

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

27-28 March 2017, Zagreb (Croatia)

Minutes

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

0. Opening

Mr. Nils König opened the meeting and welcomed the participants.

- Ring tests organization and evaluation: ideas for improvements

Next ring tests are planned for foliar: 20th ring test in 2017/18, for deposition and soil solution: 9th ring test in 2018/2019, and for soil: 9th ring test in 2018.

Ms Kowalska on behalf of Mr. Fürst presented the ideas for improvements in ring test organization and evaluation. In the last deposition/soil solution ring test there was a problem with alkalinity results. Alkalinity should be determined from the labs only if $\text{pH} > 5$. But in case the pH determination was wrong not all samples were analyzed for alkalinity. This decision should be done in future from the ring test organizer. Only the samples will be shown where results must be submitted. So a completeness check can be done during data submission. In case of alkalinity only positive values can be reported. If the LOQ is reached minus LOQ (-LOQ) must be reported. In case of Gran titration or if no LOQ is determined the max. accepted LOQ must be reported (-LOQ). But this is very unpalausible because this samples should be excluded from the ring test provider before.

To avoid errors during data submission (for monitoring and for ring test results) a harmonization between the units in deposition and soil solution is needed. All parameters in monitoring should be checked in ring tests too. For a new parameter changes in the web interface for ring test data submission and an extra statistical evaluation to exclude outliers must be made. Experts had to check the sufficient data quality, tolerable limits, max. accepted LOQ and evaluation limits must be set up before this parameter is monitored.

- Problematic parameters in the ring tests for water and foliar analysis: do we need special methodical presentations during the meeting of the heads of the labs? (Anna Kowalska, Alfred Fürst)

Based on the results of the requalification process of the 8th Deposition and Soil Solution ring test Ms Kowalska concluded that laboratories are capable of identifying the reasons for wrong results. Most of the problems were related to low concentration range of parameters. Therefore it was proposed to prepare a presentation on measuring of samples with low concentrations for next meeting of the heads of the labs: contamination problems and clean working conditions.

Results of the 17th - 19th Foliar ring test show that for two parameters labs deliver about 15% of nontolerable results in successive ring tests: K and P. For Mg, Zn and Fe about 12% -14% results is non tolerable in the last two ringtests. There was proposed to prepare a special

presentation on the phosphorus determination and pretreatment. The problem with nontolerable P results may come from digestion method.

- Preparation of the meeting of the heads of the labs Sept. 2017 Palanza, Italy (Nils König)

The next meeting of the heads of the labs has been scheduled for 7-8 September 2017 in Pallanza, Italy at the kind invitation of Mr Marchetto from National Research Council – Institute of Ecosystem Study.

At the meeting there will be discussed the results of 8th water and 18th and 19th foliar ring test, problematic parameters in the ring tests, analytical problems, new methods, and method comparisons in water, foliar, and soil analyses.

Among the other proposed topics are:

- Preparation, evaluation, timetable and financing of future ring tests,
- New features in the Ring test Web Interface 2.0,
- Aqua regia digestion with microwave or reflux method,
- Proposal for better coding of the methods for C-CO₃ and Corg determination with element analyzers,
- Heavy metals in the ICP Forests monitoring program,
- Problems and possible changes in data submission (different units Depo/Soil Solution ring tests; problems with data submissions of elder or corrected data),
- Data submission (Corrections in the quality forms, new evaluation of QA forms, consequences),
- New methods proposed in other expert panel meetings: presentation of the methods, experiences with the methods and decision about the acceptance for the ICP Forests manual.

Participants of the meeting are invited to prepare short presentations on analytical problems, method comparisons, instruments used in labs and other topics related to laboratory work. More information will be given in invitation for the meeting.

- Proposal for better coding of the methods for C-CO₃ and Corg determination with element analyzers (Nils König)

Determination of carbonates in Manual part X Sampling and Analysis of Soil is described only for the method based on calcimetric analysis using Scheibler unit. In present, the other methods using macro-elemental analysers are available and already used by labs and should be coded. Therefore, four new codes are proposed:

- DA06 - Macro Elemental-analyzers for C for solids with variable temperature-programming for Corg- and CO₃-determination
- DA07 - Macro Elemental-analyzers for C for solids with CO₃-unit (acid digestion of carbonates)
- DA08 - Macro Elemental-analyzers for C for solids; CO₃-determination as difference between C_{tot} and Corg (after acid carbonate-digestion)
- DA09 - Macro Elemental-analyzers for C for solids; Corg-determination after acid carbonate-degasing

Soil Expert Panel has to decide whether those methods will be allowed in the Manual. The decision has to be made based on what precision and what quantification limit is needed in relation to the purpose of the study. From the other part, the information on the instruments used by labs has to be gathered at the coming meeting of the heads of the labs to see how many labs use specific instruments for carbonate content analysis.

- Aqua regia digestion with microwave or reflux method: are they comparable? Do we should open the manual for both methods? (Nathalie Cools, Nils König)

In Manual part X Sampling and Analysis of Soil the only allowed method for digestion in aqua regia is the reflux method. The microwave digestion is not allowed because results are not comparable. In Germany there was made a comparison of both methods for 22 elements in 10 types of soil. A linear regression was found for both methods and for most of the elements but the results differed depending on the type of the soil and the element. The German study confirms that both methods can not be used interchangeably. In the last soil ring test higher % of labs that failed had used microwave digestion. However, facing up to the fact that the new ISO standards for microwave digestion in soil has been released (ISO 12914:2012) and taking into account increasing popularity of microwave systems, the admission of microwave method has to be considered by Soil Expert Panel. The problem may be prominent with comparability of data for long time series in ecological research when the digestion methods have changed in time.

- Problems and possible changes in data submission (Different units Depo/Soil Solution/ring tests; Problems with data submissions of elder or corrected data) (Anna Kowalska, Till Kirchner)

Al, Fe, and Mn are analysed in deposition as optional parameters and in soil solutions as mandatory parameters if pH is lower than 5. In the former, results have to be reported in µg/l while in the latter in mg/l. Different units can lead to mistakes in reported values especially when the same labs analyse deposition and soil solution samples. In 8th Deposition and Soil solution ring test a few labs reported results in mg/l despite the fact that µg/l were required. The same errors are apparently present in LQA files for both: deposition and soil solutions. Therefore there was proposed to use the same units in deposition, soil solution and ring tests, preferably mg/l. For the data already stored in the database the units have to be recalculated, and the improbable values: too low or too high detected. NFC's will be asked for verification or correction of the data. The availability of the old data for the correction of the LQA files will be discussed at the coming meeting of the heads of the labs. The ICP-Forest community has to be informed about the changes through the official web-page.

(At the Expert Panel Soil and Soil Solution meeting in Zagreb it was accepted that the meeting of the heads of the labs shall decide about the acceptable tolerable limits and LOQ's for the parameters Mn, Fe and Al in ringtests.)

Information about ring test results will be removed from the LQA file; this information will be delivered directly to the database by the ring test providers. Labs will not have to deliver info about ring test results or requalification results to LQA files any more. This way the problem with matching up of the correct number of the ring test to the dataset from a specific survey year will be solved too. LQA forms will not be skipped totally as still much information has to come from the labs.

For soil both dates are important in the database: date of sampling and date of analysis. Up to now there is no possibility to code two different dates of analysis in the same sample for variables. To overcome this problem the database manager proposed to add an additional column in the submission file for year of analysis/variable.

- Heavy Metals in the ICP Forests monitoring program (Which elements are needed in which survey; Analytical methods and problems; Integration of these elements into the ring test program) (Nils König, Alfred Fürst)

Mr König on behalf of Mr Fürst presented the actual situation about the parameters (elements) in different surveys and in the ring tests. For foliage (litterfall) and soil the lab

quality of all monitored chemical parameters are checked in ring tests. The ring test providers were/are the coordinating centers FSCC and FFCC. They cooperate strict with the expert panels and were organising the ring tests. Problematic parameters with inaccurate results in the ringtest were skipped from survey and from ring test (e.g. Al, Na for foliage and litterfall).

For deposition and soil solution there was a different situation. Two Expert panels were responsible and the organization of the ring tests was done from the Expert Panel Deposition in cooperation with the WG QA/QC in labs. Due to this the parameter list in monitoring and in ringtests are different and the units between monitoring and ring tests are still not harmonized. It is mandatory to check the data quality of all chemical parameters in ring tests! A harmonization between the monitored parameters and the parameters in the ring test is needed. Analytic difficult monitoring parameters, which are not needed or not surveyed should be skipped.

Heavy metals that are optional in deposition or soil solution and are not integrated in the deposition/soil solution ring tests can be tested in EMEP ring tests. ICP-Forests labs are invited to participate there without charge. This possibility will be presented to the heads of the labs at the coming meeting.

B. Combined Meeting with EP Foliar and EP Deposition

0. Opening

Mr König opened the meeting and welcomed the participants.

- 2015 Soil Ring test results (Tamara Jakovljević)

Ms Jakovljević presented the results of the 8th Soil Interlaboratory comparison test. The number of participants is almost the same as in 2012 (32 in 2015, 30 in 2012). 31 lab sent results. In the test 42 parameters could be analyzed, 25 are mandatory parameters. The best results are obtained for pH in CaCl₂, OC and total nitrogen. Problematic parameters in the ring test were exchangeable cations. Some labs did not use the reference method. For CaCO₃ 2 labs need requalification because they had 10 times less result; it seems to be a problem with calculation and units. 14 labs out of 31 failed in at least 1 mandatory element. Requalification was finished at end of January 2016. The new ring test will be in 2018.

- 2017 Deposition Ring test results (Anna Kowalska)

Ms Kowalska presented the results of the 8th Deposition and Soil Solution Ring test. Compared to the previous ring test, time for analyses and for requalification was shortened to 4 months starting from the registration due to the risk of instability of the samples. 40 labs (25 countries) registered and 39 of them submitted results. Five of the samples were natural waters: stemflow (beech), throughfall (spruce), bulk open field, two soil solutions. Labs were requested to analyse in these samples all the mandatory parameters and P-PO₄, Fe, Al, and Mn. Sixth sample was syntetic for alkalinity measurements only.

P-PO₄ in samples 2, 3, and 4 and N-NH₄ in sample 4 were excluded from the evaluation due to the low concentration – more than 33% of results was <LOQ. DOC in one sample was excluded from evaluation because it did not pass the stability test. Alkalinity in soil solutions (sample 4 and 5) was not evaluated because pH was <5.

For mandatory parameters, 13% of N_{tot}, 11% of DOC and 7% of alkalinity results were missing. Nine labs did not submit all the mandatory parameters.

Percentage of acceptable results was above 90% for 15 labs, between 80% and 90% for next 14 labs. Three labs reported less than 40% of acceptable results. Requalification was

necessary for 25 labs but most of them failed for only 1 or 2 parameters; 20 of the labs successfully requalified.

Too high limit of quantification was reported by 1 - 3 labs for Cl, DOC, Mg and N-NO₃ and these results did not pass the test.

The most problematic parameters were: Ca, pH, alkalinity, and N-NH₄; less than 80% of acceptable results was recorded for those parameters and more than 5 labs had to requalify for them. As much as 10 labs failed for Ca.

Labs reported in requalification the following reasons for failure:

- technical problems (instruments, sensors, electrodes failure/ageing, poor compensation of temperature): Ca, alkalinity, N_{tot}, pH, N-NH₄, DOC, conductivity;
- Quality control material or standards of poor quality: Ca, Alkalinity, N_{tot}, pH, DOC;
- Calibration (failed for low concentration samples): Ca, N_{tot}, DOC;
- Contamination of samples, spectral interferences: Ca

The common problem was reporting wrong units or lack of recalculation for alkalinity, S-SO₄, N-NH₄, N-NO₃, P-PO₄. It happened also to the labs participating regularly in WRT's. Some of the common errors could be avoided if labs would read the instruction delivered with samples and if the quality tests (conductivity, ionic balance, N check) would be performed as a routine.

Percentage of non tolerable results although remarkable lower than in ring tests organized between 2002 and 2009, stays at the level comparable with two previous rounds of ring tests (2013 and 2015). For most of the parameters, except for Ca, less than 20% results falls outside the tolerable limits. Obviously, concentration of the analytes in samples can influence the score of the labs. Higher % of unacceptable results was recorded in samples with low concentration.

Three parameters that are obligatory in soil solutions if pH<5: Al, Fe, and Mn were not measured in 6th and 7th WRT but were requested in 8th WRT. Al, Fe, and Mn are going to be included in the next ring tests. The number of labs that submitted results (i.e 31-32 labs) was high enough to make the statistical evaluation of the results. Maximum tolerable quantification limits (LOQ) and tolerable limits for future ring tests were calculated. For Aluminium and Iron, maximum LOQ was proposed to be 0,015 mg/L, for Manganese 0,01 mg/L. Tolerable limit for Al is proposed to be 30% for concentration ≤0,1 mg/L and 15% for concentration >0,1 mg/L. For Fe in whole concentration range, proposed tolerable limit is 30%. For Mn, proposed tolerable limit is 15% for concentration ≤0,025 mg/L and 10% for concentration >0,025 mg/L. The proposal will be presented and discussed at the meeting of the heads of the labs in September 2017.

In future ring test submission of all requested parameters in all the samples will be mandatory for labs; the list of requested parameter per sample will be delivered with samples by ring test provider. 9th Deposition and Soil Solution ring test is planned to start in autumn 2018; timetable to be discussed at the meeting of the head of the labs.

- 2016/17 Foliar Ring test results (Alfred Fürst)

In the 'Combined session with EP Foliage and Deposition and EP Soil and Soil Solution' Mr. König on behalf of Mr. Fürst presented the results of the 18th and 19th Needle/Leaf Interlaboratory Comparison Tests. The numbers of participants were in both tests lower than before (18th:53 labs; 19th:45 labs). This is also a consequence of the stop of funding of the monitoring program.

The samples in the 18th test were: beech leaves, pine branches and two spruce needles; in the 19th test: three samples spruce needles and one pine needle. In the 19th test there is a big group of laboratories with correct results but on the other side there is a big group with

very bad results (one lab failed with nearly all results). Mr. Fürst try to compare the results with the answers of the QA/QC questionnaire:

Participating in more than one ringtest per year has a positive influence on data quality. Laboratory accreditation and a higher number of analyzed samples per year have a small positive influence on data quality. The results are not so good if the lab has the opinion that the staff is good trained on the method and the matrix!

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

Cadmium results are really good in both tests (only between 2.1-8.0% non tolerable results).

P, Mg, K, Cu and Pb are the most "problematic" parameters with more than 15% of non tolerable results in one or in both tests.

A good ringtest result means that the % Recovery is close to 100% and the variation between the replicates is small. A requalification is mandatory for all laboratories, if they plan to submit monitoring results to PCC! Use your labcode, if you submit the requalification papers per email. Use only the Excel sheet to summarize your requalification results and don't forget to submit additional printouts (as pdf) about calibration, dilution factors.... It should be possible to recalculate your results! Submit your ideas about your opinion for missing the qualification and how you avoid the same error in future.

FFCC offers reference samples (<http://bfw.ac.at/rz/bfwcms2.web?dok=5146>) and a new spruce sample with known content of heavy metals. The registration for the next Needle/Leaf Interlaboratory comparison test is open till 2017-07-10.

Because of the use of multi-element determination methods (ICP-AES and ICP-MS) a lot of labs already analyze more and more elements without extra costs. A special evaluation for heavy metals (As, Co, Cr, Hg, Mo, Ni, Tl, V) was made for the 18th and 19th test. A repetitious accuracy was reached in both tests for these elements and the reached results are comparable to them for Cu, Cd and Pb. For As, Co, Cr, Hg and Ni (more than 10 participants) it is planned to include them in the normal ring test evaluation and to include them as optional parameter in the monitoring program for foliage and litterfall. This will be discussed in the EP meeting Foliage & Litterfall afterwards.

- Heavy metals in the ICP Forests program: needs and possibilities (to be discussed in detail during the EP's sessions) (Nils König)

Mr König presented the actual situation about the heavy metals in different surveys (optional/mandatory) and in the ring tests. The different Expert Panels have to discuss and to decide if something should be changed in the program. But it is important that check the quality of the heavy metal measurements for all types of samples.

For foliage (litterfall) and soil the lab quality of all monitored chemical parameters are checked in ring tests but not for deposition and soil solution. Therefore it is important to have also ringtests for heavy metals in water samples.

Therefore Mr König proposed that ICP-Forests labs should participate in the EMEP ringtests which is possible for ICP Forests labs without charge. This possibility will be discussed with the heads of the labs at the coming meeting.

- Different units Depo/Soil Solution/ring tests (Anna Kowalska)

See the same topic under the meeting of WG QA/QC