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Analytical Chemistry in High-Alpine Environmental Research

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Abstract. Snow and ice chemistry studies in the high-altitude regions of the Alps give insight into present and past atmospheric chemistry. Impurities found in snow originate from atmospheric aerosol particles or reactive trace gases and, thus, represent a broad spectrum of chemical species such as water-soluble inorganic and organic ions, insoluble minerals, organic components, soot, trace metals, *etc.* Consequently, a variety of analytical techniques need to be applied in snow chemistry studies, including ion chromatography, inductively coupled plasma optical emission or mass spectrometry, atomic absorption spectrometry *etc.* A few details of the respective methods used in our laboratory are discussed here. Since snow samples are characterised by low impurity concentrations, they are particularly sensitive with respect to stability and contamination. Thus, special care in sample handling is required. Investigations of the geographical, seasonal and year-to-year variations of the concentrations and deposition fluxes of major ionic species were carried out in the Alps. Concentrations of ammonium, nitrate and sulphate showed a West to East increase, which was, however, not reflected in the total flux, since precipitation heights exhibited an opposite pattern. Long-term records from an alpine glacier revealed substantial increases of sulphate, ammonium, nitrate, and lead in the course of the last 100 years.

1. Introduction

The high-altitude regions of the Alps are of particular interest for environmental researchers for a variety of reasons. First of all, they are located rather remote from anthropogenic sources of air pollution and allow, therefore, to study the background atmosphere [1]. For this purpose, one can take advantage of the alpine snow cover which serves as natural collector of precipitation and atmospheric fluxes of pollutants or nutrients since it integrates the input of atmospheric trace components by wet and dry deposition. Where the snow cover persists over longer time periods of up to hundreds of years in form of cold glaciers, the alpine environment even produces unique archives for the reconstruction of paleoclimate information [2][3]. While from polar ice sheets environmental records on a global scale

have been gained, glaciers in the Alps provide more local data of atmospheric history, which is important for species with short lifetimes in the atmosphere such as aerosol particles. Last but not least, the alpine ecosystems are highly sensitive and their response to environmental changes can be detected more easily than the response of an already disturbed ecosystem.

In order to extract the environmental information from the alpine archives, a range of chemical species is usually investigated applying various analytical techniques. In the following, after a description of the sample characteristics, the applied techniques are discussed and a few outstanding results are presented. Finally, a relation of high-alpine snow and ice chemistry research with similar work in the polar regions is attempted.

2. Characteristics of Alpine Snow and Ice Samples

The chemical composition of snow is assumed to reflect the concentrations of the various impurities present in the atmosphere at the time of snow formation. These can be either species contained in atmospheric aerosol particles (*e.g.*, am-

monium, calcium, hydrogen ion, nitrate, sulphate, soot, organic components, insoluble minerals, trace metals) or reactive trace gases (*e.g.*, hydrochloric acid, nitric acid, formaldehyde, hydrogen peroxide). Nonreactive trace gases such as carbon dioxide, methane, and nitrous oxide are not captured by snow crystals and can be determined in air bubbles formed in glacier ice. They will not be discussed in this context, since only preliminary work has been carried out on samples from the Alps so far [4]. Most of the chemical analyses are performed after melting of the snow samples which subdivides the species into water-soluble and insoluble ones. The concentrations of the trace species can vary by at least two orders of magnitude showing very low values in clean winter snow of 1–10 µg/l of the major components such as Ca^{2+} , NH_4^+ , NO_3^- , SO_4^{2-} , and 10–100 ng/l for trace metals. Concentrations in alpine winter snow and Greenland surface snow are comparable, whereas those in precipitation at low elevation sites (< 1000 m) in Europe are a factor of 10–100 higher [5][6]. Thus, the snow samples are particularly sensitive with respect to stability and contamination [7]. Furthermore, the high porosity of snow compared to ice, *e.g.*, requires special care in sample handling, since contaminating gases can more easily diffuse into the snow. This fact has to be taken into account not only for fresh snow samples but also for ice cores where the upper part consist of porous firn, with the firn-ice transition being located normally at a depth of *ca.* 30 m. In most cases, the snow samples are transported to the laboratory in a frozen state, and are melted directly prior to chemical analysis.

3. Applied Analytical Techniques and Sample Preparation Procedures

The major anionic species, *i.e.*, Cl^- , $\text{C}_2\text{O}_4^{2-}$, F^- , HCOO^- , H_3CCOO^- , NO_3^- , SO_4^{2-} , are usually analysed by ion chromatography (IC) with conductivity detection. In our laboratory, *e.g.*, a NaOH gradient elution is applied for simultaneous determination of the above anions (DX-500, Microbore, column: AS11, suppressor: ASRS-I, Dionex). By direct injection of 100 µl of sample, sufficiently low detection limits are obtained (0.2–1 µg/l depending on the species) without a preconcentration step. For methanesulphonate (MSA) a preconcentration of the sample is necessary [8], whereas for Br^- electrochemical detection is used after preconcentration [9]. Ion chromatography with conductivity detection seems the pre-

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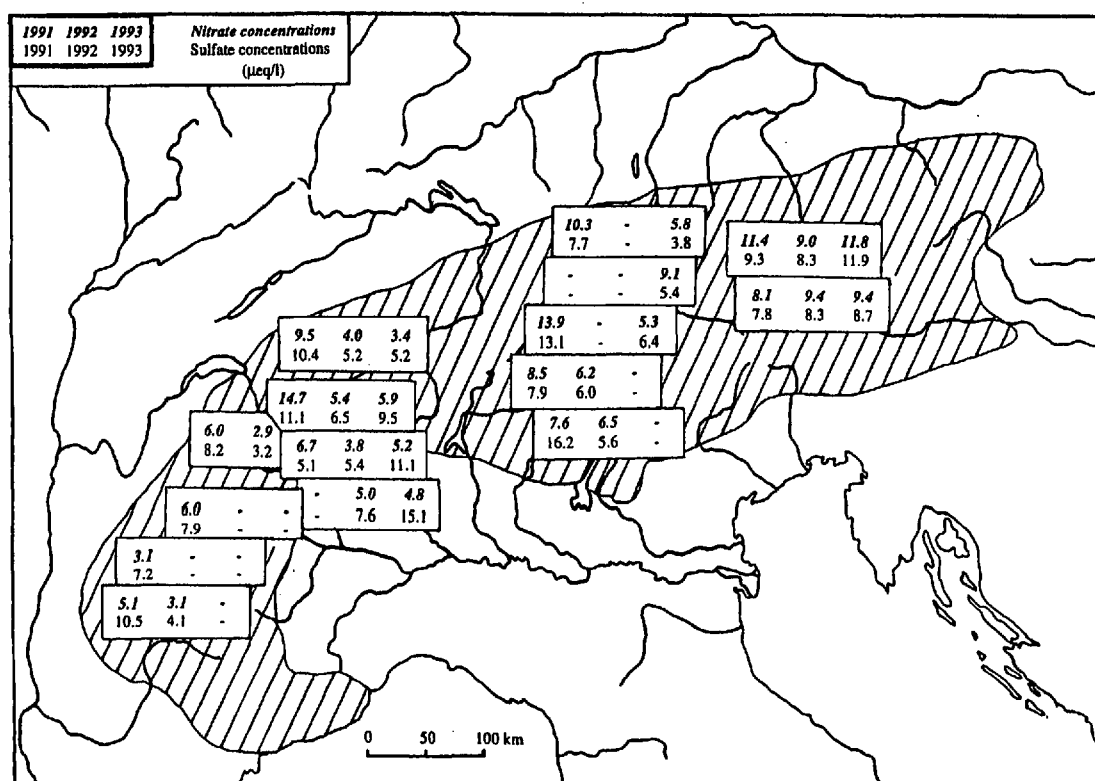


Fig. 1. Mean nitrate and sulphate concentrations ($\mu\text{eq/l}$) of the snow cover formed by the winter and spring accumulation at the different sampling sites in 1991, 1992, and 1993. Reproduced by courtesy of Tellus from Nickus *et al.*, *Tellus* 1997, 49B, 56–71.

ferred method for the major cations Ca^{2+} , K^+ , Mg^{2+} , Na^+ , NH_4^+ , too, although inductively coupled plasma optical emission spectrometry (ICP-OES) or mass spectrometry (ICP-MS), and atomic absorption spectrometry (AAS) are also used. The advantage of IC is the simultaneous determination of NH_4^+ , which is an important species in environmental research. In our laboratory, a methanesulphonic acid eluent is applied without preconcentration yielding detection limits of 1–10 $\mu\text{g/l}$ [10] (S2000, Sykam, column: CS12, suppressor: CSRS-I, Dionex). Materials like bottles, tubes, and vials are carefully cleaned with ultrapure water (18 M Ω cm quality) prior to use for the snow samples. For the determination of carboxylic acids, melting of the samples is performed under inert gas atmosphere to avoid contamination from laboratory air [8].

Only few techniques like ICP-MS and graphite furnace AAS are sensitive enough for the analysis of trace metals (Al, Cu, Pb, Zn, *etc.*) in snow and ice samples. ICP-MS is a particularly attractive method, since it offers, besides sensitivity, the possibility of isotopic ratio determinations (*e.g.*, $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$). In our laboratory we use a double focusing ICP-MS (ELEMENT, Finnigan MAT) equipped with a Micro Concentric Nebulizer (MCN-100, Cetac) [11]. Snow and ice samples are introduced in a self aspirating mode of the nebulizer with an uptake of 40–60 $\mu\text{l}/\text{min}$ under class 100 clean room conditions. Detection limits ($3\sigma_b$ criterion) for Cu (5

ng/l), Pb (2 ng/l), and Zn (10 ng/l), *e.g.*, are controlled by the blank and not by the sensitivity of the instrument. Lead isotopic ratios are determined with a standard error of 0.14% for a concentration level of ca. 100 ng/l and an analysis time of 12 min [11]. Sample preparation and handling is even more critical for trace metal determination. Fresh snow samples are collected in precleaned, acid washed polypropylene tubes, and melted under acid conditions (0.1N HNO_3 , Baker Ultrex II) directly before analysis. Sample handling is always performed under class 100 clean room conditions. Firn and ice core samples which might be contaminated by contact with the drill are prepared by a method adapted from *Boutron et al.* [12]. Core sections of 10–50 cm are mechanically decontaminated in a clean bench in our cold room by chiselling successive layers of snow or ice progressing from the outside to the centre of the core. The centre of the core represents the sample which is analysed after melting in precleaned low-density polyethylene bottles under acid conditions [13].

4. Alpine Wide Geographical Distribution of Trace Species in Snow

In the framework of the EUROTRAC subproject ALPTRAC [14], a snow sampling programme was carried out in the Alps in the years 1991–1993 in order to study the chemical composition of the

high alpine snow pack [7][15]. The main focus of this programme was the investigation of geographical, seasonal and year-to-year variations of the mean concentrations and the deposition fluxes of major ionic species, *e.g.*, ammonium, calcium, nitrate, and sulphate. At up to 17 glaciers from the south-western part of the French Alps (Dauphiné) *via* Monte Rosa, Bernese Alps, Tyrolean Alps to the eastern part of the Austrian Alps (Sonnblick region) samples from the entire winter and spring accumulation of snow were collected and analysed for major ions. Sampling sites were located at an altitude range of 2900–4050 m a.s.l. in order to guarantee that the onset of the snowmelt was not before May. The data revealed that the mean impurity levels of the winter and spring snow pack appeared to be determined by the amount of spring accumulation, showing clearly enhanced concentrations of major ions compared to the winter background values. Another important feature was the rather regularly occurring deposition of Saharan dust, contributing substantially to the input of alkalinity, which is capable of neutralising most of the mineral acid content of the snow pack [16]. Mean concentrations of ammonium, nitrate, and sulphate showed a West to East trend with an increase by about one third, illustrated in *Fig. 1* for nitrate and sulphate. However, this trend in concentrations was not reflected in the total flux of the impurities, since precipitation heights exhibited an opposite pat-

tern. Although no geographical preference of the flux was observed for single winter half-years along the main alpine ridge, a pronounced year-to-year variation was found indicating that large scale meteorological phenomena influence the deposition pattern.

5. Long-term Concentration Records of Trace Species from an Alpine Glacier

In order to illustrate the amount of air chemistry information stored in alpine glacier archives, concentration records of sulphate, ammonium, nitrate, and calcium as well as of lead for the period 1750–1980 A.D. are shown in Fig. 2. These continuous records of trace species in precipitation represent a unique paleoclimatic data set regarding time resolution and geographical scale. They were obtained in our laboratory by analysing an ice core which was drilled on Colle Gnifetti, a glacier saddle in the Monte Rosa massif at an altitude of 4450 m a.s.l. [17]. So far, the top most 70 m of the 109 m long ice core have been investigated after being cut into 2.5–5.0 cm pieces resulting in 1535 subsamples. Dating of the ice core was performed by continuous measurements of ^{210}Pb (until 1900) and by using distinct stratigraphic markers such as historically known Saharan dust events in 1901/02, 1936/37, and 1977 (identified by yellowish layers accompanied by high concentrations of calcium), the atomic bomb horizon in 1963 (identified by tritium measurements) and volcanic eruptions (identified by high sulphate concentrations along with high sulphate to calcium ratios) [3]. For the volcanoes, the time of eruption was used (1912: *Katmai*, Alaska, 1883: *Krakatau*, Indonesia, 1815: *Tambora*, Indonesia, 1783: *Laki*, Iceland). In order to obtain a continuous time scale the time markers were used to fit the accumulation rate of a simplified ice flow model allowing for thinning of the ice [18]. The ten-year averages shown in Fig. 2 clearly demonstrate the dramatic impact of anthropogenic activities on atmospheric chemistry of aerosol related species by the perturbation of the snow chemistry at this high-alpine glacier. Exponential increases of the concentrations were observed for sulphate (period 1870–1980), ammonium (1870–1980), nitrate (1930–1980), and the factors of increase, based upon the preindustrial background levels, amounted to 5.8 ± 0.9 , 2.2 ± 0.4 , 2.3 ± 0.3 , respectively [3]. These increases reflect the anthropogenic emissions of the precursor gases

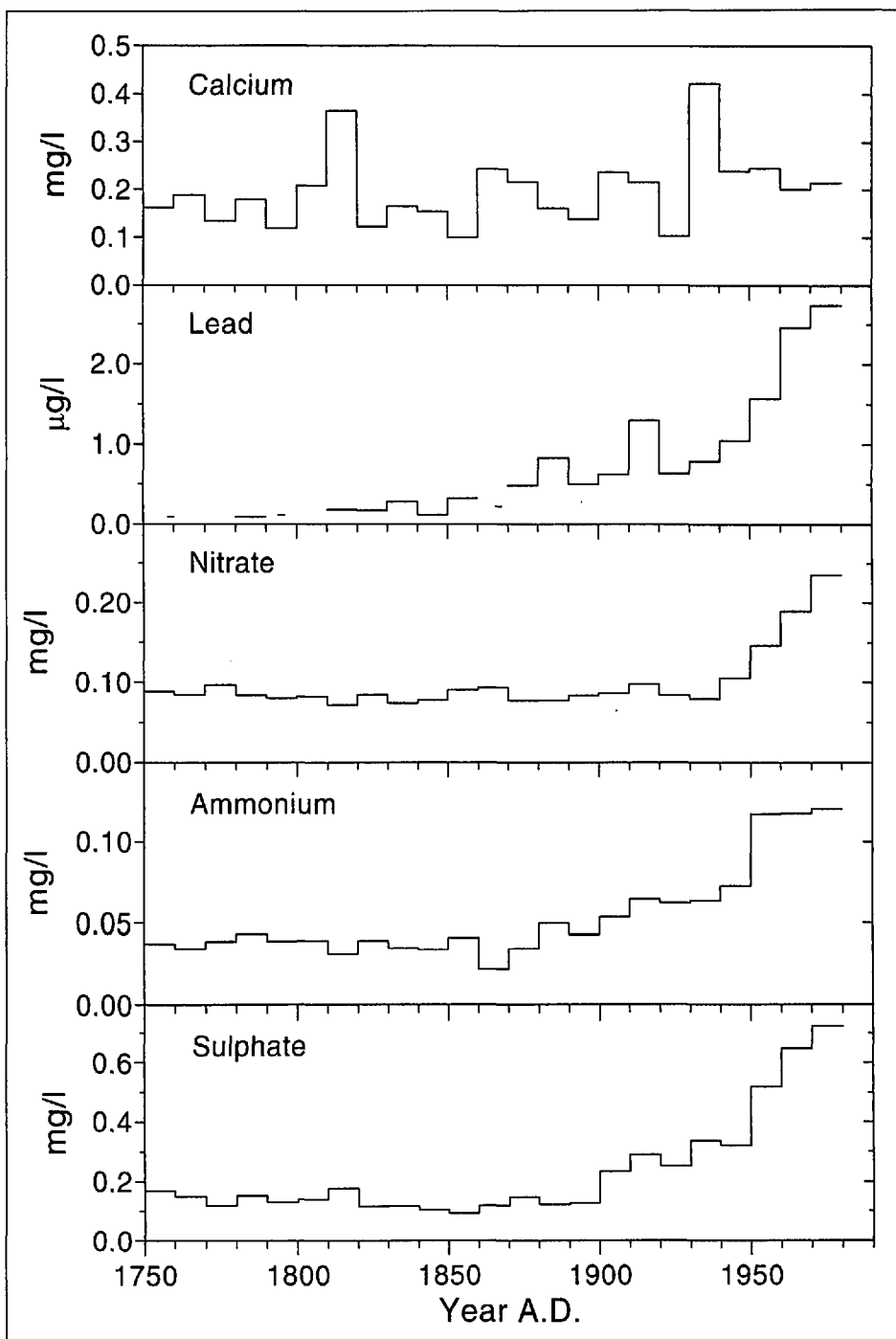


Fig. 2. Ten-year averages of the concentrations of sulphate, ammonium, nitrate, lead, and calcium obtained from an alpine ice core drilled at Colle Gnifetti, Monte Rosa. Note that the averages of lead are given in $\mu\text{g/l}$, and that they are calculated from selected samples covering the ten-year period. Data adopted from Döscher et al. [19] and Döring et al. [13].

SO_2 , NO_x and NH_3 from fossil fuel consumption, traffic, and agricultural sources. For the heavy metal lead no levelling off was detected going back until 1750, indicating that the preindustrial concentrations were still enriched by mining and smelting activities, and thus, no natural background value could be determined from this record so far [13]. After about 1950 lead shows the most pronounced increase of all studied species due to the use of alkyl lead additives in gasoline, which is also reflected in its isotopic composition [19]. For calcium, on the other hand, no obvious trend could be observed,

and the pronounced concentration maxima were attributed to periods with high Saharan dust inputs [20].

6. High-alpine Snow and Ice Chemistry in Relation to Polar Research

Generally, similar analytical methods are applied for snow and ice chemistry studies in high-alpine and mid-latitude as well as polar regions. However, the characteristics of the samples differ significantly. In samples from the Alps anthropogenically derived species together with

mineral dust contribute a major portion of the impurities, and in snow and ice from remote continental mid-latitude glaciers mineral dust dominates. In polar regions, on the other hand, a large contribution of ocean derived compounds like methanesulphonic acid and seasalt is observed in samples from areas near the coast, whereas snow and ice from inland sites show extremely low impurity concentrations (down to the sub ng/l level for trace elements) due to their remote location. For the purest samples from pristine Antarctica preconcentration steps or large sample volumes are still required [21], whereas for general applications in the field of paleoclimate research the sensitivity and precision of modern analytical techniques seem sophisticated enough. However, to carry out the entire process of collection, transportation, preparation, and introduction of the sample without any further contamination is even now a major challenge in analysing such samples.

In order to overcome this problem, one interesting approach is the continuous melting technique, combined with continuous flow analysis which was applied very successfully for the parallel determination of H₂O₂, HCHO, NH₄⁺, and Ca²⁺ in Greenland [22]. The major advantages of this method, besides being nearly contamination-free, are the high spatial resolution attainable (ca. 1 cm) and the significant reduction of sample handling compared to conventional sampling and analysis procedures. However, the number of species which can be determined simultaneously is limited, and the technique cannot be applied in the firm part of the core so far.

7. Outlook

Chemical analyses of snow and ice samples in environmental and paleoclimate research seems well established for a number of inorganic species. The application of quasi on-line techniques seems promising and will certainly get more emphasis in the future. Up to now, one of the major gaps in snow and ice chemistry are the organic compounds, although it is known that a significant portion of aerosol particles is organic matter of probably biogenic origin. Chemical analysis is limited to a few species like, e.g., HCHO, carboxylic acids, or bulk signals such as dissolved organic carbon, particulate total organic carbon and elemental carbon [23]. Thus, more work is needed to improve or even develop analytical techniques for organic compounds going beyond bulk analysis in the direction of speciation.

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