Sources of particulate selenium in the Baltic Sea atmosphere*

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Abstract

To determine the atmospheric concentrations and size distributions of particulate selenium (Se), aerosols were collected by air filtration and impactor sampling at the Kap Arkona coastal weather station on the Island of Rügen. Total reflection X-ray fluorescence analysis was used to determine Se and numerous other elements as well. The dependence of the Se concentration on the wind direction and the results of a regression analysis indicated that Se associated with sub-micron particles is mainly derived from anthropogenic sources. The pronounced relationship between Se and Cu indicated that copper smelting is a major source of atmospheric selenium. A marine Se contribution was identified for particles larger than 2 μm.

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1. Introduction

The deposition of atmospheric trace elements has been recognised for many years as a significant contribution to the trace metal load discharged into the Baltic Sea. Trace metal studies as part of the EU BASYS subproject 'Atmospheric Load' included selenium (Se) which, though it has important physiological control functions, may be toxic at higher concentrations. On a global average, about 75% of atmospheric Se is particulate, the remaining fraction being gaseous. The first investigations on particulate Se in the marine atmosphere by Duce *et al.* (1975) revealed a significant anthropogenic impact, even in remote oceanic regions. According to Smith & Campbell (1979), copper smelting and the combustion of coal are the principal processes contributing to anthropogenic emissions. During these high-temperature processes, Se is emitted in gaseous form which during cooling condenses on fine particles. A study by Mosher & Duce (1983) compared particulate Se concentrations in urban areas with those in remote oceanic regions. They found particulate Se gradients that were much less steep than those of other anthropogenic trace metals and concluded that gaseous Se is released by the ocean and subsequently adsorbed on particles. Measurements by Schneider (1985) in the atmosphere over the subtropical North Atlantic also indicated the existence of a marine source of Se.

Investigations of atmospheric trace metal concentrations and deposition over the Baltic Sea, especially those within the HELCOM monitoring programme, have concentrated on the potentially toxic elements Hg, Cd, Pb and Cu. Here we report the first data on atmospheric concentrations and size distributions of particulate Se in the Baltic Sea area and attempt to identify the sources of atmospheric Se.

2. Experimental

2.1. Sampling

Samples for particulate Se were collected at the German weather station at Kap Arkona on the Island of Rügen (Fig. 1), located on a cliff at a height of about 40 m above sea level. The sampling equipment was mounted on a platform about 3 m above the ground. The surrounding area is closed to the public; moreover, there are no other potential local contamination sources in the vicinity of the station. During the eight week experiment (15 May 1997 to 15 August 1997), 33 aerosol samples were collected. The sampling time varied between 1 and 2 days.

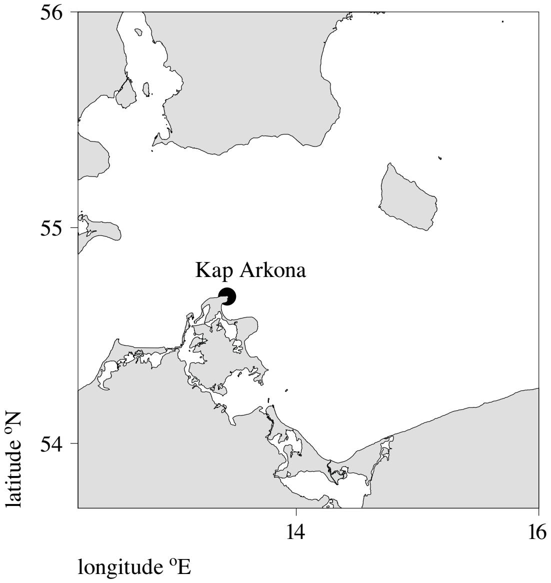

Fig. 1. The location of the Kap Arkona sampling station

To determine the atmospheric Se concentrations, air filtration units were used. Air was sucked through nitro-cellulose filters (50 mm diameter) at a flow rate of about 25 l min^{-1}. To measure the Se size distributions, four stages of a single-orifice cascade impactor (PIXE type) were used. At a flow rate of about 1 l min^{-1}, the cut-off aerodynamic diameters were:
stage 1: $0.25\ \mu\text{m} < \text{d} < 0.5\ \mu\text{m}$,
stage 2: $0.5\ \mu\text{m} < \text{d} < 1.0\ \mu\text{m}$,
stage 3: $1.0\ \mu\text{m} < \text{d} < 2.0\ \mu\text{m}$,
stage 4: $2.0\ \mu\text{m} < \text{d} < 4.0\ \mu\text{m}$.
Sample holders for the total-reflection X-ray fluorescence analysis (TRXF) consisting of 30 mm quartz discs were used as impaction slides in order to enable the direct analysis of the deposited particles without any chemical manipulation (Schneider 1989).

2.2. Analytical method

The nitro-cellulose filters were digested with 4 ml HNO_3 to which 100 ng yttrium (Y) were added as an internal standard. Using PTFE beakers placed in steel containers, digestion was performed under pressure at about 200°C. After cooling, 10 μl of the solution were pipetted onto the centre of the TRXF sample holders and evaporated to dryness. By excitation with the Mo(K_α) line for 1000 seconds, a multi-element fluorescence spectrum was obtained. The intensity of the Se peak was related to the standard

Y peak. Thus, by the application of a previously determined calibration factor, the Se concentration in the digestion solution and thus in the air could be calculated. A detailed description of the trace element analysis by TRXF and its application to atmospheric trace metals is given by Stoessel (1987).

For the determination of the blank Se value, a series of 15 blank filters was analysed. In all cases the Se content was below the detection limit, which was estimated at 0.75 ng ml^{-1} and corresponded to an atmospheric Se concentration of 0.04 ng m^{-3}.

For the analysis of the impactor samples, the impaction slides were introduced into the TRXF analyser and exposed to $Mo(K_\alpha)$ excitation for 1000 seconds. The Se/Fe mass ratios were calculated from the fluorescence spectrum. Standardisation was performed in the second step by the addition of 1 ng Y to the spot left by the impacted aerosol particles and the TRXF measurement was repeated. From this second spectrum, the absolute Fe mass was determined and used to calculate the absolute Se mass from the Se/Fe ratio. This procedure was applied because Se and many other elements are soluble in the acidic Y solution and may diffuse out of the excitation area after standardisation, whereas this chromatographic effect is very unlikely for the mainly mineral and insoluble Fe.

Since the TRXF method is a multi-element analysis, data for many other elements were obtained incidentally, among them Cu and Cl, which will be used to support the interpretation of the Se data.

3. Results and discussion

3.1. Concentrations and size distribution

The total Se concentrations obtained from the sum of the four impactor stages were only about 70% of the concentrations determined by air filtration. This discrepancy is attributed to particles adhering to the inner walls of the impactor. The total particulate Se concentrations are presented as a time series in Fig. 2. The mean concentration (0.34 ng m^{-3}) is significantly larger than those reported from remote marine areas, but less than those observed at urban sites (Table 1). The variability of the data (0.12–0.88 ng m^{-3}) is less pronounced than for other trace elements (*e.g.* Pb: 0.5–14 ng m^{-3}) measured at the same time at Kap Arkona and confirms the observations by Mosher & Duce (1983).

Since the wind direction was variable during most of the sampling intervals, it was not possible to discern characteristic Se concentrations for individual wind sectors and thus to identify the main Se transport directions. Stable wind conditions were observed only between 12 and 19 July, when the

Table 1. Concentrations of atmospheric particulate selenium

Location	Particulate selenium concentration [ng m^{-3}]	References
Coastal Rhode Island	0.93 ± 0.59	Mosher & Duce (1983)
North-West Atlantic	0.15 ± 0.07	Mosher & Duce (1983)
South Pole	0.006 ± 0.001	Maenhaut *et al.* (1979)
Kap Arkona	0.33 ± 0.17	this paper

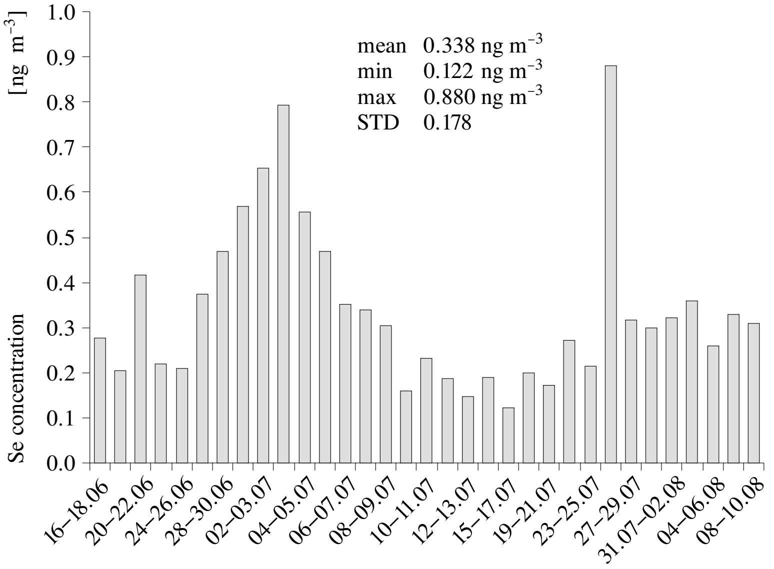

Fig. 2. Time series (16.06.–10.08.1997) of particulate Se concentrations at Kap Arkona

wind blew continuously from the central Baltic Sea (ENE, 60°–90°). During this period the concentrations were lowest, indicating that the main sources of these Se concentrations lie south of the Baltic Sea. Two concentration peaks of about 0.8 ng m^{-3} could not be related unequivocally to the wind direction.

The mean Se size distribution is shown in Fig. 3. About 60% of the particulate Se was found in the small particle fraction with diameters between 0.25 μm and 0.50 μm. This is typical of anthropogenic elements emitted by high-temperature processes.

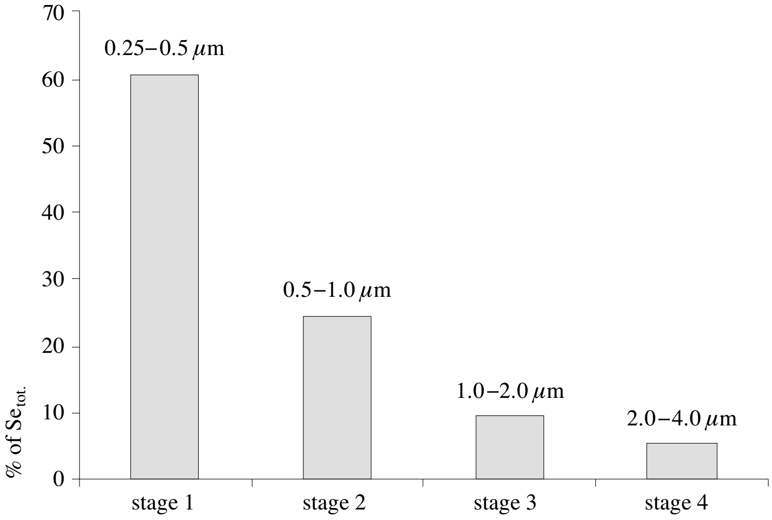

Fig. 3. Percentage of total particulate selenium for the four stages of the impactor

3.2. Source identification

The characteristics of the Se concentrations and size distributions clearly demonstrate that anthropogenic emissions are largely responsible for the concentrations of particulate Se at Kap Arkona. In order to detect the specific processes by which Se is released into the atmosphere, correlations between Se and other elements (Cd, Pb, Zn, Cu) containing a strong anthropogenic component (*e.g.* Schneider 1987) were examined in that linear regressions were performed. These showed that the closest relationship existed between Se and Cu. After eliminating one extreme Cu value, the calculations showed that 66% of the variation in Se can be explained by the Cu variation ($R^2 = 0.66$). Therefore, the regression analysis was repeated with the Se/Cu concentrations in the different size classes. The results (Fig. 4) indicate that the Se and Cu concentrations are highly correlated ($R^2 = 0.81$) for sub-micron particles, especially in the smallest size range (0.25–0.50 μm). These findings confirm the supposition that copper smelting is a source of atmospheric Se (Germani *et al.* 1981) and very probably accounts for most of the particulate Se at Kap Arkona.

Since the ocean is also a potential source of atmospheric Se, we examined our data for a possible marine component. The Cl concentrations are used as an indicator of the abundance of sea salt particles found in the coarse mode of the particle size spectrum (Marks 1990) and which were collected mainly (70%) on stage 4 (2–4 μm) of the impactor. A sea salt contribution has therefore been taken into account only for this size class. Assuming that sea salt particles are associated with a characteristic amount of Se

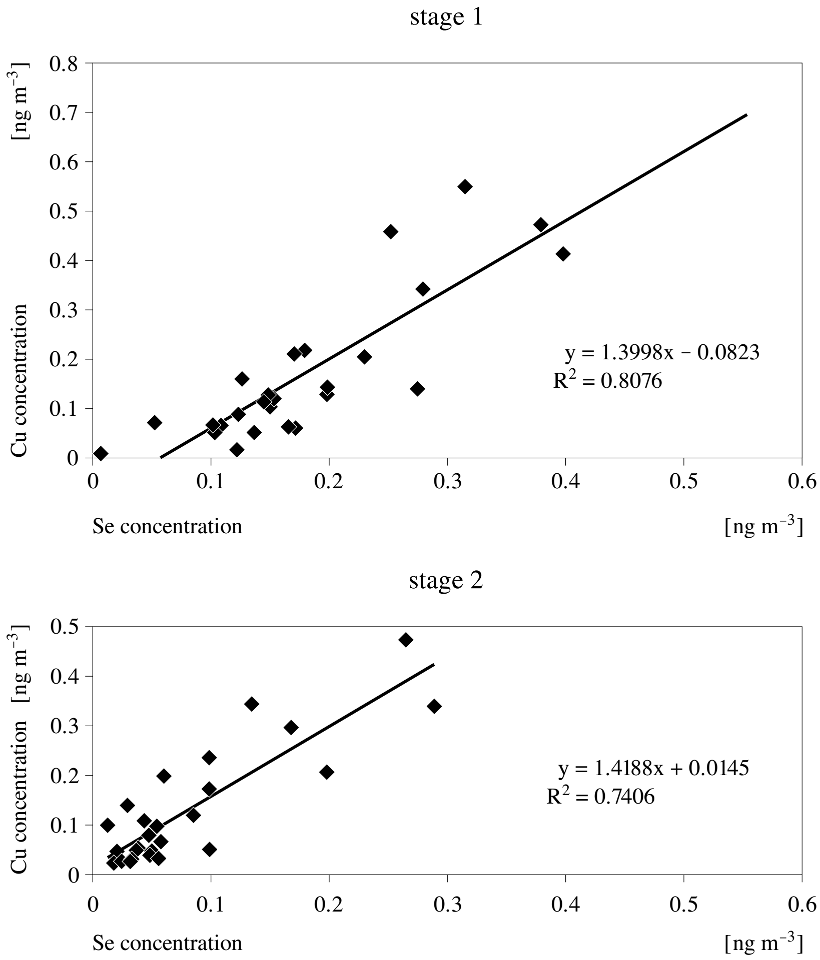

Fig. 4. Correlations between Se and Cu for different particle size ranges

($\mathrm{Se_{marine}} = \mathrm{f_{ss}} \times \mathrm{Cl}$) and that the anthropogenic Se at stage 4 is an almost constant fraction ($\mathrm{f_4}$) of the total anthropogenic Se ($\mathrm{Se_{tot.\ anthr.}}$), we can express the Se concentration for this size range $\mathrm{Se_4}$ by

$$\mathrm{Se_4} = \mathrm{Cl_4} \times \mathrm{f_{ss}} + \mathrm{Se_{tot.\ anthr.}} \times \mathrm{f_4}. \tag{1}$$

Since the expected marine contribution to impactor stage 4 is only a small contribution with regard to the total Se ($\mathrm{Se_{tot.}}$), $\mathrm{Se_{tot.\ anthr.}}$ is approximately equal to $\mathrm{Se_{tot.}}$, and eq. (1) can be rewritten as

$$\mathrm{Se_4}/\mathrm{Se_{tot.}} = \mathrm{f_{ss}} \times \mathrm{Cl_4}/\mathrm{Se_{tot.}} + \mathrm{f_4}. \tag{2}$$

This relationship was tested by plotting $\mathrm{Se_4}/\mathrm{Se_{tot.}}$ versus $\mathrm{Cl_4}/\mathrm{Se_{tot.}}$ (Fig. 5). Despite the data points being scattered quite widely around the regression line, a distinct correlation does exist, indicating that sea salt particles act as a carrier for Se. About 30% of Se in the 2–4 μm size range can be attributed to sea salt particles; however, with regard to the total Se, this contribution is only about 2%.

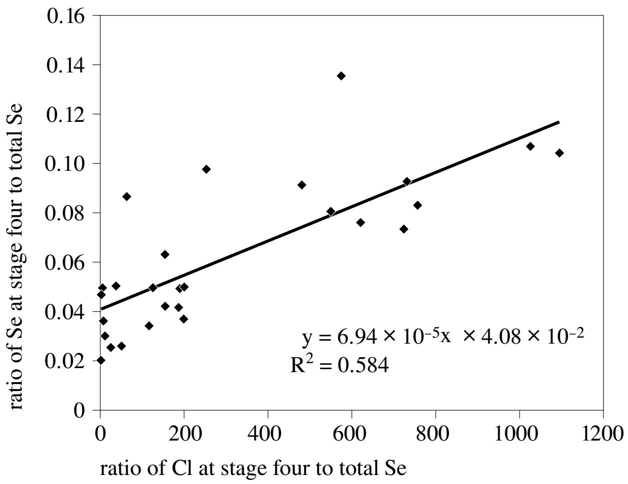

Fig. 5. Identification of the marine contribution to particulate Se by relating $Se_4/Se_{tot.}$ to $Cl_4/Se_{tot.}$ (according to eq. (2))

The ratio between Se and Cl associated with sea salt is represented by the slope of the regression line and amounts to 6.9×10^{-5}. In view of the geochemical variability, this is consistent with the Se/Cl ratio for atmospheric sea salt particles over the subtropical North Atlantic (2.3×10^{-5}) determined by Schneider (1985) using completely different methods. The Se/Cl ratio in bulk seawater is lower by about four orders of magnitude (Measures & Burton 1980) and so a process must exist by which sea salt particles are enriched in Se. Enrichment at the surface of bursting bubbles, which generate sea spray, must be considered. However, this process is usually based on the adsorption of cations on negatively charged organic films and will probably not be effective for Se, which occurs in anionic forms in seawater. Therefore, we suggest that gaseous Se, possibly $Se(CH_3)_2$, released at the sea surface (Mosher & Duce 1983), is adsorbed on sea salt particles and causes this enrichment.

4. Conclusions

The atmospheric concentrations of particulate Se on the southern Baltic Sea coast range between those reported from urban areas and from remote marine regions. Anthropogenic origins and copper smelting are probably the major sources. Detected in the coarse particle mode, the marine Se contribution is of minor importance to the atmospheric Se budget in the anthropogenically highly influenced Baltic Sea area, but could be significant on a global scale, especially if the gaseous phase Se is taken into account.

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