Meeting of the heads of the Labs
19./20. September, Zadar (Croatia)

Effects of storage in field and in laboratory and influence of temperature and light on the chemistry of forest water samples


1 IVL Swedish Environmental Research Institute, Sweden (Experiment D)
2 Department of Geosciences and Natural Resource Management, University of Copenhagen, Denmark (Experiment D)
3 WSL, Swiss Federal Institute for Forest, Snow and Landscape Research, Switzerland (Experiments I,J,K,L,M,N,O)
4 Northwest German Forest Research Station, Germany (Experiments E,F)
5 CNR-ISE, Institute of Ecosystem Study, Italy (Experiment G)
6 Forest & Nature Lab, Ghent University, Belgium (Experiment C)
7 Research Institute for Nature and Forest, Belgium (Experiments A,B)
8 Slovenian Forestry Institute, Slovenia (Experiment H)
The chemical composition of water samples can vary over time due to

- biological activity in the sample,
- exchanges and adsorption on the walls of the storage vessel,
- abiotic particle formation,
- dissolution.

Factors influencing these processes include

- the initial composition of the sample, e.g. pH, temperature and light conditions, which directly determine the activity of microorganisms such as nitrifiers,
- storage duration (in the field or the laboratory),
- cleaning of the storage vessels,
- pre-treatment of the samples before analysis (e.g. filtering, acidification).
Types of experiments:

Fourteen different storage experiments:

1. **Storage in the field - influence of the sampler design:**
   Experiment A, D, I - sample bottle hanging in a tube (A) versus sample bottle in a soil pit (B).

2. **Storage in the laboratory simulating field conditions:**
   Experiment E, G, H - storage of unfiltered bulk open field (BOF), throughfall (TF), stemflow (SF) and soil solution (SS) samples 1 to 86 days at different temperatures (4, 8, 20, 30, 40 °C). Samples collected after 1 day, 1 or 2 weeks.

3. **Long-term storage in the laboratory:**
   Experiment B, E, J, K, L, M, N, O - storage of filtered bulk BOF, TF, SF and SS samples at 2-4 or -20 °C. 1 day to 1 year, acidified and not acidified.
1. Storage in the field - influence of the sampler design
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2. Storage in the laboratory simulating field conditions:

storage in bottles, filtrated and unfiltrated

different temperatures: 8 °C, 20° C, 30 °C, 40 °C
3. Long-term storage in the laboratory:

storage in bottles, filtrated

different temperatures: 2-4 °C, -20°
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**influencing variables:**
- sample type (bulk precipitation, throughfall, stemflow, soil water)
- light
- temperature (-20 °C, 2-4 °C, 8°C, 20°C, 30°C, 40°C)
- filtration (without, with paper filters, with membrane filters)
- sample pretreatment (acidification)
- storage time (0, 2, 5 days; 1, 2, 4 weeks; 1, 2, 3, 4, 6 month; 1, 2 years)

**measured compounds:**
- anions, cations, pH, conductivity, alkalinity, N tot, DOC
Results (1):

1. Storage in the field - influence of the sampler design:

Experiment A, D, I:
(A): large daily variations in temperature, high temperature peaks (up to 45 °C), higher mean temperature;
(B): better protected from light, lower variations in temperature, lower mean temperature (max. 20 °C)

Experiment I:
lower pH in (B), higher conductivity and higher DOC in (B). No signifikant pattern for Ntot
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Results (2):

1. Storage in the field - influence of the sampler design

light, temperature
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Results (3): Example from Experiment A

Temperature (°C)

- bottle in pit below soil surface
- bottle above ground level

Time (5 minutes interval)
Results (4):

2. Storage in the laboratory simulating field conditions:

Experiment E (fresh collected samples, 1 day after rainfall):
evident changes in DOC, pH and \( \text{NH}_4^+ \) and \( \text{N}_{\text{tot}} \); the changes were often higher and faster at higher temperatures and in unfiltered samples; DOC decreased and pH increased

Experiment G (samples collected after 1 week):
evident changes in DOC, pH and N compounds; but not clear how it is related to temperature

Experiment H (samples collected after 2 weeks; 15 days storage of TF at room temperature, sunny and hot places):
high evaporation at the warm places after 15 days; no changes for pH, N compounds, small changes for \( \text{Na}^+ \) and \( \text{Ca}^{2+} \)
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Results (5):

Example from Experiment E
Results (6):

Example from Experiment E

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N-Compounds in Throughfall at different Temperatures, filtered and unfiltered (pH5.6)
Results (7):

Example from Experiment G

NH$_4^+$ (mg-N L$^{-1}$)

Measurement after storage vs. measurement immediate
Results (8):

3. Long-term storage in the laboratory:

Experiment B:
no systematical changes of $\text{NO}_3^-$, $\text{NH}_4^+$, $\text{SO}_4^{2-}$, $\text{Cl}^-$, cations after storage at -20 °C for up to 1 year

Experiment J:
no changes for N compounds but decrease in DOC in SS at 2-4 °C and -20°C after 4 months; no or little difference when stored at 2-4 °C or -20 °C

Experiment L:
no changes for pH and conductivity during 1 month, no changes of DOC during 2 months, no changes of cations (acidified) during 4 months; slightly decrease of $\text{NO}_3^-$ during 4 months at 2-4 °C
Results (9):

Experiment M:
no changes in DOC after 2 weeks at 2°C and additional 3 months at -20°C; decrease in conductivity in samples with pH > 8; after 3 weeks at -20 °C

Experiment O:
no alteration of the samples in systematic way during long time storage at -20 °C

Experiment E:
no changes of pH < 4,9; increase at higher pH; decrease of DOC; changes for NH₄⁺, no changes for NO₃⁻ at 2-4 °C

Experiment K (storage at 2 °C):
no large differences for elements measured by ICP-OES between acidified and not-acidified storage
Results (10):

Example from Experiment N

Relative difference for storage acidified vs. not acidfied [%] in absolute values

- Al
- Ca
- Mg
- Mn
- Na
- Si
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Example from Experiment E

4 °C / filtr. / 85 days
Conclusions:

- during the sampling period outside on the plot (2 weeks) the conditions are continuously changing; high temperature peaks up to 45 °C are possible
- high temperature can promote changes in the (unfiltered) samples
- mostly changing parameters are DOC, pH, NH4+, Ntot
- the changes in unfiltered samples normally were higher than in filtered samples, but in filtered samples changes were also observed
- in most cases the changes were higher at higher temperatures
Conclusions (2):

- in filtered samples stored at 2-4 °C or at -20 °C only the TC /DOC content sometimes decreased; the other parameters normally didn´t change

- the storage experiments with unfiltered samples stored up to 2 weeks at different temperatures show different changes for pH, DOC, NH4+ and Ntot. Many changes can happen in the field before sample collection for these parameters

- Overall, shorter sampling periods (weekly), early filtration and storage of the samples at 2-4 or -20 °C is the best way to minimize changes. Changes can not be avoided totally.