

**European Mountain lake Ecosystems: Regionalisation,  
diaGnostics & socio-economic Evaluation**

**EMERGE**

**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 and snow pack

### 1. Introduction and aims of the measurements

The lakes considered in the EMERGE 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

### 2. Direct deposition

Evaluation of the effects on surface waters and comparison with the critical loads requires 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 precipitation. 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 wind and snow.

**bulk deposition** = total flux of ions from the atmosphere during both dry and wet periods (with precipitation). 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 limitations 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 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 (major ions and nutrients, heavy metals, radionuclides, SCPs and organic micropollutants), it will be necessary to deploy a number of collectors. These will include:

- ◆ 1 collector for major ions and nutrients (wet-only or, if not possible, bulk);
- ◆ 1 to 3 NILU-type bulk collectors - heavy metals, 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;
- ◆ 1 wet and dry collector suitable for organic micropollutants (see procedures given by Joan Grimalt *et al.*, in this manual);

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**

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 EMERGE 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

These information, together with other details of the area, must be summarised on the annexed form, and sent to the person in charge of the different projects (major ions and nutrients, SCP, micropollutants, etc.).

## **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, 1.0 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

Samples for heavy metal analyses will be collected from the following WP3 sites:

		Analytical Laboratory
Redó	monthly	Liverpool
Ladove	monthly	Liverpool
Lochnagar	biweekly	UCL
Paione	biweekly	Liverpool

#### 2.3.1 Principles for heavy metal determination

The precipitation is collected with NILU-type bulk collectors, which consists of a funnel and a collection bottle made of polyethylene. A plastic filter is placed in the bottom of the funnel to avoid collection of local debris. All equipment coming in contact with the samples are soaked in HNO<sub>3</sub> (3%) at least overnight before use.

Collection bottles are changed according the schedule indicated in the Work Plan. Funnels are replaced every second month. The site operator and laboratory will agree in advance on a procedure for supplying replacement funnels and collection bottles.

At the end of each month the filled sample bottles will be marked clearly and sent to the analytical laboratory. The samples will be analysed for heavy metals using inductively coupled plasma - mass spectrometry (ICP-MS). The heavy metals analysed will be Cd, Pb, Cu, Co, and Zn.

At sites where samples are being analysed both for heavy metals and radionuclides (Redó, Ladove), combined samples will be collected for both analyses (see section 2.4).

Samples from Redó, Ladove and Paione should be sent to Peter Appleby at the University of Liverpool. Samples from Lochnagar should be sent to Neil Rose at University College London. Data required for each sample include:

Start date, stop date, diameter of collector, total volume of rainfall collected.

#### 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 containing 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 pre-treatment and analysis for heavy metal determination**

When received at the analytical laboratory, the samples in the collection bottles are acidified with concentrated HNO<sub>3</sub> (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% HNO<sub>3</sub> (suprapure) and 50 ng/ml Sc, In, Ho and Re (internal standards).

#### **2.4 Radionuclides**

Samples for radionuclide analyses will be collected from the following WP3 sites:

		Analytical Laboratory
Redó	monthly	Liverpool
Ladove	monthly	Liverpool

The sample collection methods are exactly the same as for heavy metals (see section 2.3), though substantially larger samples (preferably at least 1 litre) are needed. Deposition will be analysed both for heavy metals and radionuclides and combined samples sufficient for both analyses and collected from the same NILU-type collector should be sent (with appropriate site information, date, collection period etc.) to Peter Appleby at University of Liverpool.

#### **2.5 SCPs**

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

### 2.5.1. Bulk Deposition

- From WP3 sites. Fortnightly from Lochnagar & Paione. Monthly from GKS, Redo, Ladove.
- As much volume as possible to be filtered (GF/C) for SCPs.
- Use as small a diameter filter as possible.
- Fold each filter in half (sample inside) and place each in a separate bag labelled with site name, 'bulk deposition' and sampling interval.
- Along with the samples send a data sheet as follows:

Site Code	Start Date	End Date	Collector Area	Total vol. collected	Filtered volume	Rainfall (mm)
SCOT1	4/9/2000	18/9/2000	200 cm <sup>2</sup>	2500ml	2000ml	53.2 mm
SCOT1	18/9/2000	2/10/2000	200 cm <sup>2</sup>	1300ml	1000ml	35.8 mm

## 2.6 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

In order to evaluate the accumulation of atmospheric trace substances in the snow cover it is absolutely necessary to perform sampling before the onset of snow melt.

### 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 which depends 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 recognise the vertical sequence of snow layers.

- and lie in the shadow: incident sun may rapidly alter stratigraphy or even cause local melting.

- b. 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.

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/m<sup>3</sup>!).

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.

- c. Determine the density profile. It is most convenient to measure snow density at the same intervals as you take the snow samples.
- d. 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.
- e. 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.
- f. 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).

### **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 deionised 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 stabilised 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 cm<sup>3</sup>) and weigh it with a spring balance. Density has to be determined along a vertical profile similar to sampling snow for the chemical analysis.

$$\text{weight} / \text{volume} = \text{density} [ \text{kg/m}^3 ]$$

weight / area = water equivalent [cm ]  
tube)

(with area = cross section of the

### 3.5 Analysis

#### 3.5.1 Major Ions and Nutrients

The analysis will follow agreed methods for water samples (Mosello and Wathne, this manual).

#### 3.5.2 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

Historic fallout of radionuclides, trace metals and persistent organic pollutants at the WP3 sites Redó and Ladove will be determined via the accumulated inventories in soil cores.

### 4.2 Sampling procedure

The cores will be from undisturbed locations selected (as far as is possible) 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 <sup>222</sup>Rn escape),
- V. the soil depth should be sufficient contain the entire fallout inventory,
- VI. there should be reliable precipitation data.

The 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 the soil extruded at 1 cm sections for the top 10 cm and 2 cm sections thereafter.

Suitability of the core tubes and of the extrusion and sub-sampling tools against contamination should be checked in advance with Joan Grimalt (POPs) and Gloria Lacort (metals).

The extruded samples should be weighed and then split into two equal halves. The first half should be stored in acetone rinsed aluminium foil, **frozen** as soon as possible and transported frozen to CSIC for POPs analysis.

The second half should be weighed. Sub-samples for metals analysis (3g wet) should be placed in acid-washed glass vials and sent for metals analysis. The remaining part should be reweighed, dried, stored in sealed, labelled plastic bags and sent for radiometric analysis.

### 4.3 Handling, storage and transport requirements

#### ***POPs analysis***

Sub-samples for organic micropollutant analysis must be double wrapped in aluminium foil. Two aluminium sheets must be used. One in direct contact with the sample should have been previously rinsed in acetone. The second foil layer should be used to wrap the first. The outer layer should be clearly labelled. A paper label with a water resistant marker is preferred.

Samples should be frozen as soon as possible and stored frozen. If this is not feasible, they should be kept as cool as possible. These conditions must be maintained during transport, using boxes of dry-ice. Samples should be sent to ICER-CSIC.

Contacts: Joan Grimalt: jgoqam@cid.csic.es  
Pilar Fernandez pfrqam@cid.csic.es

Address: Department of Environmental Chemistry  
IIQAB-CSIC  
Jordi Girona, 18  
08034 Barcelona  
Spain

Tel: +34 93 400 61 00

Fax: +34 93 204 59 04

#### ***Radiometric analysis***

Samples should be dried (either freeze-dried or air-dried in a 'clean air' laboratory), the wet and dry weights recorded, and sent in clearly labelled plastic bags (site code and soil depth) to ULIV.

Contact: Peter Appleby appleby@liverpool.ac.uk

Address: Department of Mathematical Sciences  
University of Liverpool  
P.O. Box 147  
Liverpool  
L69 3BX  
UK

Tel: +44 151 794 4020

Fax: +44 151 794 4061

#### ***Metals***

Samples should be stored wet in acid cleaned glass vials provided by the analytical laboratory, frozen and sent to the laboratory without further treatment. Vials must be clearly labelled with site code and soil depth.

Contact: Gloria Lacort gloria@giga.sct.ub.es

Address: Serveis Científico-Técnicos. University of Barcelona  
Lluís Solé i Sabarís, 1  
E-08028 Barcelona

Tel: +34 93 402 16 99

Fax: +34 93 411 13 98

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# EMERGE

## European Mountain lake Ecosystems: Regionalisation, diagnostics & socio-economic Evaluation

### Atmospheric deposition chemistry

#### Sampling site

Responsible person \_\_\_\_\_

Institute \_\_\_\_\_

Laboratory \_\_\_\_\_

EMERGE lake(s) \_\_\_\_\_

Name of the sampling site \_\_\_\_\_

Country \_\_\_\_\_

Latitude \_\_\_\_\_ North

Longitude (Greenwich) \_\_\_\_\_  East  West

Altitude \_\_\_\_\_ m a.s.l.

Vegetal cover of the surroundings \_\_\_\_\_

Geo-lithology of the surroundings \_\_\_\_\_

Distance from EMERGE lake(s) \_\_\_\_\_ Km

Number of months in which the site is accessible during the year \_\_\_\_\_

Local disturbs (unpaved roads, etc.) \_\_\_\_\_

Type of sampler  bulk  wet-only

Sampling frequency  weekly  other (specify) \_\_\_\_\_

Snowpack measurement  yes  No

Precipitation amount measurement  by a meteorological station  
 by calibrated gauge  
 by the weight of collected samples