European Union / United Nations Economic Commission for Europe
International Co-operative Programme on Assessment and
Monitoring of Air Pollution Effects on Forests

1st Meeting of the Heads of the Laboratories
(9.-10. June 2008, Hamburg, Germany)

DOC in ion balance of atmospheric deposition solutions

Validation criteria of water chemical analyses
(atmospheric deposition, runoff, soil water)

Rosario Mosello and Gabriele Tartari

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WG on QA/QC in laboratories within ICP Forests

Plan of the presentation

✓ DOC in ion balance of atmospheric deposition solutions
  - Validation criteria for chemical analyses: the ICP Forests manual
  - The first collective study on validation criteria for atmospheric deposition
  - The second collective study: role of DOC in ion balance, results and discussion

✓ Presentation of an excel sheet for the validation of chemical analysis
Aspects to be considered to assure good analytical quality of results

<table>
<thead>
<tr>
<th>Field</th>
<th>Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Sampling, transport and conservation of samples</td>
<td>• Skilled personnel</td>
</tr>
<tr>
<td></td>
<td>• Validated and written analytical methods</td>
</tr>
<tr>
<td></td>
<td>• Properly constructed, equipped and maintained laboratory facilities</td>
</tr>
<tr>
<td></td>
<td>• Use of high-quality glassware, reagents, deionised water and other testing material</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Internal QC</th>
<th>External QC</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Calibration, adjustment, and maintenance of equipment</td>
<td>• Interlaboratory exercises</td>
</tr>
<tr>
<td>• Use of blanks, DL, QL</td>
<td>• Certified reference materials</td>
</tr>
<tr>
<td>• Use of replicate samples</td>
<td>• Use of control samples and standard samples, with proper records (control charts)</td>
</tr>
<tr>
<td></td>
<td>• Validation and critique of results</td>
</tr>
<tr>
<td></td>
<td>• Archiving results</td>
</tr>
</tbody>
</table>

Validation criteria for chemical analyses: the ICPF manual

- Ionic balance;
- Comparison between measured and calculated conductivity;
- Na/Cl ratio validation test;
- Organic nitrogen validation test.
Part VI of the ICP Forests Manual

Download from web page ICP Forests
http://www.icp-forests.org/Manual.htm

Validation criteria

Ionic balance

\[
PD = 100 \times \frac{(\Sigma \text{cat} - \Sigma \text{an})}{0.5 (\Sigma \text{cat} + \Sigma \text{an})}
\]

\[
\Sigma \text{anions} = [\text{HCO}_3^-] + [\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{Org}^-]
\]

\[
\Sigma \text{cations} = [\text{Ca}^{++}] + [\text{Mg}^{++}] + [\text{Na}^+] + [\text{K}^+] + [\text{H}^+] + [\text{NH}_4^+]
\]

Sampling and Analysis of Deposition

updated: 09/2004
Comparison between measured (CM) and calculated conductivity (CE)

\[
CD = 100 \frac{\text{(CM-CE)}}{\text{CM}}
\]

for conductivity \( \leq 100 \mu\text{S cm}^{-1} \)

\[
\text{CE}_{\infty} = \sum \lambda_i c_i
\]

for conductivity \( > 100 \mu\text{S cm}^{-1} \)

\[
\text{CE} = \sum \lambda_i f_i c_i
\]

\( \lambda_i \) equivalent ionic conductance

\( C_i \) Concentration of the ion \( i \)

\( f_i \) activity coefficient

<table>
<thead>
<tr>
<th>Units</th>
<th>Factors to ( \mu\text{eq L}^{-1} )</th>
<th>Equivalent conductance at 25°C kS cm(^2) eq(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>( 10^6 \times 10^{-pH} )</td>
<td>0.3500</td>
</tr>
<tr>
<td>Ammonium</td>
<td>mg N-NH(_4) L(^{-1})</td>
<td>71.39</td>
</tr>
<tr>
<td>Calcium</td>
<td>mg L(^{-1})</td>
<td>49.90</td>
</tr>
<tr>
<td>Magnesium</td>
<td>mg L(^{-1})</td>
<td>82.29</td>
</tr>
<tr>
<td>Sodium</td>
<td>mg L(^{-1})</td>
<td>43.50</td>
</tr>
<tr>
<td>Potassium</td>
<td>mg L(^{-1})</td>
<td>25.58</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>meq L(^{-1})</td>
<td>1000</td>
</tr>
<tr>
<td>Sulphate</td>
<td>mg S L(^{-1})</td>
<td>62.37</td>
</tr>
<tr>
<td>Nitrate</td>
<td>mg N-NO(_3) L(^{-1})</td>
<td>71.39</td>
</tr>
<tr>
<td>Chloride</td>
<td>mg L(^{-1})</td>
<td>28.21</td>
</tr>
</tbody>
</table>
Acceptance threshold values in data validation based on the ionic balance and conductivity

<table>
<thead>
<tr>
<th>Conductivity of the sample 25 °C</th>
<th>Ionic balance</th>
<th>Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>≤ 10 µS cm⁻¹</td>
<td>± 20%</td>
<td>±30%</td>
</tr>
<tr>
<td>&lt; 20 µS cm⁻¹</td>
<td>± 20%</td>
<td>±20%</td>
</tr>
<tr>
<td>&gt; 20 µS cm⁻¹</td>
<td>± 10%</td>
<td>±10%</td>
</tr>
</tbody>
</table>

Conductivity

Ionic balance

Conductivity

Acceptance threshold values in data validation based on the ionic balance and conductivity

Working Ring Test 1 (2002)
Working Ring Test 2 (2005)
Complete analysis → Ionic balance

Low conc. samples
(≤ 20 µS cm⁻¹)

- Δ % ions
  - ≤ 20
    - Analyses accepted
  - > 20
    - Analyses repeated

Medium-high conc. samples
(> 20 µS cm⁻¹)

- Δ % ions
  - ≤ 10
    - Analyses accepted
  - > 10
    - Analyses repeated

Complete analysis → Conductivity comparison

Low conc. samples
(≤ 10 µS cm⁻¹)

- Δ % cond
  - ≤ 30
    - Analyses accepted
  - > 30
    - Analyses repeated

10 - 20 µS cm⁻¹

- Δ % cond
  - ≤ 20
    - Analyses accepted
  - > 20
    - Analyses repeated

Medium-high conc. samples
(> 20 µS cm⁻¹)

- Δ % cond
  - ≤ 10
    - Analyses accepted
  - > 10
    - Analyses repeated
Hypothesis:
Na⁺ and Cl⁻ in atmospheric deposition originate *manly* from sea spray, so that the ratio Na/Cl is close to those in sea water (0.86, molar or equivalent concentrations).

Consequences:
other ions, such as Mg²⁺, SO₄⁻, should in part derive from sea water.

**Na/Cl ratio validation test**

**Organic nitrogen validation test**

\[ TN = N-NO_3^- + N-NH_4^+ + (N-NO_2^-) \cdot \text{Org}_N \]

\[ \text{Org}_N = TN - N-NO_3^- - N-NH_4^+ \]

The concentration of organic nitrogen can not be negative!

\[ TN - N-NO_3^- - N-NH_4^+ \geq 0 \]
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✓ Presentation of an excel sheet for the validation of chemical analysis

First collective study on the application of the validation criteria

➢ About 5000 analyses of deposition samples done from 7 different laboratories
➢ Samples were representative of different geographic and climatic situations

Validation of chemical analyses of atmospheric deposition in forested European sites

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4Centro Forestale del Nord, Via Trento 3, 20089 Giussani, Italy
5Institut National des Forêts, Boisard & Cie, 77510 Fontainebleau, France
6Central e-mail: antonio.morello@onera.fr
Applicability of ion balance and conductivity tests to different type of solutions

<table>
<thead>
<tr>
<th></th>
<th>ion balance</th>
<th>conductivity</th>
<th>Na/Cl</th>
<th>nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>wet-only</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>bulk open field</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>throughfall</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>stemflow</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>soil water</td>
<td>no</td>
<td>?</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>runoff</td>
<td>?</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>

? = applicable if TOC is lower than 5 mg C L⁻¹

Questions

- Why organic anions contribute to ion balance and do not contribute to conductivity?
- Why soil water is different from atmospheric deposition and runoff?
In the case of soil water both organic carbon and trace metals are important in the ion balance.

However there are problems in evaluating the ionic contribution of trace metals to the ion balance, because of the dependence of the metal speciation from pH and the possibility of complexation with organic substance (DOC).

These aspects do not exclude the possibility to check for correlations among variables, assuming a full dissociation of trace metals.
Is Na/Cl ratio close to 0.86, the value in sea water?

Criteria proposed for the data validation are not rigid and mandatory, but should be used merely as guidelines for the person in charge of validation in each laboratory.

Analyses which do not fit with the validation criteria should be repeated and, if data are confirmed, they should be accepted and included in the database.
**Plan of the presentation**

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- **Presentation of an excel sheet for the validation of chemical analysis**

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**Criteria for the Validation of the Results of Chemical Analyses (atmospheric deposition, run off)**

**Second Step**

**Aims**

- Emphasise the use of data validation in the analyses routine practice
- Include DOC in the ion balance validation
- Increase the number of laboratories involved in the exercise
- Investigate on the meaning and relationships of DOC in atmospheric deposition and soil water
Second collective study on the application of the validation criteria

- About 6000 analyses of deposition samples done from 8 different laboratories
- Emphasis given to the role of DOC and organic anions
Data used in the study

Number of samples used for the statistical analysis of each type of solution (in brackets: number of samples used for testing the regressions).

<table>
<thead>
<tr>
<th>Tree</th>
<th>Solution</th>
<th>BE</th>
<th>CH</th>
<th>DE</th>
<th>FIN</th>
<th>FR</th>
<th>IT</th>
<th>NO</th>
<th>UK</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conifers</td>
<td>BOF</td>
<td>144</td>
<td>106</td>
<td>92</td>
<td>162</td>
<td>214</td>
<td>167</td>
<td>79</td>
<td>964</td>
<td>964</td>
</tr>
<tr>
<td>Conifers</td>
<td>THR</td>
<td>186</td>
<td>70</td>
<td>243(443)</td>
<td>121</td>
<td>306(513)</td>
<td>214(80)</td>
<td>216(236)</td>
<td>301(397)</td>
<td>1657(1699)</td>
</tr>
<tr>
<td>Broad</td>
<td>leaves</td>
<td>BOF</td>
<td>199</td>
<td>136</td>
<td>88</td>
<td>604</td>
<td>78</td>
<td>1105</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Broad</td>
<td>leaves</td>
<td>STF</td>
<td>275</td>
<td></td>
<td>143</td>
<td>179</td>
<td></td>
<td>597</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Broad</td>
<td>leaves</td>
<td>THR</td>
<td>253</td>
<td>126</td>
<td>121(210)</td>
<td>372</td>
<td>299(300)</td>
<td>283</td>
<td>1454(510)</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>1057</td>
<td>438</td>
<td>544 (653)</td>
<td>283</td>
<td>821 (513)</td>
<td>1510 (380)</td>
<td>383 (236)</td>
<td>741 (397)</td>
<td>5777 (2179)</td>
</tr>
</tbody>
</table>

Data Handling

- Each laboratory data were validated using the standard excel file for data validation, available on the web. Only complete analyses were considered. Each laboratory data were aggregated on the basis of: (1) each single plot and (2) the type of vegetation.

- Other graphs were added to those already present in the validation file, including the relationship between DOC and $\Sigma$ cations – $\Sigma$ anions. They were useful for general data exploration.

- The data used in the evaluation of DOC Formal Charge included those not fitting the conductivity test criteria and did not include the highest values (strong skewness).

- The evaluation of DOC Formal Charge using the linear regression slope must be considered as a preliminary approach.
\[ \Sigma \text{ anions} = \text{Alk} + [\text{SO}_4^{\text{n}}] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{Org}^-] \]
\[ \Sigma \text{ cations} = [\text{Ca}^{++}] + [\text{Mg}^{++}] + [\text{Na}^+] + [\text{K}^+] + [\text{H}^+] + [\text{NH}_4^+] \]

[\text{Org}^-] is measured as DOC (mg C L\(^{-1}\))

We indicate as DOC formal charge (\(\beta_1\)) the apparent ionic charge of 1 mg/L of DOC assuming that:
- no errors are affecting ion concentrations
- no other ions are present in solutions

\[ \text{PD} = 100 \times \frac{(\Sigma \text{ cat} - \Sigma \text{ an})}{0.5 (\Sigma \text{ cat} + \Sigma \text{ an})} \]

\[ \Sigma \text{ anions} = [\text{HCO}_3^-] + [\text{SO}_4^{\text{n}}^-] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{Org}^-] \]

\[ \Sigma \text{ anions} = [\text{HCO}_3^-] + [\text{SO}_4^{\text{n}}^-] + [\text{NO}_3^-] + [\text{Cl}^-] + f(\text{DOC}) \]

\[ f(\text{DOC}) = \text{slope} \times \text{DOC} + \text{intercept} \]
\[ f(\text{DOC}) = \beta_1 \times \text{DOC} + \beta_0 \]
Evaluation of the DOC Formal Charge Using the Regression Slope of DOC (mg C L\(^{-1}\)) vs Cat-An (μeq L\(^{-1}\))

Slope \(\beta = \frac{\Delta y}{\Delta x} = \frac{\mu \text{ eq L}^{-1}}{\text{mg C L}^{-1}} = \frac{\mu \text{ eq}}{\text{mg C}}\)

- **Italy Conifers Throughfall**
  - \(y = 2.95 x + 3.63\)
  - \(R^2 = 0.63\)
  - \(n = 168\)

- **Switzerland Throughfall**
  - Oak
  - \(y = 6.0725 x - 3.4499\)
  - \(R^2 = 0.71\)

- **Italy Conifers Throughfall**
  - \(y = 12.571 x - 6.9841\)
  - \(R^2 = 0.88\) (uncorrected)
Hypotheses tested on the data set from different laboratories and type of solutions (1-4), and on the regression coefficients $\beta_1$ (formal charge) of the significant regression $\Delta$ vs DOC.

1) Do differences in the data set from different laboratories exist?
2) Are there differences between data set from different type of solutions?
3) Are there differences between data set from solutions deriving from broadleaves or conifer plots?
4) Are there differences between data set of deposition with high or low marine salt content?
5) Are there differences between the coefficients ($\beta_1$) from different types of solutions?
6) Are there differences between coefficients from different plots?
7) Are there differences between coefficients related to geographic/climatic conditions of the plots?

1) Do differences in the data set from different laboratories exist?
   Yes, the statistical analysis shows highly significant differences between the data set with a 30% of the variability explained by the variable "laboratory".

2) Are there differences between data set from different type of solutions?
   The comparison between the data set of THR and STF solutions was possible only in the case of BE, FR and IT; in all these cases the differences resulted significant with a relative contribution to the total variance of 19, 4 and 2% respectively.

3) Are there differences between data set from solutions deriving from broadleaves or conifer plots?
   The comparison was possible in the case of six countries (BE, DE, FR, IT, UK, CH) and resulted in all cases being highly significant, although the contribution to the total variance of the model was very low (0.5 %).

4) Are there differences between data set of deposition with high or low marine salt content?
   Yes, this variable explains 3% and 9% of the total variability of the model for THR (8 labs) and STF solutions (3 labs), respectively.
Hypotheses tested on the data set from different laboratories and type of solutions (1-4), and on the regression coefficients $\beta_1$ (formal charge) of the significant regression $\Delta$ vs DOC.

1) Do differences in the data set from different laboratories exist?  
2) Are there differences between data set from different type of solutions? 
3) Are there differences between data set from solutions deriving from broadleaves or conifer plots? 
4) Are there differences between data set of deposition with high or low marine salt content? 

5) Are there differences between the coefficients ($\beta_1$) from different types of solutions? 
6) Are there differences between coefficients from different plots? 
7) Are there differences between coefficients related to geographic/climatic conditions of the plots?

The slopes $\beta_1$ of the regressions do not show significant differences for the solutions STF and THR; this is limited to the solutions of BL plots from IT, BE, FR, for which both THR and STF data are available.

6) Are there differences between coefficients from different plots?

7) Are there differences between coefficients related to geographic/climatic conditions of the plots?
6) Are there differences between coefficients from different plots?

Tab. 8 - Range, mean values and standard deviations of $\beta_1$ and $\beta_0$ in different plots and types of solutions

<table>
<thead>
<tr>
<th></th>
<th>Throughfall conifers</th>
<th>Throughfall broad leaves</th>
<th>Stemflow broad leaves</th>
</tr>
</thead>
<tbody>
<tr>
<td>n. of plots</td>
<td>46</td>
<td>32</td>
<td>11</td>
</tr>
<tr>
<td>$\beta_1 \pm \sigma$</td>
<td>4.73 ± 1.58</td>
<td>5.91 ± 1.99</td>
<td>4.95 ± 1.60</td>
</tr>
<tr>
<td>range $\beta_1$</td>
<td>2.33, 9.08</td>
<td>2.22, 10.65</td>
<td>2.98, 8.34</td>
</tr>
<tr>
<td>$\beta_0 \pm \sigma$</td>
<td>-3.06 ± 15.87</td>
<td>-4.46 ± 14.81</td>
<td>-4.97 ± 13.08</td>
</tr>
<tr>
<td>range $\beta_0$</td>
<td>-48.47, 34.85</td>
<td>-43.46, 27.21</td>
<td>-22.61, 14.42</td>
</tr>
</tbody>
</table>

7) Are there differences between coefficients related to geographic/climatic conditions of the plots?

Geographic variables: latitude, longitude, altitude

Climatological variables: mean annual temperature and amount of precipitation

The statistical analyses did not give any significant indication on regular variations of $\beta_1$ using these variables.

It is not possible to verify how much weight the broad approach in the definition of the tree types (broad leaves and conifers) and the associated errors to the chemical data have on this result.
5) Are there differences between the coefficients ($\beta_1$) from different types of solutions?

<table>
<thead>
<tr>
<th>Units</th>
<th>THR</th>
<th>STF</th>
<th>THR</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>1454</td>
<td>597</td>
<td>1657</td>
</tr>
<tr>
<td>pH range</td>
<td>4.0 - 7.9</td>
<td>3.8 - 8.1</td>
<td>4.1 - 7.0</td>
</tr>
<tr>
<td>pH mean± σ</td>
<td>5.8±0.6</td>
<td>5.6±0.6</td>
<td>5.3±0.5</td>
</tr>
<tr>
<td>DOC range</td>
<td>mg C L$^{-1}$</td>
<td>0.37</td>
<td>14246</td>
</tr>
<tr>
<td>DOC mean± σ</td>
<td>mg C L$^{-1}$</td>
<td>8±6</td>
<td>11±7</td>
</tr>
<tr>
<td>$\sum$ cat range</td>
<td>μeq L$^{-1}$</td>
<td>37-2736</td>
<td>30-5287</td>
</tr>
<tr>
<td>$\sum$ cat mean± σ</td>
<td>μeq L$^{-1}$</td>
<td>418±321</td>
<td>593±539</td>
</tr>
<tr>
<td>$\sum$ an range</td>
<td>μeq L$^{-1}$</td>
<td>29-2606</td>
<td>22-5303</td>
</tr>
<tr>
<td>$\sum$ an mean± σ</td>
<td>μeq L$^{-1}$</td>
<td>377±304</td>
<td>545±523</td>
</tr>
<tr>
<td>$\sum$ cat - $\sum$ an range</td>
<td>μeq L$^{-1}$</td>
<td>258</td>
<td>263</td>
</tr>
<tr>
<td>$\sum$ cat - $\sum$ an mean± σ</td>
<td>μeq L$^{-1}$</td>
<td>41±59</td>
<td>48±58</td>
</tr>
<tr>
<td>Slope $\beta_1$</td>
<td>μeq (mg C)$^{-1}$</td>
<td>6.80±0.16</td>
<td>5.04±0.25</td>
</tr>
<tr>
<td>Intercept $\beta_0$</td>
<td>μeq L$^{-1}$</td>
<td>-12.32±1.63</td>
<td>-6.67±3.29</td>
</tr>
<tr>
<td>P-value</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>R²</td>
<td>0.56</td>
<td>0.4</td>
<td>0.47</td>
</tr>
</tbody>
</table>
Use of DOC Formal Charge in the evaluation of the ion balance

Norway, conifers

Italy, broadleaves
Percent of analyses validated based on conductivity and ion balance tests

1) no correction  
2) regression calculated for each country  
3) regression calculated from the mean of all countries

<table>
<thead>
<tr>
<th>Country</th>
<th>BL n. samples</th>
<th>BL Conductivity test %</th>
<th>BL Ion balance test %</th>
<th>CON Conductivity test %</th>
<th>CON Ion balance test %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belgium</td>
<td>BL 120</td>
<td>81</td>
<td>60</td>
<td>92</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>BL 91</td>
<td>82</td>
<td>70</td>
<td>77</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>CON 60</td>
<td>90</td>
<td>73</td>
<td>92</td>
<td>73</td>
</tr>
<tr>
<td>Switzerland</td>
<td>BL 148</td>
<td>58</td>
<td>27</td>
<td>93</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>CON 111</td>
<td>56</td>
<td>26</td>
<td>87</td>
<td>78</td>
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Conclusions

The investigations done on about 6000 data from 8 laboratories indicates DOC concentrations can helpfully be used to evaluate the formal charge of DOC in the ion balance to check the results of THR and STF samples analyses.

Statistical analyses indicate that the main cause of variability is linked to “laboratory”, i.e. to systematic (and random) errors associated to chemical analyses.

The comparison between formal charges associated to DOC/TOC in atmospheric deposition and freshwater does not indicate relevant differences.

The large range of geographic and climatic conditions of the plots used in the study indicates that as a first approach the mean values of $\beta_1$, $\beta_0$ evaluated in this paper can be considered for general use, but...

Specific studies carried out in each laboratory, aimed at testing the regression between $\Delta$ and DOC, are strongly recommended as part of the validation of the analytical results.

Future Work

A complete set of analyses was available only for 8 labs out of 52-59 laboratories participating in the WRT1 and WRT2. The number of laboratories performing all the analyses indicated from the ICP Forests manual should increase.

Differences between the results obtained in laboratories was the most important cause of variability, explaining about 30% of the total variance. The comparability of data produced in different laboratories must be improved.

To reach this goal it is essential an improvement in QA/QC both in and between laboratories. Working Ring Tests and collaborative studies such as the present one, and the following discussions, can greatly help in improving the quality of analytical data.
**Acknowledgements**

All the colleagues who provided data and commented different aspects of the elaboration:

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