Atmospheric Pb and Cd input into the Baltic Sea: a new estimate based on measurements

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Abstract

Bulk deposition samples were collected during a summer (1997) and a winter (1998) measurement campaign at four coastal stations along the southern Baltic Sea coast and on the Island of Gotland. The data were used to construct Pb and Cd deposition fields over the Baltic Sea. A weak gradient with decreasing deposition rates from the southwest towards the east and north was obtained for Pb. In the case of Cd, the spatial distribution pattern was characterized by an extreme deposition maximum at the Polish station on the Hel Peninsula. The total atmospheric input of Pb and Cd into the Baltic Sea was 550 and 33 t/year, respectively, and exceeds the riverine input by approximately about 50%. Previous measurement-based estimates were higher by a factor 2–3 and indicate a decrease of the atmospheric deposition during the past 10–15 years. The comparison with modelled deposition data yielded partly large differences and was impaired by the fact that 1990 emission inventories were used whereas our measurements were performed in 1997/1998.

Relating our deposition estimate and the Pb/Cd input by rivers to the mean concentrations in Baltic Sea water, residence times of 0.29 and 3.6 years were obtained for Pb and Cd, respectively. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Atmospheric deposition; Cadmium; Lead; Baltic Sea

1. Introduction

The Baltic Sea is exposed to the input of many anthropogenically derived chemicals which are released into the environment mainly in the highly industrialized and densely populated areas in central Europe. These substances enter the Baltic Sea via atmospheric deposition and riverine input where they may accumulate and potentially exert toxic effects on the ecosystem. Accumulation of contaminants in the Baltic Sea is favoured by the low water depth (mean: 52 m) and the limited water exchange with the North Sea which results in a mean seawater residence time of 20–30 years (HELCOM, 1986), which is much longer than in other coastal seas, e.g. in the North Sea (1–2 years; Otto et al., 1990).

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About 20–30 years ago, it became evident that atmospheric deposition plays an important role for the marine cycles of trace metals (e.g., Buat-Menard, 1986) and, in particular, for the contamination of coastal seas (e.g., Rodhe et al., 1980). This applies especially to the Baltic Sea where strong trace metal emission sources exist in countries bordering on the southern and eastern coast. However, the impact of these sources on the deposition into the Baltic Sea depends on the atmospheric transport pattern. The frequency distribution of the wind direction in the central Baltic Sea shows that southwesterly winds prevail. The relative frequency for the 60° southwest sector is 26%, whereas the corresponding southeast sector accounts for only 9%. As a consequence, sources located southwest of the Baltic Sea are of enhanced importance. Model studies have shown that emissions in Western European countries that are not neighbouring the Baltic Sea account for about 25% of the trace metal deposition to the Baltic Sea (Krüger, 1996).

Several attempts have been made to estimate the atmospheric input of trace metals into the Baltic Sea on the basis of measurements. A very first estimate was presented by Rodhe et al. (1980). Although based on fragmentary data, the results indicated the importance of atmospheric deposition for the trace metal budget of the Baltic Sea. In the following years, the Helsinki Commission for the Protection of the Baltic Sea Environment (HELCOM) initiated an airborne pollution monitoring programme (EGAP) which included the deposition of trace metals. Based on these data and on results from research projects (Grassl et al., 1989), new experimental input estimates were established, mainly for Pb, Cd and Zn (HELCOM, 1989, 1991; Duce et al., 1989; Schneider, 1993). The data for Pb and Cd (Table 1) reveal discrepancies as large as a factor 2, which is probably due to inadequate sampling/analytical techniques, shortcomings in the sampling strategy, and different methods for extrapolation of coastal data to the entire Baltic Sea. Moreover, the estimates refer only to the time span between 1980 and 1990. Subsequent EGAP monitoring data were not used for input calculations due to questionable data quality (HELCOM, 1997).

In parallel to the experimental efforts, progress was achieved in modelling the long-range transport and deposition of atmospheric trace metals. Petersen and Krüger (1993) published modelled input fluxes (Pb, Cd, Zn, As), and the latest HELCOM deposition estimate (Pb, Cd) was based on model computations (HELCOM, 1997) as well. The differences between the model results (Table 1) are also considerable. However, it has to be taken into account that the computations refer to different years (1984/1985 vs. 1990) and therefore are based upon different emission inventories. Also, the fact that Petersen and Krüger (1993) applied a Langrangian transport model, whereas an Eulerian-type model was used for the HELCOM (1997) estimate, and that different process parameterizations were included in the two models, may have contributed to different results. The agreement between the experimental and modelled estimates is also not satisfactory. For 1989/90, the input estimates for both Pb and Cd differ by a factor of 2–3.

In view of this situation, trace metal deposition was included in the “Atmospheric Load” subproject within the EU research project Baltic Sea System Studies (BASYS). By the use of both measurements and models, it was intended to establish an improved

<table>
<thead>
<tr>
<th>Year</th>
<th>Pb [t/year]</th>
<th>Cd [t/year]</th>
<th>Reference</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1980</td>
<td>2400</td>
<td>80</td>
<td>Rodhe et al., 1980</td>
<td>measurements</td>
</tr>
<tr>
<td>1983–86</td>
<td>1560</td>
<td>35</td>
<td>HELCOM, 1989</td>
<td></td>
</tr>
<tr>
<td>1985–87</td>
<td>1000</td>
<td>60</td>
<td>Duce et al., 1989</td>
<td></td>
</tr>
<tr>
<td>1986–89</td>
<td>1600</td>
<td>77</td>
<td>Schneider, 1993</td>
<td></td>
</tr>
<tr>
<td>1984–85</td>
<td>1400</td>
<td>18</td>
<td>Petersen and Krüger, 1993</td>
<td>models</td>
</tr>
<tr>
<td>1990</td>
<td>640</td>
<td>27</td>
<td>HELCOM, 1997</td>
<td></td>
</tr>
</tbody>
</table>
current atmospheric input estimate as part of an overall trace metal budget for the Baltic Sea. Here we describe our experimental approach and present the results in comparison to model calculations (Sofiev et al., 2000). We concentrate on Pb and Cd since these elements show opposite biogeochemical characteristics in seawater. Cd is linked to the cycling of nutrients ("nutrient-like element") and has relatively long residence times in seawater, whereas Pb is easily removed from the water column by adsorption to mineral particles and subsequent sedimentation ("scavenged element") resulting in much shorter residence times.

2. Experimental

2.1. Sampling

Deposition samples were collected during a summer (June 16–August 8, 1997) and a winter period (February 1–March 31, 1998) at four coastal stations (Fig. 1) located at Kap Arkona on the Island of Ruegen (KAP), the Hel Peninsula (HEL), at Preila (PRE), and at Hoburg on the Island of Gotland (HOB). The main criterion for the selection of these sites was the absence of local sources such as heavy traffic or other human activities. Simple precipitation samplers consisting of a PE funnel with a surface area of 110 cm² screwed to a PE collection bottle (150 cm³) were deployed at each station. All materials that get in contact with the samples were carefully cleaned with HNO₃ (pH = 0) and subsequently rinsed with suprapure deionized water. Since the samplers were kept open during dry periods, the samples comprised wet and dry deposition as well (bulk deposition). During most of the sampling periods, the collection bottles were changed each second day, provided that precipitation had occurred. During two 2-week periods in July 1997 and March 1998, daily samples were collected. In some cases, e.g. during the winter experiment at PRE, the funnel was rinsed with 30–50 cm³ suprapure water after sampling intervals with no precipitation in order to get pure dry deposition samples.

A total of 175 deposition samples were obtained and shipped to the Baltic Sea Research Institute which acted as the central laboratory for the trace metal analysis.

2.2. Chemical analysis

For the determination of Pb and Cd in the deposition samples, total-reflection X-ray fluorescence (TXRF) and graphite furnace atomic absorption spectrometry (GFAAS) were applied using the following stepwise procedure.

Prior to the analysis, the samples were acidified with concentrated suprapure HNO₃ to a pH of about 0 in order to avoid adsorption of dissolved trace metals on the walls of the collection bottle. To suspend particles homogeneously, the samples were shaken vigorously and 20 μl of the sample were pipetted onto the center of the TXRF sample holder. Ten microliters of yttrium standard solution containing 1 ng Y was added, the sample was evaporated to dryness, and the X-ray fluorescence spectrum obtained by excitation with the Mo(Kα) line was recorded for 1000 s (Atomika, Model EXTRA II). By multiplication of the Pb/Y fluorescence intensity ratio with a calibration factor, the Pb concentration in the sample was calculated. For each deposition sample, two TXRF subsamples were prepared and measured. Details of trace metal analysis by TXRF are given by Knoth and Schwenke (1980).

Since the sensitivity of the TXRF method is low for Cd, GFAAS was applied (Perkin-Elmer, Model 5000). However, the concentrations in most of the samples were also too low for direct Cd determina-
tion by GFAAS. Therefore, these samples were freeze-dried and then redissolved in a volume of 1 N HNO₃ that was 1/10 of the original sample volume. After this enrichment procedure, the detection limit for Cd in bulk deposition was reduced to 0.018 nmol/l. The uncertainty of the method is estimated to be about 15%.

The concentrated samples were also used to determine Pb by GFAAS and to repeat the TXRF determination. Hence, the Pb data were obtained using three different procedures: direct TXRF, GFAAS and TXRF after enrichment by freeze-drying. Since the differences between the results did not show any systematic trend, the mean was used to represent the Pb concentration. The mean differences between the three determinations indicated that the uncertainty of the Pb values is about 10–15%. Due to the freeze-drying enrichment, the sensitivity of the Pb determination was increased and a detection limit of 0.1 nmol/l was attained for both the TXRF and GFAAS method.

At the beginning of each measurement period, a field blank test was performed at each station using ultra-clean deionized water to simulate a rain event. Handling of the samples and chemical analysis were identical with the treatment of the real samples. For Pb, the concentrations in the blank samples (30–50 cm³) varied between 0.15 and 1.9 nmol/l with a mean value of 0.87 nmol/l. In the case of Cd, only three samples contained detectable Cd concentrations with a mean of 0.09 nmol/l, which thus represents an upper blank limit.

3. Results and discussion

3.1. Pb and Cd concentrations in the deposition samples

The Pb and Cd concentrations in the bulk deposition samples at the four stations are plotted as a function of the precipitation height in Fig. 2. No blank corrections were performed because of the uncertainties of blank determination and because the effect on the measured concentrations was within the uncertainty of the method.

The Pb data cover a range of approximately two orders of magnitude and increase during periods of low precipitation (Fig. 2a). To compare the concentrations at the different stations, means weighted to the amount of precipitation were calculated (Table 2). The mean values for Pb refer to both measurement periods and show a steady decline in the sequence KAP–HEL–PRE–HOB, indicating a west/east and a south/north gradient.

The variability of the Cd concentrations is similar to that of Pb if only the stations KAP, PRE and HOB are considered (Fig. 2b). However, at station HEL exceptionally high Cd concentrations were observed mainly, but not only, during sampling periods with little precipitation. Some samples contained as much as 240 nmol/l Cd and, when associated with relatively high precipitation amounts, yielded strong deposition pulses. Hence, a completely different regional distribution pattern was obtained for the mean Cd concentrations in the bulk deposition samples (Table 2). Whereas almost uniform values were found for KAP, PRE and HOB, an extremely high mean concentration was observed at HEL, which exceeded those at the other stations by a factor of about 20.

In view of these unexpected results, the question arises whether the samples could have been contaminated during handling. We think this is unlikely because only the Cd concentrations were high in the respective samples, whereas other elements such as Zn and Pb, which are known as indicators for contamination, did not show any anomaly. Moreover, data from the HELCOM monitoring station Leba, located about 75 km east of HEL, have also shown markedly elevated (factor 5) Cd concentrations in bulk deposition compared to the neighbouring stations in Germany and Lithuania (HELCOM, 1997). From these findings, we conclude that a strong Cd source must exist in northern Poland, which has a pronounced impact on the deposition at HEL. Backward trajectories calculated by the Finnish Meteorological Institute (M. Hongisto, K. Jylha, pers. communication) are presented (Fig. 3) for the sampling interval with the maximum concentration in bulk deposition (Fig. 2b). The trajectories show that the air masses passed the area south/southeast of HEL before arriving at the sampling site. Hence, one may speculate that the City of Gdansk, which is located about 25 km south of HEL, is the suspected Cd emission source. However, for the other sampling intervals with high Cd deposition, the trajectories...
were not unequivocally indicative of a Gdansk Cd source.

3.2. Dry deposition of Pb and Cd

To approximately estimate the contribution of dry deposition to the bulk deposition, the data from the winter experiment at PRE were analyzed, where nine dry-only samples were collected during 2 weeks without any precipitation. The concentrations in water used to rinse the funnel ranged over one order of magnitude and showed mean values of 3.1 nmol/l for Pb and 0.13 nmol/l for Cd, respectively. Although the blanks may have contributed significantly
Table 2
Mean Pb and Cd concentrations in bulk deposition (c), measured precipitation (h) and deposition rates (D), and deposition rates normalized to the mean annual precipitation rate (Dh).

<table>
<thead>
<tr>
<th></th>
<th>Pb [nmol/l]</th>
<th>h [mm/year]</th>
<th>Ds [μmol/m² year]</th>
<th>Dh [μmol/m² year]</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAP</td>
<td>25</td>
<td>454</td>
<td>12.0</td>
<td>14.6</td>
</tr>
<tr>
<td>HEL</td>
<td>17</td>
<td>447</td>
<td>7.5</td>
<td>9.3</td>
</tr>
<tr>
<td>PRE</td>
<td>14</td>
<td>326</td>
<td>4.9</td>
<td>7.5</td>
</tr>
<tr>
<td>HOB</td>
<td>11</td>
<td>266</td>
<td>3.4</td>
<td>6.1</td>
</tr>
</tbody>
</table>

Cd [nmol/l] h [mm/year] Ds [μmol/m² year] Dh [μmol/m² year]

| KAP   | 0.69        | 454         | 0.32              | 0.39              |
| HEL   | 16.2        | 447         | 7.24              | 8.91              |
| PRE   | 0.72        | 326         | 0.25              | 0.38              |
| HOB   | 0.89        | 266         | 0.28              | 0.49              |

3.3. Input estimates for Pb and Cd

The mean precipitation (h) and bulk deposition (Dh) rates include the contribution of the dry-only samples for each station in Table 2. To estimate the annual total deposition (D) of Pb and Cd to the Baltic Sea requires extrapolation of the local bulk deposition rates in time and space. Whereas the concentrations in bulk deposition were assumed to be representative for an entire year, the deposition rates were adjusted to the climatological mean precipitation rate (H). Since normalization to H must be confined to the wet fraction (Dwet) of the bulk deposition, the total deposition (Dt) is expressed by:

\[ D_t = D_{dry} + D_{wet} * H/h \]

Using the previously determined ratio \( D_{dry}/D_t = 0.20 \) and replacing \( D_{wet} = D_b - D_{dry} \) gives:

\[ D_t = D_t * [1/(0.20 + (1 - 0.20) * h/H)] \]

On the basis of Eq. (2), \( D_t \) was calculated for each station using the bulk deposition and precipitation rates (Table 2) and the mean annual precipitation rate for the Baltic Sea \( H = 584 \) mm/year (HELCOM, 1986). The uncertainties related to the

Fig. 3. Air mass trajectories for the sampling interval with the maximum Cd deposition at station HEL (see Fig. 2b).
determination of the $D_{\text{day}}/D_0$ are relevant for the determination of $D_0$ only if the measured precipitation rates deviate strongly from the climatological mean. This effect was tested for the stations HOB and PRE where a low ratio $h/H$ of about 0.5 was observed. However, a reduction of $D_{\text{day}}/D_0$ to the model-derived value of 0.1 (Petersen and Krüger, 1993; HELCOM, 1997) affected $D_0$ only by about 5%.

In order to extrapolate the annual Pb and Cd deposition rates from the four stations to the entire Baltic Sea, the following simplifications and assumptions were made.

(a) The Baltic Sea (415 000 km$^2$) is considered as a rectangle (Fig. 4) with the line KAP–HEL–PRE (500 km) representing the so-called “continental” coast, whereas HOB represents the conditions 300 km north of the “continental” coast. In order to extrapolate the deposition measurements to the areas north of HOB, bulk deposition measurements made in 1995 at the Finnish monitoring station Hailuoto (HAI) on the northern coast of the Bothnian Bay (HELCOM, 1997) were assumed to be representative of the upper boundary of the Baltic Sea rectangle. The mean concentrations at HAI were 8.7 and 0.44 nmol/l for Pb and Cd, respectively. The calculation of the total deposition rates followed the procedure for our data and yielded 4.49 μmol/m$^2$ year for Pb and 0.23 μmol/m$^2$ year for Cd.

(b) Due to dispersion and deposition, concentrations of atmospheric trace substances decrease approximately exponentially with increasing distance from the source area. Therefore, it was assumed that deposition between the stations also follow an exponential function. Fields for the total deposition were calculated by interpolation, first between the stations along the “continental” coast, then between this baseline and the uniform deposition at a distance of 300 km (HOB) and finally between HOB and HAI. The calculations were performed for cells of 50 km × 50 km.

Fig. 4a shows the calculated spatial distribution of the Pb deposition, which is characterized by a weak gradient with decreasing deposition from the southwest (KAP) towards the east and north. The mean deposition rate was 6.37 μmol/m$^2$ year and corresponds to a Pb input into the Baltic Sea of 550 t/year. The distinct decrease of the Pb deposition with regard to previous experimental estimates (Table 1) is consistent with the reduction of Pb emissions due to the restricted use of Pb additives in gasoline and with the decreasing trend of Pb concentrations in Baltic Sea surface water (Kremling and Streu, 2000). However, we cannot exclude that methodological improvements also contributed to the differences in the estimates.

Sofiev et al. (2000) calculated the Pb input into the Baltic Sea for the period of our measurements by model simulations that are based on modifications of the ADOM model (Venkatram et al., 1988) and the HILATAR model (Hongisto, 1998). Extrapolating their monthly data to an entire year yields Pb inputs of 680 and 596 t/year for the ADOM and the HILATAR model, respectively, which agrees well with HELCOM (1997) model estimate (Table 1). The agreement with our estimate (550 t/year) seems also reasonable, taking into account the uncertainties involved in both the model calculations and the experimental approach. However, the comparison is impaired by the fact that the model calculations are based on a 1990 Pb emission inventory which, due to emission reductions in Europe, does not apply to 1997/1998.

The distribution of the Cd deposition (Fig. 4b) is centered around the deposition hot spot at HEL with about 9 μmol/m$^2$ year. The relative contributions of the individual deposition events to the total deposition during the sampling campaigns are presented in Fig. 5 and show that the three highest deposition peaks accounted for about 70% of the total deposition. With increasing distance from HEL, the gradient decreased, but it still existed between HOB (0.49 μmol/m$^2$ year) and HAI (0.23 μmol/m$^2$ year). A mean Cd deposition rate of 0.71 μmol/m$^2$ year was calculated, yielding a total input of 33 t/year. About 20% of this input occurred in a narrow 50-km band along the southern coast. Most of the previous experimental input data (Table 1) were higher than our estimate by a factor of about 2. Again, it is difficult to assess the effect of methodological artefacts on these differences. However, the decreasing Cd concentrations in Baltic Sea surface waters during the time span 1982 to 1993/1995 (HELCOM, 1996; Kremling and Streu, 2000) support the conclusion that a real decrease of the Cd input occurred during the past 10–15 years.
The comparison with model calculations by Sofiev et al. (2000) revealed major differences. Both the ADOM (9.4 t/year) and the HILATAR (9.0 t/year) model produced input estimates which were a factor of 3.7 below the values based on measurements. This discrepancy can only partly be attributed to the extreme deposition at HEL, which is not reproduced by the model (Sofiev et al., 2000). If the HEL data are excluded from our deposition calculations, a total Cd input of 18 t/year is still obtained. On the other hand, the HELCOM (1997) Cd model calculations generated an input of 28 t/year, which differs by only 20% from our estimate.

The comparison between our input data and the model results must consider the uncertainties of the different approaches. With regard to model calcula-
tions, inaccurate and obsolete emission inventories are very likely the main error sources, which according to Sofiev et al. (2000) may lead to uncertainties of roughly a factor 2. To give a well-grounded estimate of the uncertainty of our estimate is difficult as well. The error of 10–15% given for the chemical analysis of the samples is probably magnified by the procedure to extrapolate the deposition data in space and time.

Considerable effort has been made to estimate the atmospheric trace metal deposition to the North Sea since the neighbouring countries are highly industrialized and many potential emission sources are concentrated close to the coast. A compilation of measured deposition rates covering the period up to 1993 is given by Injuk and van Grieken (1995). Mean Pb and Cd deposition rates for the entire North Sea area are reported (e.g. Rojas et al., 1993) exceeding those in the Baltic Sea by a factor of 4–5. Subsequent investigations by Injuk et al. (1998), which did not include Cd, yielded somewhat lower Pb deposition rates. However, their Pb flux estimate of 17.9 μmol/m² year, which included a dry contribution of about 14%, is still a factor 3 higher than our data and indicates that the North Sea is more heavily subjected to atmospheric trace metal deposition than the Baltic Sea.

3.4. Importance of the atmospheric input for the Baltic Sea Pb and Cd budget

In addition to atmospheric deposition, riverine input plays an important role for the Baltic Sea Pb and Cd budget. According to HELCOM (1998), the Pb and Cd river loads are approximately 340 and 24 t/year, respectively. Thus, the atmosphere contributes about 60% to the total input of both Pb and Cd into the Baltic Sea.

To establish a mass balance, the water exchange between the Baltic Sea and the North Sea must be considered as a potential sink/source for Pb and Cd. Mean concentrations for dissolved Pb and Cd in the central Baltic Sea surface waters are 0.041 and 0.080 nmol/l, respectively (Kremling and Streu, 2000). Taking into account a particulate Pb and Cd fraction of about 30% and 5% (Pohl and Hennings, 1999) results in total concentrations of 0.058 and 0.085 nmol/l, respectively. For the northeastern North Sea, Haarich and Schmidt (1993) reported total Pb and Cd concentrations of 0.21 and 0.19 nmol/l, respectively. Combining these data with the water exchange rates between the Baltic Sea and the North Sea (HELCOM, 1986: outflow = 947 km³/year; inflow = 471 km³/year) yields a net import into the Baltic Sea of 11 t/year for Pb and of 1 t/year for Cd. Compared to the atmospheric and riverine inputs, these are negligible quantities.

Whereas decreasing trends of the Pb and Cd concentrations in Baltic Sea surface waters were identified for the time span between 1982 and 1993/1995 (Kremling and Streu, 2000; HELCOM, 1996), the concentrations have stabilized during the
last 5 years (Pohl and Hennings, 1999; Pohl, unpublished monitoring data). This indicates that the present Pb and Cd inputs are compensated by sedimentation and that the budget is at steady state. Relating the sum of the input fluxes to the mean concentrations (Fig. 6) results in mean residence times of 0.29 and 3.6 years for Pb and Cd, respectively. This confirms and specifies the “scavenged” behaviour of Pb and “nutrient-like” properties of Cd.

4. Conclusions

Pb and Cd input estimates for the Baltic Sea are presented which, with the exception of the HAI data, are based on a sampling network with uniform sampling equipment and on identical analytical methods. A methodological bias of the data was thus avoided and a homogeneous data set was obtained. The discrepancy between the experimental and modelled Pb/Cd input data that we were confronted with at the start of the project could not be resolved. The fact that the emission inventories used by the models do not apply to the time of the measurements is the major obstacle to identifying the reasons for the deviations.

Uncertainties in the experimental estimates are related to the representativeness of our measurements. Although seasonal differences in the air mass transport pattern and deposition were taken into account by performing a winter and a summer experiment, our measurements covered only one third of a year. The question of representativeness also arises with regard to the selection of sampling sites. The site selection is especially critical along the southern Baltic Sea coast, which is closest to the source areas. This was demonstrated by the input estimate that ignored the deposition maximum at HEL and yielded an input of 18 t/year instead of 33 t/year. To achieve representativeness, the stations must be located both in “low” and “high” deposition areas, but must avoid local sources which have no long-range effect. This is an extremely difficult task because it requires knowledge of the deposition distribution pattern along the coastline and because the establishment of a sampling network is restricted by logistical limitations. Future measurement programmes should use model calculations to optimize the site selection, presuming that the models are based on correct emission inventories.

Despite these potential sources of errors, we are confident that our effort has improved the knowledge about the present Pb and Cd deposition to the Baltic Sea. The data indicate that atmospheric deposition of Pb and Cd exceeds the input by rivers and thus has a major impact on the Pb and Cd budget of the Baltic Sea. Compared to estimates for the time before 1990, the input of Pb and Cd decreased by a factor of 2–3. This is consistent with the decreasing trends for Pb and Cd in Baltic Sea surface waters reported by HELCOM (1996) and Kremling and Streu (2000).

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References


