



Working Group on QA/QC in Laboratories
8th Meeting of the Heads of the Laboratories
12-13 May 2022, WSL/Birmensdorf (Switzerland)

Minutes

The meeting was attended by 58 participants (15 online) from 20 countries. **Mr. Alfred Fürst** opened the meeting, welcomed the participants and thanked the team of WSL for the invitation and for the organization of this meeting. **Mr. Peter Waldner** (NFC Switzerland) on behalf of Mr. Marco Ferretti (Chairman of ICP Forests) and **Mr. Arthur Gessler** (Steering committee SwissForestLab) welcomed the participants at WSL/Birmensdorf. Mr. Arthur Gessler presented a short overview to new possibilities for forest monitoring.

The agenda of the meeting was adopted.

Mr. Michael Tatzber presented the results of the 23rd and 24th Needle Leaf Interlaboratory Comparison Tests. The number of participating laboratories decreased slightly compared to previous tests (23rd: 48 and 24th: 47).

Following samples were analyzed in these two tests: beech leaves, two samples consisting of spruce needles and ash leaves in the 23rd test and spruce twigs, pine needles, beech leaves and spruce needles 24th test. Sample 3 of the 21st and sample 1 of the 24th Interlaboratory Comparison Test were identical (spruce twigs) and their determined values in a satisfying agreement. The most prominent pre-treatment methods were microwave digestion and pressure digestion; the most prominent analytical methods were ICP-AES and ICP-MS.

The five rather new parameters arsenic (analyzed by 12 labs), cobalt (17 labs), chromium (21 labs), mercury (17 labs) and nickel (25 labs) had enough participants for a statistical evaluation. For determinations of such parameters ICP-MS appears as the best choice, especially for low concentrations – for mercury the element analyzer appears as well appropriate.

The results for sulfur could be improved slightly over the last five years; the result for nitrogen and calcium were quite constant (except nitrogen in the 21st test). It is assumed that the most prominent error sources for Ca-analyses are application of ICP-MS in too high concentrations and no right buffering against P and Si in the AAS-flame technique, also matrix adapted standards appear important for this method (with focus on acid mixture & concentration). The numbers of non-tolerable results for lead, arsenic and cobalt decreased over the last five years. In most cases most of the non-tolerable results originated from other used methods than ICP-MS. Hence this method

appears clearly as the best choice for analyses of such parameters; especially when the concentrations of these elements are low.

The registration for the 25th Needle/Leaf Interlaboratory Comparison test is still open until 23 June 2022, the actual number of participants is 25 (March 2022). There is a need for samples, especially (but not only) heavy metal polluted ones and/or samples from deciduous trees! Please contact Mr. Tatzber if you want to prepare a ringtest sample and keep in mind its value for its further use as a control sample!

A list of the instruments used per laboratory was sent out as part of the ring test. For methodological questions, each lab can contact colleagues who use the same method or instrument.

Mrs. Tamara Jakovljević Results of the 10th Soil Ring test 2021

Laboratory for physically and chemical analysis, Croatian Forest Research Institute has organized the soil interlaboratory comparison in 2021 for 32 European labs. The samples A-E were from Slovenia (A), Turkey (B), Austria (C), Croatia (D) and Latvia (E). The organization included: preparations for the registration of participants, pre-treatment, homogenization and homogeneity comparison. One sample, sample B, was with CaCO₃ content between 10 – 20% and one organic, sample E. During the statistical procedure some samples were excluded because of the low results, e.g. Sample B was excluded for parameters Al_{exch}, Fe_{exch}, Mn_{exch}, Free_H, Org_C, and all samples were excluded for CaCO₃ except sample B. Parameters passed by all labs were pH_CaCl₂, Org_C, Total_N. Most failed parameters were Ca_{extr} and K_{extr}. 11 of 32 labs passed all parameters. 13 of 21 labs failed at least one mandatory parameter.

In requalifications, 17 of 21 labs submitted requalification report. Still some labs did not submit all needed documentation (e.g. control chart) for requalification and fail because of that. After the meeting all laboratories which fulfil the needs of the requalification will get an extra sample set to confirm their requalification.

Mrs. Tamara Jakovljević has offered reference material to the labs that did not qualify. She also asked countries to help with soil samples for the next ring test.

Mrs. Anna Kowalska - Results of the 11th Deposition & Soil solution Ring test 2021/2022:

39 laboratories from 22 countries registered to the 11th Deposition and Soil Solution Ring test. Five of the samples were natural waters (samples 1-5): bulk open field, throughfall (coniferous), stemflow (beech) from Poland, soil solution from mixed stand in Romania and soil solution from coniferous stand in Poland. Sixth sample was synthetic for alkalinity and phosphate measurements. Additionally 28 labs received 4 samples of natural water (samples 7-10) for heavy metals: Cd, Cu, Co, Cr, Ni, Pb, Zn. The recommended method for analysis of heavy metals is ICP-MS.

Alkalinity in soil solutions (sample 4 and 5) was not evaluated, pH in sample 4 was excluded from evaluation due to instability. Phosphates and manganese in sample 4, ammonium in samples 3, 4 and 5, iron in sample 1, 2 and 3, and Cr in sample 7 were excluded from the evaluation due to too low concentration.

The overall score of the labs improved compared with previous rounds of ringtests: the groups of labs that deliver above 90% of correct results is more numerous than in previous ringtests (27 labs in 11th WRT) and fewer labs (4 labs) delivered below 80% of correct results than before.

Requalification was necessary for 16 labs; 11 labs made the effort to requalify for bad results. The most problematic parameter was Alkalinity with 5 labs that failed the qualification.

Percentage of non-tolerable results is comparable with two previous rounds of ring tests (2019 and 2020). For mandatory parameters except Alkalinity and pH no more than 10% results falls outside the tolerable limits. For alkalinity 25% and for pH 14% of results exceeds tolerable limits.

Next 12th Deposition and Soil Solution ring test is planned to start in summer/autumn 2022 and finish in spring 2023.

Mr. Alfred Fürst presented the history and progress of the ringtest programme and the current qualification/re-qualification procedure. All important information to the ringtest are available on the webpage of ICP-Forests (<http://icp-forests.net/page/working-group-on-quality>). The final verification of the measures set in the laboratory for improvement the data quality during re-qualification is done by a successful participation in the next test (for foliage & litterfall or deposition & soil solution), or with a successful analysis of an extra soil sample set.

The documents required for re-qualification by the ringtest provider must be submitted in time. The provider checks them and it must be possible for him to derive the content found by the lab from the measured values and control cards are obligatory. The person responsible for the laboratory must be available for queries.

In order to be able to send information to the NFCs and to the persons responsible for the laboratory, the e-mail addresses must be kept up to date (ringtest web interface and the expertlist on the ICP-FORESTS page).

Mr. Till Kirchner presented “Lab data in the ICP Forests database - improved check routines and other news”

Quality information is currently located in various places in the database. The aim is to make this information easily accessible to data users so that data quality can also be used as a selection criterion for evaluations. For this purpose, the monitoring data in the DEM, FOM, LFM, SOM and SSM files must be linked with data from the LQA files (e.g. method codes, LOQ) and with the ring test results coming from the test providers (e.g. labcodes, percentage ringtest result). This is not so easy, because of the long key an extra generated code number (QIF) is introduced in the monitoring data tables to link them easily with the quality information (LOQ, ringtest results,...). A check matrix for method codes of the foliage and litterfall survey was set up and checked successfully with older available data in the database (<https://icp-forests.org/documentation/ExplanatoryItems/211.html>).

In case the data check during data submission does not work properly, e.g. warnings or errors are displayed and are obviously wrong, Mr. Till Kirchner can be contacted directly.

The new check of the correct allowed method codes during data submission should be enlarged to deposition, soil solution and soil.

Mrs. Carmen Iacoban presented “Possibilities of avoiding errors in the laboratory”. The laboratory Campulung Moldovenesc is located in North Romania. ICP Forests monitoring analyses performed at the chemistry lab from INCDS Câmpulung Moldovenesc are:

- Deposition and soil solution (no DOC), since 1998
- Air quality: ozone, NH₃ and NO₂ measurements, using passive samplers, since 2009 (FutMon)
- Litterfall, including determination of content in Ca, Mg, K and P, since 2009 (Futmon)

QA/QC, including intercalibration exercises for needles/leaves since 2005 (8th Test 2005/2006), water since 2009 (3rd Test) were performed. In 2009 we participated with good results to the intercomparison test for O₃, within the FutMon Project.

At the beginning, we participated to the AQUACON- MedBas project exercises No 6 - acid rain (1/1996, 1/1997 and 1/1998) and No 5-freshwater analysis (1/1996, 1/1997 and 1/2000), organized by Istituto Italiano di Idrobiologia.

We had problems with the determination of Ca using ion chromatography in the WRTs (2011-2020), special for low concentrations (<2 mg/l). For the 2021/2022 WRT, we used AAS technique instead of ion chromatography, with lanthanum nitrate addition. All the results for calcium were within the mean of the labs, so we passed the exercise with 100% good results. We decided to analyze all the samples with concentrations lower than 2 mg/l, determined by ion chromatography, by AAS with lanthanum addition.

At the 11th WRT we got two wrong results for total nitrogen dissolved analysis, because we confused the samples 4 and 5 with each other.

In the database, instead of a concentration of 6.13 mg/l K, by mistake we wrote 613.00 mg/l. This mistake determined a change in the annual mean concentration from the correct value of 1.53 to the wrong one of 13.78 mg/l and the annual deposition from the correct value of 8.51 to the wrong one of 79.91 kg/ha/year. The quantity of precipitation collected between 06 and 20.09.2021 for the considered sample was 11.3 mm and the annual quantity was 558.1 mm.

The requalification reports published on the ICP Forests webpage (11th WRT and the 23rd needle/leaves Interlaboratory Ring Test) are very useful because it consist in a way to convince people in lab to requalify for the failed parameters.

Mr. Steen F. Hansen presented an overview on “Optimizing the Thermo iCAP-Q ICP-MS for ICP-Forests samples” inspired by the experiences gained when taking over an instrument that has been running for a couple of years by different users. There are many compromises to consider when optimizing the instrumental settings and details in the physical setup of system that might influence the overall performance. The laboratory conditions and reagent quality also affect the overall quality especially for some elements. The continuous focus by staff to avoid contamination, carryover etc. is the key to have multi-element methods running both trace elements and macro elements running simultaneously. An attempt was made to give some guidance on how to adjustment different parts of the setup to obtain better performance.

Mrs. Luisa Minich presented “Change in composition of archived soil solution samples”. Dissolved organic carbon (DOC) in soil solution is a complex mixture of substances. DOC can be distinguished

into the hydrophobic and hydrophilic fraction. The hydrophobic fraction mainly consists of aromatic moieties of humic substances, is low in nutrients, and rather refractory. The hydrophilic fraction mainly consists of carbohydrates of microbial and plant origin, is enriched in nutrients, and more susceptible to microbial degradation. As the hydrophobic fraction is more stable, it can be associated with a greater radiocarbon (^{14}C) age than its counterpart. The chemical composition of soil solution can vary over time due to various processes such as biological activity, exchange and adsorption processes with the storage vessel or precipitation of specific substances. The storage duration of soil solution samples can be expected to influence some of these processes. Previous experiments revealed a decrease in the DOC concentration in soil solution samples that were subjected to long-term storage. This decrease was more pronounced for samples that were characterized by high DOC concentrations initially. Here, we aim to elucidate the effect of long-term storage on the composition of DOC in soil solution samples. We compared repeated results of UV-Vis spectroscopy as well as radiocarbon data from archived samples (2007). We found that the hydrophobic fraction of DOC decreased by 15-20 % from 2007 to 2018, but remained unchanged from 2018 to 2022. Radiocarbon data of archived soil solution revealed DOC to be very old for the mineral soil horizons. These findings do not complement results of a previous study which revealed rather young and constant ^{14}C values across the soil profile for recent soil solution samples. This difference in the soil depth pattern of ^{14}C between archived and recent soil solution samples can have several reasons. The young DOC (hydrophilic fraction) could be preferentially lost during storage, old carbon could be released from the material of the PE bottles and deplete the ^{14}C content of the sample, or the observed old ^{14}C age might be an artefact. The remaining uncertainties require repeated measurements of DOC concentration of the archived samples, as well as radiocarbon analysis of another set of recent soil solution samples.

Mr. Jörg Luster presented tree nutrient status by bark analysis: first experience and results (Jörg Luster, Angélique Herzig, Antonia Ulmann, Stephan Zimmermann, Lorenz Walther, Katrin Meusburger, Forest Soils and Biogeochemistry, WSL). Foliar nutrient concentrations are widely used as diagnostic indicators of the nutritional status of trees. However, there are some drawbacks to this method, including the need to climb trees for sampling, potential contamination of the exposed surfaces, and strong temporal and spatial variation requiring well-constrained sampling protocols. Replacing the analysis of foliage by the analysis of a well-defined bark segment holds some intriguing advantages, including easy sampling on breast height, good protection from contamination, a relatively large seasonal time window with constant concentrations, and integration over several years.

Here, we report on first experiences with bark analysis in our group. Samples were taken from 43 forest sites across Switzerland representing a soil moisture gradient. Tree species comprised beech (*Fagus sylvatica*), oak (*Quercus sp.*), spruce (*Picea abies*) and pine (*Pinus sylvestris*). For sampling, sample preparation and analysis we followed the protocol of the Göttelein group (TU Munich). Measured concentrations of N, P, Mg, K, and Ca were in the same range as found in a study by the aforementioned group on German forest sites. Disappointing some hopes, the concentrations in bark did not reflect the supply of major nutrients in the soil, except for Mg and K in spruce and pine.

Taking together our results with those from the Göttelein group, we conclude (i) that – while operationally attractive – bark analysis cannot replace foliar analysis to assess the nutrient status of trees, and (ii) that concentrations in bark are in general no better indicators of soil nutrient availability than foliar concentrations.

Mr. Michael Tatzber presented results from determinations of mercury in tree rings from different Austrian emission sites. This method is based on sampling via drill dust from tree rings. Stems disks from Linz and Donawitz (primary iron production), Brückl (chloralkali electrolysis) and Brixlegg (copper recycling and/or production) were investigated. The sampling of all four quadrants of each tree ring allowed for very reliable results, because the different quadrants of similar tree rings contained in many cases distinctly different mercury concentrations. There was a tendency to increasing differences in mercury concentrations in different quadrants of similar tree rings when the overall mercury concentrations in tree rings were higher. Two stem disks which originated from two different places close to Donawitz (Styria) showed one maximum in the 1970s and two different stem disks originating from Brückl showed two maxima; one situated in the 1970s and one in the mid 1980s. The courses of the two stem disks from Brückl could be compared with information about technical changes in the chlor-alkali-electrolysis and were plausible against their background. For Brixlegg, several maxima were obtained: One maximum was detected in the end of the 1970's, a local maximum in the end of the 1920's, in the end of the 19th century and the highest maximum in 1813 (whereas its real maximum could be situated earlier). The maximum in 1813 and especially its height is especially remarkable, because the industrial revolution did not reach Austria until the second half of the 19th century at the earliest. In sum, the applied methodology could contribute to both closing a gap of knowledge about an important mercury pool in forest ecosystems which is contained in wood and to determining differences of emissions with mercury which occurred decades or even centuries ago, depending on the age of the investigated stem disk.

It is particularly important to avoid contamination by bark when taking samples. Ingrown branches also interfere and contaminate the sample.

Mr. Michael Krinninger, Mr. Theodor Alpermann, Mr. Nils König presented "Measurement of mercury in deposition samples".

The determination of mercury in deposition samples requires a suitable analytical instrument (AFS or ICP-MS) as well as a multitude of precautions during sampling and sample preparation steps in the laboratory to prevent mercury bleeding or carryover in sample bottles or tubing as well as mercury adsorption at walls of bottles or tubing. Therefore, suitable material for the treatment and storage of samples prior to mercury determination is limited to PFA and borosilicate vessels and all equipment in contact with deposition samples have to be cleaned thoroughly several times with diluted HCl (and demineralized water) prior to use. The determination of mercury in deposition samples requires samplers with sample bottles that are closed, thermally insulated and that contain diluted HCl. A multistep procedure for the preparation of deposition samples in the lab includes the acid-induced desorption, oxidation of mercury by BrCl, mixing of samples and filtration. If no ICP-MS system is available, AFS provides a rather cost-efficient method for the determination of mercury. For quality assurance of mercury quantification, certified reference material (e.g. NIST or NRC standards) should be employed. Heavy metals and mercury in deposition solutions can be collected and further analysed only by using suitable mercury samplers with its specific demands.

At the moment, no further Hg measurements are planned after the completion of the project.

Mr. Alfred Fürst & Mrs. Anna Kowalska: Mrs. Lena Wohlgemuth could not come to the meeting. The article “Physiological and climate controls on foliar mercury uptake by European tree species” is published and can be downloaded here: <https://doi.org/10.5194/bg-19-1335-2022>

Mr. Alfred Fürst and Mrs. Anna Kowalska will publish in the ICP-FORESTS Technical Report 2022 an article “History and progress of the ICP Forests ringtest programme and the Working Group QA/QC in Laboratories”, see: <http://icp-forests.net/page/icp-forests-technical-report>

Mr. Alfred Fürst will retire on 1.8.2022. Mrs. Anna Kowalska will take over the chair of the WG QA/QC in laboratories; new co-chair will be Mrs. Tamara Jakovljević - *the group agreed with it.*

These personnel changes will come into effect after the next TF meeting at the beginning of June 2022.

The next meeting of the heads of the laboratory should be a hybrid meeting too and Turkey (Mrs. Rabia Günhan) offered to organize it in spring 2024.

Mr. Alfred Fürst thanked the team of WSL for the perfect organization of the meeting and closed the meeting.

All presentations can be downloaded from the ICP Forests website:

<http://icp-forests.net/group/qualityinlaboratories/page/document-archive#Birmensdorf>

