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## Manganese in tree rings of Norway spruce as an indicator for soil chemical changes in the past

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**Abstract** Element concentrations in tree rings can be used to monitor changes in environmental quality. With regard to the detection of incipient soil acidification, the manganese concentration in soils and plants is a significant marker for the switch of acid buffering in soils mainly with the exchange of base cations or with the dissolution of aluminium oxides. This is a site-specific non-linear event, indicating the onset of  $\text{Al}^{3+}$  dominance in the soil solution, where damages to vegetation due to acid stress become possible. This turning point is also a marker for the attainment of pH 4.2 in soils, the critical threshold used for critical load calculations. On a plot of the German environmental monitoring in forests the element concentrations in tree rings of 60-year-old spruces reveal a distinct decline in the Mn concentration, beginning in the late 1960s ending in the late 1970s. With this information it was possible to assume a base saturation in the soil of about 15–20% in the late 1960s, and to model the development of the base saturation of the site. A decline from 17.5 to 6% within one decade could be related to the deposition. This is in accordance with the base saturation of 6.5%, measured in 1993 for this site, but also for adjacent spruce sites on the same geological substrate. The knowledge of the time span where this site-specific non-linear event occurred is essential for

the reconstruction of the soil chemistry of a site. Moreover, it enables the assignment of observations like ‘forest damages’ to the onset of changes in environmental quality.

**Keywords** Dendroecology · Norway spruce · Soil chemistry · Soil modelling · Environmental monitoring · Critical thresholds

### Introduction

Element concentrations in tree rings can be used to monitor changes in environmental quality (Guyette and Cutter 1994; Aussenac 1996; Mohamed et al. 1997; Ferretti et al. 2002; Poszwa et al. 2003). Effects of pollution and changes in the availability of elements can be detected and assigned to a distinct time in the past.

Recently, increased soil acidification in Europe due to the long-lasting input of acidifying depositions has been proven by resampling forest soils at intervals of several years or even decades (Falkengren-Grerup 1987; Ulrich and Meyer 1987; Rampazzo and Blum 1992; Matzner and Murach 1995). Acidification of soils causes the loss of the base cations  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$  and an increase in the content of the acid cations  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{Fe}^{2+}$  on the cation exchange complex of the soils.

The buffering mechanisms of soils can be ordered according to the thermodynamic stability ranges of the predominant buffering substances (Ulrich 1991) and the actually occurring mechanism can be monitored in the chemical composition of the soil solution. With regard to the detection of incipient soil acidification, the manganese concentration is a significant marker for the switch of buffering mainly with the exchange of base cations and the dissolution of aluminium oxides (Hildebrand 1986; Ulrich 1991). This is a site-specific non-linear event, occurring within few years, indicating a considerable change in soil quality. In this stage Al starts to dominate the soil solution and to damage the vegetation, since acid stress becomes possible. The

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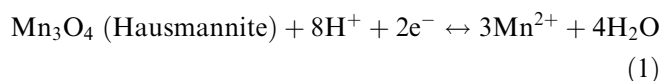
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knowledge of this time span is essential for the reconstruction of the chemical site history in backward scenarios, due to the site specificity of this non-linear event.

The manganese content of soils varies in a wide range, depending on the soil-forming geological material. According to Wedepohl (1969–1978), the content in the most common geological substrates is between 300 and 3,000  $\mu\text{g g}^{-1}$ , which is in accordance with a mean value of 600  $\mu\text{g g}^{-1}$  for soils, reported by Lindsay (1979). The dissolution of manganese oxides is triggered by the soil reaction and redox conditions, as shown, e.g. for Hausmannite in Eq. 1, according to Lindsay (1979):



In the course of the buffer reaction protons are consumed and  $\text{Mn}^{2+}$  is released to the soil solution. The ecological significance of the Mn oxide dissolution arises from the fact that it occurs in the pH range of ca. 5–4.2, so that a  $\text{Mn}^{2+}$  pulse in the soil solution is a marker for a distinct pH range in the soil. Below a value of ca. pH 4.2 the dissolution of Al oxides begins, and the trivalent  $\text{Al}^{3+}$  starts to dominate in the soil solution and the cation exchange complex of the soil solid phase. In contrast to the Mn oxides, the reserves of Al oxides in soils are large, due to the weathering of clay minerals. The dissolution of Mn oxides indicates the transition from the acid buffering with base cation release via the exchange of base cations to the buffering mainly with the dissolution of Al oxides. This is the point where the base saturation of the soils drop exponentially from ca. 15–20% to below 10% (Reuss 1983). Figure 1 illustrates this relation for German forest soils (0–10 cm depths,  $N=1,557$ ) at a high integration level (Wolff and Riek 1996).

In plants  $\text{Mn}^{2+}$  uptake is controlled by the content of manganese in the soil-forming material and the soil pH (Nebe 1967).  $\text{Mn}^{2+}$  is taken up by trees like the other divalent cations  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$  via the transpiration

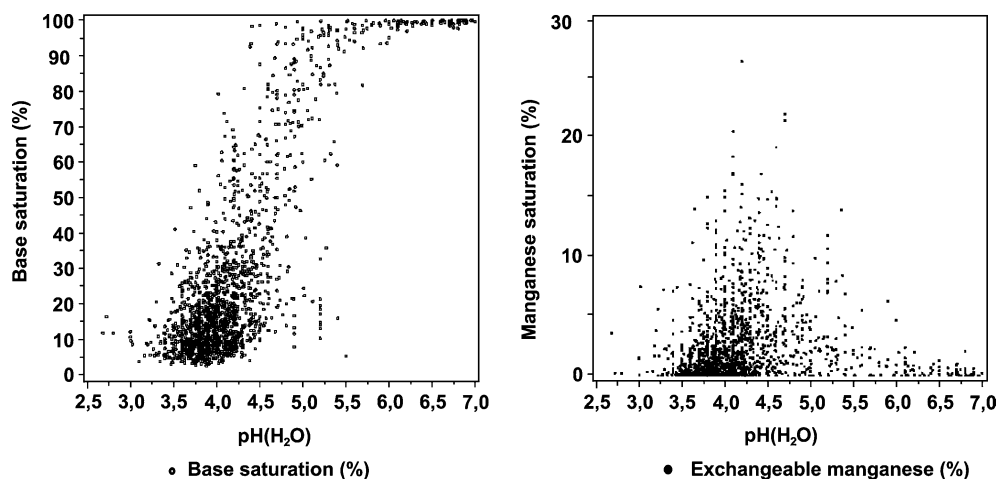
stream. In periods with high  $\text{Mn}^{2+}$  supply from the soil the uptake is high and manganese can be seen afterwards in all plant organs (i.e. Nihlgard and Lindgren 1977). Manganese is subsequently incorporated in the wood, where it can be detected in tree rings. Therefore, the Mn concentration in plant organs, as well as the relation of Mn to other elements, is a suitable indicator for ongoing or historical processes in the rooting zone of soils (Guyette et al. 1992; Guyette and Cutter 1994). It indicates the beginning of ‘critical states’ in forest ecosystems, characterised by unfavourable ratios of bases to Al in soils and unbalanced nutrient uptake by trees (Croan and Grigal 1995). In contrast, the uptake of  $\text{Al}^{3+}$  is often discriminated and the translocation in the plant is small (i.e. Godbold 1994; Kochian 1995), so that the use of  $\text{Al}^{3+}$  in plant organs as indicator in dendroecology is restricted.

## Materials and methods

The sites are part of the German environmental monitoring in forests, which is part of the ICP Forests monitoring of UN-ECE and EU (UN-ECE and EU 1998). On the so-called Level I plots of the 8 km  $\times$  8 km grid net the annual crown condition is assessed, and until now one soil survey and one foliar survey (1986–1993) have been carried out. The Level II sites are intensive monitoring plots, where element fluxes through the ecosystem were assessed in high temporal resolution.

The sites used for this study are situated in the Thuringian Forest. For the Level I site 16063 dendrochemical data, and for the adjacent Level II plot measured deposition data were available. The Level II plot ‘Pfanntalskopf’ (No. 1604) is a 61 to 80-year-old Norway spruce (*Picea abies* L. Karst.) stand on a podzol soil, the humus form is raw humus. The site is southwest exposed in an altitude of 800–850 m a.s.l. Soil characteristics and deposition (No. 1604) are given in Tables 1 and 2.

**Fig. 1** Relation between soil pH ( $\text{H}_2\text{O}$ ) and base saturation of the exchange complex (%), left, and soil pH ( $\text{H}_2\text{O}$ ) and exchangeable manganese (%), right, in German forest soils (0–10 cm depths,  $N=1,557$ )



**Table 1** Soil chemical characteristics of the Level II site 'Pfann-talskopf' (No. 1604) of the German environmental monitoring in forests

Depth (cm)	Base saturation (%)	pH (KCl)	pH (H <sub>2</sub> O)	CEC (molc kg <sup>-1</sup> ) <sup>a</sup>
0–10	6.5	3.3	4.1	0.06
10–30	7.0	3.8	4.4	0.05
30–60	7.0	3.9	4.5	0.05

<sup>a</sup>The cation exchange capacity (CEC) is the mean value of the adjacent Level I sites in the Thuringian Forest on sandstone; base cations in percentage on the exchanger for Level I plot No. 16063

Information on the growth of selected Level I plot No. 16063 were collected by means of tree cores. The diameter of the increment auger was 8 mm, samples were taken at 1.3 m height of the trees. Samples from three 60-year-old Norway spruces (*P. abies* L. Karst.) were taken.

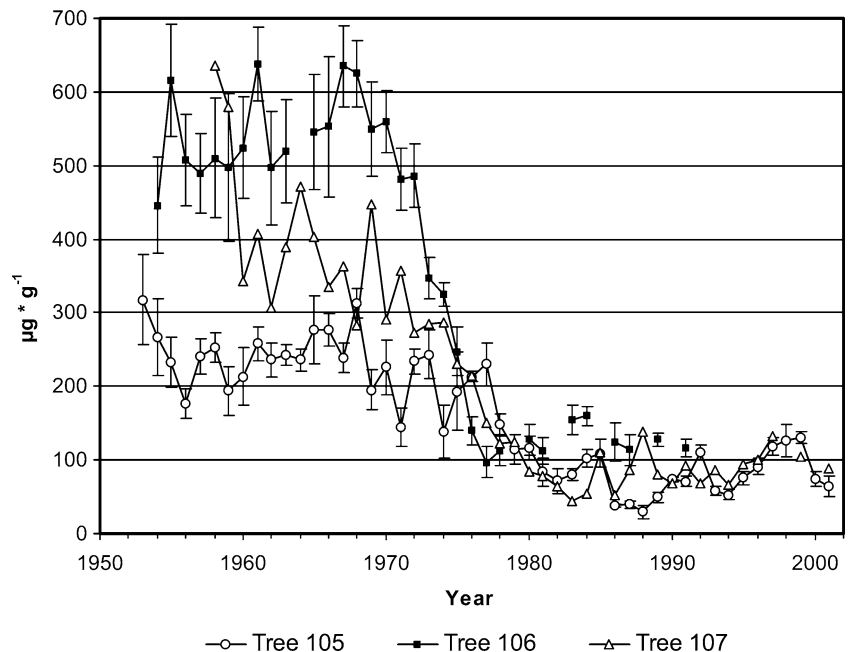
The soil model BODEN was used to reconstruct the chemical site history (Augustin et al. 1998). It includes a soil chemical equilibrium model and a water balance model. All data used for the modelling are given in Table 1 and 2. For the formulation of the cation

**Table 2** Mean deposition 1968–1994 (interpolated according to Ulrich 1994; since 1994: measured at Level II site 1604)

Mean deposition (kg ha <sup>-1</sup> a <sup>-1</sup> ) 1968–1994 <sup>a</sup>						Seepage water (mm ha <sup>-1</sup> a <sup>-1</sup> )
K	Ca	Mg	NO <sub>3</sub> -N	SO <sub>4</sub> -S	Cl	
25	30	4	14	70	20	400

<sup>a</sup>Mean annual values of deposition for the years 1968–1994

**Fig. 2** Mn concentration (µg g<sup>-1</sup>) in tree rings of 60-year-old spruces (*Picea abies* L. Karst.) on Level I site 16063



exchange (Ca, Mg, Al) mean Gaines–Thomas coefficients were taken from the soil condition survey of Lower Saxony (Germany), where soil solution data were available (Schall et al. 1998).

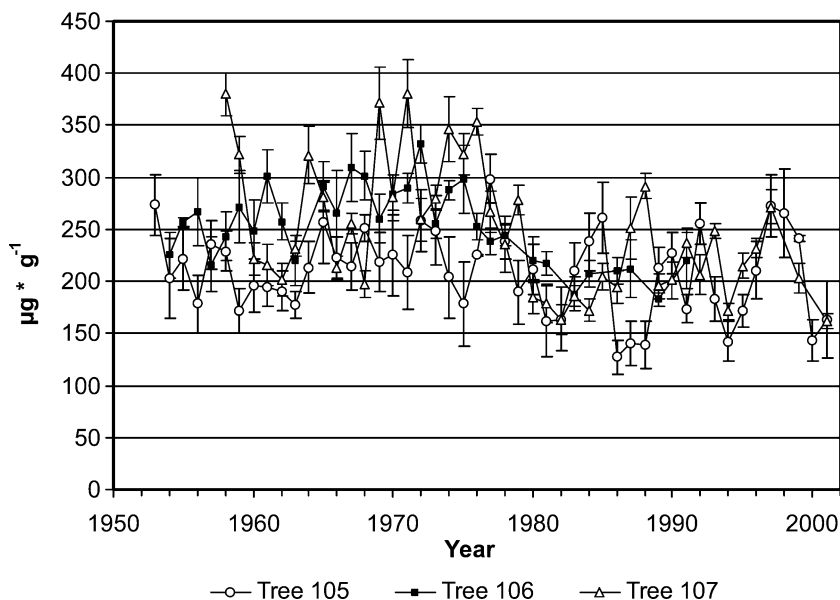
The detection and quantitative analysis of elements in tree rings were carried out using an ICP mass spectrometer ELAN 6000 in conjunction with laser sampler 320 (Perkin-Elmer SCIEX, Thornhill, ON, Canada), according to Hoffmann et al. (1994).

## Results and discussion

The manganese concentration in the tree rings of the spruces are shown in Fig. 2. The relatively high Mn concentrations of 400–600 µg g<sup>-1</sup> in the 1950s and 1960s drop down to a level of 50–100 µg g<sup>-1</sup> within one decade. This decline of the Mn concentration starts in 1968 and ends in 1980. All spruces on the site show the same reaction pattern.

On the radial transport of Mn in tree stems the information is sparse. During the conversion of sapwood into heartwood, extensive translocations of chemical compounds occur (Meerts 2002). In gymnosperms the concentrations of the divalent cations Mg and Ca are slightly enhanced in the heartwood, but the variation is high (Meerts 2002). The proportion of sapwood in Norway spruce depends on the age of the tree and the nutritional state (Schmidt-Vogt 1986). Assuming a sapwood proportion for Norway spruce of 20 tree rings in 1.3 m height, 3.5–4 cm of the stem diameter can be regarded as sapwood, both of which are in accordance with the data given in Schmidt-Vogt (1986). The detected change in the late 1960s is beyond this zone in

**Fig. 3** Mg concentration ( $\mu\text{g g}^{-1}$ ) in tree rings of 60-year-old spruces (*Picea abies* L. Karst.) on Level I site 16063



the heartwood of the tree core and can be seen as unaffected by the tree-aging process.

Simultaneously, the concentrations of  $\text{Mg}^{2+}$  in the stems had been on the decline slightly from the mid-1970s to the mid-1980s (Fig. 3). Since then the concentrations have remained on the same level. Obviously, magnesium becomes increasingly depleted in the rooting zone, leading to a reduced availability of Mg for the trees. However, the decline was somewhat delayed after the Mn depletion, which is in accordance with the soil chemical relations mentioned above.

This is consistent with the fact that, if the depletion of base cations from the cation exchange complex proceeds, a further influx of protons causes the soil pH to decrease rapidly (Bruggenwert et al. 1991).

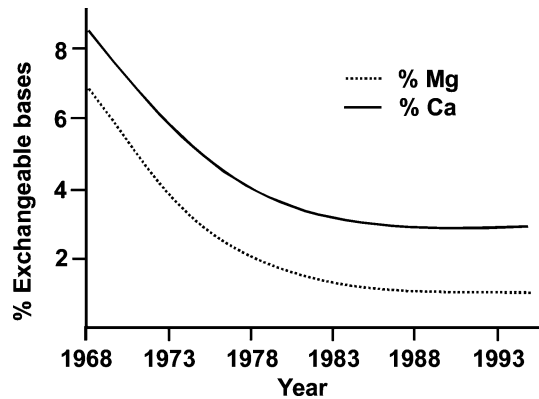
In the Thuringian Forest the first studies on the 'novel forest damage' in the former German Democratic Republic were conducted in 1984, since the damages could no longer be disregarded (Heinsdorf et al. 1991). The results revealed unexpected low contents of Mg in spruce needles, leading to the deficiency symptom 'yellowing'. The authors had mentioned that those deficiencies in the region were not known 20 years ago (Heinsdorf et al. 1988).

The dissolution of Mn oxides in soils precede the onset of an 'acid-stress situation' for trees (i.e. low availability of magnesium, low pH and increasing concentrations of aluminium). Therefore, elevated Mn concentrations in soils and plant organs discern often damaged from undamaged tree collectives, and indicate the beginning of 'novel forest damages' (Becher 1986; Gärtner et al. 1990). Becher (1986) found that high manganese concentrations in spruce needles and low magnesium contents characterise the discriminant function between damaged and undamaged Norway spruces.

### Modelling

With the dendroecological information from the tree rings it is possible to detect the non-linear site-specific turning point in the chemical site history, which is marked by the dissolution of the Mn oxides. In Fig. 2 the slope of the curve shows the downward drift of the Mn depletion. It is plausible to assume that the base saturation in this phase would still have been about 15–20% (Reuss 1983). Afterwards, beginning with the Al oxide dissolution, a depletion of bases from the exchange complex to <10% base saturation is supposed to have been reached. Therefore, the base saturation for the year 1968 was set at 17.5% (i.e. 15–20%).  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were taken as base cations, since  $\text{K}^{+}$  was nearly below the detection limit. The element input in the respective region is known from the intensive monitoring plot 'Pfanntalskopf' (Level II site 1604), where wet deposition is measured since 1994 in a Norway spruce stand of the same age. The deposition between 1968 and 1994 was calculated according to Ulrich (1994) based on data from the German Environmental Agency. For the data see Table 1, the time step for the modelling was 1 year. Figure 4 shows the model result for exchangeable  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in 0–10 cm depths.

The base saturation decreased within a decade from 17.5 to ca. 5–6%, which is the value measured in 1993 in the German soil survey for this site, and for adjacent Norway spruce sites of the Level I monitoring net on the same geological substrate (sandstone). The time period of about 10 years to deplete 10% of the bases from the exchange complex corresponds well to the decline of the Mn concentration in tree rings from the late 1960s to the late 1970s, and even later than the 1970s.



**Fig. 4** Saturation of the exchanger with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (0–10 cm depth) between 1968 and 1993, as modelled with the soil chemical model BODEN

## Conclusions

The example shows that in principle it is possible to link information on the environmental monitoring in forests with indicators from tree ring analysis to reconstruct soil chemical history on the medium time scale. It is possible to use the time span of Mn depletion in the soil, and subsequently in tree rings, as an indicator for the assessment of the transition phase between the acid buffering mainly with silicate weathering and the dissolution of Al oxides, which occur at pH values between 5 and 4.2. This turning point is a marker for the time when the soil reaches the critical threshold of pH 4.2, used for critical load calculations, below which acid stress to forest trees become possible.

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