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

---

Combined meeting of the Expert Panels Foliar, Deposition Soil/Soil Solution, Crown Condition and Ambient Air Quality together with the Working Group QA/QC in Laboratories

Meeting of the Working Group QA/QC in Laboratories

22. April 2015, Göttingen (Germany)

Minutes

A. Meeting of the Working Group QA/QC in Laboratories

0. Opening

Nils König opened the meeting and welcomed the participants.

1. Preparation of the next meeting of the heads of the labs

Next meeting of the heads of the laboratories participating in the ICP-Forests programme is going to be held at 17 and 18 September 2015 in Vienna, kindly hosted by Austrian Federal Research and Training Centre for Forests, Natural Hazards and Landscape (BFW), FFCC represented here by Alfred Fürst. Deadline for registration and booking of the hotels is 1 August 2015. The agenda of this meeting will include:

- Presentation of the results of the 7th Deposition and Soil Solution Interlaboratory Comparison Test (by Kirsti Derome),
- Presentation of the results of the 16th and 17th Foliar Interlaboratory Comparison Test (by Alfred Fürst),
- Presentation of the results of the 8th Soil Interlaboratory Comparison Test (by Tamara Jakovljević),
- Special presentation about pH and alkalinity, the most troublesome analyses in water, as proved by the preliminary results of 7th and earlier editions of the Deposition and Soil Solution Interlaboratory Comparison Tests,
- Comparison of acidic digestion methods (by Nils König),
- Flow injection analysis as possible source of error in determination nitrates in water due to oxidisation of NO_2^- to NO_3^-,
- Using control charts (by Alfred Fürst) with examples of control charts delivered by participants (see also part B: Combined Meeting with EP Foliar and EP Deposition),
- Problems with ionic balance with examples delivered by participants,
- Discussion and decision about acceptance of the new methods if there are any proposals from Expert Panels,
- New functionalities and current state of database ICP-Forests (by Till Kirchner),

- Other presentations about analytical problems, delivered by participants.

Questionnaire about analytical problems will not be send round to heads of the labs prior to the meeting; presentations are the sufficient basis for detection and solving common problems.

Assistance programme for laboratories facing analytical problems is permanently open. However, due to a lack of financial support the assistance activity (e.g visits in experienced labs, visits of experts) has to be financed by the laboratory searching for help.

Last evaluation of the QA forms submitted to the ICP-Forests database revealed many mistakes. Some countries have not corrected them until now. There is no plan to evaluate QA forms in near future as many checks can be done automatically under submission.

2. New method code for ring tests and data submission

As agreed at 4th meeting of the heads of the labs in 2013 in Zadar/Croatia, members of the WG QA/QC, Nils König and Alfred Fürst elaborated new method codes for sample preparation, pretreatment, and determination. All method codes have been harmonized for deposition, soil solution, soil and foliage analyses and apply for the ring tests as well as for the QA forms. Data entry in the ICP-Forests database have been already related to the new method codes. New codes were already used in ring test and from now on are also to be used in data submission.

3. Next ring tests

Future ring tests: foliar and soil will be organized as before, i.e. by FFCC-BFW and Croatian Forest Research Institute. For now it is uncertain if LUKE (former METLA) is going to organize next round of water ring test. If not, a new organizer will have to be appointed.

Tamara Jakovljević presented the progress of the ongoing 8th Soil Interlaboratory Comparison Test. The ring test is for the first time organized by Croatian Forest Research Institute. Total cost of participation is 350 €, paid within 30 days from registration. Registration is still open. Deadline for the submission of the results is 9 August 2015, first results are expected in September this year, and requalifcation procedure starts in October 2015.

Alfred Fürst informed about preparation to the 18th Needle and Leaf Interlaboratory Comparison Test. Registration is open till 6 July 2015. Cost of participation is 210 €. Deadline for data submission is 1 January 2016.

Soil and foliar ring tests are open also for laboratories that do not participate in the ICP-Forests programme, that helps to keep the participation fee low.

4. Miscellaneous:

Next meeting of the Working Group of Quality Assurance and Quality Control will be held back-to back with the meeting of the other Expert Panels. The date has not been fixed yet.

B. Combined Meeting with EP Foliar and EP Deposition

0. Opening

Nils König opened the meeting and welcomed the participants.

1. 16th and 17th Needle/Leaf Interlaboratory Comparison Test

Alfred Fürst gave a presentation about the results of the 16th and 17th Needle/Leaf Interlaboratory Comparison Tests. The numbers of participants were in both tests a little bit lower than before (16^{th}:57 labs; 17^{th}:54 labs). This could be a consequence of the stop of founding of the monitoring program.

Microwave methods are the most used pretreatment method. For nitrogen and carbon element analyzers are the common determination method. ICP-AES, ICP-MS and Flame-AAS are the most used determination methods for all other parameters.

Based on the results of the questionnaire Mr. Fürst tries to identify influences of the data quality. A small influence can be found between accredited labs and not accredited labs. The most improvement can be found, if labs participating in more ringtests/year. Almost all labs declared that they use control charts. How is it possible to use a control chart and fail with most parameters in the ringtest? This should be one important topic for the next labheads meeting. “Bring your control chart” and how to use a control chart. There is a plan to enlarge the QA/QC-DARQ in the web interface for foliage to get information about the frequency of foliage sample in the lab and about the staff training (method and instrumentation).

Nitrogen results are really good in both tests (only between 2-3% non tolerable results). P, Ca, Mg and Cu are the most “problematic” parameters with approx. 12-16% of non tolerable results.

Possible reasons for bad calcium results could be: Influence of chemical interferences in Flame-AAS and the use of Air/C2H2 flame, use of „strange methods“ for Calcium determination (e.g. ICP-MS, ICP-AES with ultrasonic nebuliser) and ionisation interference in axial ICP-AES or calibration errors.

Possible reasons for wrong phosphorous results could be the use of sensitive photometric methods. Oxidizing acids influence most of these methods (e.g. molybene blue methods) the results are then usually lower. The lab standard deviation is usually bigger compared with ICP-AES methods.

Possible reasons for wrong copper results could be contamination effects and the use of flame AAS, because this method is not sensitive enough for low Cu concentrations.

Ringtest results can be cross-checked also per different parameters (in case of multi-element methods), per sample (complex sample matrix, mistaken identity) and with results from older tests (same problematic parameters/results) to get more information about possible reasons for errors.

How to avoid errors in future? Should be an important question, if a lab failed in a ringtest! FFCC can and give support and offers reference samples for method validation and ringtests for external quality checks. The registration for the 18th Needle and Leaf Interlaboratory Comparison Test is open up from now till 06. July 2015.

In case of a standard ringtest evaluation (no separate printed report) there is a need for a minimum reporting. All web-evaluations are shown only temporary! The new Webinterface 2.2 allows now to printout a pdf-file with all this information.

All ringtest reports and the printouts of the standard evaluated report must be stored somewhere and should be assessable via internet. Due the fact that ringtest providers

changed over time and webpages changed, Mr. Fürst strongly recommends to send at least all these ringtest reports as documentation to PCC!

2. 7th Deposition and Soil Solution Interlaboratory Comparison Test

Kirsti Derome gave a presentation about the results of the 7th Deposition and Soil solution Interlaboratory Comparison Test. The number of participants was in this test a little bit lower than before (5th: 43 labs/ 23 countries; 6th: 41 labs/ 22 countries; 7th: 37 labs/ 24 countries). This could be a consequence of the stop of founding of the monitoring program after the 5th ring test. The changing of participating laboratories makes it difficult to analyze the development of a unique laboratory and link the results of the ring tests to the Monitoring data in the past.

Three of five natural intercalibration samples were deposition from Denmark, UK and Finland, and two soil solution samples from Belgium and Finland. The sixth sample was synthetic sample for measuring alkalinity only. Because of low concentrations (33% or more of results < LOQ) some parameters had to be excluded before final evaluation of the results. Those were Phosphate-P (sample 1), Ammonium-N, Nitrate-N, Phosphate-P and total Nitrogen (sample 3) and alkalinity (samples 2, 3 and 4).

Percentage of accepted results for each parameter was mostly over 85 %. Only alkalinity, pH and Phosphate-P did not reach that. 19 % of laboratories did not analyze Phosphate-P, but this parameter is optional for both deposition and soil solution. 13 % of participants did not measure DOC and total Nitrogen and 11 % alkalinity although these parameters are mandatory for both deposition and soil solution.

Some laboratories have the limits of quantifications (LOQ) too high for some parameters (ref. maximum allowable LOQ's in the QA/QC manual); these results are not passing the ring test. At the same time some labs have extremely low LOQ's for alkalinity and Phosphate-P, especially. In these cases method validation is needed. It's possible that there's a fault in units, too. Problems in measuring pH must be taken into agenda on the next meeting of the laboratory heads, including proper controlling of calibration and condition of the electrode and other practical issues. Some laboratories have obviously submitted the result of Nitrate+Nitrite-N instead of Nitrate-N ((according to the method used), and this has caused some failed results. Normally there's no Nitrite-N in our samples, but this time especially sample 1 had quite high pH with both Nitrite-N and Nitrate-N in about equal concentrations.

The overall results (requalification not yet done!) of the 7th ring test after rejection of low concentration parameters were clearly better than in the 6th ring tests. 17 participants had percentage of acceptable results over 90 %, 9 laboratories over 80 %, 5 over 70 %, 5 between 50 to 70 % and only 1 under 50 %. Only 2 laboratories had remarkably lower percentage compared to the 6th ring test, but 22 laboratories had better overall percentage. Percentages of non-tolerable results for all parameters have decreased clearly during all the intercalibration tests (years 2002 -2015). When comparing the two last ring tests, only for pH (24 %) and alkalinity (18 %) these percentages are now slightly higher, it means that overall results were not staying at the earlier level or becoming better for these parameters. Methodological problems will be on the agenda on the meeting of the laboratory heads in September in Vienna.

Requalification process is going on, there are 20 laboratories with 44 parameters (1 to 5 parameters/ laboratory) to reanalyze or send other explanations latest on 9th May. After agreement of the requalification data final results are loadable from the database.

In conclusion, there are some issues to take into account when planning the next ring test:

- Not all mandatory parameters are involved in ring test (e.g. Fe, Mn in soil solution)
- Feedback for the next ring test is valuable, like type of samples, samples collected by participants, concentrations of parameters, time table of the ring test etc.
- Organizer of the next ring test