Chemical composition of a polluted snow cover

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Abstract. The meltwaters of snow cover samples taken in Munich during five consecutive days were analysed for contents of solids, C, Na, K, Mg, Ca, CaO, CaCO$_3$, SO$_4$, NO$_x$, NH$_4$, NH$_3$, Cl, Fe, Pb and pH. Concentrations of some of these constituents in newly fallen snow exceed those in 'clean' alpine snow by up to 10 times, except for alkaline-earth metals and calcium compounds. The chemical character of individual snowfalls locally varies very little, but there are distinct differences with regard to different snowfall events, different regions or old snow. The latter is found to be most polluted at centres of motor traffic, and least polluted in fresh air areas like parks. Due to important inhomogeneities in the samples a progressive increase of concentrations with time is not found, except for Cl and solids.

INTRODUCTION

Today, measurements of pollutants in the atmosphere and in the waters of the earth are a matter of routine, but this is not so for temporary snow covers. On the one hand, the meltwaters of a temporary snow cover contain some or all of the major constituents usually found in surface water and groundwater. On the other hand, a snow cover is subject to the influences of ground level air masses and can therefore be regarded as a temporary depot of air pollutants.

This report sums up some aspects of the chemical composition of a snow cover in Munich, compared with that of a 'clean' snow cover in a nearly 'untouched' alpine valley. It follows examples given by Feth et al. (1964), who successfully tried to make the results of chemical analysis of snowmelt waters suitable for use in geochemical considerations, or by Ricq-de Bouard (1973), who recently reported comprehensively on the chemical composition of meltwaters from alpine snow fields. In spite of early observations by Batta and Leclerc (1934) little attention has since been paid to interactions between air pollution and the chemical composition of a snow cover.

PRECONDITIONS

Snow sampling points

In total, 11 snow sampling points were installed in Munich (Fig. 1): nine in the immediate vicinity of the city, which usually suffers from high concentrations of pollutants in the air, and two (Englischer Garten and Patentamt) in the open area near the Isar River. Industries which produce air pollutants are concentrated at about 3–4 km southeast, west and north of the city.
FIGURE 1. Snow sampling points in Munich with mean concentrations expressed as percentages of maximum values. pH values are also given.

The 'clean' samples of snow cover were taken from the alpine valley of Lainbachtal which is situated on the northern periphery of the Bavarian Alps, 60 km south of Munich.

Snow sampling and meltwater analysis
Snow samples were taken from untouched ground by means of a cutting frame with a surface area of 0.5 m² between 13.00 and 14.00 hours. They were immediately put into plastic bags, and then allowed to melt. The meltwaters subsequently passed through a millipore filter, the remaining solids being dried, weighed and their C content determined. After the hydrogen-ion concentration (pH) had been ascertained, the meltwaters were transferred to polyethylene bottles before they were finally analysed according to standardized procedures
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(Gesellschaft Deutscher Chemiker, 1960) for C, Mg, Ca, CaO, CaCO₃, SO₄,
NO₂, NO₃, NH₄, Cl, Fe and for Na, K and Pb by atomic absorption and emission
spectrophotometer.

As a result of the small random sample sizes the differences found in mean
chemical concentrations cannot implicate any statistical significance.

Snow cover data and meteorological conditions
At the beginning of five consecutive snow sampling days in Munich on
26 February 1973, the snow cover at the sampling points was 7-9 cm deep,
corresponding to a water equivalent of 9-12 mm. The first snowfall was on
23 February with further accumulations on 24 February (2.8 mm) and 25
February (1.2 mm). On the following two days a further 2.6 mm was added.

In the alpine area, 125 cm or 335 mm water equivalent are stored during the
same period.

Finally, some basic data of meteorological parameters influencing pollution
loads: the daily mean temperature in Munich varied between 0 and —4.8°C,
the minimum ground temperatures varied between —6.4 and —12°C. Only on
2 and 3 March did shallow temperature inversions exist. On all observation days
relatively low average wind velocities of about 3 m s⁻¹ predominated. Winds
from south to southwest prevailed except on 26–27 February when the wind
blew from west to northwest.

ANALYTICAL RESULTS

Newly fallen snow

With regard to a single snowfall event, few important local variations were
found in the chemical composition of newly fallen snow which was sampled not
later than 2 h after snowfall, but there are variations if different events and
different regions respectively are examined (Table 1).

Meltwaters of newly fallen snow contain important concentrations of Cl and
Na which according to the ratio Na to Cl substantially originate from land
sources. In Munich these concentrations exceeded those of the alpine snow
cover by about 10 times. The solid content which primarily constitutes silicate
minerals that make up most of the snow-crystal nuclei is also higher in
Munich.

Similar high concentration rates were found for the alkaline-earth metals Mg
and Ca and for some calcium compounds, which result from continental dust
and therefore are much more concentrated in the mountain area of the limestone
Prealps. According to their chemical composition, meltwaters of newly fallen
snow in the metropolitan area usually showed acid reactions, which correspond
to results found in Vienna by Steinhauser (1958), whereas basic reactions
predominated in the mountains (high contents of calcium compounds).

Old snow

Mean concentrations

A regional distribution pattern of mean concentrations is given in Fig. 1,
covering a period of four consecutive days with permanent snow cover at all
sampling points. The average concentrations on 23 February (Table 1) are
estimated to represent the basic chemical composition.

Pollution rates are highest in the centres of motor traffic which correspond to
densely built-up areas (Justizpalast in Fig. 1 and Table 2). They are lowest in
well ventilated open areas such as Englischer Garten. Because of winds during
the whole observation period, pertinent pollutant centres are undoubtedly to be
<table>
<thead>
<tr>
<th>Location</th>
<th>Solids [g m^-2]</th>
<th>(organic)</th>
<th>Na</th>
<th>K</th>
<th>Mg</th>
<th>Ca</th>
<th>CaO</th>
<th>CaCO_3</th>
<th>[ppm]</th>
<th>SO_4</th>
<th>NO_2</th>
<th>NO_3</th>
<th>NH_4</th>
<th>Cl</th>
<th>Fe</th>
<th>Pb</th>
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<td>Munich</td>
<td>25.11.72</td>
<td>0.012</td>
<td>0.5</td>
<td>0.2</td>
<td>0</td>
<td>1.5</td>
<td>5.05</td>
<td>0</td>
<td>0.02</td>
<td>6</td>
<td>0.7</td>
<td>6.3</td>
<td>0.05</td>
<td>0</td>
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<td></td>
<td>23.2.73</td>
<td>0.037</td>
<td>0.5</td>
<td>0.2</td>
<td>0</td>
<td>3</td>
<td>5.05</td>
<td>0</td>
<td>0.0075</td>
<td>8</td>
<td>0.075</td>
<td>9.8</td>
<td>0.03</td>
<td>0</td>
<td>5</td>
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<td></td>
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<td>Lainbachtal</td>
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<td>0.05</td>
<td>0.05</td>
<td>1.2</td>
<td>3</td>
<td>20</td>
<td>0</td>
<td>0.05</td>
<td>2.5</td>
<td>0.05</td>
<td>3.3</td>
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<td>0</td>
<td>7.15</td>
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<td></td>
<td>16.1.73</td>
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<td>0.005</td>
<td>0.05</td>
<td>0</td>
<td>10</td>
<td>15.1</td>
<td>0</td>
<td>0.01</td>
<td>2</td>
<td>0.05</td>
<td>4.2</td>
<td>0</td>
<td>0</td>
<td>9.45</td>
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</table>
located in the neighbourhood of the sampling points (cf. $\text{SO}_4$), where dust from nearby buildings and streets precipitates.

According to Table 1, concentrations of Fe differ little from the regional mean of 0.045 ppm. Unexpectedly Pb was not detected in any of the samples. Apart from Justizpalast which showed high concentrations, moderate regional differences of concentration were shown by alkali and alkaline-earth metals, calcium and nitrogen compounds, and sulphates whereas the concentrations of the remaining constituents varied distinctly. (Table 2).

Although the bottom layers of the alpine snow cover were at least 13 weeks old, the total constituents of this 'clean' snow reached only an average of 201 points (Table 2) which was equivalent to scarcely one third of the most polluted metropolitan snow. In the alpine snow there was a relatively high content of solids, alkaline-earth metals and calcium compounds, but there was no C, $\text{SO}_4$, Fe or Pb.

Daily variations
Except for Cl and solids, progressive increases of concentrations with time were not detected; in one case (Englischer Garten: $\text{CaCO}_3$) an inverse development even appears.

Some important daily concentration variabilities observed allow more critical evaluations of the average concentrations mentioned above. These variations are essentially due to:

(1) inhomogeneities in samples resulting from inevitable but small displacements of the sampling points from day to day,

(2) interferences of new snow additions up to 27 February and/or uncontrolled concentration variabilities through water losses by evaporation and snowmelt which depend on the solubility of the chemical constituents.

For the second reason, calculations of daily pollutant increases become dubious, even if we had quantitative knowledge of the water balance of the snow cover.

CONCLUSION

In contradiction to the early records of Batta and Leclerc (1934), by means of chemical analysis of snow cover meltwaters, some up to now unconventional aspects of air pollution are isolated. During the short snow cover period in question, air pollution in Munich took an approximate normal development as far as concentrations of $\text{SO}_4$ (daily mean 0.03–0.06, half-hour maximum 0.21 mg m$^{-3}$), CO (2.5–5.8, 13 ppm) and NO$\text{X}$ are concerned.

Not on all occasions were the pertinent pollution sources definitely detected because of the lack of information regarding primary chemical compounds in the snow cover. Nevertheless, the chemical analysis of a snow cover could supplement official air pollution measurements with some interesting additional information without excessive expense.

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