Long Range Atmospheric Transport of Silver in Northern Europe

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INTRODUCTION

Very few data for the concentration of silver in air and precipitation exist in the literature so far. Nriagu and Pacyna (1988) did not even include Ag in their general assessment of worldwide contamination of air, water and soils by trace metals. The main reason for this is obviously that the environmental concentration levels of this element are generally too low to be determined reliably by most existing methods for trace element analysis.

In the author’s laboratory the atmospheric deposition of a wide variety of trace elements has been studied regularly over the last 20 years (Steinnes 1977, 1980; Steinnes et al. 1992, 1994; Berg et al. 1994, 1995; Berg and Steinnes 1997). Occasionally similar trace element studies of aerosols have been carried out at specific sampling stations run by the Norwegian Institute for Air Research (e.g. Amundsen et al. 1992). In some of the early studies where instrumental neutron activation analysis (INAA) was employed, analytical data for Ag were recorded, but these data were discussed only to a very limited extent (Amundsen et al. 1992, Steinnes et al. 1992). Recently (Berg and Steinnes 1997) apparently reliable data for Ag were also obtained by inductive-coupled plasma mass spectrometry (ICP-MS). Altogether these data for Ag allow some conclusions to be drawn concerning the atmospheric transport and deposition of this element, in particular when discussed in relation to similar data for other heavy metals studied simultaneously.

LONG RANGE ATMOSPHERIC TRANSPORT OF POLLUTANTS IN NORTHERN EUROPE

The aspect of long range atmospheric transport of pollutants (LRTP) in Northern Europe most frequently focused on in public discussion as well as in the scientific literature is the continuous supply of many chemical substances to the southern parts of Scandinavia from other, more densely populated and strongly industrialized parts of Europe. The extinction of fish in thousands of lakes and rivers strongly affected by atmospheric deposition of sulfur and nitrogen compounds from LRTP is clearly the most serious result of this transboundary pollution (Overrein et al. 1981). However, the polluted air masses arriving to Scandinavia also contain appreciable amounts of other pollutants such as ozone, heavy metals, and persistent organic pollutants. At episodes with southerly winds the pollutants
from other European countries are frequently deposited particularly in southern Norway and south-western Sweden by orographic precipitation.

The atmospheric deposition of selected heavy metals has been followed regularly over the last 20 years at the Birkenes station in southernmost Norway. More recently this monitoring has been gradually extended to other stations (Berg et al. 1994). Every 5 years the atmospheric deposition of a large number of trace elements is monitored in a network of about 500 sites by collection and analysis of naturally growing moss (e.g. Steinnes et al. 1992), a method originally introduced by Swedish scientists (Rühling and Tyler 1973). Air concentrations of 20 elements were studied on a daily basis at Birkenes by air filter sampling during two periods in 1978-79 and 1985-86 (Amundsen et al. 1992). Altogether these data have documented that elements such as Pb, Zn, Cd, V, As, and Sb are supplied to southern Norway almost exclusively by LRTP.

THE PLACE OF SILVER IN LONG RANGE ATMOSPHERIC TRANSPORT

Concentrations of Ag in moss were registered by INAA in 1976 at about 40 sites (Steinnes 1977) and in 1977 at about 500 sites (Steinnes et al. 1992) all over Norway. Silver data by INAA also exist from the 1985-86 aerosol sampling at Birkenes (Amundsen et al. 1992). In a moss survey in 1995 (Berg and Steinnes 1997), data for Ag were obtained by ICP-MS. Unfortunately it has not succeeded so far to determine Ag in precipitation samples from the Norwegian monitoring network (Berg et al. 1994). Nevertheless the data now available for Ag, when combined with similar data for other elements associated with LRTP, allow some conclusions to be drawn with respect to concentration levels in air and atmospheric deposition, as shown in the following.

Air concentrations

Diurnal aerosol samples from the 1978-79 and 1985-86 campaigns at Birkenes were assigned to sectors representing different source areas by using trajectory data (Amundsen et al. 1992). Eight sectors of equal size were defined. The highest concentrations of elements predominantly supplied by LRTP were observed in sectors 4, 5, and 6, representing mainly source areas in eastern Europe, central/western Europe, and Great Britain, respectively. Average median values (in ng m\(^{-3}\)) for V(2.3), Zn(21), As(0.69), Se(0.54), Cd(0.12), Sb(0.47), and Pb(11) in these sectors were generally 5-10 times higher than those representing air from sectors 1 (Norway) and 8 (North Atlantic). The 1985-86 values for Ag followed the same sector distribution with maximum concentrations in air derived from sectors 4-6, which clearly places this element among those associated with LRTP. The average median value however was only 0.035 ng m\(^{-3}\), i.e. much lower than for the other elements.

Atmospheric deposition.
Isoleths for Ag from the national surveys in 1977 (Steinnes et al. 1992) and 1995 (Berg and Steinnes 1997) both show a geographic distribution in the moss where the southernmost part of Norway receives 5-10 times higher deposition than the northern part of the country, similar to that of the other LRTP-derived elements. The 1995 level in southernmost Norway is about 40% of that observed in 1977, which indicates a reduced deposition similar to that evident for As, Cd and Sb, but less than that of Pb, during this period of time.

Sampling of bulk precipitation at six Norwegian background stations in 1989-1990 (Berg et al. 1994), using clean techniques for sampling and analysis, made it possible to determine bulk deposition fluxes at these sites. Even though Ag concentrations in precipitation were too low to be determined, it is possible to estimate the deposition of Ag at Birkenes, assuming that the ratio between Ag and other LRTP elements in the aerosol is the same as in bulk deposition, and accounting for differences in deposition trends of different elements between 1985 and 1990 as indicated by the moss analysis. Thus, the bulk deposition of Ag at Birkenes in 1990 is estimated to be 32±11 μg/m²·y, which corresponds to an average concentration in precipitation of 23±8 ng L⁻¹.

Natural surface soils

Large-scale investigations of organic-rich surface soils in Norway have shown that the topsoil in southern Norway is strongly contaminated with elements such as Pb, Cd, As, and Sb, derived from LRTP (Allen and Steinnes 1980; Steinnes et al. 1989; Page and Steinnes 1990; Steinnes et al. 1997). Samples from a nationwide program in 1995, taken from the upper 3 cm of the soil, were analyzed recently (Nygård et al. 1997) with respect to Ag, which was not included in any of the previous soil surveys. Generally values are of the order of 0.4 - 0.8 ppm, and the geographical distribution does not indicate any significant contribution from LRTP. One trend, however, appears to be very pronounced: soils from areas along the western coast generally show much lower concentration levels than elsewhere in the country, often 0.2 ppm or less. Apparently the higher input of airborne seasalt components in these coastal areas lead to weaker binding of Ag in the humus layer, possibly due to the formation of the AgCl complex in the soil.

CONCLUSIONS

The main conclusions from the present work may be formulated as follows:

1. Long range atmospheric transport from other parts of Europe is a primary source of airborne silver in Scandinavia.

2. Atmospheric deposition of silver in southern Norway has declined by over a factor of 2 over the last 20 years.
3. Current concentrations of silver in precipitation falling in different parts of Norway can be estimated to be of the order of 2-20 ng L⁻¹.

4. Airborne silver is not a major source to contamination of soils and surface waters except perhaps near strong point sources of air pollution.

5. Components of marine aerosols appear to affect the chemistry of silver in organic topsoils.

REFERENCES

Allen, R. O. and E. Steinnes, Contribution from long-range atmospheric transport to the heavy metal pollution of surface soil, in D. Drablos and A. Tollan (Eds), Ecological Impact of Acid Precipitation, SNSF Project, Oslo - Ås, 1980, pp 102-103.


Questions & Answers: Long Range Atmospheric Transport of Silver in Northern Europe

Q. GARY GILL (Texas A&M University): You showed a relationship - I believe it was for lead - between deposition and the levels of lead that were in the moss. I'm curious whether that correlation is a relationship between wet deposition or if it also includes some dry deposition component? Then sort of a corollary question: Is the moss reflecting predominantly a wet or dry component, or a compilation of both?

A. Well, the situation in Norway is that lead deposition is mainly wet deposition. And what we used there was bulk deposition collectors which collect all wet deposition and only part of the dry deposition. We don't know so well how good this moss reflects the dry deposition, but in our case it's not so important.

Q. ANDERS ANDREN (UW-Madison): Eliiv, I'm not sure I really understand your argument about the marine influence part. Are you saying that silver comes in the precipitation as a silver chloride, and it doesn't adsorb as effectively as that silver which might come from other sources?

A. No. What I'm saying is that whatever the source of silver is in the surface soil, that the binding of silver is affected by the marine ions coming in.

Q. Oh, I see what you mean. So you have the anions in the soil already.

A. Yes.

Q. ALINA KABATA-PENDIAS (IUNG-Poland): The data you present for your country for silver in surface soils are very much comparable with data which we have for our kind of soil in our countries, which are not necessarily enriched in humus. Most of our surface soils are very poor in humus. But anyway, results are pretty comparable, there is 1 ppm silver in soil. But what we could see is a kind of a halo phenomenon, if you know what I mean by halo, around any larger city. This 1 ppm of silver doesn't exist very much elsewhere, but is quite visible around each city. And I hadn't seen this on the map showing distribution for your country. Do you observe such an influence of municipal activity on silver levels in surface soils?

A. I think that depends on how dense your network is.

(Balance of answer and follow-up question lost due to tape malfunction)

Q. ARUN MUKHERJEE (University of Helsinki-Finland): Is it possible that we can calculate or find out the load of silver in the Baltic Sea? I know that would not have very much data on silver loading to the whole Scandinavian area, but we know now mercury, lead, we know very much about cadmium on the Baltic Sea, but is it possible that in the near future we can do something on the load of silver in the Baltic Sea?

A. If you mean the anthropogenic load over all times, I think that would be difficult. If it was to calculate the load at a certain time I think you could use, for example, measured lead deposition data and assume a certain ratio. But calculating the load over all time, I think would be very difficult. I think that's better done by taking sediment samples.