

MEASURING AND MODELLING THE DYNAMIC RESPONSE
OF REMOTE MOUNTAIN LAKE ECOSYSTEMS TO
ENVIRONMENTAL CHANGE

A programme of **MO**untain **LA**ke **R**esearch

MOLAR

ATMOSPHERIC DEPOSITION

**SAMPLING AND ANALYSIS OF DIRECT DEPOSITION,
SNOW PACK AND SOIL CORES**

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ATMOSPHERIC DEPOSITION

Sampling and analysis of direct deposition, snow pack and soil cores

1. Introduction and aims of the measurements

The lakes considered in the MOLAR project are located in remote areas, far from the direct influence of human activities, so that it can be assumed that the main disturbing factors are the deposition of pollutants from the atmosphere and climatic variations. For this reason, evaluation of the input of ions from the atmosphere is of major importance.

The main aims of the measurements of atmospheric deposition are:

- a. to evaluate the flux of ions and nutrients from the atmosphere to the watershed/lake surface, on a seasonal and annual basis;
- b. to compare critical loads and actual loads of pollutants from the atmosphere;
- c. to compare atmospheric deposition and lake water chemistry, as a starting point for studying watershed and in-lake processes which influence water chemistry.
- d. to validate quantitative models for reconstruction the history of atmospheric deposition from lake sediment records.

Atmospheric deposition will be determined using several methods:

- ◆ Direct deposition
- ◆ Snow pack
- ◆ Soil cores

2. Direct deposition

Evaluation of the effects on surface waters and comparison with the critical loads require quantification of the total flux of ions from the atmosphere. This is very difficult, as there are generally marked difficulties in the evaluation of dry deposition. As an aid to clarifying the different methods of measuring atmospheric deposition, we may define the following terms:

wet-only deposition (of ions) = flux of ions from the atmosphere with rain, snow, hail. The sampling equipment used avoids collection of dust during dry periods, as the container opens automatically at the onset of precipitation.

Advantages: gives valuable information on the chemistry of atmospheric deposition.

Disadvantages : needs electric power and maintenance; does not work correctly in case of heavy snow.

bulk deposition = total flux of ions from the atmosphere during both dry and wet periods (with rain, snow, hail). It is sampled with a continuously exposed bottle and plastic funnel.

Advantages: cheap and simple to use, does not need electric power; nor maintenance.

Disadvantages: very sensitive to dust from neighbouring areas; in calcareous soils bulk deposition gives incorrect information on pH, calcium, magnesium, potassium and alkalinity of atmospheric deposition.

dry deposition = flux of ions, gases, particles from the atmosphere during dry periods. The flux of dry deposition is due to gravity (sedimentation), impaction, interception, and is strongly influenced by:

- type of surface (broad leaves, needles, rocks, water, etc.)
- humidity of surfaces
- macro- and micro-meteorology

It is very difficult and extremely expensive to measure dry deposition; there are several techniques (see e.g. Ruijgrock *et al.* 1995), but all have limits and different degrees of difficulty. An alternative is to evaluate dry deposition through the use of large scale models, e.g. the EMEP model (Iversen 1992; Sandness & Styve 1992).

Chemical data collected on atmospheric deposition in most of the cases refer to bulk or wet-only samples. Several studies have considered a comparison between the two types of samples (Galloway & Likens 1978; Slanina *et al.* 1979; Söderlund 1982; Mosello *et al.* 1988). In general there is no relationship between the two types of samples collected at the same site. The collection efficiency of wet-only collectors is approximately 80-90% of that of bulk collectors. The reasons are a) possible delays in lid-opening as a result of difficulty in detecting the onset of precipitation; b) a lower collection efficiency for small droplets owing to the height of the dry sampler (about 2 m) above the ground or increased disturbance of the air flow.

The differences in the chemistry of bulk and wet-only samples vary in relation with the calcareous or silicic nature of the soil near the sampling site and with the relative importance of dry deposition. In calcareous areas wind-blown dust influences bulk more than wet-only samples, increasing pH and alkalinity, calcium and magnesium concentrations. The likelihood of differences is higher with low sampling frequency. In silicic areas this disturbance is much lower. Bulk samples, because of the partial collection of dry deposition, show slightly higher concentrations of sulphate, nitrate and ammonium. However, it is important to remark that the dust collected by bulk samples is not equivalent to the total dry deposition, nor in general can be assumed as a rough estimate of it.

To cater for the various needs (ions and nutrients, heavy metals, radionuclides, SCPs and organic micropollutants), it will be necessary to deploy a number of collectors. These will include:

- ◆ collectors for major ions and nutrients.
- ◆ NILU-type bulk collectors - heavy metals (except Hg), radionuclides & SCPs. These consist of a funnel (diameter 20cm) and a bottle made of polythene (PE). A PE filter is placed in the bottom of the funnel to avoid collecting local debris. For an annual rainfall of 1000 mm, the sampler will collect (on average) 0.60 L per week, or 2.6 L per month.
- ◆ IVL-type bulk collectors - Hg.

- ◆ wet and dry collectors - SCPs (Redo only).
- ◆ collectors suitable for organic micropollutants.

In all cases accurate records will be kept of the amount of precipitation that each sample represents, in order to be able to calculate fluxes.

2.1. Site selection

The site selection is the responsibility of the site operator. The selected sites should not be subject to any strong influence from local sources of pollution in the catchment that may lead to misinterpretation of the chemical data. A site should be representative of the atmospheric deposition which falls on the MOLAR lake/watershed. If the site is at some distance from the lake, the representativity of the station must be evaluated on the basis of paired samplings for short periods of time or/and using data of other stations in regional studies. Measurement of meteorological variables provides additional information of some importance; in its absence at least one double measurement of the volume of precipitation through a calibrated gauge is required. Sites with long-term series of data are preferable if the other main criteria are met.

The information required for describing each site (both lakes and atmospheric deposition sites if they are different) is:

- name and site code
- latitude, longitude, altitude
- distance from the studied lake(s)
- historical data (if available)
- presence/absence of local sources of pollution
- forest/vegetation present
- roads (paved, unpaved) and rough quantification of traffic
- geology of bedrock

2.2. Sampling for major ion and nutrient chemistry

On the basis of the considerations made in the introduction, wet-only sampling appears to be the most reliable technique for quantifying the deposition of atmospheric pollutants.

Sampling strategies will vary according to the accessibility and facility of the sampling site. In sites accessible the whole year by car and where electric power is available, the best choice is wet-only sampling on a weekly basis. In this way it is possible to evaluate seasonal variations in deposition concentrations and the time lag between precipitation and analysis is kept to a minimum.

If sites are not easily accessible, fortnightly or monthly samples are to be collected. If samples are taken less frequently than every month, they must be taken at the same times of year each year, preferably evenly spaced in time.

Difficulties in wet sampling arise with heavy snow events. In this case a bulk collector, comprising a polyethylene cylinder, 1.5 m high, raised about 0.5 m from the ground, may be used. Differences between wet-only and bulk chemistry are minimal during winter time, when the ground is covered with snow and the amount of mineral dust is negligible.

2.3. Heavy metals (except mercury) for WP2

2.3.1 Principle for heavy metal determination

The precipitation is collected with NILU-type bulk collectors which consist of a funnel and a bottle made of polyethylene. A plastic filter is placed in the bottom of the funnel to avoid collection of local debris. The collection bottles are changed weekly whereas the funnels are replaced every second month. The samples are analysed for heavy metals using inductively coupled plasma - mass spectrometry (ICP-MS). The heavy metals analysed will be Cd, Pb, Cu, Co, and Zn.

All equipment coming in contact with the samples are soaked in HNO₃ (3%) at least overnight before use. Four new sampling bottles are sent from NILU each month, whereas one new funnel is sent every second month. Four weekly samples should be returned to NILU in one batch in the beginning of a new month. The samples should be marked clearly:

MOLAR - name of site

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Phone: + 47 63 89 80 00

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2.3.2 Field operation for heavy metal determination

The samples can easily be contaminated and it is extremely important not to touch parts of the equipment coming in contact with the sample during the field operation procedure. Plastic gloves should be worn during all handling of the bottles or other sampling equipment.

Placement of the sampler:

- a. Open the plastic bag, and fold it around the funnel
- b. Put on gloves, and open the plastic bag which contains the bottle
- c. Unscrew the bottle cap and place it in the plastic bag
- d. Screw the funnel and the bottle together
- e. Open the plastic bag which contains the plastic filter and transfer the filter into the funnel without touching it.
- f. Install the funnel/bottle carefully in the stand.

Placement/removal of sample bottles

- a. Open the first plastic bag containing the sampling bottle and fold it back

- b. Put on gloves, and open the second plastic bag
- c. Unscrew the bottle cap and place it in the plastic bag
- d. Remove the funnel/bottle from the stand and unscrew
- e. Place the old bottle in double plastic bags
- f. Rinse the funnel with demineralized water
- g. Screw the funnel and new bottle together, and carefully install in the stand
- h. Screw the bottle cap tightly on the bottle
- i. Mark the bottle with station name and period of exposure (from - to)
- j. Close the plastic bags

2.3.3 Sample pretreatment and analysis for heavy metal determination

When received at NILU, the samples in the collector bottles are acidified with concentrated HNO₃ (suprapure) to a total acid concentration of 1%. They are occasionally shaken to release any adsorbed elements on the inner walls of the bottles in a period of 2 to 3 days before transferring to storage bottles made of polyethylene. The acidified samples are subsequently stored at +5°C before analysis.

Analysis of heavy metals are carried out using ICP-MS. Calibration is accomplished by using standard solutions at 1 and 10 ng/ml. All calibration standards, blanks and samples are added 1% HNO₃ (suprapure) and 50 ng/ml Sc, In, Ho and Re (internal standards).

2.4 Mercury (Hg) determination

2.4.1 Principle for mercury (Hg) determination

The precipitation is collected with IVL-type bulk collectors on monthly basis. The rack is made of black polyethylene, whereas all parts of the collector coming in contact with the sample (funnel, filter, capillary, bottle) are made of borosilicate glass. The bulk sampler is protected from the interference of dry deposits of Hg through the capillary attached to the funnel. A filter is placed in the bottom of the funnel to avoid collection of litter and insects. The collection bottle is fitted with a wide polyethylene collar to protect it from sunlight penetration. Two collectors are placed at each station. Mercury is determined by using cold vapor atomic fluorescence spectroscopy (CV-AFS)

All the equipment which comes into contact with the sample is washed with HCl/BrCl at NILU. The sampling bottles are distributed by NILU each month to the sampling stations. For preservation, the bottles are preacidified with 2.5 ml Suprapure HCl when sent out from NILU. The bottles are packed in double plastic bags and sent by mail to and from the sampling stations. The sample bottle should be returned to NILU together with the four weekly heavy metal bottles in the beginning of a new month. The parcel should be marked clearly:

MOLAR - name of site

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2.4.2 Field operation for mercury determination

This field operation procedure following below is the one recommended for use in the Oslo and Paris Commissions (PARCOMs) monitoring network (Munthe 1996)

Collection bottles containing the precipitation samples should be exchanged according to a fixed procedure taking great care to avoid contamination. Plastic gloves should be worn during all handling of the bottles or other sampling equipment.

- a. Remove outer plastic tube
- b. Prepare new collection bottle, plastic bags and container (squeeze bottle) with high purity water. All equipment needed for the bottle exchange should be placed on a plastic cover either on the ground or other available surface.
- c. Open double bags of new collection bottle.
- d. Carefully remove the ground glass joint connecting the bottle to the capillary. Use both hands; one for loosening the glass fittings the other for holding the funnel.
- e. Remove the stopper from the new collection bottle and stopper the bottle containing the sample. Remove the bottle containing the sample from the plastic casing and put in double plastic bags.
- f. Without bottle in place rinse the funnel and capillary with high purity water. If visible materials (dust, insects etc.) are present in the funnel this can be disconnected from the capillary and rinsed separately. New plastic gloves should be used if handling of the watch glass or touching the inside of the funnel is necessary. If the funnel and capillary are visibly dirty even after rinsing, they should be exchanged for newly washed pieces.
- g. Remove new collection bottle from plastic bags and place in the plastic casing. Connect the ground glass fitting and check all connections. Make sure that all connections are without gaps where the silicon tubing is exposed to the precipitation sample unnecessarily.
- h. Replace outer plastic tube.
- i. Mark the double plastic bags containing the sample bottle with station name and period of exposure (from - to)

Field blank samples should be taken regularly (every 6 month):

- Two extra sampling bottles are brought to the site; one containing diluted HCl (pH 3 to 4) and one empty. After removing the sample bottle (step 5) the empty bottle is installed and the diluted HCl is poured through the funnel and capillary. The bottle is stoppered, double bagged and brought to the laboratory for analysis. The mercury content is compared to that of samples stored in a clean laboratory environment.

The sample bottles should be transported as soon as possible to NILU. If delays are unavoidable, storage outside or in wooden shed etc. are preferable to analytical laboratories with unknown history of mercury handling. The bottles containing the samples are stored in a clean room until analysis.

2.4.3 Analysis of precipitation samples for total mercury

The mercury is oxidated by adding BrCl to the precipitation samples one hour before analysis. Mercury is subsequently determined by using cold vapor atomic fluorescence spectroscopy (CV-AFS) using SnCl₂ as reduction agent (aqueous Hg is reduced to Hg⁰).

2.5 Radionuclides

Precipitation will be collected using a separate NILU-type collector following the same procedures as for heavy metals, preserved in 2M high purity HNO₃, and sent (with appropriate site information, date, collection period etc.) to Peter Appleby at University of Liverpool.

2.6 SCPs

Reference is the two sections of Neil Rose's SCP protocol:

2.6.1 Bulk Deposition

SCP are to be analysed from every bulk deposition sample for WP2. i.e. weekly samples for Jorisee, Gossenkollersee, Redo, Øvre Neådalsvatn and weekly in summer and bi-weekly in winter at Lochnagar and Starolesnienske Pleso from October 1996 - March 1998. Please refer to the bulk deposition sampling protocols.

A note should be made of the total wet deposition before removing the sample and then the walls of the collector should be washed with deionised water to remove any particulate matter sticking to the walls.

If a bulk deposition sampler is used for SCP only then the whole sample should be filtered through a Whatman GF/C filter, if more analyses are to be done then a known fraction of the deposition should be filtered through a Whatman GF/C filter. As much sample as possible should be filtered for SCP. Filters should be folded once to include any particles and stored flat in an individual, labelled (site name, 'Bulk deposition', dates) plastic bag. These can be sent in batches (e.g. every 2 months) to Neil Rose.

If the bulk deposition collector contains snow or ice, again, a known fraction should be sub-sampled for SCP, and melted before filtration. If no rain or snow has fallen over the sampling period then the walls of the collection vessel should be washed with deionised water and a known fraction of the resulting suspension filtered for SCP.

With each sample it is essential to know:

- The sampling interval dates
- The total amount of wet deposition that has fallen over the sampling period
- The fraction of the total that has been filtered for SCP.

2.6.2 Dry and Wet deposition

At Redo only initially for a trial period, dry and wet deposition samples will be analysed for SCP. Filters will first be analysed for organics and then passed on for SCP. If this approach fails to work, the bulk deposition sampling outlined above will be undertaken. Samples should be labelled with date, 'Redo', and 'dry' or 'wet deposition'.

2.7 Organic Micropollutants

Reference is the procedures given by Joan Grimalt et al. in this manual. A full description of both sampling and analysis is given in the special section: "Protocols for the Analysis of Organic Micropollutants in Fish, Sediments, Wet-only deposition, Bulk deposition, Snow, Water, Air."

3. Snow pack

At Gossenöllesee, snow pack samples will be analysed monthly for major ions and nutrients, heavy metals (Pb, Cd, Cu, Co, Zn), radionuclides, SCPs and organic micropollutants. For the other WP2 sites sampling will be at least once during snow season.

3.1. Sampling site

Select the sampling site according to your local knowledge of the catchment area. However, good accessibility should not be the only reason to select the site. There are several requirements a sampling site has to meet:

- a. The selected site should be as representative as possible for the catchment area in respect to snow accumulation. Checking the snow depth with an avalanche sonde along various transects within the catchment may help you to get an impression on the distribution of snow.
- b. The site should not be influenced by avalanches or frequent snow drift causing either additional snow accumulation or ablation.
- c. The site must not be influenced by any human activity. For instance, it should be situated away from hiking or skiing routes, roads, etc.

3.2. Sampling procedure

- a. Dig a snow pit at a size depending on the depth of the snow pack. For a 2 meter snow cover a pit of 1 x 2 m might be a practicable size. The wall where you will take the samples and determine snow density and stratigraphy should be
 - plane: smooth it with a not rusty shovel, e.g. an avalanche shovel made of glassfiber. This will help you to recognize the vertical sequence of layers.
 - and lie in the shadow: incident sun may rapidly alter stratigraphy or even cause local melting.
- b. Mark the location of your pit. For instance, put a stick at the exact position of that pit wall where you did all your sampling ("front wall"). Next time you dig another pit move ahead about 1 m from the stick. You should be sure the snow cover had not been disturbed anyhow before. Thus never step close to the front wall of the pit or throw snow there during digging the pit (only left and right of the pit).

- c. Take snow samples along a vertical profile at intervals of e.g. 10 cm. Extra samples of layers with mineral (Saharan) dust or ice might be of interest and reveal additional information.

Sampling at intervals of 10 cm is especially recommended at sites with weather stations. If the height of the snow cover reaches values of 3 to 4 m sampling intervals of 20 or 30 cm may be more convenient. Bigger sampling intervals, but more than one snow pit within the catchment are recommended, if no representative site can be found.

- d. Determine the density profile. It is most convenient to measure snow density at the same intervals as you take the snow samples.
- e. Determine the stratigraphy of the snow cover. A detailed description of grain size, grain form, dirty layers, ice layers and lenses may help you to interpret results.
- f. Optional: measurement of snow temperature at several levels. Snow temperatures in the range of -2 to 0°C indicate snow melt, that either will begin within the next time or already occurred. If snow temperature is around 0°C at all levels you should be aware that a big amount of trace substances accumulated in the snow pack will already have been released with the percolating melt water.

3.3 Precautions against sample contamination

- a. All material expected to come into contact with the sampled snow has to be carefully cleaned in the lab before (with diluted HCl , soaked and rinsed with deionized water).
- b. During sampling wear non fibrous cloths (inclusive a cap), mouth masks and cleaned rubber gloves. Never touch the snow to be sampled, sample bottles, tools etc. with bare hands.
- c. If not stabilized keep samples frozen until analysis.

3.4 Snow density and water equivalent

In order to calculate (estimate) ionic loads, i.e. the amount of atmospheric trace substances accumulated in the snow cover, you need to know the density, respectively the water equivalent (W.E.) of the snow pack.

To measure density fill a tube of well defined volume (e.g. 500 cm³) and weigh it with a spring balance. Density has to be determined along a vertical profile similar to sampling snow for the chemical analysis.

weight / volume = density [kg/m³]
weight / area = water equivalent [cm]
(with area = cross section of the tube)

3.5 Snow samples

Estimate the amount of sample liquid you need for chemical analysis before selecting the sample bottles (fresh snow will only have a density of about 200 kg/m³!).

The following procedure has evolved from experiences of previous snow investigations: The snow is cut off with a tube of stainless steel at intervals of 10 cm. The cross section of the tube fits with that of the sample bottles (about 3.5 cm for the 500 ml bottles we use). With a stopper we cram the snow into the bottle taking as many parallel samples from the respective interval as are needed to completely fill the bottle. In this way you will get enough sample liquid and - what is quite important - you will get a mean concentration of trace substances for the respective snow layer (ion concentrations may vary considerably even within a few centimeters!).

The 10 cm intervals are marked with a plate of stainless steel horizontally stuck into the snow thus guarantying that you will take the parallel samples always from the same 10 cm interval.

To put the tube and the plate you will need a hammer (glassfiber) as soon as the snow becomes harder and more dense.

3.6 Analysis

3.6.1 Major Ions and Nutrients

The analysis will follow agreed methods for water samples.

3.6.2 Heavy Metals

The analysis will follow agreed methods for precipitation and water samples.

3.6.3 Radionuclides

Snow pack samples for radionuclide analyses will be collected monthly. Sub-samples of c.250mL (sufficient to generate a total melted volume of 2L) will be taken from c.12 evenly spaced depths in a vertical profile, amalgamated and melted in storage bottles that have been cleaned and acid washed according to the same protocol as for heavy metals, preserved by acidifying to 2M strength with high purity HNO₃, and sent to Peter Appleby at Liverpool ERRC.

3.6.4 SCPs

Reference is the appropriate section of Neil Rose's SCP protocol:

Snow pack samples for SCP analysis will be collected monthly. Two litre samples (unpacked volume) will be taken from each 10cm layer of the snow pack. The snow should be melted, filtered through a Whatman GF/C filter. The filter paper should then be folded in half once (so that any filtered particles are enclosed) and stored flat in an individual plastic bag clearly labelled 'Snow' with the site name, date, sampling depth (e.g. 50-60cm) and volume (water equivalent). The bags should then be sent to Neil Rose at ECRC

3.6.5 Organic micropollutants

Reference is the procedures given by Joan Grimalt et al. in this manual. A full description of both sampling and analysis is given in the special section: "Protocols for the Analysis of Organic Micropollutants in Fish, Sediments, Wet-only deposition, Bulk deposition, Snow, Water, Air."

4. Soil cores

4.1 Introduction

At each of the WP2 sites, long-term values of the mean atmospheric flux of radionuclides will be assessed from radionuclide inventories retained in soil cores.

4.2 Sampling procedure

Soil cores will be collected using sharpened plastic tubes of 7-10 cm internal diameter. These should be driven into the soil to a depth of at least 30 cm taking care to avoid compaction, dug out and then extruded into 1 cm sections for the top 10 cm and 2 cm sections thereafter.

The cores should be from undisturbed locations selected according to the criteria:

- I. there should have been no major soil disturbance for at least 30 years, and preferably longer,
- II. soil types should be of a type that inhibits radionuclide migration through the soil column,
- III. they should be on open level ground not subject to erosion or flooding by surface waters,
- IV. the soils should be relatively compact and saturated (so as to minimise *in situ* ^{222}Rn escape),
- V. the soil depth should be contain the entire fallout inventory,
- VI. there should be reliable precipitation data (rain and snow).

At least three cores should be collected from each site. If there are no suitable sampling locations in the catchment itself, cores may be taken from the nearest suitable location.

4.3 Sample preparation and transport

The *in situ* volume of each core slice will be recorded, and the dry weight fraction determined by drying overnight following the same procedure as for the lake sediment samples. The dried samples will then be securely packed, sealed and labelled in polythene sample bags, and sent to Peter Appleby at Liverpool University ERRC.