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Atmospheric Heavy-metal Deposition on Land and Sea.

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ABSTRACT

During a period of four years (1975-78) atmospheric deposition of heavy metals has been measured in Denmark at 8 to 18 stations.

Pb, Cd, Cu, Zn, Na, Mg, Mn og Ni have been determined in monthly samples.

Anthropogenic sources are expected to be responsible for the emission of Pb, Cd, Cu and Zn to the atmosphere.

The atmospheric deposition (expressed in kg metal/km^2/year) of the metals Pb, Cd, Cu and Zn gives a major contribution of the total sea input of these metals.

Déposition atmosphérique de métaux lourds à terre.

ABSTRACT

Au Danemark, depuis une durée de 4 ans (1975-78) on a analysé la déposition atmosphérique de métaux lourds dans 8 a 18 stations.

On a analysé des preuves mensuelles de Pb, Cd, Cu, Zu, Na, Mg, Mn et de Ni.

On est convaincu que les sources anthropogéniques soient responsables de l'émission de Pb, Cd, Cu et de Zn a l'atmosphère.

La déposition atmosphérique exprimée en (kg métaux/km^2/an) des métaux Pb, Cd, Cu et de Zn est un supplément considérable à l'input total à la mer de ces métaux.

Atmospheric Heavy-metal Deposition on Land and Sea

Introduction.

The atmosphere is a transport medium for gases and aerosols. The sea produces aerosols by spray and bubble mechanisms which give a marine-atmosphere rich in sea-salt aerosols. Sea-salts are transported to the continent through the atmosphere leading to a pronounced deposition of Na, K and Mg in the coastal regions.

From the continents aerosols originate in soil-dust and anthropogenic activities are spread to the sea.

It has been shown that heavy-metals are long range transported from the industrial centers in Europe to the Atlantic (Prahm 1976) and Southern Scandinavia. (Hovmand, 1979).

Precipitation (defined as the sum of wet and dry material deposited in a funnel) gives a minimum value of the total atmospheric deposition on an area. It is the purpose of this paper to show that atmospheric deposition of anthropogenically emitted metals is similar over land and sea. The atmosphere contributes significantly to the total sea-input of Pb, Zn and Cd.

Material and methods.

The sampling device is a standard funnel (NILU, Norwegian Institute for Air Research) with a sampling diameter of 20 cm (sampling area 0,0314 m^2). A polyester net (200 µm mesh) in the bottom of the gauge prevents sampling of bigger particles and insects.

The funnel is connected to a 10 ℓ bottle (Kautex); the bottle and funnel are made of polyethylene (Fig. 1). 10 ml concentrated HNO_3 (Merck p.a.) is added to the bottle prior to the start of the one month sampling period.

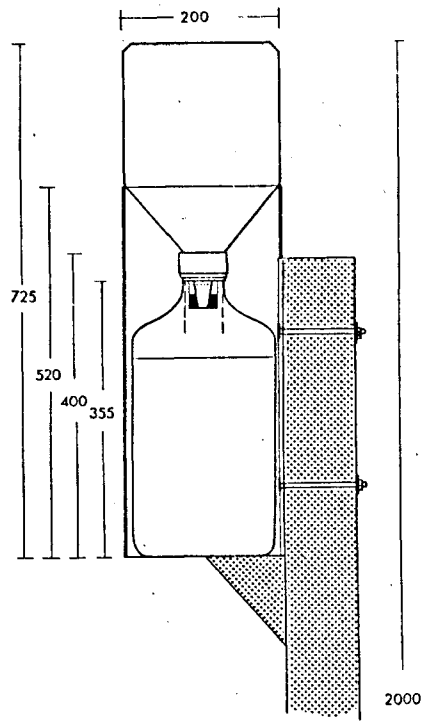

Fig. 1. Bulkprecipitation collector. All dimensions in millimetre. Total height 2000 mm.

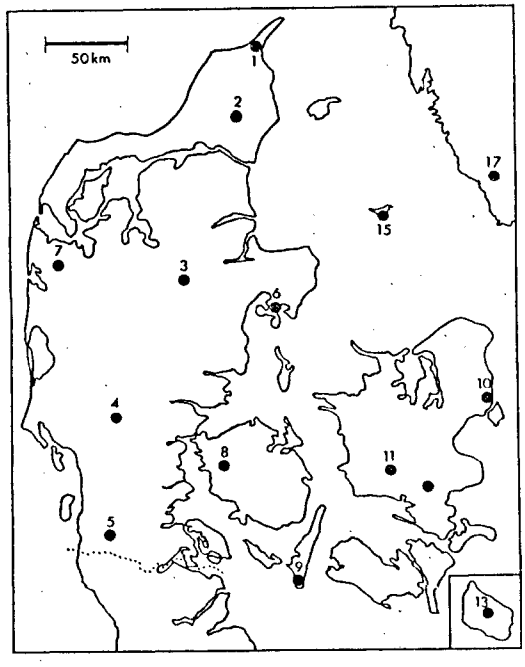

Fig. 2. Location of sampling stations for atmospheric metal deposition.

Atomic Absorption with graphite oven and flame is used for metal analysis. Pb, Cd and Ni are analysed after a solvent extraction (1% DDDC in xylene, extracts metals from acid solutions buffered to pH 4-5). The other elements are determined directly in the acidified solution.

Fig. 2 shows the location of the sampling stations. Station 10 situated in Central-Copenhagen is not included in the computations. All the other stations are situated in the countryside, far from contaminating sources. The minimum distances from the sampling stations to the following sources are:

Greater cities	($>10^4$ inhab.)	>10 km
Power plants and big factories		>10 km
Highways and small cities		>1 km
Small roads		>0,1 km

The stations 7-9-13-15-16 are maritime stations, expected to give atmospheric deposition values, close to deposition over open sea. The other stations are land-stations, but no continental station (more than 100 km to the shore) is in operation.

Results.

The samples taken during a four year period 1975-78 were analysed for the eight metals (Pb, Cd, Cu, Zn, Na, Mg, Fe, Mn). Mean values per year are shown in Table 1. Mean values are calculated on basis of all stations except No 10, Copenhagen and No 16, Faeroe Islands.

Table 2. gives atmospheric deposition values for five maritime stations.

The sampling stations have been in operation two to four years. Table 3 shows the proportion between the deposition at the maritime station during the period of operation and mean deposition for all stations in the same period.

Discussion.

It can be seen from table 3. that atmospheric deposition measured at land stations and maritime stations do not differ significantly. This emphasizesthat aerosols are long range transported and the atmospheric deposition is a wide spread phenomenon. Atmospheric deposition determined as bulk precipitation is believed to show a minimum value of the "total atmospheric deposition" which includes aerosol adsorption and impaction to surfaces.

Comparative evaluations of the input of some heavy metals to the Baltic Sea (Hansen et al, 1976) shows that atmospheric deposition of Pb, Cd, Zn is greater or of the same magnitude as the sum of other sources. Estimated inputs to the Baltic from waste water, and river waters are compared with atmospheric deposition in table 5. Table 4 gives a comparison between rate of sedimentation in the Bornholm Basin (Pheiffer Madsen, 1979) and the atmospheric deposition values from table 1.

Conclusion.

It is shown that atmospheric input of heavy metals to the Baltic surface is a significant contribution to the total loading, especially for the metals Pb and Cd.

Need for further research.

As the bulk precipitation of heavy metals is belived to give a minimum value for the "total atmospheric deposition" it is desirable to measure the aerosol adsorption to the sea surface.

The atmospheric deposition of heavy metals is a wide spread phenomenon covering large areas of the seas compared to the local input from wastewater and rivers. Consequently the uptake of atmospheric deposited material by plankton seems to be an importent object for further research.

References.

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Table 1.

Atmospheric metal deposition. Mean values for danish background stations.
Acid activated (a.a.) bulk precipitation. Monthly samples.

Year	Precipitation	Pb	Cd	Cu	Zn	Na	Mg	Fe	Mn	Number of samples
	mm	$mg \cdot m^{-2} \cdot year^{-1}$								
1975+	539	7.9	0.24	1.60	17.2	1256	207	98	11.2	140
1976	475	8.1	0.19	1.24	13.2	1595	233	100	8.9	180
1977	701	10.7	0.17	2.00	14.9	1912	296	-	8.2	147
1978	717	9.1	0.21	1.30	14.7	1308	209	71	7.4	80
mean values 1975-1978	608	9.0	0.20	1.5	15.0	1518	236	90	8.9	551++

+ Calculated from a period of 11 months
++Total number of samples.

Table 2.

Atmospheric metal deposition at some maritime sampling stations. Annual averages computed from stated periodes.

Station No. (location)	Sampling period	Precipitation	Pb	Cd	Cu	Zn	Na	Mg	Fe	Mn
	month/year	mm	$mg \cdot m^{-2} \cdot year^{-1}$							
St 13 (Bornholm Baltic Sea)	02/75-09/77	537	10.1	0.25	1.5	17.0	588	153	76	11.9
St 09 (Langeland Baltic Sea)	02/75-09/77	305	5.2	0.15	1.2	16.8	1439	215	61	5.4
St 15 (Anholt, Kattegat)	02/76-09/77	412	7.2	0.14	1.2	9.3	1246	166	41	3.5
St 07 (West Jutland North Sea)	02/75-12/78	738	6.9	0.18	1.2	12.5	2483	385	50	4.1
St 16 (Faeroe Is. Atlantic)	01/77-11/78	1621	4.2	0.05	1.3	5.8	9615	1654	36	2.2

Table 3.

Proportion between atmospheric deposition at the maritime stations during the period of operation and the mean deposition at all stations in the same period. Location and sampling period as in table 2.

Station No	Precipitation	Pb	Cd	Cu	Zn	Na	Mg	Fe	Mn
St 13	1.01	1.17	1.42	1.02	1.18	0.45	0.75	0.80	1.00
St 09	0.58	0.60	0.72	0.82	1.17	1.10	0.82	0.64	0.61
St 15	0.75	0.75	0.77	0.76	0.65	1.19	0.96	0.70	0.41
St 07	1.24	0.78	0.92	0.81	0.86	1.66	1.66	0.78	0.99
Mean	0.90	0.83	0.96	0.85	0.97	1.10	1.05	0.73	0.75
St 16	2.29	0.41	0.22	0.72	0.37	5.9	6.6	0.23	0.27

Table 4.

Sedimentation rate of heavy metals in the Bornholm Basin. Deposition period 1962-68. Data from Pheiffer Madsen (1979).

Pb	Cd	Cu	Zn	Ni
		$mg \cdot m^{-2} \cdot year^{-1}$		
16	0.22	10	71	~10

Table 5.

Estimated input of heavy metals to the Baltic Sea. Atmospheric deposition is estimated from mean concentrations in bulk precipitations (table 1) and total rain fall of 172 $km^3 \cdot year^{-1}$.

Sources	Pb	Cd	Cu	Zn	Ni
			$tons \cdot year^{-1}$		
*Waste water + Industrial waste	884	54	731	1833	489
*Rivers	944	94	3304	9440	1416
Atmospheric deposition	2500	57	420	4200	200

*Hansen et al. (1976).