixture (500 ml 0.8 N $K_2Cr_2O_7$ + 500 ml concentrated H_2SO_4) is added. The whole is dried at 125°C for 45 minutes. The residue is titrated against 0.2 N $Na_2S_2O_3$ until the colour turns green.

Calcium Carbonate

Quantitative determination of soil carbonate minerals commonly is done by acidifying the soil and measuring the amount of CO_2 evolved. The procedures normally make no distinction between the various carbonate minerals, but express the carbonate content as the calcium carbonate equivalent (Doner and Lynn, 1989). The most common methods used are:

- Gravimetric method. A pre-weighed soil sample containing carbonates is reacted with a strong acid. The resultant loss in weight from CO_2 released permits a measurement of inorganic C from carbonates.
- Volumetric method. The pressure of the CO_2 vapour released in the reaction of the sample with the strong acid is used to displace a water column. The volume of displaced water is calibrated against the carbonate content.
- Titration method. The sample is treated with a diluted acid and the residual acid, not neutralised by carbonates, is titrated.

An accurate quantitative gravimetric measurement of carbonate content requires the elimination of the loss of water vapour evolved with CO_2. This is achieved by connecting a trap containing anhydrone ($Mg(ClO_4)_2$) to the flask where the reaction is taking place (Tee Boon Goh et al., 1993).

The apparatus used to measure the water displacement in the volumetric method is termed a calcimeter. Because the solubility of CO_2 in the acid varies with temperature, more accurate results are obtained by calibrating each calcimeter under the conditions of use (Allison and Moodie, 1965). When dolomite is present, the decomposition time must be considerably extended.

The titration method tends to overestimate the $CaCO_3$ equivalent because some non-carbonate components of the soil may react with the acid. The error can be relatively high at very low carbonate contents (< 10 g/kg) (ISRIC, 1987). The accuracy in this range is rather low for most methods.

The accuracy of these methods can be improved by addition of an antioxidant, such as $SnCl_2$ or $FeSO_4$, to the acid (Allison and Moodie, 1965). These conditions decrease the tendency for CO_2 to evolve from soil organic matter, in part from decarboxylation reactions and in part from an oxidation induced by reaction between the acid and any MnO_2 present in the soil. The error resulting from the release of CO_2 from organic matter is kept to a minimum by using the shortest possible reaction time.

Reference method: Volumetric method

Take a sample amount of 0.25 to 10 g, according to the predicted $CaCO_3$ content. Bring the sample in the reaction vessel, place a tube with 10 ml of hydrochloric acid (1/1) in the vessel and close the calcimeter system. Mix the hydrochloric acid with the sample by shaking the reaction vessel. Follow and equilibrate permanently the height of the water column with the ampoule of the calcimeter. Read the volume of displaced water when no further change occurs in the liquid level.

The calcimeter is calibrated with samples of 0.050g, 0.100g, 0.150g and 0.200g of calcium carbonate. The calibration curve allows the conversion of the volume displaced water into the amount of $CaCO_3$ in the sample.

Both standard samples were carbonate-free.

Total Nitrogen

Two categories of total N analysis are recognised (McGill and Figueiredo, 1993):

- Wet oxidation techniques, such as the Kjeldahl method, involve conversion of organic and inorganic N to NH_4^+ and its subsequent measurement.
- Dry combustion normally involves an initial oxidation step followed by passage of the gases through a reduction furnace to reduce NO, to N_2. The quantity of N is normally determined using a thermal conductivity detector.

In the Kjeldahl method, the N in the sample is converted to ammonium by digestion with concentrated H_2SO_4. The ammonium is determined from the amount of NH3 liberated by distillation of the digest with alkali (Bremner, 1965).

Kjeldahl procedures are the most widely used and continue to be modified, in particular to revise the digestion of nitrates and ammonium. Because the Kjeldahl digestion includes some, but not all, NO, modifications using reductants for NO_3^- and NO; have been proposed. In soils with a high proportion of their N as fixed NH_4^+, not all of the ammonium is quantitatively measured, unless a pre-treatment with HF-HCl is applied to destroy the clay minerals. Selection of the combination of variables for the Kjeldahl method is often based **on** local requirements and facilities. Digestion **options** include: addition of H_2SO_4 **or** H_2O_2; heating mantles **or** digestion blocks; macro- **or** semi-micro digestion; inclusion **or** omission of NO; plus NO; Subsequent measurement of NH_4^+ may use the Berthelot reaction, NH_4^+ electrode, diffusion, steam distillation, macro- **or** semi-micro distillation **or** titration (McGill and Figueiredo, 1993). The various methods for direct determination of ammonium in Kjeldahl digests have been proposed, but the determination involving distillation of the digest is more reliable and accurate (Bremner, 1965).

Combustion techniques can be performed manually in sealed tubes **or** with automated analytical instruments using helium carrier gas. In the classical Dumas method of determining N, the sample is heated with copper oxide at a high temperature (usually above 600°C) in a stream of purified CO_2. The gases liberated are led over hot Cu to reduce nitrogen oxides to N_2, and then over copper dioxide to oxidise CO to CO_2 (Bremner, 1965). The automated dry combustion method includes all forms of N without lengthy pre-treatments (McGill and Figueiredo, 1993). Sample variability is a concern with combustion techniques because of the small sample size required. Total N results obtained by instrumentation that secures complete dry combustion may be significantly higher than those obtained by the Kjeldahl procedure (Bremner, 1965).

Method 1 : Reference method. Dry combustion.
(country codes FR, BEw, DL, IT, DK, ES, LX, FI, SR, NO, CH, HU, SL)

Method 2 : Wet oxidation (Kjeldahl) followed by steam distillation.
The nitrogen in the sample is converted to ammonium bonded compounds, such as $(NH_4)_2SO_4$, by wet digestion with concentrated H_2SO_4 in the presence of a catalyst (K_2SO_4 **or** Na_2SO_4 + $CuSO_4$ + Se). After **5** hours digestion at a temperature of maximum 380°C, the digest is made alkaline by adding NaOH and then distilled by steam, trapping the evolved ammonia in H_3BO_3. The distillate is titrated with 0.01M H_2SO_4 or HCl until pH 5.4 is reached.
(country code AU, Ll, CR, ET, BL)

countrv code BEf : To 250 mg of sample 1 g of catalyst ($NaSO_4$:$CuSO_4$:Se - 190:3:4) and 10 ml of concentrated mixture of sulphuric and salicylic acid (50 g C_6H_4OH-COOH dissolved in 1 l concentrated H_2SO_4) is added. The temperature is slowly raised until a clear liquid remains. Boil for another 15 minutes. After cooling, the solution is diluted with 30 ml H_2O and 45 ml NaOH (40%) is slowly added. Distillation during 15 minutes. The distillate is intercepted in 10 ml H_3BO_3 (10%) and titrated with 0.05 N HCl using a colour indicator (0.15 g bromocresol green + 0.10 g methyl red dissolved in 200 ml ethanol 96%).

country code NL : Exactly 5.000 g of sample (2.000 g for humus samples) is mixed with 15 ml of phenol-sulphuric acid mixture (400 g phenol dissolved in 4 l of concentrated H_2SO_4) and one half hour later with 6g of catalyst (Na_2SO_4:$CuSO_4$.H_2O:Se - 190:3:2). During destruction (1.5 hour), assisted by an additional 20 ml of concentrated H_2SO_4, the reaction bottle is regularly overturned. To the solution, separated from the residue, 125 ml 12.5 N NaOH is added. During distillation, the evolved ammonia is trapped in 50 ml of a 1%H_3BO_3 solution with **bromocresol** green indicator. The distillate is titrated against 0.1142 N H_2SO_4 until the green colour changes to blue.

countrv code UK : 2g of air dry soil is folded into a pellet with N-free paper. The pellet is dropped in a digestion tube to which 1 catalyst tablet (1g K_2SO_4, 0.03g $CuSO_4$, 0.03g TiO_2), 10 ml of concentrated H_2SO_4 and 10 ml of 30% H_2O_2 is added slowly. The temperature is controlled in a 4 phase procedure: (1) desiccation at 220°C for 20 min., (2) digestion at 380°C for 40 min, (3) reheating at 380°C for 60 min and (4) cooling to 40°C during 20 min. In the mean time a water jet pump prevents fumes escaping from the digestion tubes. Once fuming has subsided, the tubes are removed for distillation with a Gerhardt Vapodest apparatus. The digestion solution is first made alkaline by adding 25 ml of 50% NaOH for every **5** ml of remaining acid. Distillation during 12 minutes. The distillate is intercepted in an erlenmeyer flask placed beneath the condenser containing 50 ml boric acid solution (3% H_3BO_3) plus indicator mixture (1000:7.5). The indicator solution contains 140mg Bromocresol Green dissolved in 5 ml alcohol, 4 ml 0.1 N NaOH, 8.8 ml of 1%water-soluble new-coccin solution and 300 mg P-Nitrophenol dissolved in 2 ml alcohol, which is diluted to 100 ml. Titration of the distillate with 0.02 N HCl, using phenolphthalein as colour indicator.

countrv code EL : 30 ml concentrated H_2SO_4 and 20 ml H_2O is added to the mixture of catalyst (K_2SO_4 + $CuSO_4$ + Se) and soil sample.

countrv code PO : 1 g of catalyst ($NaSO_4$:$CuSO_4$:Se - 100:10:1) and 8 ml concentrated H_2SO_4 is added to the soil sample.

Method 3 : Wet oxidation (Kjeldahl) without steam distillation.
The nitrogen in the sample is converted to ammonium bonded compounds, such as $(NH_4)_2SO_4$, by wet digestion with concentrated H_2SO_4 in the presence of a catalyst (K_2SO_4 or Na_2SO_4 + $CuSO_4$ + Se) and mineralisation at a temperature of maximum 370°C.

countrv code FR : Total N in organic layer samples is determined by dry combustion (method 1), mineral soil samples by wet oxidation. Extraction in sulphuric acid (H_2SO_4) with a Se catalyst at 350°C for 2 hours. NH_4 formed is determined by colorimetry on a segmented flow analyser.

countrv code CZ : To 0.4 g of mineral soil sample 0.2 g of catalyst (K_2SO_4 or Na_2SO_4 + $CuSO_4$ + Se - 16:4:1) and 5 ml of H_2SO_4 is added. The solution is mixed up. After mineralisation at 370°C the mixture is diluted to 75ml. The N concentration is measured by spectrophotometry. For humus samples, 0.15 g of sample is mixed with 0.05-0.1 g of powder Se, 5 ml of H_2SO_4 and 1.5 ml of H_2O_2 (30%). Temperature is raised until 200°C during the first hour, then till 370°C for another hour. Dilution and measurement are done as for mineral soil samples.

Method 3.1 : Wet oxidation (Modified Kjeldahl) without steam distillation.

countrv code IR : The sample is wet-ashed in concentrated H_2SO_4 at a ratio 1:10 (M:V). Oxidation is assisted by addition of 30% H_2O_2 and heating to maximum 200°C. Any nitrogen present is converted to $(NH_4)_2SO_4$. N is determined colorimetrically.

Element Analysis

Total element analysis requires a complete destruction of both organic and mineral fraction of the soil matrix. The two main decomposition methods are:

- Acid decomposition: samples are digested in concentrated strong acids or combinations of them to convert elements to soluble forms.
- Dry-ashing: decomposition by fusion at medium temperature results in a melt which can then be dissolved in water or acid to give a solution containing the constituent elements.

Total analysis is often used for a mineralogical characterisation of a soil. It is not very useful in characterising a soil as a medium for plant growth because unavailable forms of macro- and micronutrients make up an appreciable part of the total amount of these elements in the soil (Heald, 1965). However, few of the wide range of decomposition methods available cause complete dissolution of all types of minerals (Bain and Smith, 1987).

Strong acid extractants are generally used to determine so-called "total" element concentrations, although they mostly leave a residue of silicate minerals. Complete decomposition of both organic and mineral materials, including siliceous materials present in the soil, is achieved when the extracting solution contains concentrated hydrofluoric acid (Karam, 1993). Unless HF is used to dissolve also the silicate residue, the acid decomposition methods give a measure of the amounts present in relatively soluble mineral and organic forms, i.e. potentially available for natural leaching and biological processes. Elements added to soils as non-silicates from industrial sources, are also determined (Soon and Abboud, 1993).

Concentrated HNO_3 (Soon and Abboud, 1993), aqua regia (Cottenie et al., 1982) and many other combinations of concentrated acids have been used to determine "total" element concentrations in soils. A complete dissolution of the organic material is also achieved with HNO_3-$HClO_4$ (Mathur et al., 1980) and H_2O_2-$HClO_4$-H_2SO_4 oxidative mixtures (Van Lierop, 1976). Aqua regia-HF digestion for 1 hour at 100°C is a rapid and reasonably precise total element analysis method that also includes metals trapped within the crystal lattice (Soon and Abboud, 1993).

During the acid decomposition process mineral salts are formed together with oxidation products of the organic matrix (CO_2, H_2O, NO, NO_2, SO_2). In open digestion systems, these gaseous products may escape and the organic compounds are completely removed. Losses of metals by volatilisation is minimised by using low working temperatures. When digestion takes place under pressure, as in the Teflon-lined bombs, the organic matrix is solubilised. This approach allows rapid decomposition of the sample without loss by volatilisation, but may cause difficulties during measurement of dissolved trace metals (Cottenie et al., 1982). In the reagent mixture, the oxidising agent (HNO_3, $HClO_3$, $HClO_4$, HF, H_2O_2) takes the major part followed by solvents or neutralising agents (HCl, H_2SO_4, H_2O). Catalysts are sometimes added in small amounts. HNO_3 can be obtained as a very pure reagent, while HCI, H_2SO_4 and $HClO_4$ generally contain greater amounts of contaminating elements that may falsify the results (Cottenie et al., 1982).

In the dry-ashing procedure, the soil material is ignited in a furnace at medium temperature (400-550°C) to oxidise organic matter and the ions are usually extracted from the ash with acid solutions. The dry-ashing method is simpler, faster and more economical than wet digestion (Ali et al., 1988). Wet digestion in concentrated acids is somewhat more accurate and rapid (Karam, 1993). The main problem during ashing is the risk of loosing volatile elements, such as Hg, Pb *of* Cd at higher temperatures. However, it has been shown that in organic materials ashed at 450-500°C the losses of most trace elements including Pb and Cd are minimised (Cottenie et al., 1982).

The most common analytical techniques to quantify the concentration of dissolved elements are inductively coupled plasma (ICP), atomic absorption spectrometry (AAS) and flame emission spectrometry (FES). Conventional spectrometry techniques (AAS , FES) have the disadvantage of being single element techniques, but the advantage of easy sample presentation and low cost.

Phosphorus

> *Note: In some procedures under method 3 the mixture of acids and soil is heated in a digestion block. Block temperature is much higher than the solution tempemture. Block heating to ± 170°C is assumed similar to boiling.*

Method 1 : Reference method. Aqua Regia Extraction.
The soil is treated with a mixture of concentrated HCl, HNO_3 and H_2O_2 (3:1:2). The mixture is boiled for 2 hours. After cooling to room temperature, the solution is filtered. The residue is rinsed **5** times with 1M nitric acid. P is measured by AAS, **FES** or ICP spectrophotometry.
(country codes BEf, BEw, IT, DK, PO, LX, FI, SR, HU, CR, CZ, BL, UR)

Method 2 : Extraction in diluted acid (heated near boiling temperature).
country code CH : Extraction with 2M HNO_3. 5 g of sample is digested in a 50 ml solution of 2M HNO_3. The solution is kept at boiling temperature for 2 hours on a sandbath. The element is determined with ICP-AES.

Method 3 : Extraction in concentrated acid (heated near boiling temperature).
country code DL : Extraction in concentrated HNO_3. The sample is digested with HNO_3 under pressure. 100-200 mg of the sample is mixed with 2 ml of concentrated HNO_3. This is heated up slowly to 170°C for 10 hours overnight. After cooling down the digestion solution is filtered to glass funnels. In the digestion solution the elements are measured directly with ICP and/or AAS (flame *of* graphite furnace). P is measured with ICP.
country code UK : Extraction in aqua regia. 0.5 g of sample is moistened with 1ml deionised water and then mixed with 15 ml HCl and 5 ml HNO_3. The mixture of acids and soil is left at least 2 hours to effect initial oxidation. Then 4 ml H_2O_2 is added in 1 ml aliquots while foaming is prevented. An hour later, the tubes are entered in a digestion block where the temperature is first raised to 110°C for 30 minutes and then to 170°C for 2 hours. After cooling to about 40°C the sides of the tubes are washed down with as little as possible 1M HNO_3 and then the solution is reheated to 175°C for 30 minutes. When the tubes have cooled to room temperature the contents are filtered and washed with 1M HNO_3. Phosphorus is measured using ICP-optical emission spectroscopy techniques.
country code IR : Extraction in concentrated H_2SO_4. The sample is wet-ashed in concentrated H_2SO_4 at a ratio 1:10 (M:V). Oxidation is assisted by addition of 30% H_2O_2 and by heating to maximum 200°C. Any phosphorous present is converted to H_3PO_4. Phosphorous forms are determined colorimetrically.
country code **ES** : Mineralisation in concentrated HNO_3: and HCl in a microwave oven. 0.2 g of soil sample is first digested in 3 ml 63.01M HNO_3. In a second phase 2 ml concentrated HCl and 0.5 ml H_2O_2 are added. The extract is filtered and diluted with 1 N HNO_3 to 50 ml. P is measured by ICP in the filtrate.
country code AU : Extraction in concentrated HNO_3 and $HClO_4$ (five parts HNO_3 and one part $HClO_4$).
country code SL : Extraction in concentrated HNO_3 and $HClO_4$. 20 ml of acid mixture (HNO_3:$HClO_4$ - 5:1) is added to 2g of sample and boiled for 2 hours. Allow to cool slowly to about 50°C, add 20 ml H_2O and boil

gently for another 15 minutes. After cooling to room temperature, dilution with deionised water and filtering, P is measured in the filtrate colorimetrically.

country code BU : Extraction in concentrated $HClO_4$ and HNO_3. To 1 g of sample 10 ml acid mixture (70% nitric and 72% perchloric acid, 1:3 V:V) is added. Heat at 180-190°C **on** a sandbath until nearly dry. Add 10 ml 0.1 N HCI and heat again until vapours appear. Filter the sample cold and make to volume (50 ml) with deionised water. P is determined by UV-VIS spectrophotometer.

Method 4 : Wet digestion in concentrated acid (heated above boiling temperature).

country code **NL** : Wet digestion in a mixture of concentrated sulphuric acid and nitric acid. 2-5 g of sample is mixed with **5** ml H_2SO_4 and **5** ml HNO_3. The samples are digested in a heating block at 350°C until white fumes are formed. After cooling for 1 minute, 1 ml HNO_3 is added and the mixture is again heated until fumes appear. This procedure is at least 3 times repeated. The mixture is boiled for 10 minutes (block temperature at 140°C), cooled to room temperature, 20 ml H_2O is added and it is finally boiled again for 10 minutes. After cooling to room temperature the solution is filtered and diluted with H_2O. Phosphorus is determined by ICP spectrometry.

country code FI : Wet digestion in aqua regia. To 0.5-1.5g of sample 1 ml ion-exchanged water, 7.5 ml concentrated HCl and 2.5 ml concentrated HNO_3 is added in an open tube. Let it stay overnight. The samples are digested in an aluminium heating block without reflux. Raise temperature carefully, after the most violent foaming, to 200°C (100°C in tubes) for 1 hour. After cooling 5 ml of 30% H_2O_2 is added and temperature is raised till 300°C for 1.5 hours. After cooling the solution is filtered and the residue is washed with distilled water. P is determined by ICP spectrophotometry.

Method 5 : Dry ashing, followed by dissolution in concentrated acid.

country code FR : The dried and ground sample is ignited at 500°C for 4 hours. After cooling, concentrated hydrofluoric and perchloric acids are added to the material and evaporated to dryness. The residue is dissolved in hydrochloric acid and then diluted with water. P is determined by colorimetry of a phosphomolybdic complex.

country code EL : The sample is first dried at 105°C and subsequently heated to 500-550°C until constant weight is achieved (4 to **5** hours). The ash is dissolved in a HCI solution (1 ml H_2O + code 9.5 ml 20% HCl) and kept at boiling temperature. After filtering, P is determined in the solution with $(NH_4)_6 MO_7O_{24} . 4H_2O$ using $SnCl_2 . 2 H_2O$ **as** a reducing agent.

country code LI : After dry ashing and subsequent cooling, the sample is mixed with concentrated HCl (1:1).

country code ET : The sample is ignited at 400-450°C. After cooling it is mixed with a 25 % HCl solution. P is determined colorimetrically.

Potassium, Calcium, Magnesium and Sodium

Note: In some procedures under method 3 the mixture of acids and soil is heated in a digestion block. Block temperature is much higher than the solution temperature. Block heating to ± 170°C is assumed similar to boiling.

Method 1 : Reference method. Aqua Regia Extraction

The soil is treated with a mixture of concentrated HCl, HNO_3 and H_2O_2 (3:1:2). The mixture is boiled for 2 hours. After cooling to room temperature, the solution is filtered. The residue is rinsed 5 times with 1M nitric acid. The different elements are measured by AAS, FES or ICP.
(country codes BEf, BEw, IT, DK, PO, LX, FI, SR, HU, CR, CZ, BL, UR)

Method 2 : Extraction in diluted acid (heated near boiling temperature).

country code CH : Extraction in 2M HNO_3. **5** g of sample is digested in a 50 ml solution of 2M HNO_3. The solution is kept at boiling temperature for **2** hours **on** a sandbath. The elements are determined with ICP-AES.

Method 3 : Extraction in concentrated acid (heated near boiling temperature).

country code DL : Extraction in concentrated HNO_3. The sample is digested with HNO_3 under pressure. 100-200 mg of the sample is mixed with **2** ml of concentrated HNO_3. This is heated up slowly to 170°C for 10 hours overnight. After cooling the digestion solution is filtered to glass funnels. In the digestion solution K, Ca and Mg are measured directly with ICP.

country code UK : Extraction in aqua regia. 0.5 g of sample is moistened with 1ml deionised water and then mixed with 15 ml HCl and 5 ml HNO_3. The mixture of acids and soil is left at least 2 hours to effect initial oxidation. Then 4 ml H_2O_2 is added in 1 ml aliquots while foaming is prevented. An hour later, the tubes are entered in a digestion block where the temperature is first raised to 110°C for 30 minutes and then to 170°C for 2 hours. After cooling to about 40°C the sides of the tubes are washed down with as little as possible 1M HNO_3 and then the solution is reheated to 175°C for 30 minutes. When the tubes have cooled to room temperature the contents are filtered and washed with 1M HNO_3. The concentration of the different cations is measured using ICP-optical emission spectroscopy techniques.

country code IR : Extraction in concentrated H_2SO_4. The sample is wet-ashed in concentrated H_2SO_4 at a ratio 1:10 (M:V). Oxidation is assisted by addition of 30% H_2O_2 and by heating to maximum 200°C. Any K is converted to K_2SO_4, Ca to $CaSO_4$ and Mg to $MgSO_4$. The concentration of the different cations is determined by AAS.

country code EL : Extraction in concentrated $HClO_4$ and HNO_3. 5 ml concentrated HNO_3 and 5 ml $HClO_4$ are added to 1 g of sample and heated to 200-300°C on a hot plate until 2-3 ml of clear solution remains. The solution is filtered with water. Ca and Mg are determined by AAS, K by FES.

country code ES : Mineralisation in concentrated HNO_3: and HCl in a microwave oven. 0.2 g of soil sample is first digested in 3 ml 63.01M HNO_3. In a second phase 2 ml concentrated HCl and 0.5 ml H_2O_2 are added. The extract is filtered and diluted with 1 N HNO_3 to 50 ml. Ca and Mg are measured by ICP in the filtrate, K by AAS.

country code AU : Extraction in concentrated HNO_3 and $HClO_4$ (5 parts HNO_3 and 1 part $HClO_4$).

country code NO : Extraction in aqua regia and concentrated HCl. A 2 g sample is heated to 60°C in 20 ml aqua regia overnight, in an open system. The next day the sample is boiled for two hours. The cooling cap is then removed and the sample is evaporated to nearly dry. Concentrated HCl is added to dissolve the residue, which is then filtered. The different elements are measured in the filtrate by ICP.

country code SL : Extraction in concentrated HNO_3 and $HClO_4$. 20 ml of acid mixture (HNO_3:$HClO_4$ - 5:1) is added to 2g of sample and boiled for 2 hours. Allow to cool slowly to about 50°C, add 20 ml H_2O and boil gently for another 15 minutes. After cooling to room temperature, dilution with deionised water and filtering, the elements are measured in the filtrate; K by flame spectrophotometry, Ca and Mg by AAS.

country code BL : Extraction in HF.

country code BU : Extraction in concentrated $HClO_4$ and HNO_3. To 1 g of sample 10 ml acid mixture (70% nitric and 72% perchloric acid, 1:3 V:V) is added. Heat at 180-190°C on a sandbath until nearly dry. Add 10 ml 0.1 N HCl and heat again until vapours appear. Filter the sample cold and make to volume (50 ml) with deionised water. Determination of the elements by AAS.

Method 4 : Wet digestion in concentrated acid (heated above boiling temperature).

country code NL : Wet digestion in a mixture of concentrated sulphuric acid and nitric acid. 2-5 g of sample is mixed with 5 ml H_2SO_4 and 5 ml HNO_3. The samples are digested in a heating block at 350°C until white fumes are formed. After cooling for 1 minute, 1 ml HNO_3 is added and the mixture is again heated until fumes appear. This procedure is at least 3 times repeated. The mixture is boiled for 10 minutes (block temperature at 140°C), cooled to room temperature, 20 ml H_2O is added and it is finally boiled again for 10 minutes. After cooling to room temperature the solution is filtered and diluted with H_2O. Potassium, calcium, magnesium and sodium are determined by ICP spectrometry.

country code FI : Wet digestion in aqua regia. To 0.5-1.5g of sample 1 ml ion-exchanged water, 7.5 ml concentrated HCl and 2.5 ml concentrated HNO_3 is added in an open tube. Let it stay overnight. The samples are digested in an aluminium heating block without reflux. Raise temperature carefully, after the most violent foaming, to 200°C (100°C in tubes) for 1 hour. After cooling 5 ml of 30% H_2O_2 is added and temperature is raised till 300°C for 1.5 hours. After cooling the solution is filtered and the residue is washed with distilled water. Ca, Mg, K and Na are measured by ICP spectrophotometry.

Method 5 : Dry ashing, followed by dissolution in concentrated acid.

country code FR : The dried and ground sample is ignited at 500°C for 4 hours. After cooling, concentrated hydrofluoric and perchloric acids are added to the material and evaporated to dryness. The residue is dissolved in hydrochloric acid and then diluted with water. The element contents of the extract are determined using listed methods : Ca, Mg, FES, K : FAES.

country code LI : After dry ashing and subsequent cooling, the sample is mixed with concentrated HCl (1:1). K is determined by flame photometer, Ca and Mg by AAS.

country code ET : The sample is ignited at 400-450°C. After cooling it is mixed with a 25 % HCl solution. K is determined by flame photometer, Ca by titration.

Al, Fe, Cr, Ni, Mn, Zn, Cu, Pb and Cd

Note: In some procedures under method 3 the mixture of acids and soil is heated in a digestion block. Block temperature is much higher than the solution temperature. Block heating to ± 170°C is assumed similar to boiling.

Method 1 : Reference method. Aqua Regia Extraction
The soil is treated with a mixture of concentrated HCl, HNO_3 and H_2O_2 (3:1:2). The mixture is boiled for 2 hours. After cooling to room temperature, the solution is filtered. The residue is rinsed **5** times with 1M nitric acid. The different elements are measured by **AAS, FES,** ICP spectrophotometry.
(country codes BEw, DK, PO, LX, FI, SR, HU, CR, CZ)

Method 2 : Extraction in diluted acid (heated near boiling temperature).

country code ES : Extraction in 0.1M HCl.

country code CH : Extraction in 2M HNO_3. **5** g of sample is digested in a 50 ml solution of 2M HNO_3. The solution is kept at boiling temperature for 2 hours on a sandbath. The elements are determined with ICP-AES.

country code LI : Extraction in 2M HNO_3. The sample is treated with 1M HNO_3 (ratio 1:20). Fe, Cr, Ni, Mn, Zn, Cu, Pb and Cd are determined by AAS.

Method 3 : Extraction in concentrated acid (heated near boiling temperature).

country code DL : Extraction in concentrated HNO_3. The sample is digested with HNO_3 under pressure. 100-200 mg of the sample is mixed with 2 ml of concentrated HNO_3. This is heated up slowly to 170°C for 10 hours overnight. After cooling down the digestion solution is filtered to glass funnels. In the digestion solution Al, Fe and Zn are measured directly with ICP. Mn and Cu are measured with ICP *or* FES. Cd, Pb and sometimes Cu are determined by AAS with a graphite furnace.

country code UK : Extraction in aqua regia. 0.5 g of sample is moistened with 1ml deionised water and then mixed with 15 ml HCl and **5** ml HNO_3. The mixture of acids and soil is left at least 2 hours to effect initial oxidation. Then 4 ml H_2O_2 is added in 1 ml aliquots while foaming is prevented. An hour later, the tubes are entered in a digestion block where the temperature is first raised to 110°C for 30 minutes and then to 170°C for 2 hours. After cooling to about 40°C the sides of the tubes are washed down with as little as possible 1M HNO_3 and then the solution is reheated to 175°C for 30 minutes. When the tubes have cooled to room temperature the contents are filtered and washed with 1M HNO_3. The concentration of the different elements is measured using ICP-optical emission spectroscopy techniques.

country code AU : Extraction in concentrated HNO_3 and $HClO_4$ (**5** parts HNO_3 and 1 part $HClO_4$).

country code NO : Extraction in aqua regia and concentrated HCl. A 2 g sample is heated to 60°C in 20 ml aqua regia overnight, in an open system. The next day the sample is boiled for two hours. The cooling cap is then removed and the sample is evaporated to nearly dry. Concentrated HCl **is** added to dissolve the residue, which is then filtered. The different elements are measured in the filtrate by ICP, except for low levels of Cd, which are determined using a graphite furnace.

country code SL : Extraction in concentrated HNO_3 and $HClO_4$. 20 ml acid mixture (HNO_3:$HClO_4$ - 5:1) are added to 2g of sample and boiled for 2 hours. Allow to cool slowly to about 50°C, add 20 ml H_2O and boil gently for another 15 minutes. After cooling to room temperature, dilution with deionised water and filtering, Al, Fe, Mn and Zn are measured in the filtrate by AAS.

country code BL : Extraction in HF.

country code BU : Extraction in concentrated $HClO_4$ and HNO_3. To 1 g of sample 10 ml acid mixture (70% nitric and 72% perchloric acid, 1:3 V:V) is added. Heat at 180-190°C on a sandbath until nearly dry. Add 10 ml 0.1 N HCl and heat again until vapours appear. Filter the sample cold and make to volume (50 ml) with deionised water. Determination of the elements by AAS.

Method 4 : Wet digestion in concentrated acid (heated above boiling temperature).

country code **NL** : Wet digestion in a mixture of concentrated sulphuric acid and nitric acid. 2-5 g of sample is mixed with **5** ml H_2SO_4 and **5** ml HNO_3. The samples are digested in a heating block at 350°C until white fumes are formed. After cooling for 1 minute, 1 ml HNO_3 is added and the mixture is again heated until fumes appear. This procedure is at least 3 times repeated. The mixture is boiled for 10 minutes (block temperature at 140°C), cooled to room temperature, 20 ml H_2O is added and it is finally boiled again for 10 minutes. After cooling to room temperature the solution is filtered and diluted with H_2O. Al, Fe, Cr, Ni, Mn and Cu are determined by ICP spectrometry.

country code FI : Wet digestion in aqua regia. To 0.5-1.5g of sample 1 ml ion-exchanged water, 7.5 ml concentrated HCl and ***2.5*** ml concentrated HNO_3 **is** added in an open tube. Let it stay overnight. The samples are digested in an aluminium heating block without reflux. Raise temperature carefully, after the most violent foaming, to 200°C (100°C in tubes) for 1 hour. After cooling **5** ml of 30% H_2O_2 is added and temperature is raised till 300°C for 1.5 hours. After cooling the solution is filtered and the residue is washed with distilled water. Element concentrations are determined by ICP spectrophotometry.

Method 5 : Dry ashing, followed by dissolution in concentrated acid.

countrv code FR : Digestion with concentrated HF and $HClO_4$. The sample is ignited at 500°C for 4 hours. After cooling, concentrated hydrofluoric and perchloric acids are added to the material and evaporated to dryness. The residue is dissolved in hydrochloric acid and then diluted with water. Zn is measured in the solution by FES. Copper, Cd and Pb are determined by electrothermal AAS (graphite furnace).

countrv code LI : After dry ashing and subsequent cooling, the sample is mixed with concentrated HCI (1:1). Na is determined by flame photometer, Fe by AAS.

Cation Exchange Properties

The principle of the methods used to measure exchangeable cations is to saturate the exchange complex with some cation, termed index ion, that forces the cations already present on the charged surfaces to go into solution (Baize, 1993). Exchange capacity can then be calculated as the sum of displaced cations from the soil (summation method); or the index ion can be displaced with a concentrated solution of a different salt and the exchange capacity calculated as the amount of index ion displaced (displacement methods).

The measurement of CEC is complicated by:

- errors due to the dissolution of soluble salts, such as $CaCO_3$ and gypsum,
- specific adsorption of K and NH_4 in the interlayer position of phyllosilicates,
- specific adsorption of trivalent cations such as Al^{+3} and Fe^{+3} on the surface of soil particles.

In general, the errors can be reduced by using a method of CEC determination that employs reagents of similar concentration and pH to those of the soil to be analysed. Methods using relatively high concentrations of saturating and extracting solutions buffered at pH 7 or 8.2 are commonly used with agricultural soils providing a measurement that is independent of recent fertilisation and liming practices. For forest soils and in particular low-pH soils, it is often preferable to measure CEC at the pH of the soil, thus providing a more accurate measure of the exchangeable cations under field conditions (Hendershot et al., 1993). The CEC of acid forest soils is largely composed of pH-dependent charges. This is particularly true of soils whose colloidal fraction is composed of organic matter, 1:1 clay minerals and Fe and Al oxides. As a consequence, the actual CEC of those soils is much lower than that measured in neutral salt solutions (Pritchett and Fisher, 1987).

The $BaCl_2$ method provides a rapid means of determining the exchangeable cations and the "effective" CEC of a wide range of soil types. Barium is a good flocculant and is able to displace trivalent cations. The relatively low ionic strength of the equilibrating solution causes a small change in pH than do more concentrated salt solutions. The CEC is calculated as the sum of exchangeable cations, Ca, Mg, K, Na, AI, Fe, Mn and H (optional). In soils with large amounts of pH-dependant exchange sites the value measured at pH 7 will be considerably higher than that measured by this method. Problems may arise with saline soils containing very high levels of SO„ since $BaSO_4$ will precipitate.

Basic Exchangeable Cations

Basic exchangeable cations are defined as the alkali and alkaline earth metals (Ca, Mg, K and Na) attached to the clay and organic constituents of soils and which can be exchanged with each other and with other positively charged ions (Chapman, 1965).

Method 1 : Reference method. Extraction with unbuffered 0.1M $BaCl_2$.
In the 0.1M $BaCl_2$ solution the exchangeable cations are measured. Place 2 g of sample plus 20 ml of 0.1M bariumchloride in a 30 ml plastic centrifuge tube and shake for 2 hours. Centrifuge and retain the supernatant solution for analysis. The base cations (Ca, Mg, K, Na) are measured by AAS, FES or ICP.
(country codes BEf, BEw, PO, LX, SR, HU, CZ, BL)

countrv code IR, FI : The sample is soaked in the unbuffered solution (1:10 V:V), rotated and filtered. The basic cations are measured in the filtrate by ICP spectrophotometry.

Method 1.8 : Na is not determined.

country code FR, **AU**, SL : Identical procedure as for method 1, except that exchangeable Na is not determined.

<u>Method 2</u> : Extraction with a diluted unbuffered salt (not 0.1M $BaCl_2$) solution (< 1 N).

<u>country code **NL**</u> : Extraction with unbuffered 0.01M AgTU. The AgTU solution is formed by mixing 3.4g $AgNO_3$ and 15.2g thiourea (CH_4N_2S) in 2 litre H_2O. Dependant on the estimated CEC value 0.5 to 10 g of sample is mixed with 50 ml AgTU. The exchangeable cations are extracted in the 0.01M solution during four hours of shaking. Ca, Mg, K and Na are determined by ICP directly in the extract. Exchangeable NH_4 contents are extracted with 1M KCl and measured with a colorimetric technique (flow injection analyser).

<u>Method 2.1</u> : Extraction with unbuffered 0.1M HCl, followed by titration to pH 8.2.

<u>country code ET</u> : The sum of base cations is determined by titration of the 0.1M HCl extract with 0.1M NaOH to pH 8.2.

<u>Method 3</u> : Extraction with an unbuffered salt solution (2 1 N).

<u>country code DL</u> : Extraction with unbuffered 1M NH_4Cl. 2.5 of the soil sample is soaked with a few ml NH_4Cl (1M) solution over night. The next morning 100 ml of the NH_4Cl solution is slowly percolated through the sample during 4-5 hours. The cations (Ca, Mg, Na, K) are measured directly in the percolate by AAS.

<u>country code NO</u> : Extraction with unbuffered 1M NH_4NO_3. 10 **g** of mineral soil sample or ***2.5*** g of organic sample are soaked in 50 ml 1M NH_4NO_3, stirred, stored overnight, stirred again and then filtered. Washing is done with 1M NH_4NO_3. Ca, Mg, K and Na are determined in the extract by ICP.

<u>country code CH</u> : Extraction with unbuffered 1M NH_4Cl. To 5 **g** of sample an unbuffered solution of 50 ml NH_4Cl (1M) is added. After 1 hour of shaking the cations (Ca, Mg, K, Na) are determined by ICP-AES in the filtrate.

<u>country code UR</u> : Extraction with unbuffered 1M CH_3COONa.

<u>Method 4</u> : Extraction with a salt solution buffered at pH > 7.

<u>country code BU</u> : Extraction with a 1M CH_3COONa and 0.2M K-maleinate mixture buffered at pH 8.25. The filtrate is titrated with 0.04M NaOH for the determination of total acidity and then back titrated with 0.04 N EDTA for exchangeable Ca and Mg.

Acid Exchangeable Cations

The soil is leached with a relatively diluted solution of $BaCl_2$ at soil pH, resulting in the replacement of acid cations, mostly Al and H ions, from the exchange sites. Methods using a buffered solution usually measure lower amounts of exchangeable acid cations, due to the high pH of the extracting solution. Iron and manganese may be quite abundant in some acid soils.

<u>Method 1</u> : Reference method. Extraction with unbuffered 0.1M $BaCl_2$.
In the 0.1M $BaCl_2$ solution the exchangeable cations are measured. Place **2 g** of sample plus 20ml of 0.1M bariumchloride in a 30 ml plastic centrifuge tube and shake for 2 hours. Centrifuge and retain the supernatant solution for analysis.
(country codes FI, HU)

<u>Method 1.1</u> : H is determined by the "German" method

<u>country codes AU. SL. BL</u> : After centrifugation, the acid cations are measured in the supernatant solution:
Al, Fe and Mn by AAS or ICP.
H by the "German" method; based on the difference in pH before and after extraction.

<u>Method 1.2</u> : H is determined by titration of the 0.1M $BaCl_2$ extract.
After centrifugation, the acid cations are measured in the supernatant solution:
Al, Fe and Mn by AAS or ICP.
H by titration of the 0.1M $BaCl_2$ extract.

<u>Method 1.3</u> : H is determined by titration of the 1M KCl extract.

<u>country code SR</u> : After centrifugation, the acid cations are measured in the supernatant solution:
Al, Fe and Mn by AAS or ICP.
H by titration of the 1M KCl extract.

<u>Method 1.7</u> : H is not determined.

<u>country code IR, CZ. FI</u> : The sample is soaked in the unbuffered solution (1:10 M:V), rotated and filtered. The acid cations are measured in the filtrate.
Al, Fe and Mn by ICP spectrophotometry

<u>Method 1.9</u> : Fe is not determined.

<u>country code FR</u> : cf. method 1.2, except that Fe is not measured.

<u>Method 2</u> : Extraction with a diluted unbuffered salt (not 0.1M $BaCl_2$) solution (< 1 N).

<u>country code **NL**</u> : Extraction with unbuffered 0.01M AgTU. The AgTU solution is formed by mixing 3.4g $AgNO_3$ and 15.2g thiourea (CH_4N_2S) in 2 litre H_2O. Dependant on the estimated CEC value 0.5 to 10 g of sample is mixed with 50 ml AgTU. The exchangeable cations are extracted in the 0.01M solution during four hours of shaking. ACE is calculated as the difference between CEC and BCE.

<u>Method 3</u> : Extraction with an unbuffered salt solution (2 1 N).

<u>countrv code DL</u> : Extraction with unbuffered 1M NH_4Cl. 2.5 of the soil sample is soaked with a few ml NH_4Cl (1M) solution over night. The next morning 100 ml of the NH_4Cl solution is slowly percolated through the sample during 4-5 hours. The cations (Fe, Al and Mn) are measured directly in the percolate by AAS. The exchangeable protons are calculated by a computer programme. The programme regards the hydrolytic reactions of Al and its different species as a function of pH.

<u>country code DK</u> : Extraction with unbuffered 1M KCl. 20 g soil sample is mixed with 50 ml 1M KCl. AI is determined by **AAS** in the filtrate.

<u>country code NO</u> : Extraction with unbuffered 1M NH_4NO_3. 10 g of mineral soil sample or 2.5 g of organic sample are soaked in 50 ml 1M NH_4NO_3, stirred, stored overnight, stirred again and then filtered. Washing is done with 1M NH_4NO_3. Ca, Mg, K and Na are determined in the extract by ICP.

<u>country code CH</u> : Extraction with unbuffered 1M NH_4Cl. To 5 g of sample an unbuffered solution of 50 ml NH_4Cl (1M) is added. After 1 hour of shaking the cations (Al, Fe and Mn) are determined by ICP-AES in the filtrate. Exchangeable H is obtained by subtracting exchangeable Al (titration) from exchangeable acidity (Al + H). Exchangeable acidity is determined by titrating a KCl extract.

<u>country code UR</u> : Extraction with unbuffered 1M CH_3COONa.

<u>Method 4</u> : Extraction with a salt solution buffered at pH > 7.

<u>country code BU</u> : Extraction with a 1M CH_3COONa and 0.2M K-maleinate mixture buffered at pH 8.25. The filtrate is titrated with 0.04M NaOH for the determination of exchangeable protons. Exchangeable AI is determined by subtracting exchangeable H from the exchangeable acidity, determined by titration of the $CaCl_2$ extract.

Exchangeable Acidity

Exchangeable acidity (AcExc) is the acidity released upon exchange by an unbuffered salt solution (ISRIC, 1987). After equilibrium is reached, the solution is titrated against NaOH using phenolphthalein as colour indicator. When using an automatic titrator the end-point is set at pH 7.8.

<u>Method 1</u> : Reference method. Titration of a 0.1M $BaCl_2$ extract to pH 7.8.
Place 2 g of sample plus 20 ml of 0.1M bariumchloride in a 30 ml plastic centrifuge tube and shake for 2 hours. Centrifuge and titrate the supernatant solution to pH 7.8.
(country code BEf, BEw, PO, LX, SR, CZ, SL, BL)

<u>Method 2</u> : Titration of a salt extract (not 0.1M $BaCl_2$) to pH 7.8.

<u>country code CH</u> : A 5:50 KCl (1M) extract is titrated with NaOH till an end point of pH 7.8 is reached to obtain exchangeable acidity (Al + H). The solution is then back titrated with HCl to determine exchangeable Al.

<u>Method 3</u> : Titration of a salt extract to pH 7.0.

<u>country code FI</u> : The sample is soaked in an unbuffered 0.1M $BaCl_2$ solution (1:10 V:V), rotated and filtered. The filtrate is titrated to endpoint pH 7.0.

<u>countrv code NO</u> : Extraction with an unbuffered 1M NH_4NO_3 solution followed by titration with 0.05 NaOH to endpoint pH 7.0.

<u>Method 4</u> : Titration of a salt extract to pH 8.2.

<u>countrv code DK</u> : 20 g soil sample is mixed with 50 ml 1M KCl. Titration of the filtrate with 0.02M NaOH, using phenolphthalein as colour indicator.

<u>country code ET</u> : Titration of a 1M CH_3COONa extract with 0.1M NaOH to pH 8.2.

<u>country code BU</u> : Titration of a 1M $CaCl_2$ extract with 0.04M NaOH, using phenolphthalein as colour indicator.

Cation Exchange Capacity

In non-calcareous soils, and particularly in acid soils, the sum of exchangeable cations provides a very accurate estimate of CEC. It is not as accurate with neutral, calcareous or saline soils, due to difficulties of making proper corrections for water-soluble basic cations and additional basic cations in the extract dissolved from carbonates (Chapman, 1965).

<u>Method 1</u> : Reference method : Extraction with an unbuffered 0.1M $BaCl_2$ solution.
(country code FI, HU)

<u>Method 1.1</u> : CEC = exchangeable (Ca+Mg+K+Na+Al+Fe+Mn+H)
<u>country code BL</u> : The CEC **is** calculated by making the sum of all exchangeable cations (sum base cations + sum acid cations). Exchangeable protons are measured by the “German” method.

<u>Method 1.3</u> : CEC = exchangeable (Ca+Mg+K+Na+Al+Fe+Mn+H)
<u>country code SR</u> : The CEC is calculated by making the sum of all exchangeable cations (sum base cations + sum acid cations). Exchangeable protons are determined by titration of a 1M KCI extract.

<u>Method 1.5</u> : CEC = exchangeable (Ca+Mg+K+Na) + exchangeable acidity (pH 7.8)
<u>country code BEf, BEw, PO, LX, CZ</u> : The CEC is calculated by making the sum of exchangeable base cations and exchangeable acidity (titration to pH 7.8).

<u>Method 1.7</u> : CEC = exchangeable (Ca+Mg+K+Na+Al+Fe+Mn)
<u>country code FI</u> : Extraction with an unbuffered 0.1M $BaCl_2$ solution. The CEC is calculated by making the sum of all exchangeable cations. Exchangeable protons are not determined.

<u>Method 1.8</u> : CEC = exchangeable (Ca+Mg+K+Al+Fe+Mn+H)
<u>country code AU, SL</u> : The CEC is calculated by making the sum of all exchangeable cations (sum base cations + sum acid cations). Exchangeable Na is not measured. Exchangeable protons are determined by the “German” method.

<u>Method 1.9</u> : CEC = exchangeable (Ca+Mg+K+Al+Mn+H)
<u>country code FR</u> : The CEC is calculated by making the sum of all exchangeable cations (sum base cations + sum acid cations). Exchangeable protons are determined by titration of the 0.1M $BaCl_2$ extract. Exchangeable Na and Fe are not measured.

<u>Method 2</u> : Extraction with a diluted unbuffered salt solution (< 1 N)

<u>countrv code **NL**</u> : CEC = exchangeable (Ca+Mg+K+Na+NH_4) + ACE
Extraction with unbuffered 0.01M AgTU. The AgTU solution is formed by mixing 3.4g $AgNO_3$ and 15.2g thiourea (CH_4N_2S) in *2* litre H_2O. Dependant on the estimated CEC value 0.5 to 10 g of sample is mixed with 50 ml AgTU. The exchangeable cations are extracted in the 0.01M solution during four hours of shaking. The CEC is determined from the decrease in Ag concentration before and after the extraction. Ag is measured by ICP spectrometry.

<u>Method 2.6</u> : CEC = exchangeable (Ca+Mg+K+Na) + exchangeable acidity (pH 8.2)
<u>country code ET</u> : Extraction with an unbuffered 0.1 N HCl solution. The CEC is calculated by making the sum of base cations (titration of the HCl extract) and exchangeable acidity (titration of the 1M CH_3COONa extract).

<u>Method 3</u> : Extraction with an unbuffered salt solution ($\geq$ 1 N).

<u>Method 3.1</u> : CEC = exchangeable(Ca+Mg+K+Na+Al+Fe+Mn+H)
<u>countrv code DL, CH</u> : Extraction with an unbuffered 1M NH_4Cl solution.

<u>Method 3.4</u> : CEC = exchangeable (Ca+Mg+K+Na) + exchangeable acidity (pH 7.0)
<u>country code NO</u> : Extraction with an unbuffered 1M NH_4NO_3 solution. The CEC is calculated by making the sum of base cations and the exchangeable acidity (titration to pH 7.0).

<u>Method 4</u> : Extraction with a salt solution buffered at pH > 7.

<u>Method 4.6</u> : CEC = exchangeable (Ca+Mg+K+Na) + exchangeable acidity (pH 8.2)
<u>countrv code BU</u> : Extraction with a 1M CH_3COONa and 0.2 N K-maleinate mixture buffered at pH 8.25. The CEC is calculated by making the sum of base cations (titration of the CH_3COONa extract) and exchangeable acidity (titration of the $CaCl_2$ extract).

Base Saturation

The degree to which all cation exchange sites of a soil are occupied by basic cations such as Ca, Mg, K and Na is termed the percent base saturation.

<u>**Methods 1 to 4.6**</u> :
Base saturation is a calculated parameter. The calculation method is identical for all laboratories :

$$\frac{\sum base\ cations}{CEC}''100$$

With CEC = Σ base cations + Σ acid cations
or CEC = Σ base cations + exchangeable acidity

The differences between these laboratories are caused by their different measuring procedures for CEC and exchangeable (base) cations. Therefore, the method description for the base saturation can not be regarded separately from the method descriptions of these *2* parameters. The same list as for the CEC (cfr supra) is applied.

A.5. Statistical Analysis of Intercalibration Results

The objective of the intercalibration exercise was to assess the comparability of the data stored in the transnational database. For this purpose, the analysis results of the two standard samples (samples A and B), reported by the laboratories of the countries participating in the transnational inventory, are compared.

The list of analysis methods describes all methods applied in the framework of the Second Intercalibration Exercise, and thus includes method descriptions that are not relevant in the scope of the evaluation of the large-scale inventory results. Countries that participated in the intercalibration exercise, but for which national datasets were not loaded in the European database at the time of writing this report, are separated from the 23 countries that comprise the actual transnational database. Belarus, Ukraine, Estonia and Bulgaria participated in the Second Intercalibration Exercise, but were unable to meet the deadline for submission of the national soil condition inventory results. Their soil condition data were unavailable for the transnational report. In order to make a relevant evaluation of the interlaboratory variability, related to the transnational report, the standard sample results of these countries are not presented in the data tables on the following pages.

The tables present the average (in case replicate measurements were made) intercalibration results of samples A and B for each parameter. The following statistical procedure was used :

- The intercalibration results of the countries considered are sorted based on the analysis method applied and their country code. The countries using a reference method are identified (country codes in slightly shaded cells).
- For every sample, the median of the intercalibration results, obtained by those countries using a reference method, and the median of all the intercalibration results are calculated.
- For every sample and for each country the absolute deviation from the median is calculated. For the pH one has to take into account that this is a logarithmic quantity, for example a pH of 3.4 corresponds to a [H^+] concentration of $1.0x10^{-3.4}$ M.

To combine the results of the two samples, the relative deviation in percent is calculated, comparing the absolute deviation with the respective median reference value. For every country, the relative deviations of the two samples are averaged. The mean deviations are presented in the far right column and shown in a barchart below the table. For the parameters organic carbon, nitrogen and cadmium only sample A is considered, because the amount of these elements in sample B are negligible.

Furthermore, to assess the overall comparability, the mean and median of those deviations are calculated, for all countries as well as for the subset of countries using the reference method. The discussion in Section 1.3 of Part I is based on the results presented below.

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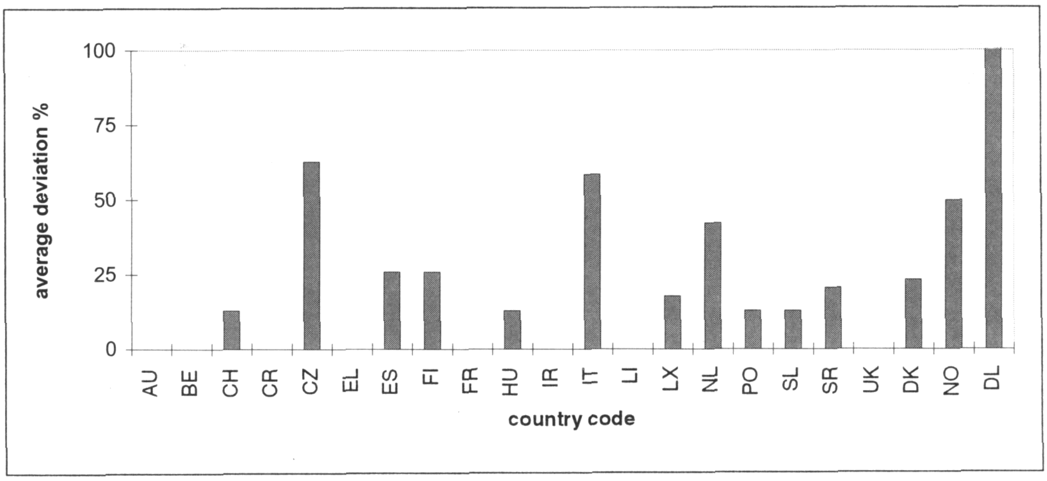
A.6. Analysis Results of Standard Samples

Intercalibration results of pH (delogarithmised values - H^+ concentrations)

		Standard Sample A			Standard Sample B			
country code	method	no. of replicates	average result	deviation from median	no. of replicates	average result	deviation from median	average deviation %
1	1	2	4.0E-04	0.0E+00	2	6.3E-05	0.0E+00	0
2	1	4	4.0E-04	0.0E+00	4	6.3E-05	0.0E+00	0
3	1	1	6.3E-04	2.3E-04	1	7.9E-05	1.6E-05	42
5	1	1	6.3E-04	2.3E-04	1	1.0E-04	3.7E-05	58
6	1	3	4.0E-04	0.0E+00	3	6.3E-05	0.0E+00	0
7	1	2	4.0E-04	0.0E+00	2	6.3E-05	0.0E+00	0
9	1	2	4.0E-04	0.0E+00	2	6.3E-05	0.0E+00	0
10	1	3	4.0E-04	0.0E+00	3	7.9E-05	1.6E-05	13
11	1	3	5.0E-04	1.0E-04	3	7.9E-05	1.6E-05	26
12	1	1	5.0E-04	1.0E-04	1	6.9E-05	6.1E-06	18
14	1	3	4.0E-04	0.0E+00	3	6.3E-05	0.0E+00	0
15	1	2	5.0E-04	1.0E-04	2	7.9E-05	1.6E-05	26
18	1	1	3.2E-04	8.2E-05	1	5.0E-05	1.3E-05	21
20	1	3	5.0E-04	1.0E-04	3	6.3E-05	0.0E+00	13
21	1	3	4.0E-04	0.0E+00	3	7.9E-05	1.6E-05	13
22	1	4	4.0E-04	0.0E+00	4	6.3E-05	0.0E+00	0
23	1	3	4.0E-04	0.0E+00	3	6.3E-05	0.0E+00	0
24	1	3	5.0E-04	1.0E-04	3	1.3E-04	6.3E-05	63
26	1	3	5.0E-04	1.0E-04	3	6.3E-05	0.0E+00	13
8	1.1	1	3.2E-04	8.2E-05	1	7.9E-05	1.6E-05	23
19	1.1	2	4.0E-04	0.0E+00	2	1.3E-04	6.3E-05	50
4	2	3	6.3E-04	2.3E-04	3	2.0E-04	1.4E-04	137

	no. of countries	median ref. value	average deviation	no. of countries	median ref. value	average deviation	average deviation %	median deviation %
All Labs	22	4.0E-04	6.7E-05	22	6.6E-05	1.9E-05	23	13
Reference Labs	19	4.0E-04	6.1E-05	19	6.3E-05	1.1E-05	16	13



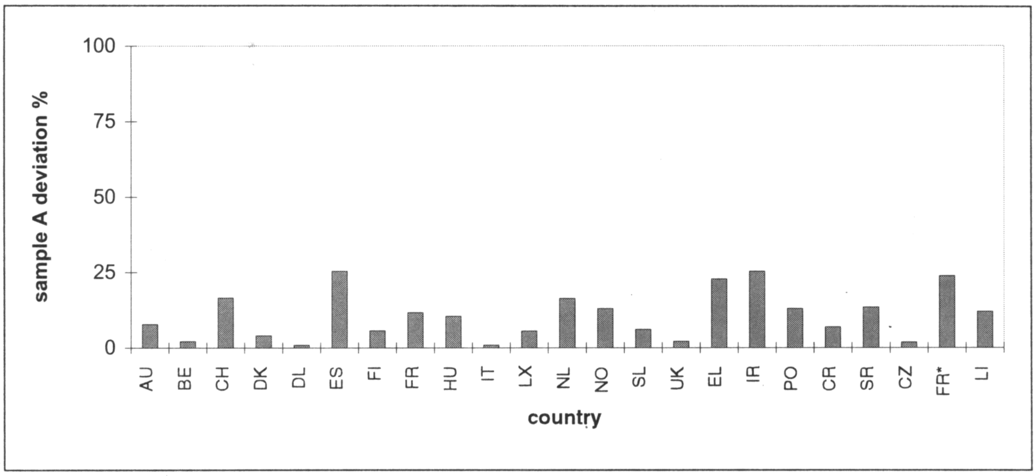
Intercalibration results of organic carbon (g kg^{-1})

		Standard Sample A			Standard Sample B		
country code	method	no. of replicates	average result	deviation from median	no. of replicates	average result	deviation from median
AU	1	3	237	17	3	1	1
BE	1	3	225	5	3	5	3
CH	1	2	257	37	0		
DK	1	1	229	9	1	2	0
DL	1	3	222	2	3	1	1
ES	1	3	164	56	3	2	0
FI	1	2	233	12	1	1	0
FR	1	2	194	26	2	1	1
HU	1	3	197	23	3	2	0
IT	1	1	218	2	1	1	1
LX	1	1	232	12	2	1	0
NL	1	1	184	36	1	4	2
NO	1	2	192	29	2	2	0
SL	1	3	207	14	3	4	2
UK	2	3	225	5	3	5	3
EL	3	1	170	50	2	1	0
IR	3	2	164	56	2	1	1
PO	3	3	191	29	3	1	0
CR	4	3	205	15	3	2	0
SR	4	1	191	30	1	2	0
CZ	5	3	216	4	3	1	1
FR*	5	2	168	52	2	1	0
LI	?	3	194	26	4	2	0

sample A deviation %
8
2
17
4
1
25
6
12
10
1
6
16
13
6
2
23
25
13
7
13
2
24
12

	no. of countries	median ref. value	average deviation	no. of countries	median ref. value	average deviation
All Labs	23	205	24	22	2	1
Reference Labs	14	220	20	13	2	1

average deviation %	median deviation %
11	9
9	6



Fr : method for organic layers (France)
Fr* : method for mineral layers (France)

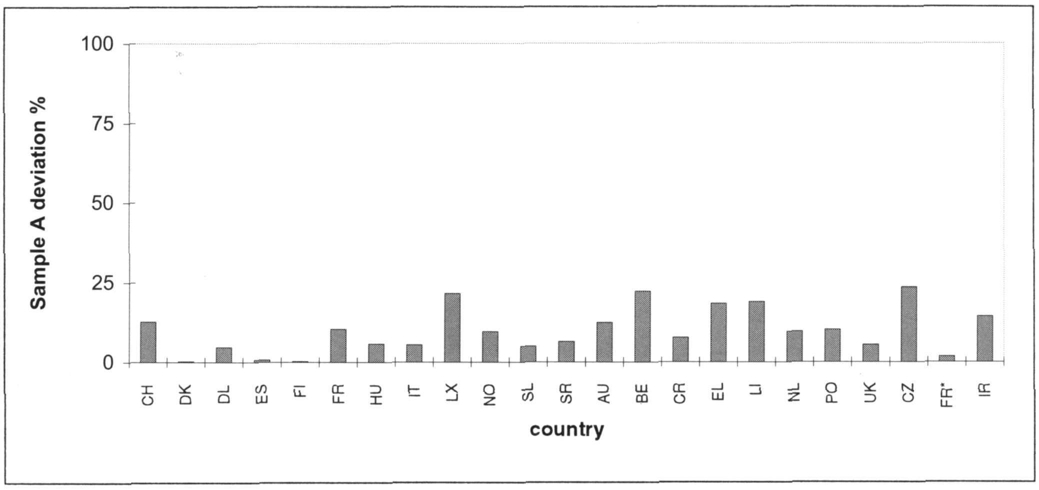
Intercalibration results of total nitrogen (g kg^{-1})

		Standard Sample A			Standard Sample B		
country code	method	no. of replicates	average result	deviation from median	no. of replicates	average result	deviation from median
CH	1	2	10.9	1.2	0		
DK	1	1	9.6	0.0	1	0.3	0.0
DL	1	3	10.1	0.5	3	0.2	0.1
ES	1	3	9.7	0.1	3	0.3	0.0
FI	1	2	9.7	0.0	2	0.5	0.2
FR	1	2	8.6	1.0	2	0.2	0.1
HU	1	3	9.1	0.6	3	0.2	0.1
IT	1	1	9.1	0.5	1	0.4	0.1
LX	1	1	11.7	2.1	2	0.7	0.4
NO	1	2	8.7	0.9	2	0.3	0.0
SL	1	3	10.1	0.5	3	0.2	0.1
SR	1	1	9.0	0.6	1	0.2	0.1
AU	2	3	8.4	1.2	3	0.1	0.2
BE	2	3	7.5	2.1	3	0.3	0.0
CR	2	3	10.4	0.7	3	0.3	0.0
EL	2	2	7.9	1.8	2	0.2	0.1
LI	2	3	7.8	1.8	3	1.1	0.8
NL	2	1	8.7	0.9	1	0.3	0.0
PO	2	3	10.6	1.0	2	0.3	0.1
UK	2	3	9.1	0.5	3	0.2	0.1
CZ	3	3	7.4	2.3	3	0.4	0.1
FR*	3	2	9.5	0.2	2	0.2	0.1
IR	3.1	2	8.2	1.4	2	0.2	0.1

sample A deviation %
13
0
5
1
0
10
6
5
22
10
5
6
12
22
8
18
19
10
10
6
23
2
14

	no. of countries	median ref. value	average deviation	no. of countries	median ref. value	average deviation
All Labs	23	9.1	1.0	22	0.3	0.1
Reference Labs	12	9.6	0.7	11	0.3	0.1

average deviation %	median deviation %
10	9
7	5

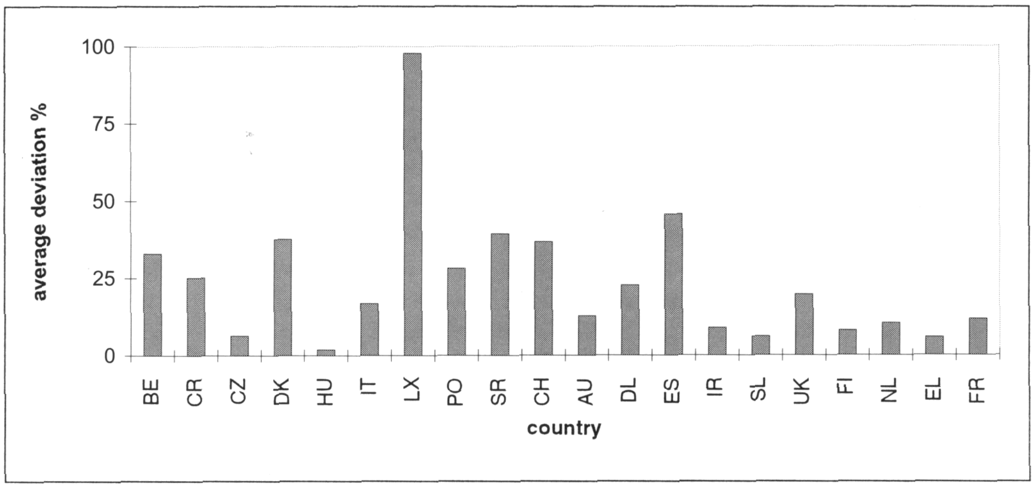


Fr : method for organic layers (France)
Fr* : method for mineral layers (France)

Intercalibration results of phosphorus (mg kg^{-1})

		Standard Sample A			Standard Sample B			
country code	method	no. of replicates	average result	deviation from median	no. of replicates	average result	deviation from median	average deviation %
BE	1	4	179	127	3	340	110	33
CR	1	1	226	79	3	341	109	25
CZ	1	3	338	32	3	460	10	6
DK	1	1	487	182	1	521	71	38
HU	1	3	305	0	3	467	17	2
IT	1	1	203	102	1	450	0	17
LX	1	1	760	455	1	660	210	98
PO	1	3	372	67	3	295	155	28
SR	1	1	143	163	1	335	115	39
CH	2	3	165	140	3	326	124	37
AU	3	3	263	42	3	397	53	13
DL	3	3	191	114	3	414	36	23
ES	3	3	257	49	3	789	339	46
IR	3	2	275	30	2	485	35	9
SL	3	2	278	28	3	436	14	6
UK	3	3	269	37	3	327	123	20
FI	4	2	340	34	2	429	22	8
NL	4	1	245	60	1	445	5	10
EL	5	1	312	7	1	408	42	6
FR	5	2	283	22	2	523	73	12

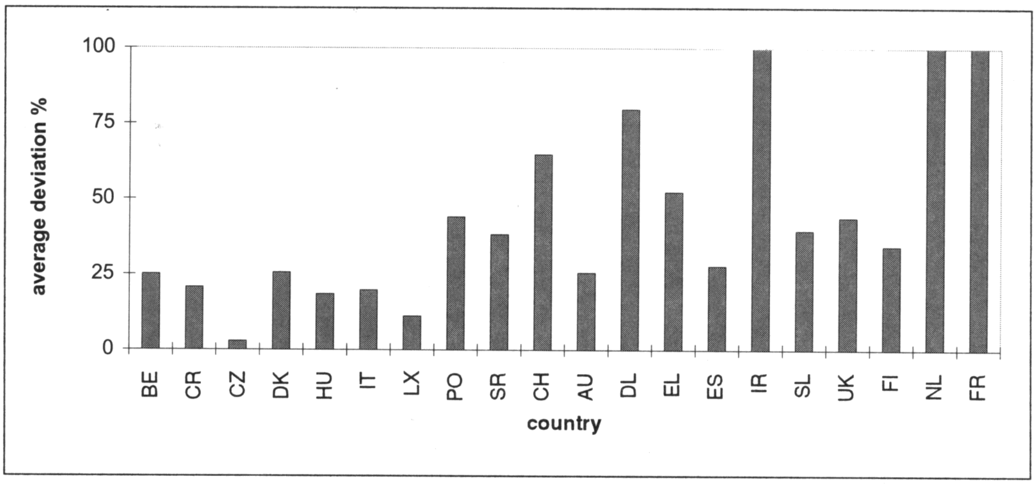
	no. of countries	median ref. value	average deviation	no. of countries	median ref. value	average deviation	average deviation %	median deviation %
All Labs	20	272	88	20	432	83	24	18
Reference Labs	9	305	134	9	450	89	32	28



Intercalibration results of potassium (mg kg^{-1})

		Standard Sample A			Standard Sample B			
country code	method	no. of replicates	average result	deviation from median	no. of replicates	average result	deviation from median	average deviation %
BE	1	4	288	137	3	2601	562	25
CR	1	1	336	90	3	2521	642	21
CZ	1	3	426	0	3	2983	180	3
DK	1	1	555	129	1	3818	655	26
HU	1	3	471	45	3	3994	831	18
IT	1	1	594	168	1	3163	0	20
LX	1	1	400	26	1	3680	517	11
PO	1	3	154	272	3	2393	770	44
SR	1	1	707	281	1	3490	327	38
CH	2	3	171	254	3	955	2208	65
AU	3	3	333	92	3	2233	930	26
DL	3	3	761	335	3	5717	2554	80
EL	3	2	702	276	3	4420	1257	52
ES	3	3	574	148	3	3823	660	28
IR	3	2	1070	644	2	7035	3872	137
SL	3	3	186	240	3	2440	723	40
UK	3	3	714	289	3	3795	632	44
FI	4	2	624	198	2	3863	700	34
NL	4	1	947	521	1	6684	3521	117
FR	5	2	5300	4874	2	17800	14637	804

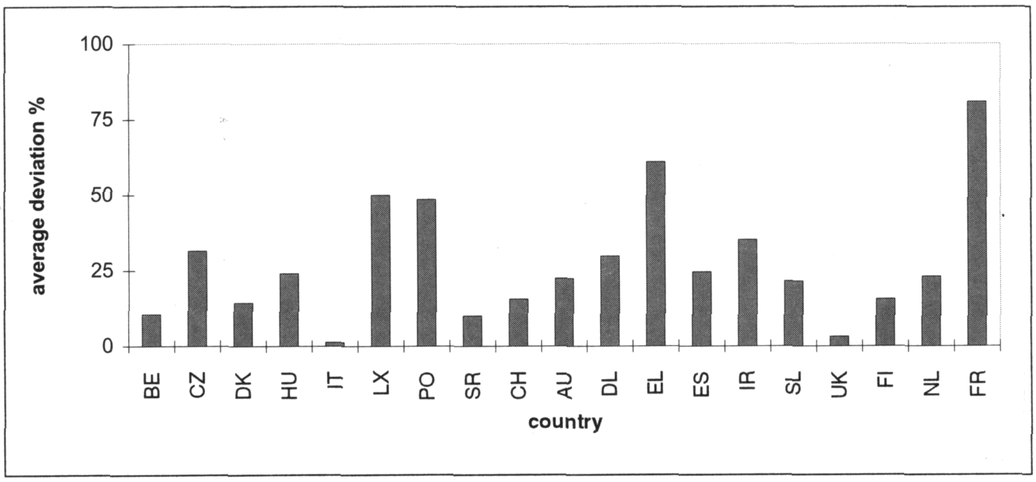
	no. of countries	median ref. value	average deviation	no. of countries	median ref. value	average deviation	average deviation %	median deviation %
All Labs	20	564	451	20	3738	1809	82	36
Reference Labs	9	426	128	9	3163	498	23	21



Intercalibration results of calcium (mg kg^{-1})

		Standard Sample A			Standard Sample B			
country code	method	no. of replicates	average result	deviation from median	no. of replicates	average result	deviation from median	average deviation %
BE	1	4	931	4	3	1111	289	11
CZ	1	3	1403	476	3	1563	164	32
DK	1	1	1114	186	1	1518	119	14
HU	1	3	1354	426	3	1430	30	24
IT	1	1	924	4	1	1369	30	1
LX	1	1	490	438	1	660	739	50
PO	1	3	607	321	3	525	875	49
SR	1	1	841	87	1	1549	149	10
CH	2	3	961	33	3	1016	383	15
AU	3	3	1167	239	3	1133	266	22
DL	3	3	844	84	3	2105	706	30
EL	3	1	218	710	1	765	634	61
ES	3	3	706	221	3	1046	354	25
IR	3	2	1085	157	2	2145	746	35
SL	3	3	1088	160	3	1758	359	21
UK	3	3	920	8	3	1321	78	3
FI	4	2	1077	149	2	1608	209	16
NL	4	1	983	55	1	1961	562	23
FR	5	2	1100	172	2	3400	2001	81

	no. of countries	median ref. value	average deviation	no. of countries	median ref. value	average deviation	average deviation %	median deviation %
All Labs	19	961	207	19	1430	457	27	23
Reference Labs	8	928	243	8	1399	299	24	19



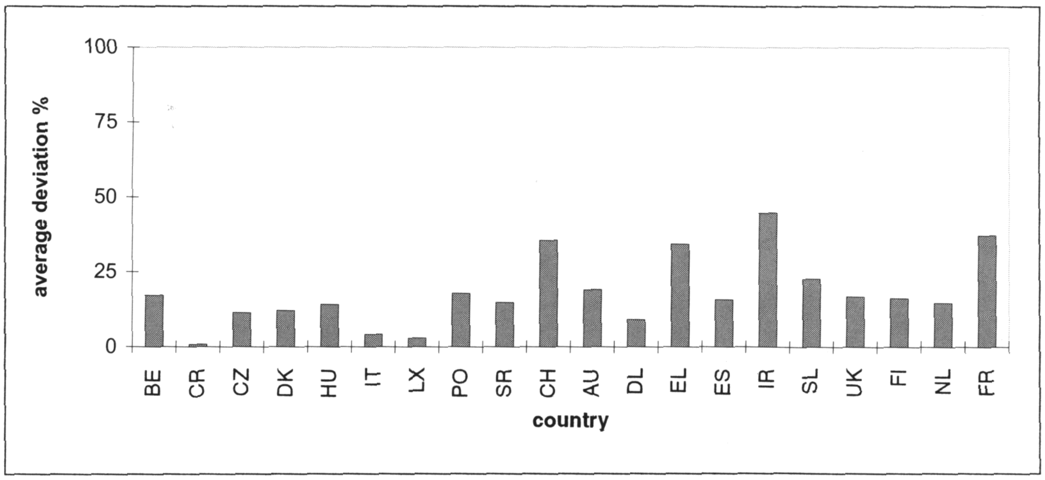
Intercalibration results of magnesium (mg kg^{-1})

		Standard Sample A			Standard Sample B		
country code	**method**	**no. of replicates**	**average result**	**deviation from median**	**no. of replicates**	**average result**	**deviation from median**
BE	1	4	317	33	3	2366	787
CR	1	1	350	0	3	3100	53
CZ	1	3	396	46	3	3453	300
DK	1	1	385	35	1	3600	447
HU	1	3	384	34	3	3743	590
IT	1	1	379	29	1	3153	0
LX	1	1	330	20	1	3150	3
PO	1	3	227	123	3	3140	13
SR	1	1	271	79	1	3378	225
CH	2	3	221	129	3	2078	1075
AU	3	3	233	117	3	3000	153
DL	3	3	355	5	3	3685	532
EL	3	3	572	222	2	3315	162
ES	3	3	315	35	3	3833	680
IR	3	2	545	195	2	4220	1067
SL	3	3	211	139	3	2970	183
UK	3	3	423	73	3	3559	406
FI	4	2	407	57	2	3666	513
NL	4	1	418	68	1	3468	315
FR	5	2	500	150	2	4150	997

average deviation %
17
1
11
12
14
4
3
18
15
36
19
9
34
16
45
23
17
16
15
37

	no. of countries	**median ref. value**	**average deviation**	**no. of countries**	**median ref. value**	**average deviation**
All Labs	20	367	79	20	3415	425
Reference Labs	9	350	44	9	3153	269

average deviation %	**median deviation %**
18	16
11	12



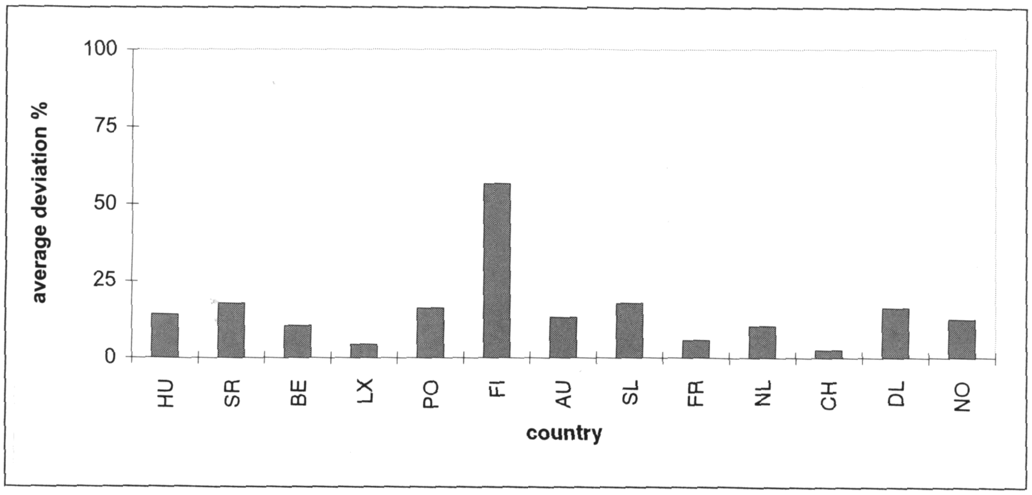
Intercalibration results of cation exchange capacity (cmol(+) kg^{-1})

		Standard Sample A			Standard Sample B		
country code	**method**	**no. of replicates**	**average result**	**deviation from median**	**no. of replicates**	**average result**	**deviation from median**
HU	1	3	14.8	3.1	3	7.3	0.1
SR	1.3	1	12.2	0.6	1	9.7	2.3
BE	1.5	3	9.2	2.4	3	7.4	0.0
LX	1.5	1	11.6	0.0	1	8.1	0.7
PO	1.5	3	10.5	1.2	3	5.8	1.7
FI	1.7	2	19.0	7.3	2	11.1	3.7
AU	1.8	3	14.5	2.9	3	7.5	0.1
SL	1.8	3	10.7	1.0	3	5.4	2.0
FR	1.9	2	10.3	1.3	2	7.4	0.0
NL	2	1	10.4	1.3	1	6.7	0.7
CH	3.1	3	11.3	0.3	3	7.6	0.2
DL	3.1	3	14.4	2.7	3	8.1	0.7
NO	3.4	3	13.4	1.8	3	8.1	0.7

average deviation %
14
18
10
4
16
56
13
18
6
10
3
16
12

	no. of counties	**median ref. value**	**average deviation**	**no. of countries**	**median ref. value**	**average deviation**
All Labs	13	11.6	2.0	13	7.5	1.0
Reference Labs	5	11.6	1.5	5	7.4	0.9

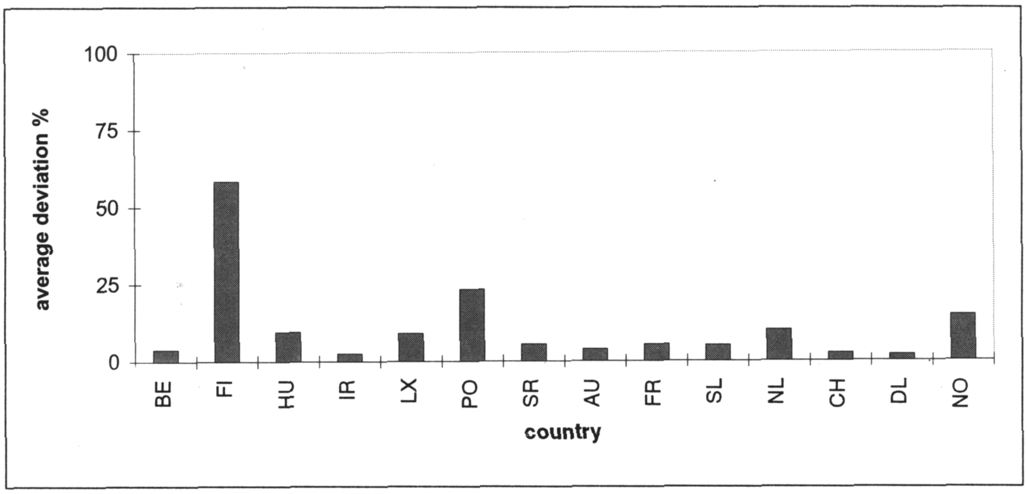
average deviation %	**median deviation %**
15	13
13	14



Intercalibration results of exchangeable basic cations (cmol(+) kg^{-1})

		Standard Sample A			Standard Sample B			
country code	**method**	**no. of replicates**	**average result**	**deviation from median**	**no. of replicates**	**average result**	**deviation from median**	**average deviation %**
BE	1	3	5.1	0.4	3	5.7	0.1	4
FI	1	2	8.8	3.3	2	9.0	3.3	58
HU	1	3	6.4	0.9	3	5.6	0.2	10
IR	1	2	5.2	0.3	2	5.8	0.0	3
LX	1	1	5.9	0.4	1	6.4	0.7	9
PO	1	3	3.9	1.6	2	4.7	1.0	23
SR	1	1	5.5	0.0	1	6.4	0.6	6
AU	1.8	3	5.7	0.2	3	5.5	0.2	4
FR	1.8	2	5.0	0.5	2	5.9	0.2	5
SL	1.8	3	5.5	0.0	2	6.3	0.6	5
NL	2	1	4.5	1.0	1	5.7	0.1	10
CH	3	3	5.2	0.3	3	5.8	0.0	3
DL	3	3	5.4	0.1	3	5.9	0.1	2
NO	3	3	6.6	1.1	3	6.3	0.6	15

	no. of replicates	**median ref. value**	**average deviation**	**no. of replicates**	**median ref. value**	**average deviation**	**average deviation %**	**median deviation %**
All Labs	14	5.4	0.7	14	5.8	0.5	11	6
Reference Labs	7	5.5	1.0	7	5.8	0.8	16	9



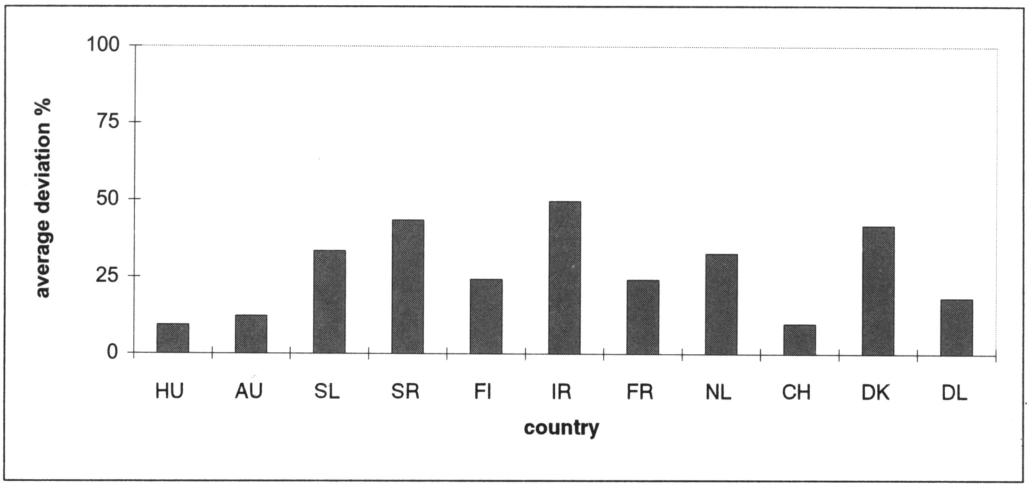
Intercalibration results of exchangeable acid cations (cmol(+) kg^{-1})

		Standard Sample A			Standard Sample B		
country code	method	no. of replicates	average result	deviation from median	no. of replicates	average result	deviation from median
HU	1	3	8.4	0.8	3	1.7	0.1
AU	1.1	3	8.8	1.3	3	2.0	0.1
SL	1.1	3	5.2	2.3	3	1.2	0.7
SR	1.3	1	6.7	0.8	1	3.3	1.4
FI	1.7	2	10.1	2.6	2	2.1	0.3
IR	1.7	2	3.0	4.6	2	1.2	0.7
FR	1.9	2	5.3	2.3	2	1.5	0.3
NL	2	1	5.9	1.7	1	1.1	0.8
CH	3	1	6.1	1.4	3	1.9	0.0
DK	3	1	4.4	3.2	0		
DL	3	3	9.0	1.5	3	2.2	0.3

average deviation %
9
12
33
43
24
50
24
33
10
42
18

	no. of countries	median ref. value	average deviation	no. of countries	median ref. value	average deviation
All Labs	11	6.1	2.0	10	1.8	0.5
Reference Labs	4	7.5	1.3	4	1.9	0.6

average deviation %	median deviation %
27	24
25	23



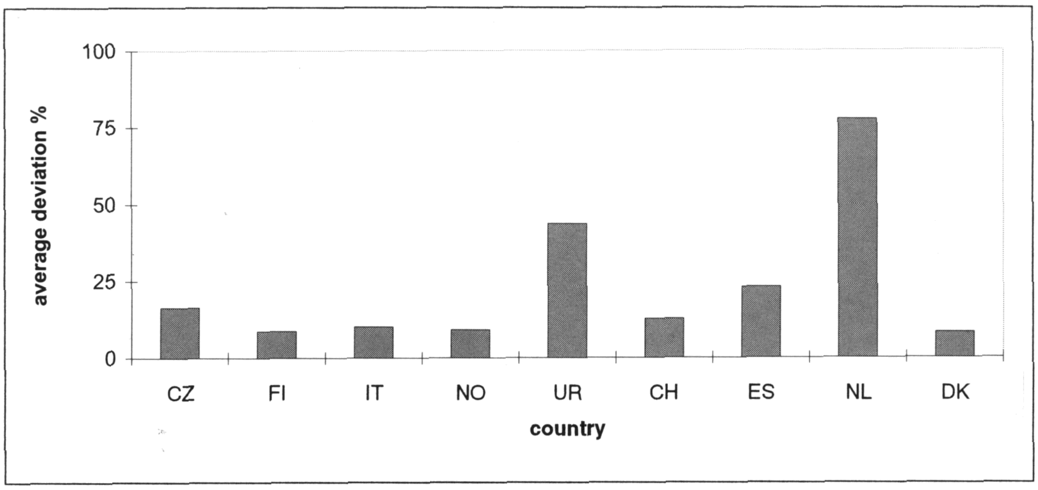
Intercalibration results of exchangeable acidity (cmol(+) kg^{-1})

		Standard Sample A			Standard Sample B		
country code	**method**	**no. of replicates**	**average result**	**deviation from median**	**no. of replicates**	**average result**	**deviation from median**
CZ	1	1	4.9	0.0	1	1.1	0.6
FI	1	3	4.1	0.8	3	1.7	0.0
IT	1	1	5.8	0.9	1	1.7	0.0
NO	1	1	4.0	0.9	1	1.7	0.0
UR	1	3	6.6	1.7	3	2.6	0.9
CH	2	3	4.9	0.0	3	2.1	0.4
ES	3	3	6.9	2.0	3	1.8	0.1
NL	3	2	11.2	6.3	2	2.2	0.5
DK	4	1	4.4	0.5	1	1.6	0.1

average deviation %
16
9
10
9
44
13
23
78
8

	no. of countries	**median ref. value**	**average deviation**	**no. of countries**	**median ref. value**	**average deviation**
All Labs	9	4.9	1.4	9	1.7	0.3
Reference Labs	5	4.9	0.8	5	1.7	0.3

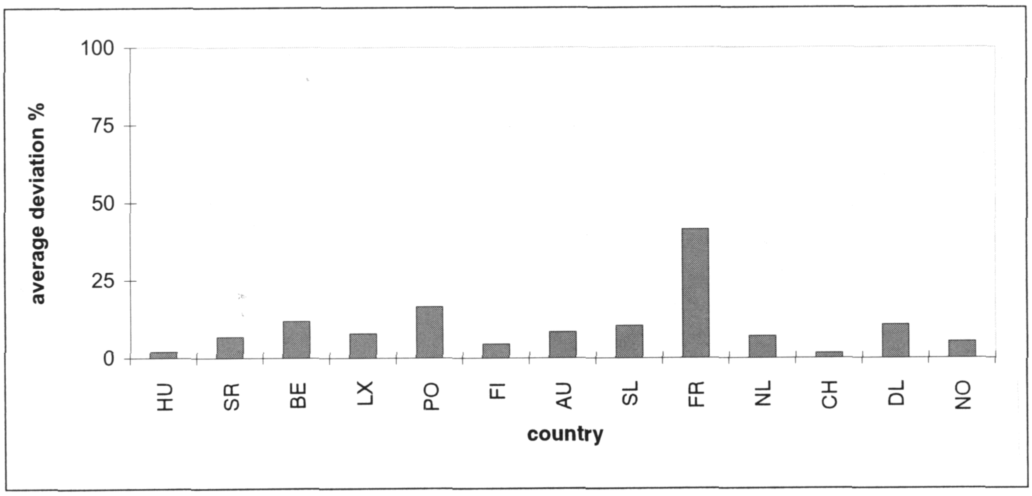
average deviation %	**median deviation %**
23	12
18	11



Intercalibration results of base saturation (%)

		Standard Sample A			Standard Sample B			
country *code*	method	no. of replicates	average result	deviation from median	no. of replicates	average result	deviation from median	average deviation %
HU	1	3	43	2	3	76	0	2
SR	1.3	1	45	0	1	66	10	7
BE	1.5	3	55	10	3	77	0	12
LX	1.5	1	50	5	1	79	3	8
PO	1.5	3	37	8	2	64	12	17
FI	1.7	2	47	1	2	81	4	5
AU	1.8	3	39	6	3	73	3	8
SL	1.8	3	51	6	2	83	6	10
FR	1.9	2	49	4	2	20	56	41
NL	2	1	43	2	1	84	8	7
CH	3.1	3	46	1	3	76	1	2
DL	3.1	3	38	8	3	73	4	11
NO	3.4	3	49	4	3	78	2	5

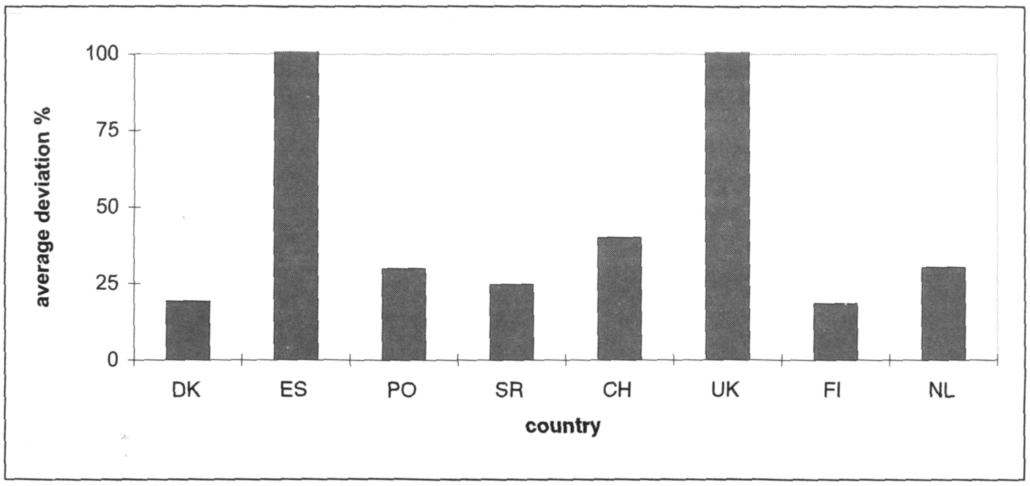
	no. of replicates	median ref. value	average deviation	no. of replicates	median ref. value	average deviation	average deviation %	median deviation %
All Labs	13	46	4	13	76	8	10	8
Reference Labs	5	45	5	5	76	5	9	8



Intercalibration results of sodium (mg kg^{-1})

		Standard Sample A			Standard Sample B			
country code	**method**	**no. of replicates**	**average result**	**deviation from median**	**no. of replicates**	**average result**	**deviation from median**	**average deviation %**
DK	1	1	59	9	1	128	23	19
ES	1	3	147	96	3	218	113	149
PO	1	3	42	9	3	60	45	30
SR	1	1	36	14	1	83	23	25
CH	2	3	45	6	3	33	73	40
UK	3	3	130	80	3	165	59	107
FI	4	2	62	12	2	91	15	18
NL	4	1	26	25	1	118	13	30

	no. of countries	**median ref. value**	**average deviation**	**no. of countries**	**median ref. value**	**average deviation**	**average deviation %**	**median deviation %**
All Labs	8	52	31	8	104	45	52	30
Reference Labs	4	51	32	4	105	51	56	27



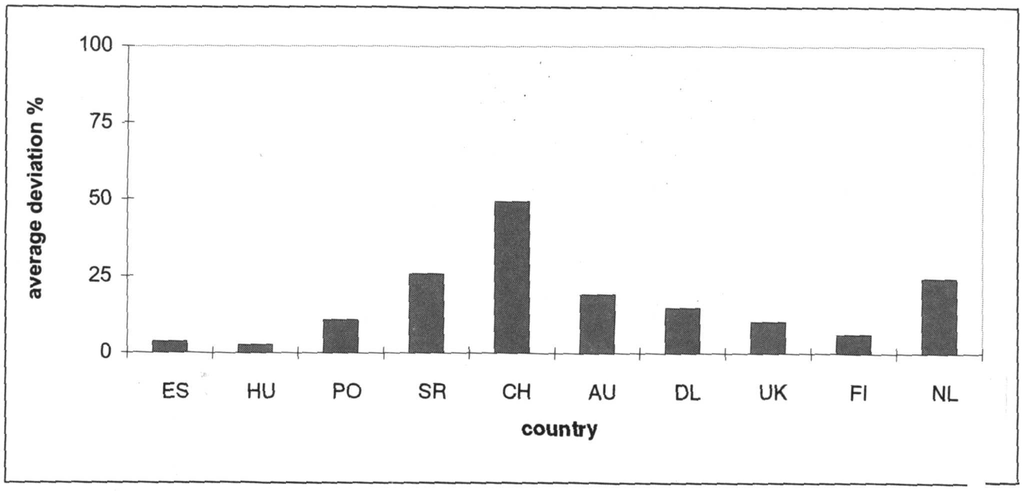
Intercalibration results of aluminium (mg kg^{-1})

		Standard Sample A			Standard Sample B		
country code	method	no. of replicates	average result	deviation from median	no. of replicates	average result	deviation from median
ES	1	3	4985	123	3	20636	921
HU	1	3	4740	123	3	19139	575
PO	1	3	3952	910	3	20289	575
SR	1	1	5908	1046	1	13785	5929
CH	2	3	2969	1893	3	7860	11855
AU	3	3	4300	562	3	14433	5281
DL	3	3	5127	265	3	24469	4755
UK	3	3	5858	995	3	19716	2
FI	4	2	5238	375	2	18771	944
NL	4	1	5918	1056	1	25084	5370

average deviation %
4
3
11
26
50
19
15
10
6
24

	no. of countries	median ref. value	average deviation	no. of countries	median ref. value	average deviation
All Labs	10	5056	735	10	19428	3621
Reference Labs	4	4862	550	4	19714	2000

average deviation %	median deviation %
17	13
11	7



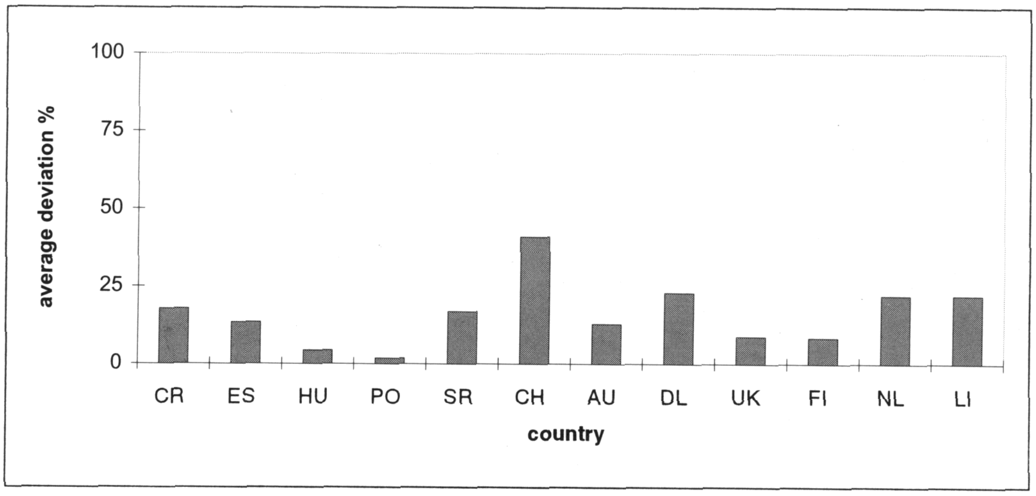
Intercalibration results of iron (mg kg^{-1})

		Standard Sample A			Standard Sample B		
country code	method	no. of replicates	average result	deviation from median	no. of replicates	average result	deviation from median
CR	1	1	3750	904	3	20467	3956
ES	1	3	3740	914	3	22656	1767
HU	1	3	5038	384	3	24526	103
PO	1	3	4824	170	3	24423	0
SR	1	1	4654	0	1	32660	8237
CH	2	3	3136	1518	3	12417	12006
AU	3	3	3933	721	3	21900	2523
DL	3	3	2977	1677	3	22030	2393
UK	3	3	5046	392	3	22171	2252
FI	4	2	4678	24	2	20442	3981
NL	4	1	3305	1349	1	20760	3663
LI	5	4	2781	1873	3	23500	923

average deviation %
18
13
4
2
17
41
13
23
9
8
22
22

	no. of countries	median ref. value	average deviation	no. of countries	median ref. value	average deviation
All Labs	12	3842	827	12	22101	3484
Reference Labs	5	4654	475	5	24423	2813

average deviation %	median deviation %
16	15
11	13



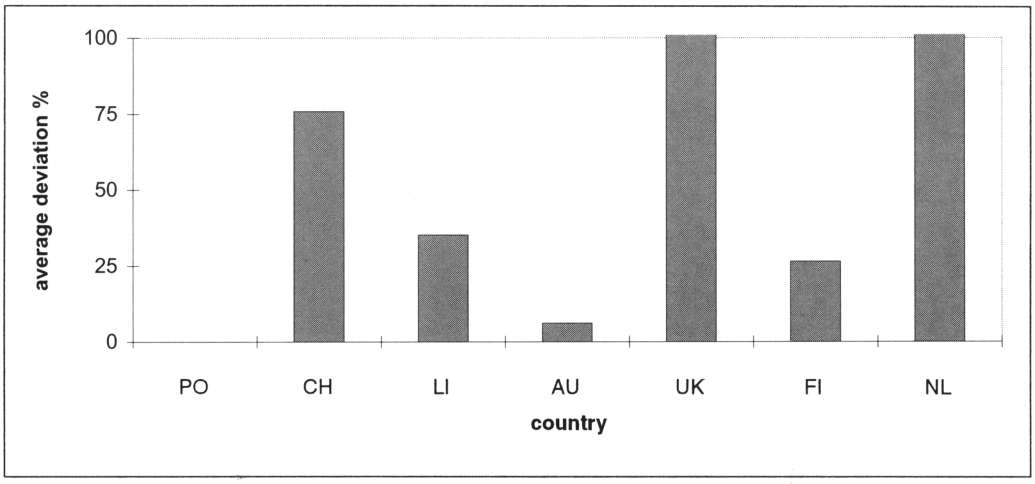
Intercalibration results of chromium (mg kg^{-1})

		Standard Sample A			Standard Sample B		
country code	method	no. of replicates	average result	deviation from median	no. of replicates	average result	deviation from median
PO	1	3	12	0	3	27	0
CH	2	0			3	6	20
LI	2	4	10	2	4	12	14
AU	3	3	11	1	3	28	1
UK	3	3	33	21	3	54	27
FI	4	2	10	2	2	37	10
NL	4	1	27	15	1	72	45

average deviation %
0
76
35
6
141
27
151

	no. of countries	median ref. value	average deviation	no. of countries	median ref. value	average deviation
All Labs	6	11	7	7	28	17
Reference Labs	1	12	0	1	27	0

average deviation %	median deviation %
62	35
0	0



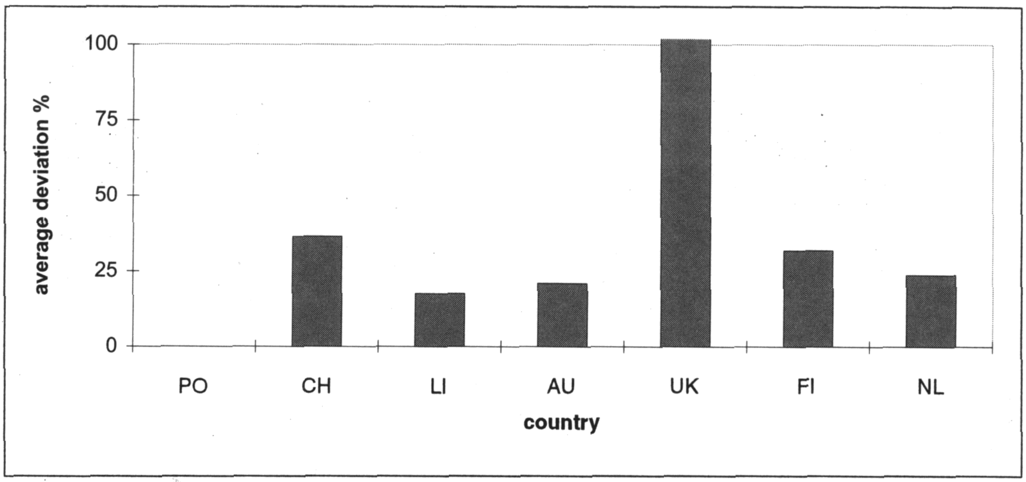
Intercalibration results of nickel (mg kg^{-1})

		Standard Sample A			Standard Sample B		
country code	**method**	**no. of replicates**	**average result**	**deviation from median**	**no. of replicates**	**average result**	**deviation from median**
PO	1	3	9	0	3	18	0
CH	2	0			3	11	7
LI	2	4	6	3	4	18	0
AU	3	3	6	3	3	20	2
UK	3	3	21	12	3	45	27
FI	4	2	7	2	2	25	7
NL	4	1	6	3	1	21	3

average deviation %
0
37
18
21
145
32
24

	no. of countries	**median ref. value**	**average deviation**	**no. of countries**	**median ref. value**	**average deviation**
All Labs	6	6	4	7	20	7
Reference Labs	1	9	0	1	18	0

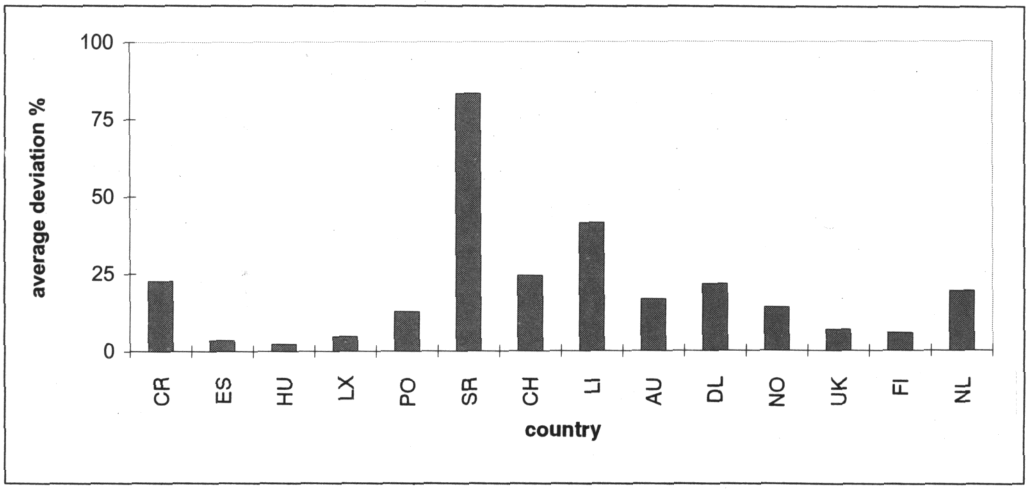
average deviation %	**median deviation %**
39	24
0	0



Intercalibration results of manganese (mg kg^{-1})

		Standard Sample A			Standard Sample B			
country code	method	no. of replicates	average result	deviation from median	no. of replicates	average result	deviation from median	average deviation %
CR	1	1	19	10	3	319	40	23
ES	1	3	31	2	3	357	2	3
HU	1	3	28	1	3	362	2	2
LX	1	1	30	1	1	340	20	5
PO	1	3	24	5	3	387	28	13
SR	1	1	54	25	1	649	290	83
CH	2	3	21	8	3	285	75	24
LI	2	4	13	16	4	261	98	41
AU	3	3	21	8	3	341	18	17
DL	3	3	37	9	3	311	49	22
NO	3	3	23	6	3	327	33	14
UK	3	3	33	4	3	361	2	7
FI	4	2	29	0	2	399	39	6
NL	4	1	39	10	1	348	12	19

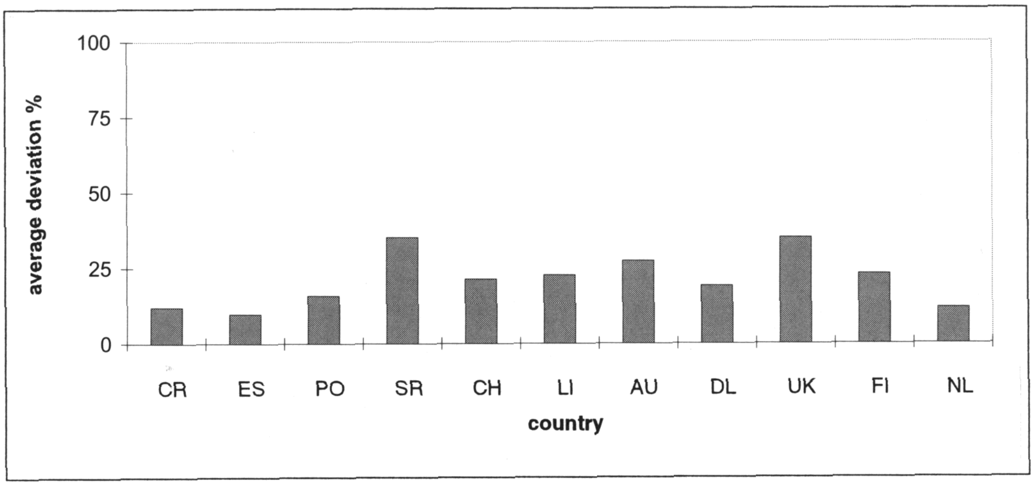
	no. of countries	median ref. value	average deviation	no. of countries	median ref. value	average deviation	average deviation %	median deviation %
All Labs	14	28	7	14	345	50	20	14
Reference Labs	6	29	7	6	360	64	22	9



Intercalibration results of zinc (mg kg^{-1})

		Standard Sample A			Standard Sample B			
country code	method	no. of replicates	average result	deviation from median	no. of replicates	average result	deviation from median	average deviation %
CR	1	1	144	15	3	41	7	12
ES	1	3	166	7	3	55	7	10
PO	1	3	172	13	3	37	11	16
SR	1	1	151	7	1	79	31	35
CH	2	3	168	9	3	30	18	21
LI	2	4	143	16	4	31	17	23
AU	3	3	211	52	3	37	11	27
DL	3	3	122	37	3	41	7	19
UK	3	3	232	73	3	59	12	35
FI	4	2	188	29	2	35	13	23
NL	4	1	154	5	1	38	10	12

	no. of countries	median ref. value	average deviation	no. of countries	median ref. value	average deviation	average deviation %	median deviation %
All Labs	11	166	24	11	38	13	21	21
Reference Labs	4	159	11	4	48	14	18	14



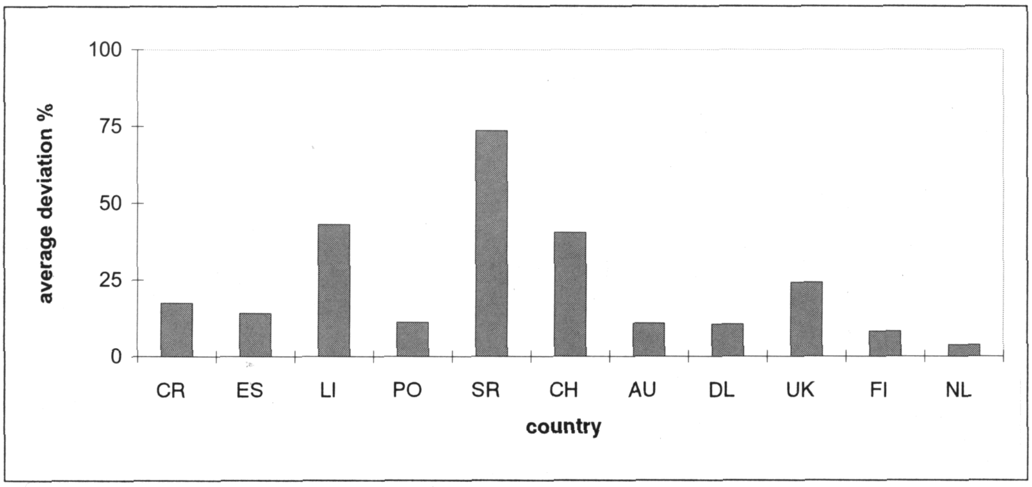
Intercalibration results of copper (mg kg^{-1})

		Standard Sample A			Standard Sample B		
country code	**method**	**no. of replicates**	**average result**	**deviation from median**	**no. of replicates**	**average result**	**deviation from median**
CR	1	1	13	2	3	13	2
ES	1	3	12	1	3	14	2
LI	1	4	5	6	4	8	4
PO	1	3	10	1	3	10	2
SR	1	1	13	2	1	26	15
CH	2	3	6	4	3	7	5
AU	3	3	11	0	3	9	3
DL	3	3	9	2	3	12	1
UK	3	3	16	5	3	11	0
FI	4	2	12	1	2	11	1
NL	4	1	11	0	1	12	1

average deviation %
17
14
43
11
74
40
11
11
24
8
4

	no. of countries	**median ref. value**	**average deviation**	**no. of countries**	**median ref. value**	**average deviation**
All Labs	11	11	2	11	11	3
Reference Labs	5	12	2	5	13	5

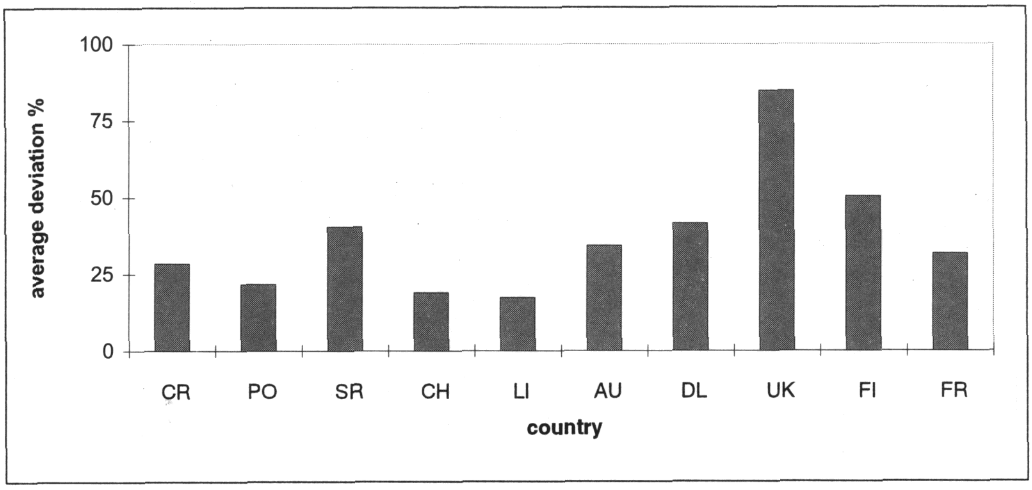
average deviation %	**median deviation %**
23	13
32	29



Intercalibration results of lead (mg kg^{-1})

		Standard Sample A			Standard Sample B			
country code	method	no. of replicates	average result	deviation from median	no. of replicates	average result	deviation from median	average deviation %
CR	1	1	89	23	3	15	3	28
PO	1	3	77	11	3	15	3	22
SR	1	1	38	28	1	7	5	40
CH	2	3	55	11	2	10	3	19
LI	2	4	50	16	4	11	1	17
AU	3	3	88	23	3	8	4	34
DL	3	3	34	32	3	8	4	42
UK	3	3	116	50	3	23	11	85
FI	4	2	97	31	2	19	6	50
FR	5	2	53	13	2	17	5	32

	no. of countries	median ref. value	average deviation	no. of countries	median ref. value	average deviation	average deviation %	median deviation %
All Labs	10	66	24	10	13	5	37	34
Reference Labs	3	77	21	3	15	3	30	25



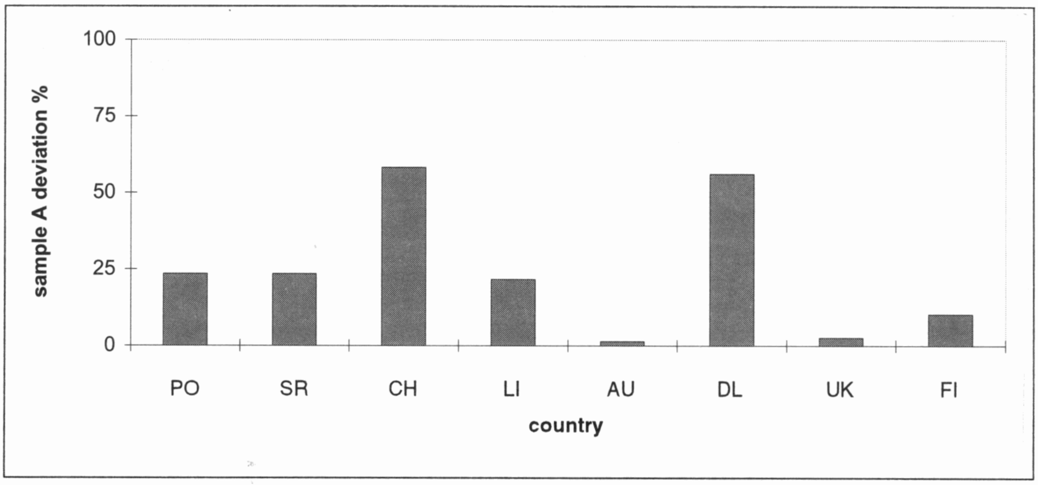
Intercalibration results of cadmium (mg kg^{-1})

		Standard Sample A			Standard Sample B		
country code	**method**	**no. of replicates**	**average result**	**deviation from median**	**no. of replicates**	**average result**	**deviation from median**
PO	1	3	4.5	0.9	3	0.0	0.5
SR	1	1	2.8	0.9	1	1.0	0.5
CH	2	3	1.5	2.1	0		
LI	2	4	2.9	0.8	4	0.9	0.4
AU	3	3	3.6	0.1	3	0.1	0.4
DL	3	3	1.6	2.1	1	0.0	0.5
UK	3	3	3.8	0.1	3	1.8	1.3
FI	4	2	4.1	0.4	2	1.7	1.2

sample A deviation %
23
23
58
22
1
56
3
10

	no. of countries	**median ref. value**	**average deviation**	**no. of countries**	**median ref. value**	**average deviation**
All Labs	8	3.2	0.9	7	0.9	0.7
Reference Labs	2	3.7	0.9	2	0.5	0.5

average deviation %	**median deviation %**
25	23
23	23



Annex B. SUPPLEMENTARY INFORMATION ON PHYSICAL SOIL PROPERTIES

B.1. Origin of Data

Data submission on parent material, texture, coarse fragments and bulk density was not foreseen for the large-scale inventory plots, but field observations were made available by several NFCs. If measured data on the requested parameters could be provided, observations made during field work often present a source of expert data. In the case of bulk density, estimations may be derived from mathematical functions or from relationships between horizons and class functions.

Information on the origin of submitted data should be given using the following codes :

M : measured data (texture, coarse fragments, bulk density)

J : expert judgement based on field observations (texture, coarse fragments, bulk density)

E : estimation derived from pedotransfer functions (bulk density)

B.2. Parent Material

Parent material refers to the material in which the soil has developed. This may differ substantially from the nature of the geological substratum. The parent material may be stratified so that the mineral material in the weathering zone might have a different composition from that in the soil horizons.

If no or inadequate field observations on parent material are made, information on parent material may be derived from detailed geological maps.

The codes for parent material are listed in annex F.

B.3. Texture

Soil mineral particles can be subdivided on the basis of particle size into coarse fragments, sand, silt and clay fractions; particle diameter ranges for each fraction are given in Figure B-1. Chemical analysis of soil samples is performed on the fine earth fraction of the soil material, i.e. after removal of coarse fragments by sieving on a 2 mm sieve. Soil texture refers to the relative proportion of sand, silt and clay particles in a given soil.

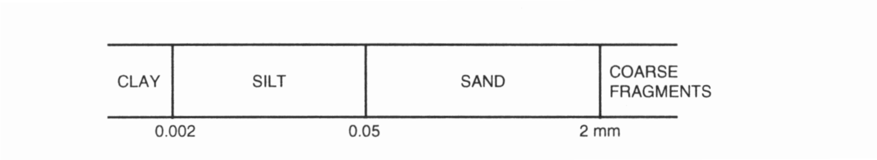


Figure B-1. Classification of soil particles according to size (particle diameter in logarithmic scale).

Each mineral horizon of the studied soils is attributed a texture class according to the key used for the Soil Map of the European Communities, which is given in Table B-1.

class	description	class limits
1	Coarse	< 18% clay and > 65% sand
2	Medium	< 35% clay and > 15% sand, or > 18% clay and > 65% sand
3	Medium Fine	< 35% clay and < 15% sand
4	Fine	35% < clay < 60%
5	Very Fine	> 60 % clay

Ideally, measured soil textures were reported. However, estimations done in the field by soil experts are accurate enough, because only a rough classification is used.

B.4. Coarse Fragments

The amount of coarse fragments (stones and gravel with a diameter > 2 mm) in the individual mineral layers was reported in volume %.

Coarse fragments are separated from the fine earth fraction during the preparation of soil samples. The content of coarse fragments is determined by weighing the residue left on a 2 mm sieve after washing and drying.

$$cf\ (weight\%) = \frac{weight\ not\ passing\ a\ 2\ mm\ sieve}{weight\ of\ the\ total\ air\ dry\ soil} \cdot 100$$

where: cf = coarse fragments

In order to convert the content by weight to an expression by volume, the bulk density of both the coarse fragments and the fine earth should be determined.

$$cf\ (vol\%) = 100 \cdot \frac{BD_{fe}}{BD_{cf}} \cdot \frac{cf\ (weight\ \%)}{\left(100 - cf\ (weight\ \%) \cdot \frac{BD_{cf} - BD_{fe}}{BD_{cf}}\right)}$$

where: BD_{fe} = Bulk density of the fine earth; and

BD_{cf} = Bulk density of the coarse fragments

The abundance of coarse fragments is usually estimated during routine soil profile descriptions. When only abundance class values (e.g. few, common, etc.) were available, the average integer value of the class limits was reported. For example, *'many'* rock fragments (15-40 vol %) is reported as 27 vol % on the data form.

B.5. Bulk Density

The bulk density (BD) is the ratio between the mass of oven-dried soil material and the external volume of the fresh sample :

$$BD = \frac{mass\ of\ the\ sample}{external\ volume\ of\ the\ sample}$$

In the case of stony or gravely soils the bulk density of the fine earth fraction (< 2 mm) was reported:

$$BD_{fe} = \frac{mass\ of\ the\ fine\ earth}{external\ volume\ of\ the\ sample - volume\ of\ the\ coarse\ fragments}$$

Several methods can be applied for the determination of bulk density, going from simple methods such as digging out holes of known volume to sophisticated gamma radiometry methods. The most common method uses steel cylinders of known volume (100 cm^3, 500 cm^3) that are driven in the soil vertically or horizontally by percussion. Sampling large volumes results in smaller relative errors but requires heavy equipment. The method cannot be used if stones or large roots are present or if the soil is too dry or too hard. In these conditions it is advised to use measuring methods based on the following principle: a hole on a horizontal surface is dug and then filled with a material with a known density (e.g. sand which packs to a calibrated volume or water separated from the soil material by an elastic membrane). Methods measuring the volume of clods or aggregates tend to underestimate macroporosity.

Annex C. DATA INTEGRITY EXPERT RULES

Table C-1. Data integrity expert rules of type A and B.

rule type	rule no.	para-meter	**description** (soil properties derived from FAO soil unit are underlined and defined in Annex E)	permissible limit values		condition(s) for application
				lower	upper	
B	1	pH	checks pH results in the presence of carbonates	6.0 5.5	- -	$CaCO_3 > 0$ and Horizon ∈ {M05,M51,M01,M12} $CaCO_3 > 0$ and Horizon ∈ {O,H}
B	2	pH	checks pH results in the presence of Salic or Sodic properties	5.0 4.0 2.8	9.0 9.0 8.0	Salic = 1 or Sodic = 1 and Horizon ∈ {M05,M51,M01,M12} Salic = 1 or Sodic = 1 and Horizon ∈ {O,H} Salic ≠ 1 or Sodic ≠ 1
B	3	C_Org	checks organic C content (g/kg) in organic layers	80	-	Horizon ∈ {O,H}
B	4	C_Org	checks organic C content (g/kg) in mineral layers in the presence of Humic properties	6	-	Humic = 1 and Horizon ∈ {M05,M51,M01}
A	5	C/N	checks the C/N ratio in organic and mineral layers	5 3	100 75	Horizon ∈ {O,H} Horizon ∈ {M05,M51,M01,M12}
A	6	C/P	checks the C/P ratio in organic and mineral layers	100 10	2500 750	Horizon ∈ {O,H} Horizon ∈ {M05,M51,M01,M12}
B	7	$CaCO_3$	checks the carbonate content (g/kg) in soils where no carbonates are expected (e.g. *Umbric* A horizon)	0	0	Calcic = 0 or Spodic = 1 or *Umbric* = 1 and Horizon ∈ {M12}
B	8	$CaCO_3$	checks the carbonate content (g/kg) in soils with low pH	0	0	$pH < 5$
B	9	AcExc	checks the exchangeable acidity value in organic and mineral layers	0.5 0	250 150	Horizon ∈ {O,H} Horizon ∈ {M05,M51,M01,M12}
B	10	ACE	checks the exchangeable acid cation concentration (cmol(+)/kg) in organic and mineral layers	0.5 0	250 150	Horizon ∈ {O,H} Horizon ∈ {M05,M51,M01,M12}
B	11	BCE	checks the exchangeable basic cation concentration (cmol(+)/kg) in organic and mineral layers	0.5 0.1	400 150	Horizon ∈ {O,H} Horizon ∈ {M05,M51,M01,M12}

Table C-1. Data integrity expert rules of type A and B (ctn.).

rule type	rule no.	para-meter	**description** (soil properties derived from FAO soil unit are underlined and defined in Annex E)	permissible limit values		condition(s) for application
				lower	upper	
B	12	CEC	checks the cation exchange capacity value (cmol(+)/kg) in organic and mineral layers	1 0.5	400 150	Horizon ∈ {O,H} Horizon ∈ {M05,M51,M01,M12}
B	13	CEC	checks the CEC values (cmol(+)/kg) in soils with Ferralic properties	0.5	24	Ferralic = 1 and Horizon ∈ {M12}
B	14	BaseSat	checks the base saturation (%) in the presence of carbonates	90	100	$CaCO_3 > 0$
B	15	BaseSat	checks the base saturation (%) in the M12 layer in the presence of Salic, Sodic, Calcic or Gypsiferous properties	80	100	Salic = 1 or Sodic = 1 or Calcic = 1 or Gypsiferous = 1 and Horizon ∈ {M12}
B	16	BaseSat	checks the base saturation (%) in the mineral layers in the presence of a *Mollic* A horizon	30	100	*Mollic* = 1 and Horizon ∈ {M05,M51,M01,M12}
B	17	BaseSat	checks the base saturation (%) in the M12 layer in the presence of a *Umbric* A horizon or Albic properties	0	80	*Umbric* = 1 or Albic = 1 and Horizon ∈ {M12}

Table C-2. **Data integrity expert rules of type C.**

rule type	rule no.	parameter	unit	maximum permissible absolute difference	minimum permissible ratio	maximum permissible ratio
Between overlying mineral layers - between overlying organic layers						
C	18	pH		2.0		
C	19/20	C_Org	g/kg	150	0.25	20
C	21/22	N	g/kg	10	0.25	20
C	23/24	P	mg/kg	400	0.25	20
C	25/26	K	mg/kg	4000	0.1	10
C	27/28	Ca	mg/kg	25000	0.01	100
C	29/30	Mg	mg/kg	25000	0.01	100
C	31	$CaCO_3$	g/kg	500		
C	32/33	Na	mg/kg	250	0.01	100
C	34/35	Al	mg/kg	15000	0.01	100
C	36/37	Fe	mg/kg	20000	0.01	100
C	38/39	Cr	mg/kg	40	0.01	100
C	40/41	Ni	mg/kg	40	0.01	100
C	42/43	Mn	mg/kg	2000	0.01	100
C	44/45	Zn	mg/kg	100	0.01	100
C	46/47	Cu	mg/kg	40	0.01	100
C	48/49	Pb	mg/kg	100	0.01	100
C	50/51	Cd	mg/kg	1.6	0.01	100
C	52/53	CEC	cmol(+)/kg	50	0.25	20
C	54/55	BaseSat	%	50	0.1	5
Between the mineral surface layer and its overlying organic layer						
C	56	pH		2.5		

Table C-3. **Data integrity expert rules of type D.**

rule type	rule no.	verification	value
D	57	CEC = BCE + ACE , or CEC = BCE + AcExc	absolute difference between CEC and BCE + ACE (or BCE + AcExc)
D	58	BaseSat = 100 * BCE/CEC	absolute difference between BaseSat and 100 * BCE/CEC
D	59	BCE ≤ CEC, ACE ≤ CEC, AcExc ≤ CEC	BCE, ACE or AcExc

Annex D. PARAMETER CLASS LIMITS

Separate class limits for organic ('org') and mineral soil layers ('min') are used for organic carbon and total nitrogen; 'tot' refers to calculated amounts for organic layers.

Class	pH	C/N	C/P	Ac_Exc	BCE	ACE	CEC	BaseSat
				cmol(+)/kg soil				%
1	≤ 3.2	≤ 16	≤ 200	≤ 0.5	≤ 0.5	≤ 0.5	≤ 2.0	≤ 10
2	3.3-4.0	17-24	201-400	0.6-2.0	0.6-2.0	0.6-2.0	2.1-5.0	11-20
3	4.1-5.0	25-30	401-600	2.1-5.0	2.1-5.0	2.1-5.0	5.1-10.0	21-50
4	5.1-6.0	31-40	601-800	5.1-10.0	5.1-10.0	5.1-10.0	10.1-20.0	51-95
5	> 6.0	> 40	> 800	> 10.0	> 10.0	> 10.0	> 20.0	> 95

Class	Org. C			N			P		$CaCO_3$
	org g/kg	min g/kg	tot g/m^2	org g/kg	min g/kg	tot g/m^2	org/min mg/kg	tot mg/m^2	min g/kg
1	≤ 200	≤ 10	≤ 500	≤ 8	≤ 0.5	≤ 5	≤ 400	≤ 500	0
2	201-300	11-20	501-1000	9-12	0.6-1.0	6 - 20	401-600	501-1500	1-20
3	301-400	21-40	1001-2000	13-16	1.1-2.5	21 - 50	601-800	1501-3000	21-200
4	401-500	41-80	2001-4000	17-20	2.6-5.0	51 - 100	801-1200	3001-6000	201-500
5	> 500	> 80	> 4000	> 20	> 5.0	> 400	> 1200	> 6000	> 500

Class	K mg/kg	Ca mg/kg	Mg mg/kg	Mn mg/kg	Na mg/kg	Al, Fe mg/kg
1	≤ 500	≤ 2000	≤ 500	≤ 100	≤ 50	≤ 2000
2	501-1000	2001-5000	501-1000	101-500	51-100	2001-4000
3	1001-2000	5001-10,000	1001-2000	501-1500	101-200	4001-8000
4	2001-4000	10,001-25,000	2001-4000	1501-3000	201-500	8001-16,000
5	> 4000	>25,000	> 4000	> 3000	> 500	> 16,000

Class	Cr mg/kg	Ni mg/kg	Zn mg/kg	Cu mg/kg	Pb mg/kg	Cd mg/kg
1	≤ 5	≤ 5	≤ 30	≤ 3	≤ 10	≤ 0.2
2	6-10	6-10	31-70	4-10	11-30	0.3-0.4
3	11-30	11-35	71-170	11-20	31-100	0.5-1.0
4	31-75	36-95	171-300	21-60	101-500	1.1-3.5
5	> 75	> 95	>300	> 60	>500	> 3.5

Annex E. SOIL TYPE AND SOIL PROPERTIES

Podzols and Cambisols together represent almost half of the forest soils in Europe (Table E-1). Other common soil types are Leptosols, Arenosols, Regosols, Luvisols, Histosols and Gleysols. The remaining 20 FAO major soil groupings occur in only 6% of the forest plots. Soil groupings typical for humid tropical conditions, such as Ferralsols, Plinthosols and Nitisols, are not represented in the European forest soil database. Gypsisols and Solonchaks, soil types occurring in areas too dry for forest growth, are also absent in the database.

Podzols are characterised by eluviation of organic matter and/or sesquioxides in the topsoil, which accumulate in the subsoil. They cover large areas in northern Europe. Haplic Podzols alone represent 12% of the forest soils and are mostly found in Sweden and Norway. Ferric Podzols, having a subsurface horizon rich in free sesquioxides, occur frequently in Finland and Lithuania. Cambic Podzols, lacking or having only a thin or discontinuous eluviated horizon, are less exclusive for northern Europe. Carbic Podzols, with a subsurface horizon containing dispersed organic matter, are less common. The second largest group, Cambisols, are soils characterised by weak weathering without important migration of weathering products within the soil profile. Cambisols occur extensively in Europe: Eutric and Calcaric Cambisols are very common in southern Europe, Dystric and particularly Gleyic and Humic Cambisols are typical for more humid areas. Leptosols, especially the Lithic subgroups are very shallow soils, mainly occurring in mountainous areas in close association with bare rock. Their major limitations for agricultural use are effective soil depth, stoniness and rockiness (CEC, 1985). The other subgroups are mostly determined by the nature of the parent material. Eutric and Rendzic Leptosols are typical for fast weathering rocks; Umbric subgroups are characteristic for acid rocks. Arenosols are weakly developed soils on loose, coarse textured materials, and are susceptible to drought. Haplic Arenosols are very common in Sweden. Regosols are soils from unconsolidated materials lacking evidence of important soil forming processes. Dystric Regosols, having a low base saturation, are the most common Regosols. Luvisols, characterised by a subsurface layer enriched in clay, are widely distributed in Europe. Haplic Luvisols are the largest subgroup. Gleyic and Stagnic subgroups show hydromorphic properties within 100 cm of the surface. Together with Chromic Cambisols, Chromic Luvisols generally correspond to the former “Red Mediterranean Soils” (CEC, 1985). Histosols, characterised by thick accumulations of organic soil materials, are largely confined to cool and cold climates. Organic soils with highly decomposed organic materials, Terric Histosols, occur twice as often as Fibric Histosols, having weakly decomposed organic materials. Soils with a poor drainage and excess of water in the subsoil during the greater part of the year are grouped under Gleysols, although they may have widely varying chemical and physical properties. Gleysols occur in alluvial plains throughout Europe; others are associated with slowly permeable subsurface horizons.

The information provided by the FAO classification name can be related to the presence or absence of diagnostic horizons and properties, used in the classification procedure (Table E-1). The classification system was developed as a key that the user should follow when classifying a soil. For example, a soil classified as a Vertisol has all the characteristics required for Vertisols, but also lacks the characteristics that are diagnostic for soil groupings that appear sooner in the key, namely Leptosols, Anthrosols and Histosols. As a consequence, judgements can be made on the presence of horizons or properties that are diagnostic for soil groupings that were eliminated by the key. The same applies to the second classification level of soil units. A Calcic Vertisol, having a Calcic horizon within 125 cm of the surface, cannot have a Gypsic horizon within the same depth limit, because it would then be classified as Gypsic Vertisol (since this soil unit appears sooner in the classification key). On the other hand a Gypsic Vertisol can also have a Calcic horizon within 125 cm of the surface.

Table E-1. Conversion of FAO soil classification names into soil properties.
(1: present; 0: absent; -1: uncertain)

Soilunit	Name	Count	Humic	Histic	Ochric	Spodic	Ferralic	Albic	Calcic	Leptic	Gleyic	Gypsiferous	Salic	Sodic
101	Eutric Fluvisols	9	0	0	1	0	-1	0	0	0	-1	-1	0	-1
102	Calcaric Fluvisols	8	0	0	1	0	-1	0	1	0	-1	-1	-1	0
103	Dystric Fluvisols	3	0	0	1	0	-1	0	0	0	-1	0	0	0
104	Mollic Fluvisols	1	0	2	0	0	-1	0	-1	0	-1	-1	-1	-1
108	Eutric Gleysols	39	0	0	1	0	-1	0	0	0	1	-1	0	-1
109	Calcic Gleysols	5	0	0	1	0	-1	0	1	0	1	-1	0	0
110	Dystric Gleysols	46	0	0	1	0	-1	0	0	0	1	0	0	0
112	Mollic Gleysols	4	0	2	0	0	-1	0	-1	0	1	-1	0	-1
113	Umbric Gleysols	19	0	2	0	0	-1	0	0	0	1	0	0	0
116	Eutric Regosols	29	0	0	1	0	-1	0	0	0	-1	0	0	-1
117	Calcaric Regosols	43	0	0	1	0	-1	0	1	0	-1	0	0	0
118	Gypsic Regosols	1	0	0	1	0	-1	0	-1	0	-1	1	0	0
119	Dystric Regosols	181	0	0	1	0	-1	0	0	0	-1	0	0	0
120	Umbric Regosols	23	1	0	0	0	-1	0	0	0	-1	0	0	0
122	Eutric Leptosols	142	0	0	1	0	-1	0	-1	1	-1	-1	-1	-1
123	Dystric Leptosols	102	0	0	1	0	-1	0	0	1	-1	0	0	0
124	Rendzic Leptosols	116	1	0	0	0	-1	0	1	1	-1	-1	-1	0
125	Mollic Leptosols	9	1	0	0	0	-1	0	-1	1	-1	-1	-1	-1
126	Umbric Leptosols	36	1	0	0	0	-1	0	0	1	-1	0	0	0
127	Lithic Leptosols	124	0	0	1	0	-1	0	-1	1	-1	-1	-1	-1
129	Haplic Arenosols	308	0	0	1	0	0	-1	0	0	0	-1	0	-1
130	Cambic Arenosols	116	0	0	1	0	0	-1	0	0	0	-1	0	-1
131	Luvic Arenosols	16	0	0	1	0	-1	-1	0	0	0	-1	0	-1
132	Ferralic Arenosols	1	0	0	1	0	1	-1	0	0	0	0	0	0
133	Albic Arenosols	1	0	0	1	0	-1	1	0	0	0	0	0	0
134	Calcaric Arenosols	10	0	0	1	0	-1	-1	1	0	0	-1	0	0
135	Gleyic Arenosols	46	0	0	1	0	-1	-1	-1	0	1	-1	0	-1
136	Haplic Andosols	8	0	0	1	0	-1	0	-1	0	0	-1	0	-1
138	Umbric Andosols	1	1	0	0	0	-1	0	0	0	0	0	0	0
139	Vitric Andosols	6	-1	0	-1	0	-1	0	-1	0	0	-1	0	-1
142	Eutric Vertisols	2	0	0	1	0	0	0	-1	0	-1	-1	-1	-1
143	Dystric Vertisols	2	0	0	1	0	0	0	0	0	-1	0	0	0
146	Eutric Cambisols	215	0	0	1	0	0	0	0	0	0	-1	0	-1
147	Dystric Cambisols	532	0	0	1	0	0	-1	0	0	0	0	0	0
148	Humic Cambisols	40	-1	0	0	0	-1	-1	0	0	0	0	0	0
149	Calcaric Cambisols	106	0	0	-1	0	-1	0	1	0	0	-1	0	0
150	Chromic Cambisols	59	0	0	1	0	0	-1	0	0	0	-1	0	-1
151	Vertic Cambisols	11	0	0	1	0	0	0	-1	0	0	-1	0	-1
152	Ferralic Cambisols	7	0	0	1	0	1	-1	0	0	0	0	0	-1
153	Gleyic Cambisols	58	-1	0	-1	0	-1	-1	-1	0	1	-1	0	-1
154	Gelic Cambisols	13	-1	0	-1	0	-1	-1	-1	0	-1	-1	0	-1
155	Haplic Calcisols	22	0	0	1	0	-1	0	1	0	0	-1	0	0
156	Luvic Calcisols	1	0	0	1	0	-1	0	1	0	0	-1	0	0
157	Petric Calcisols	6	0	0	1	0	-1	0	1	0	0	-1	0	0
163	Mollic Solonetz	1	1	0	0	0	-1	0	-1	0	0	-1	-1	1
175	Haplic Kastanozems	8	1	0	0	0	-1	-1	1	0	-1	-1	0	0
177	Calcic Kastanozems	2	1	0	0	0	-1	-1	1	0	-1	-1	0	0
179	Haplic Chernozems	2	1	0	0	0	-1	-1	1	0	0	-1	0	0
180	Calcic Chernozems	2	1	0	0	0	-1	-1	1	0	0	-1	0	0

Table E-1. Conversion of FAO soil classification names into soil properties.
(1: present; 0: absent; -1: uncertain)

Soilunit	Name	Count	Humic	Histic	Ochric	Spodic	Ferralic	Albic	Calcic	Leptic	Gleyic	Gypsiferous	Salic	Sodic
184	Haplic Phaeozems	1	1	0	0	0	-1	-1	0	0	0	-1	0	0
185	Calcaric Phaeozems	4	1	0	0	0	-1	-1	1	0	0	-1	0	0
186	Luvic Phaeozems	2	1	0	0	0	-1	-1	-1	0	0	-1	0	0
189	Haplic Greyzems	1	1	0	0	0	-1	-1	-1	0	0	-1	-1	0
191	Haplic Luvisols	83	0	0	-1	0	0	0	-1	0	0	-1	-1	-1
193	Chromic Luvisols	39	0	0	-1	0	0	0	-1	0	0	-1	-1	-1
194	Calcic Luvisols	4	0	0	-1	0	0	0	1	0	0	-1	-1	0
195	Vertic Luvisols	2	0	0	-1	0	0	0	-1	0	0	-1	-1	-1
196	Albic Luvisols	8	0	0	-1	0	0	-1	-1	0	0	-1	-1	-1
197	Stagnic Luvisols	45	0	0	-1	0	0	-1	-1	0	1	-1	-1	-1
198	Gleyic Luvisols	51	0	0	-1	0	0	-1	-1	0	1	-1	-1	-1
199	Haplic Lixisols	17	0	0	-1	0	-1	0	-1	0	0	-1	-1	-1
204	Gleyic Lixisols	7	0	0	-1	0	-1	-1	-1	0	1	-1	-1	-1
205	Eutric Planosols	14	0	0	1	0	-1	1	-1	0	1	-1	-1	-1
206	Dystric Planosols	36	0	0	1	0	-1	1	0	0	1	0	0	0
207	Mollic Planosols	1	0	2	0	0	-1	1	-1	0	1	-1	-1	-1
208	Umbric Planosols	3	0	2	0	0	-1	1	0	0	1	0	0	0
210	Eutric Podzoluvisols	2	0	0	1	0	-1	-1	-1	0	0	-1	-1	-1
211	Dystric Podzoluvisols	1	0	0	-1	0	-1	-1	0	0	0	0	0	0
212	Stagnic Podzoluvisols	6	0	-1	-1	0	-1	-1	-1	0	1	-1	-1	-1
213	Gleyic Podzoluvisols	17	0	-1	-1	0	-1	-1	-1	0	1	-1	-1	-1
215	Haplic Podzols	531	0	-1	-1	1	-1	1	0	0	0	0	0	0
216	Cambic Podzols	144	0	-1	-1	1	-1	-1	0	0	0	0	0	0
217	Ferric Podzols	267	0	-1	-1	1	-1	-1	0	0	0	0	0	0
218	Carbic Podzols	133	0	-1	-1	1	-1	-1	0	0	0	0	0	0
219	Gleyic Podzols	74	0	-1	-1	1	-1	-1	0	0	1	0	0	0
221	Haplic Acrisols	1	0	0	1	0	-1	-1	0	0	0	0	0	0
223	Humic Acrisols	1	1	0	0	0	-1	-1	0	0	0	0	0	0
226	Haplic Alisols	21	0	0	1	0	0	-1	0	0	0	0	0	0
227	Ferric Alisols	13	0	0	1	0	0	-1	0	0	0	0	0	0
228	Humic Alisols	3	1	0	0	0	0	-1	0	0	0	0	0	0
230	Stagnic Alisols	2	-1	0	-1	0	0	-1	0	0	1	0	0	0
231	Gleyic Alisols	5	-1	0	-1	0	0	-1	0	0	1	0	0	0
245	Folic Histosols	30	1	1	0	-1	-1	-1	-1	-1	0	-1	-1	-1
246	Terric Histosols	110	1	1	0	-1	-1	-1	-1	-1	1	-1	-1	-1
247	Fibric Histosols	52	1	1	0	-1	-1	-1	-1	-1	1	-1	-1	-1
250	Aric Anthrosols	6	-1	0	-1	-1	-1	-1	-1	0	-1	-1	-1	-1
251	Fimic Anthrosols	1	1	0	0	-1	-1	-1	-1	0	-1	-1	-1	-1
252	Cumulic Anthrosols	4	-1	0	-1	-1	-1	-1	-1	0	-1	-1	-1	-1
	total	***4284***												

Annex F. LIST OF PARENT MATERIALS

Table F-1. Parent material codes, attributed weathering class and number of observations.

Code	PARENT MATERIAL	WEATHERING CLASS	Count
1	**CRYSTALLINE ROCKS**	-1	1
11	ACID PLUTONIC ROCKS	1	49
111	Granite	1	91
112	Granodiorite	2	6
113	Quartzo-Diorite	1	1
12	NON-ACID PLUTONIC ROCKS		
123	Diorite	2	1
124	Gabbro	2	2
13	QUARTZITE		13
131	Quartzite	1	12
132	Micaceous Quartzite	1	10
14	GNEISS	2	39
141	Quartzic Gneiss	1	3
142	Paragneiss	2	4
15	SCHIST	2	115
151	Quartzic Schist	1	13
152	Micaschist	2	40
153	Chlorite Schist	2	4
154	Greenschist	2	2
156	Calcschist	4	5
16	PHYLLITES, SLATES		
161	Quartzo-Phyllite	1	5
162	Phyllite	2	6
163	Slate	2	49
17	OTHER METAMORPHIC ROCKS		1
172	Amphibolite	2	9
174	Peridotite	2	2
2	**VOLCANIC ROCKS**	-1	2
21	ACID VOLCANIC ROCKS		
211	Rhyolite	1	3
22	NON-ACID VOLCANIC ROCKS	3	2
221	Andesite	2	16
222	Basalt	2	20
224	Trachyte	2	3
226	Phonolite	3	2
23	CONSOLIDATED PYROCLASTIC ROCKS		
233	Tuff	3	1
24	UNCONSOLIDATED PYROCLASTIC ROCKS	3	
3	**CONSOLIDATED NON-CALCAREOUS SEDIMENTARY ROCKS**		
31	DETRITAL FORMATIONS	1	5
311	Conglomerate	1	14
312	Breche, Poudingues	1	1
313	Flysch	2	35
314	Graywacke	2	4
32	SANDSTONES	1	70
321	Quartzy Sandstone	1	21
322	Ferruginous Sandstone	1	9
323	Clayey Sandstone	2	11
324	Arkose	2	2

Table F-1. Parent material codes, attributed weathering class and number of observations.

Code	PARENT MATERIAL	WEATHERING CLASS	Count
33	SHALES	2	3
331	Siltstone	1	4
332	Claystone	2	14
4	**CARBONATE ROCKS**	4	7
41	LIMESTONES	4	268
411	Pure Limestone	4	14
412	Carbonaceous Limestone	4	3
42	MARBLE	4	
43	DOLOMITES	4	18
44	CHALK	4	7
45	MARL	4	39
451	Marl	4	4
452	Gypseous Marl	4	2
46	CALCAREOUS SHALES		2
461	Calcareous siltstone	4	2
47	CALCAREOUS SANDSTONES	4	15
471	Calcarenite	4	13
472	Macigno	4	1
48	TUFA, TRAVERTINE	4	
49	GYPSE, ANHYDRITE	4	
491	Gypse	4	1
5	**NON-CONSOLIDATED SANDY MATERIALS**	-1	8
51	OLD SEDIMENTARY SANDS		1
511	Calcareous Sandy Deposits	4	20
512	Non-Calcareous Sandy Deposits	1	113
52	ALLUVIAL OR GLACIOFLUVIAL SANDS	-1	58
521	Calcereous Alluvial Sands	4	8
522	Clayey Sands	2	24
523	Gravelly Sands	1	3
524	Sandy Till	1	11
53	COASTAL SANDS	-1	6
532	Non-Calcareous Coastal Sands	1	2
54	EOLIAN SANDS	1	4
541	Cover Sands	1	22
542	Dune Sands	1	7
6	**NON-CONSOLIDATED LOAMY MATERIALS**	-1	64
61	RESIDUAL LOAMS	2	32
611	Old Loam	1	7
612	Stony Loam	2	2
613	Clay Loam	2	25
62	EOLIAN LOAMS	2	12
621	Loess	2	23
623	Sandy Loess	1	3
7	**NON-CONSOLIDATED CLAYEY MATERIALS**	-1	1
71	OLD SEDIMENTARY CLAYS		
711	Calcareous Clayey Deposits	4	9
712	Non-Calcareous Clayey Deposits	2	26
72	ALLUVIAL AND GLACIOFLUVIAL CLAYS	2	1
721	Calcareous Alluvial Clays	4	6
723	Gravelly Clays	2	1
724	Sandy Clays	2	3
725	Clayey Till	2	2

Table F-1. Parent material codes, attributed weathering class and number of observations.

Code	PARENT MATERIAL	WEATHERING CLASS	Count
73	RESIDUAL CLAYS	2	42
8	**ORGANIC MATERIALS**		
81	PEAT		
812	Partly Decomposed Organic Materials	0	3
82	COAL	2	
83	SAPROPELIC DEPOSITS	2	
831	OilShales	2	1
9	**UNDIFFERENTIATED MATERIALS**	-1	264
91	UNDIFFERENTIATED SLOPE DEPOSITS	2	53
92	UNDIFFERENTIATED ALLUVIAL DEPOSITS	2	29
93	UNDIFFERENTIATED GLACIOFLUVIAL DEPOSITS	2	27
94	ARTIFICIAL DEPOSITS	-1	
		total	***2044***

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