

**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 - 26-27 March 2019, Brussels (Belgium)**

## **Minutes**

(All presentations can be downloaded from the ICP Forests website: <http://icp-forests.net/group/qualityinlaboratories/page/document-archive>)

### **A. Meeting of the Working Group QA/QC in Laboratories 26. March 2019**

**Mr. Alfred Fürst** opened the meeting thanked the organizers and INBO and welcomed the participants.

**Mr. Till Kirchner** presented the link between monitoring data, LQA-files and ringtest results. At the moment a user can download a zip-archive containing all monitoring data of a survey and the LQA data from labs. The zip-archive further includes a folder named "adds" which includes the ringtest results. Data from old ringtests is still part of the downloaded LQA-file. Mr. Kirchner and Mr. Fürst will discuss potential ways to "re-submit" data from old ringtest directly from the ringtest DB. After this the information could be removed completely from LQA-file. The "adds" folder will contain a list to explain the laboratory-IDs including the name of the lab and the person responsible for the ringtest/LQA.

In preparation of the next Heads of the Labs meeting 2019 Mr. Kirchner and Mr. Fürst plan to send reports about available LQA information in the central DB to the labs and ask colleagues to verify this information.

The summary of this verification will be presented and discussed at the heads of the lab meeting 2019.

**Ms. Dora Lucaci** presented the location and the dates of the meeting of the heads of the labs in Brasov/Romania. The meeting will be on the 5<sup>th</sup> and the 6<sup>th</sup> of September 2019. The fee for the meeting is 80 euro/person (before 1<sup>st</sup> of August 2019), which has to be paid by bank transfer, and it will include three meals and coffee breaks. A small excursion is planned for Friday afternoon, which will include a guided tour to the "Bran Castle" and a traditional meal, at the extra cost of 35 euro/person (before 1<sup>st</sup> of August 2019), to be paid with the registration. Details of the meeting are given in her presentation.

**Mr. Alfred Fürst** presented the topics for the meeting of the heads of the labs:

- Foliage & Litterfall (ringtest results & presentations),
- Soil (ringtest results & presentations),
- Deposition & Soil Solution (ringtest results & presentations) and
- QA/QC Manual update 2020 should be finished and ready for approval.

Special methodical presentations are foreseen:

- Microwave extraction method (soil)
- Heavy metals evaluation limits (deposition)
- ICP-MS (for foliage analyzes) Ca, Mg, S,...

He will send out the first announcement of the meeting and asked for presentations [*is already online <http://icp-forests.net/group/qualityinlaboratories/forum/topics/7th-meeting-of-the-heads-of-the-laboratories-5-6-september-2019>*]. At the moment the following presentations are named:

- Comparison of two methods for the measurement of Mercury: ICP-MS and AFS (Nils König)
- Development of a cost efficient sampler for Mercury deposition measurements (Nils König)
- Potential of mid-infrared spectroscopy for carbonate determinations in forest soil samples (Michael Tatzber)
- A fully automated system for pH measurements in soil samples (Nils König)
- Determination of mercury in natural waters (Ülis Sõukand)
- Link between monitoring data, LQA Files and Ringtest results (Till Kirchner)
- Results from verification of available LQA data (Till Kirchner / Alfred Fürst)

**Mr. Alfred Fürst** informs the participants about the planned manual update. The updated manual should be approved in the Task Force meeting 2020. There are no major changes foreseen, only the ringtest part will be harmonized, shortened and linked to the ICP-Forests webpages for the three types of ringtests. Special procedures for sample handling and evaluation, links to the ICP-FORESTS ring test webpages, the tolerable limits and max. accept. LOQs will stay in the manual. At the moment first updates of the manual were done by Anna Kowalska and Alfred Fürst. Till 15/04/2019 the updates by Tamara Jakovljević and by Aldo Marchetto will be finalized. Afterwards Nathalie Cools, Bruno De Vos and Morten Ingerslev will follow.

During the manual update it is planned to make the following changes:

“...When a lab did not qualify and did not make efforts to requalify, ~~the ring test organizers~~ **ICP Forests PCC** will send a letter to the National Focal Centre and inform them about the consequence that their data possibly cannot be used for evaluations on an European level.

The results of the ring tests are integrated in the database of the PCC. This means that the bad ring test results will be marked as disqualified and this information can be used as a selection criterion for the monitoring data used in evaluations. ...”. Mr. Kai Schwärzel agreed to this proposal, but the ringtest provider should be preparing a draft for these letters.

In addition to the named papers for the re-qualification control charts and a statement about the measures against similar errors in future will be added.

The updated version should be available before the meeting of the heads of the labs and should be adopted there.

**Ms. Nathalie Cools** started the discussion about the Microwave extraction method(s) with a presentation. DIN EN 16174 (2012) Europe/Germany: allowing both methods: reflux system

& microwave digestion and also ISO standard 12914 (2012) Soil quality - Microwave-assisted extraction of the aqua regia soluble fraction for the determination of elements allow the use of the microwave method. In the 9<sup>th</sup> soil ringtest microwave extraction method was used by three laboratories (F03, F18 and S01). Some elements are problematic to compare with the reflux method especially Al, Cr, K and Na.

New method codes will be added [*was added in the ringtest interface*]:

- PD06 Microwave extraction method (EN 16174)
- PD07 Microwave extraction method (ISO 12914)

A general code for “other microwave methods” is already in the list (PD99).

A questionnaire will be prepared and sent out (INBO-Gerrit Genouw) to get information about the digestion temperature/pressure/time, acid mixture, sample weight, used instrumentation. The outcome will be presented in the meeting of the heads of the labs. A final decision how to proceed with use of the microwave extraction method should be made before the next soil survey/next ringtest [*was prepared*].

**Ms. Anna Kowalska** presented the draft for the evaluation limits for the heavy metals in Deposition/Soil solution ringtests (see below). The frequency of deposition/soil solution ringtests should be switched to an annual ringtest repetition. A final version will be prepared for the meeting of the heads of the labs and should be adopted there [*was adopted in the EP Deposition, there is a mandate for the final decision to the meeting of the heads of the labs*].

**Mr. Alfred Fürst:** An update for soil and deposition ringtest data submission is planned. There will be a possibility to delete all results for one parameter; this will be implemented in summer 2019 [*was implemented*].

For foliage ringtest there is now a possibility for the conversion of the laboratory results to the used units in the ringtest. 14% of all results were converted with this feature, but there were still results submitted in wrong units. At the moment there is no need to add this feature in the other ringtest web-interfaces. Mr. Nils König want to add a warning in the deposition ringtest interface to report element concentrations instead of ammonia, nitrate, phosphate and sulphate [*was implemented*].

E-invoicing for the ringtest participation fees is not possible.

Available phosphorus in soils is to be implemented in the Manual part X – new parameter and new method implementation will be discussed at the meeting of the heads of the labs.

## **B. Combined Meeting with EP Foliar & Litterfall, EP Soil & Soil Solution and EP Deposition 27. March 2019**

Mr. Alfred Fürst opened the meeting and welcomed the participants.

**Results of the 20th and 21st Needle/Leaf Interlaboratory Comparison Tests (Mr. Alfred Fürst)**

He presented the results of the 20th and 21st Needle/Leaf Interlaboratory Comparison Tests. The numbers of participants were slightly increasing compared to former tests (20th: 48; 21th: 52).

The samples in the 20th test were: birch leaves, two spruce needles and a pine cone sample; in the 21th test: bears garlic, spruce needles, spruce twigs and beech leaves. Microwave digestion or pressure digestion followed by ICP-AES or ICP-MS and element analyzers are the most prominent analytical methods.

The results for nitrogen, sulphur and calcium were not so good in these tests. Mr. Fürst compared the used methods and tried to find some reasons for these bad results. Arsenic (analyzed from 14 labs), cobalt (21 labs), chromium (23 labs), mercury (16 labs) and nickel (25 labs) were new parameters in these two tests. ICP-MS methods produced for these elements the best results – for mercury element analyzers are also a good choice.

There is no or less improvement in the data quality of laboratories with a higher number of non-tolerable results. The ICP-Forests laboratories A60 (S), A62 (Ca), F07 (As, Cr) and F21 (Ca) failed with the same parameters – in bracket – in both tests. Mr. Fürst offered these labs four extra samples to check the measures against these errors in future before they start with the next regular test. Mr. Fürst remind all labs to submit the re-qualification report earlier (1st of August 2019) to discuss open questions before the final deadline (1st of September 2019). The report should contain: Your lab-code and the results of the re-analyzed ringtest samples, all printouts from the instruments (calibration curves, calibration factors, measured results, date/time), sample weights, dilution factors, moisture correction factors (if needed). There must be a statement of the reason for failing the qualification and your ideas for measures against this error in future. Additional documents e.g. control charts can be requested.

The registration for the 22nd Needle/Leaf Interlaboratory Comparison Test is open till 1st of July 2019. Ringtest samples, especially heavy metal polluted samples or samples from deciduous trees are welcome, please contact Mr. Fürst if you want to prepare a ringtest sample.

### **Results of the 9<sup>th</sup> Soil Ring test 2018 (Ms. Tamara Jakovljević)**

Laboratory for physically and chemical analysis, Croatian Forest Research Institute has organized the soil interlaboratory comparison in 2018 for 29 European labs. The samples A-E were from Check Republic (A), Slovak Republic (B), Germany(C), Spain (D) and Croatia (E). The organization included: preparations for the registration of participants, pre-treatment, homogenization and homogeneity comparison. One sample was with CaCO<sub>3</sub> content between 10 – 20% and one organic sample E. During the statistical procedure some samples were excluded because of the low values which were often below the limit of quantification.

The most successful parameters by all labs were pH- CaCl<sub>2</sub>, K exch and N tot. Most failed parameter was Mg extra. Only in 1 loam sample (D), other were excluded because pH was lower than 5.5. but still lot of labs try to analysed it.

Concerning the analyses of the semi-total elements in aqua regia extract, almost all labs applied the reflux method (which is indeed the reference method). Only 2-3 labs reported that they used the microwave digestion method. So the initial idea to use the ring test results to compare the results based on both pretreatment methods (for which even a separate reporting module was foreseen at the data submission page) could not be realised as there were too few results available based on the microwave digestion method.

19 labs of 29 failed at least in one mandatory parameter.

## Results of the 9<sup>th</sup> Deposition & Soil solution Ring test 2019 (Ms. Anna Kowalska)

In the 9<sup>th</sup> Deposition and Soil Solution Ring test participated 39 labs from 25 countries and all of them submitted results. Five of the samples were natural waters: bulk open field from Poland, throughfall (beech) from Slovenia, stemflow (beech) from Austria, and two soil solutions from coniferous stands in Poland. Labs were requested to analyse in these samples all the mandatory parameters and phosphates, Fe, Al, and Mn. Sample six was synthetic for alkalinity measurements only. All tested parameters passed the stability tests.

Alkalinity in soil solutions (sample 4 and 5) was not evaluated because pH was <5. Phosphates in samples 1, 3, 4, and 5, ammonium in samples 4 and 5, Al and Mn in sample 1, Fe in samples 1,2 and 3 were excluded from the evaluation due to the low concentration – more than 33% of results was <LOQ.

For mandatory parameters, 13% of Ntot, 11% of DOC and 7% of alkalinity results were missing. Twelve labs did not submit all the mandatory parameters.

The groups of labs that deliver above 90% and between 80% and 90% of acceptable results are as numerous as in the previous, 8<sup>th</sup> ringtest (15 and 14 labs respectively). Two labs that had the lowest percentage (below 50%) of acceptable results did not participate in the previous ringtest. From the other hand, there is a group of five labs that show little or no progress and in both ringtests submitted less than 80% acceptable results.

Requalification was necessary for 28 labs but most of them failed for only 1 or 2 parameters; 22 of the labs made the effort to requalify bad results.

The most problematic parameters across recent two ringtests remain Ca and N-NH<sub>4</sub> with less than 80% of acceptable results. Ten labs failed for Ca and eight for ammonium. Percentage of acceptable results was below 80% also for Mn. Low percentage of acceptable results (61%) for P-PO<sub>4</sub> resulted mostly from very low concentration of phosphates in ringtest samples.

Percentage of non tolerable results is comparable with two previous rounds of ring tests (2015 and 2017). Calcium, ammonium, aluminium and manganese have the highest (> 20%) percentage of non-tolerable results. For the other parameters, less than 20% results falls outside the tolerable limits.

Heavy metals that were not regularly tested in the previous ringtests, and were submitted to the ICP-Forests database, have been included in 2019 ringtest. Twenty two labs received additionally 5 samples acidified with HNO<sub>3</sub> for analysis of heavy metals: Cd, Co, Cr, Cu, Ni, Pb, and Zn. Three samples were of natural origin: throughfall, stemflow and bulk deposition of naturally low concentration of heavy metals. Two samples were synthetic with medium to high concentration of heavy metals. Results were evaluated statistically; LOQ and tolerable limits for the evaluation in future ring tests were proposed:

Parameter	Unit	Conc. Range low	Tolerable Limit low	Conc. Range high	Tolerable Limit high	max. LOQ
Cadmium	µg/l	≤ 1	± 40 %	> 1	± 30%	0.1
Cobalt	µg/l	≤ 1	± 40 %	> 1	± 30%	0.1
Chromium	µg/l	≤ 1	± 40 %	> 1	± 20%	0.5
Copper	µg/l	≤ 2	± 40 %	> 2	± 20 %	1
Nickel	µg/l	≤ 1	± 40 %	> 1	± 20 %	0.5
Lead	µg/l	≤ 1	± 40 %	> 1	± 25 %	0.5
Zinc	µg/l	≤ 30	± 35 %	> 30	± 25 %	10

The proposal will be presented and discussed and adopted at the meeting of the heads of the labs in September 2019 too. So it should be possible to include these evaluation limits in the QA/QC manual update 2020.

The timetable of 10<sup>th</sup> Deposition and Soil Solution ring test will be finally adopted at the meeting of the head of the labs.

### **Results/Feedback of the last Meeting of the Heads of the Labs in Pallanza 2017. Solved tasks from the Combined meeting Zagreb 2017 & new tasks to discuss in the EP meetings Foliage & Litterfall Deposition, Soil&Soil Solution**

Mr. Fürst reported about the last meeting of the heads of the laboratories in Pallanza 2017 and about the solved tasks from the last combined meeting in Zagreb 2017 and about open tasks, which should be discussed in the following EP meetings foliage&litterfall, soil&soil solution and deposition.

In the meeting of the heads of the laboratories in Pallanza 2017 the topic drying of foliage and litterfall samples was discussed. Clarification in the manual and in the database where done. The new parameters As, Cr, Co, Hg and Ni must be included in the foliage and litterfall manual during the update process till 2020.

The method code list for the determination of carbonates with element analyzers was enlarged (DA06-DA08). These codes are available for the soil ringtests and for the LQA-files in the database.

In the last soil ringtest 3 laboratories used the microwave extraction method. In the QA/QC session the three method codes were set up for microwave digestion methods (see above). A questionnaire will be prepared and sent out to all laboratories to know more about the used equipment, programs, temperature profiles, sample weights and acid mixtures. This topic will be further discussed at the next meeting of the heads of the laboratories.

For deposition and soil solution evaluation limits for Al, Fe and Mn were already fixed and these limits are used in the last water ringtest 2019. A proposal for the evaluation limits for different heavy metals (Cd, Co, Cr, Cu, Ni, Pb and Zn) was discussed yesterday and must be adopted in the EP deposition and the meeting of the heads of the laboratories. The meeting of the heads of the labs proposed to the expert panel deposition to skip Hg, B and Mo from the parameter list, because of methodical problems and these elements cannot be analyzed within the normal ICP-FORESTS DP survey [*B was already removed, Mo will be removed. For Hg, EP Deposition decided to keep it in the list, regarding the Minamata convention. A deposition manual update will follow.*]. These changes should be done in the next manual update 2020.

The deposition and soil solution ringtest should be made annually to check the data quality of the monitoring results more often [*was adopted in the EP Deposition*]. Ringtest results can then better be used for data selection of problematic laboratories. This must be adopted in the next meeting of the heads of the labs.

The blue marked comments (within the brackets) are decisions made in the EP meetings afterwards or after the combined EP meeting from Brussels.