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DRY AND WET DEPOSITION FLUXES OF Cd, Cu, Pb AND Zn INTO THE SOUTHERN BIGHT OF THE NORTH SEA

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Abstract—During the period from September 1988 to October 1989, 23 sampling flights were carried out over the Southern Bight of the North Sea. In this campaign, both bulk and size-segregated airborne particulate matter samples were collected. Dry deposition velocities for Cd, Cu, Pb and Zn have been estimated using a modified version of the two-layer of Slinn and Slinn and the particle size distribution obtained from size-fractionated samples. Results pointed out that the main difference between our results and those reported in the literature lies in the aerosol size distribution. Dry deposition rates calculated using these deposition velocities as a function of wind sector showed that continental air masses, particularly those associated with the wind sector west southwest, are predominant in the deposition process. Wet flux estimates were carried out using Slinn's approach. Results were also classified taking into account different wind sectors. Here, the wet flux of Pb and Zn is mainly related to wind sectors east/northeast, south southeast and local, the latter represents air masses with variable origin; whereas those of Cd and Cu correspond to wind sectors west southwest and south southeast. Results showed that wet deposition is responsible for almost 70% of the total deposition into the Southern Bight of the North Sea. However, some topics, like heavy metal content in large aerosol particles, temporal distribution of precipitation events, variation of precipitation intensity aloft, need better knowledge before accurate assessments can be made.

Key word index: Atmospheric deposition, aerosols, North Sea, heavy metals, aircraft sampling.

INTRODUCTION

There has been growing concern regarding the pollution of coastal and shelf systems of the North Sea, especially since Weichart (1973) concluded that the southern North Sea is one of the most heavily polluted areas. Recently there have been efforts to determine the relative importance of the different pathways through which trace metals and other toxic substances reach the marine environment. These sources are mainly rivers, piped discharges, dumpings, run-off from land and, last but not least, atmospheric fallout. Here, the atmospheric input is caused by processes such as cloud or raindrop scavenging of aerosol particles, known as wet deposition, and/or by the transfer of gases and solid phases, known as dry deposition. Early studies reported by IDOE (1972) suggested that the atmospheric input of trace elements represents a significant proportion of the total input, relative to other pathways.

In order to estimate the atmospheric input of heavy metals and compare it with other pathways, Cambray *et al.* (1975, 1979), Dedeurwaerder *et al.* (1982) and Dedeurwaerder (1988) conducted direct measurements of dry and wet deposition. Despite the fact that these constitute the first attempts to assess the atmospheric fallout directly, the main drawbacks to their approach are: (i) predictions are based on coastal determinations; and (ii) the lack of reliability of the sampling technique, as has recently been discussed by Liss *et al.* (1988).

Due to a large number of constraints, direct measurements of particle pollutant fluxes over the sea are scarce (Van Aalst, 1986). In order to overcome this problem, several authors have proposed, as an alternative, the use of mathematical models to predict the atmospheric input of particulate matter to the North Sea. Indeed, Van Jaarsveld *et al.* (1986) introduced a model capable of predicting such input, and also the contribution of source areas to the total deposition. Their model is based on emission inventories and a transport-dispersion approach. The main shortcoming of this model is that most of the meteorological parameters such as wind speed, friction velocity, mixing height and rainfall statistics have been obtained from in-land measurements.

Krell and Roeckner (1988) published a new approach to modeling the deposition of Cd and Pb. They use a stochastic trajectory model, emission inventories, meteorological data and estimates of precipitation

and mixing height data. Their results indicated that previous estimations of deposition data, extrapolated from coastal measurements, tend to overestimate the atmospheric input of anthropogenically generated heavy metals into the entire North Sea (Kersten *et al.*, 1988). On the other hand, their dry and wet deposition calculations take only into account particulate matter in the size range between 0.2 and 1 μm, which seems unrealistic, as will be shown throughout this work.

As an alternative method, Petersen *et al.* (1989) used the EMEP model (Eliassen and Saltbones, 1983), which was originally conceived for sulfur dioxide and particulate sulfur, to calculate dry and wet fluxes into the North Sea and the Baltic Sea. Even though the agreement between their model calculations and that of Krell and Roeckner (1988) is good, they conclude that a comprehensive validation of their approach is not possible due to the lack of long-term measurements of trace metal concentrations and deposition over the North Sea. If such long-term measurements were available, then model estimates and the uncertainties associated with them would be of no need.

In this work we concentrate on four elements of interest, namely Cd, Cu, Pb and Zn, and report on the dry and wet fluxes of atmospheric particulate matter over the Southern Bight of the North Sea. These fluxes have been calculated from total and size-fractionated airborne elemental concentrations, collected with the aid of an aircraft, during a 1-year period, in combination with calculated dry and wet deposition rates, related, *inter alia*, to the particle size distribution.

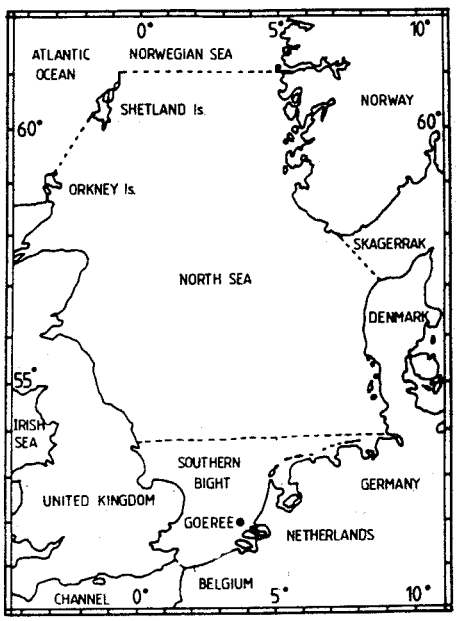

Fig. 1. Schematic representation of the Southern Bight of the North Sea. Here, the starting point of the sampling flights (Goeree platform) is also shown.

MATERIALS AND METHODS

Experimental

The sampling campaign started in September 1988, and lasted for 13 months. During this period, 23 flights were carried out using a twin-engine aircraft Piper Chieftain, PA 31-350, owned by Geosens B. V. (Rotterdam, Netherlands). All flights were performed with cloudless meteorological conditions (less than 3 oktas), and samplings did not take place during precipitation events. Each flight was planned taking into account the 36-h air mass backward trajectories provided by the Royal Netherlands Meteorological Institute (KNMI, De Bilt, Netherlands), for four different pressure levels: 1000, 925, 850 and 700 hPa, respectively. The starting point was the Goeree platform (51°55.5'N, 3°40'E), from which a spiral flight was done in order to localize the inversion layer. A map showing the area where sampling was carried out is given in Fig. 1. The aerosol sampling took place in six different tracks, each covering a distance of about 110 km towards the North Sea in the up- or downwind direction from the Goeree platform, and more or less equally spaced between the inversion height and sea level. Altitude was measured with a King Radar Altimeter model KRA 10/10a, whereas temperature and wind speed were monitored using a 102 E temperature sensor with Pt-100 element (nominal resolution 0.1°C) (Rosemount Inc., U.S.A.), and a Racall Doppler 91 radar equipped with a RSN 252 navigation compass, with a wind speed precision of 1 m s^{-1} and a position accuracy of 0.1 nautical mile. Airborne particulate matter was sampled using an isokinetic inlet designed by the Pennsylvania State University (Pena *et al.*, 1977), and collected on a set of parallel filters, namely, 0.4-μm pore size, 47-mm diameter Nuclepore membrane filter and 1-μm pore size, 47-mm diameter Millipore Teflon filter. After the air passed through the filters, it was pumped out using a Venturi system which was mounted on the wings. This had the advantage of being very light without requiring electric power. The air flow rate was 50 ℓ min^{-1}. Size-segregated aerosol samples were obtained using a multi-orifice Berner 9-stage cascade impactor (Berner *et al.*, 1979), operating at a flow rate of 30 ℓ min^{-1}. The mean particle size deposited on each stage was 11.3, 5.7, 2.8, 1.4, 0.7, 0.35, 0.17 and 0.09 μm for stages 2–9, respectively. Since the upper cut-off point for the first stage was unknown, an average size value of 23 μm was determined by least-square fitting of the mean diameter data for stages 2–9. Both Teflon filters and size-segregated samples were analysed for Cd, Cu, Zn and Pb by differential-pulse stripping voltammetry (DPSV) after extraction at a pH of 1, following the procedure used by Komy *et al.* (1988). Results of the analyses of the Nuclepore filters by energy-dispersive X-ray spectrometry (EDXRF), particle-induced X-ray emission (PIXE) and electron-probe X-ray microanalysis will be reported on in separate papers. The results reported here are based on the analysis of 108 aerosol samples. Even though the variation of the elemental concentration with height is known, the results for dry deposition are based on the elemental concentrations determined for the lowest flight level. This is not the case for wet deposition, for which all concentration values have been considered. In order to estimate the possible relationship between wind direction and airborne concentrations, all aerosol samples were classified in five different wind sectors. These were: west/southwest, north/northwest, east/northeast, south/southeast and local. The latter represents air masses with variable origin, and that in most of the cases circumscribe to the North Sea itself.

Dry deposition model description

Dry deposition velocities were calculated using a modified version of the two-layer deposition model of Slinn and Slinn (1980). In this model, the lower atmospheric boundary layer beneath a reference height of 10 m is divided into two layers. In the first layer, particle transport is mainly governed by gravitational settling and turbulence. In the second layer, also called the deposition layer and very close to the water interface, particle transfer is dominated by diffusion and phoretic effects. In the original version of Slinn and Slinn (1980), parameters such as drag coefficient, average wind speed and friction velocity were used for a height of 10 m. Since our aircraft measurements took place at a higher altitude and due to the wide range of values that the drag coefficient can have as a function of altitude and average wind speed (Smith, 1981, 1988), our approach consisted of using the Monin and Obukhov (1954) similarity theory to determine the drag coefficient, wind speed and friction velocity for a height of 10 m when the wind speed has been measured at a higher altitude. More details on this approach can be found elsewhere (Rojas *et al.*, 1991, 1993; Rojas, 1991). The motivation for this approach was that, according to Wiman *et al.* (1990), a turbulent layer of 10 m above the water surface encompasses most of the transfer zone. Once all these parameters were known, taking into account the height correction, they were introduced in the two-layer modeling described above. Atmospheric stability corrections were also included. Dry deposition velocities have been calculated following several steps. First, it was assumed that: (i) particles are hydrophobic, i.e. particles do not grow despite of the nearly saturated characteristics of the air in the deposition layer; or (ii) particles are hygroscopic (they do grow). This resulted in two dry deposition velocities as a function of particle size depending on the particle characteristics. The deposition velocity for hygroscopic particles was then weighted with the per cent number of sulfate-bearing particles. These particles have hygroscopic properties. This number per cent was obtained from single particle observations carried out using laser mass microprobe analysis (Dierck *et al.*, 1992). The complement of this number was used to weight the dry deposition velocity for hydrophobic particles. The final deposition velocity was the summation of the two weighted values. The variation of particle size with relative humidity for sulfate particles was taken from Fitzgerald (1975).

Authors like Arimoto and Duce (1986) have calculated the dry deposition rate, dividing the total mass of each element into intervals, each containing 1% of the total mass. Then, a deposition velocity is determined for each mass interval. This is known as the granulometric approach (Dulac *et al.*, 1989). However, Dulac *et al.* (1989) have shown that this procedure yielded similar results when the mass distribution is taken directly from the impactor data and used in the calculation of the dry deposition velocities. In this work we used the mass distribution given by the cascade impactor. Thus, the dry deposition velocity is given by:

$$V_d = \frac{\sum_{i=1}^{9} V_i C_i}{\sum_{i=1}^{9} C_i} \quad (1)$$

where V_i and C_i are the dry deposition velocity and aerosol elemental concentration for particle size i of the 9-stage impactor, respectively.

The uncertainties of dry deposition velocities and dry fluxes have been calculated taking into account the uncertainties associated with pure meteorological variations, namely of wind speed, sea and air temperature and wind seasonal variations. The errors related to the determination of the aerosol concentrations in both size-segregated samples and bulk samples were also considered. A strict error propagation routine was thus performed in order to assess the reliability of the generated data.

Wet deposition model description

Wet deposition estimates are based on the model of precipitation scavenging proposed by Slinn (1983). In this model, the estimation of the scavenging of airborne particulate matter by cloud and raindrops begins with the determination of the collection efficiency. This efficiency is associated with three main processes. The collection of aerosols by a falling drop can be due to inertial impaction, i.e. when particles cannot follow the streamlines around the drop, and to their inertia impact on it. The second process is called interception. Here, even though particles can follow the streamlines, their size is large enough so that their surface and that of the falling drop get in contact. Last, but not least, Brownian diffusion also contributes to the scavenging of aerosols. Due to their random motion, particles come into contact with the drop and they are removed from the atmosphere. The average collection efficiency and scavenging coefficient for a mean drop diameter (D_m) have been determined using Slinn's (1983) approximations, with an assumed average precipitation rate for the Southern Bight of the North Sea of 600 mm yr^{-1} (Schmidt, 1992). Finally, wet deposition values have been weighted by the per cent frequency of the wind direction prevailing in the zone using the compilation of meteorological data reported by Hohn (1971). Results are grouped in five wind sectors.

As will be seen from the results, no attempt has been made to calculate the error associated with the determination of the wet fluxes, even though the uncertainties of precipitation rates reported by Schmidt (1992) have a standard error of 10%. This is motivated by several reasons: (i) The average collection efficiency was determined for a D_m with a precipitation rate measured at ground level; what happens aloft is not yet fully understood. (ii) Perhaps the most important issue is that the temporal distribution of precipitation events for the North Sea is also unknown; it does not rain every day over the North Sea as is assumed in this work.

RESULTS AND DISCUSSION

Concentrations and size distributions

The average concentrations observed above the Southern Bight of the North Sea for some heavy metals are (in ng m^{-3}): 1.1 ± 0.4 for Cd, 9 ± 3 for Cu, 65 ± 5 for Pb and 72 ± 9 for Zn. As shown by Injuk *et al.* (1990), there is some agreement between these values and those reported in the literature covering a period of about 18 years. There is also an apparent decrease of the Pb concentrations in this airshed, which could be related to a reduction of the lead emissions, e.g. use of unleaded fuels.

During this work, it was possible to determine two different aerosol size distributions (see Fig. 2), depending upon the criterion used to handle missing values. Indeed, the size distribution represented by the hollow bars was obtained when all missing values were replaced by 0; whereas the replacement of the missing values by the full detection limit led to a different aerosol size distribution (filled bars). It is seen that this practice introduces drastic variations in the size distributions of Cd and Zn, while Cu and Pb seem less affected (except for the largest size class). Since this represents two extreme cases on how missing values could be treated, we adopted an intermediate position

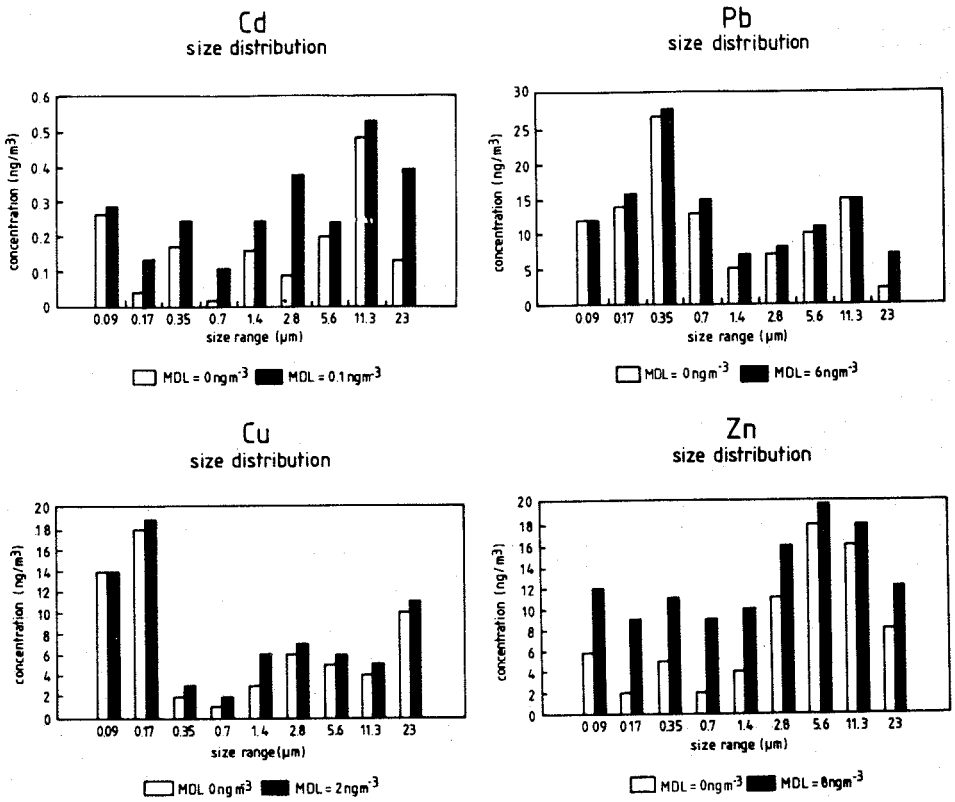

Fig. 2. Average size distribution of Cd, Cu, Pb and Zn obtained from the 9-stage Berner cascade impactor. Average obtained replacing missing values with zeros are represented by the hollow bars, whereas those obtained replacing the missing values with the detection limit correspond to the filled bars.

Table 1. Average dry deposition velocities for Cd, Cu, Pb and Zn, compared with other results reported in the literature

Reference	Cd	Cu	Pb	Zn
This work	0.39 ± 0.07	0.48 ± 0.17	0.25 ± 0.03	0.35 ± 0.07
Krell and Roeckner (1988)	0.2	—	0.20	—
Steiger *et al.* (1989)	—	—	0.14	—
Van Jaarsveld *et al.* (1986)	0.22	0.22	0.22	0.22
Dulac *et al.* (1989)	0.05	—	0.04	—

and chose, for use in our deposition calculations, the aerosol size distribution obtained when all missing values were replaced with half of the detection limit.

Dry deposition

The dry deposition velocities determined for our four elements of interest (Cd, Cu, Pb and Zn) and the respective errors are shown in Table 1. These values correspond to the average taking into account all wind sectors. Also in this table, the results reported by other researchers are listed. The standard error associated with these determinations can be considered very good, taking into account the variations related to meteorology and size-segregated elemental concentrations. These dry deposition velocities are based upon a particle size ranging from 0.09 to 23 μm aerodynamic diameter (aed), while Krell and Roeckner (1988) considered aerosols only in the size range from 0.2 to 1 μm. Steiger *et al.* (1989) used particle sizes between 0.4 and 10 μm; whereas Van Jaarsveld *et al.* (1986) used five size classes for deposition calculations, the smallest being 0.95 μm and the largest 20 μm. Of these

authors, only Dulac *et al.* (1989) included particle growth due to aerosol hygroscopicity. However, their size-segregated samples ranged from 0.67 to 8.9 μm in only five stages. This is the reason why their deposition velocity, e.g. for Pb, is a factor of 12 lower than the one reported here.

As is seen above, the main subject of discrepancy in the results concerning dry deposition velocities relies in the size distribution of the aerosols. Indeed, Van Aalst (1988) states that dry deposition velocities might vary in the range between 0.1 and 1 cm s^{-1}, and that most of this spread is caused by the lack of knowledge of the atmospheric particulate matter size distribution. Even though elements like Pb are more abundant in the sub-micrometer size range, these particles can coagulate with seasalt aerosols and reach super-micrometer dimensions. In order to give a quantitative idea on how important relatively large particles can be in the whole deposition process, Table 2 shows the percentage of the dry deposition flux accounted for by a given particle size class. Here only particle diameters larger than 1 μm are tabulated since the contribution of the sub-micrometer particles can be considered as negligible.

It is seen from this table that 98% of the dry deposition velocity for Cd is accounted for by particles larger than 4 μm; whereas for Cu, Pb and Zn, this percentage corresponds to 95, 96 and 97%, respectively. For the same North Sea area, Baeyens *et al.* (1990) concluded that the first two stages of their cascade impactor, i.e. particles larger than 4 μm, were responsible for 82% of the deposition of Pb. In the Mediterranean Sea, Dulac *et al.* (1989) reported that only 20% of the total deposition of Cd and Pb is accounted for by particles with sizes larger than 7 μm.

Table 2. Relative contribution (%) of the particle size classes in the determination of dry deposition fluxes

Diameter (μm)	Cd	Cu	Pb	Zn
1.4	1.1	1.5	1.1	0.4
2.8	0.4	3.1	1.4	1.7
5.6	2.2	6.3	14	11
11.3	50	5.7	39	27
23.0	46	83	43	59

The dry deposition rates as a function of the wind sector for the Southern Bight of the North Sea are shown in Table 3 for Cd, Cu, Pb and Zn, respectively. It was expected that continental air masses would contribute significantly to the dry deposition rate for all four elements. It is seen from this table that wind sector west/southwest is responsible for most of the deposition of Cd and Zn. The dry flux of Pb is mainly associated with this wind sector and with the south/southeast sector. The contribution of wind sector north/northwest is relatively low since the aerosol concentrations can be attributed to background levels for the Southern Bight of the North Sea. The contribution of the local wind sector to the dry deposition rate of Cu is also noticeable.

Table 4 shows a comparison of the dry deposition rates obtained in this work with those from the literature. It is seen from this table that an enormous difference exists between the results for dry deposition rates reported by Cambray *et al.* (1975), measured at a gas platform, with those from Dedeurwaerder *et al.* (1982), Baeyens *et al.* (1990) and this work. This spread suggests the possibility of contamination in the former results. It is also noticeable that Dedeurwaerder *et al.* (1982) and Baeyens *et al.* (1990), even though they measured at the same site (West-Hinder station, 50 km off the Belgian shoreline), report results that are almost a factor of four different for Zn. Our results, are comparable to those reported by Baeyens *et al.* (1990)

Table 3. Dry deposition to the Southern Bight of the North Sea for each wind sector. C is the elemental concentration in ng m^{-3}, V_d is the deposition velocity in cm s^{-1} and the flux is in kg km^{-2} yr^{-1}

Wind frequency:		West southwest 31.7%	North northwest 19.8%	East northeast 18.8%	South southeast 18.2%	Local 11.5%
Cd	C	1.47 ± 0.36	0.20 ± 0.38	2.20 ± 1.90	0.82 ± 0.44	0.43 ± 0.15
	V_d	0.69 ± 0.52	0.33 ± 0.21	0.26 ± 0.16	0.39 ± 0.25	0.29 ± 0.08
	Dry flux	0.33 ± 0.26	0.02 ± 0.04	0.19 ± 0.13	0.09 ± 0.07	0.04 ± 0.01
Cu	C	13.8 ± 5.8	1.02 ± 0.36	2.5 ± 0.4	11.7 ± 10.8	15.7 ± 6.5
	V_d	0.49 ± 0.35	0.27 ± 0.15	0.22 ± 0.13	0.19 ± 0.05	1.24 ± 0.15
	Dry flux	2.2 ± 1.8	0.09 ± 0.06	0.17 ± 0.10	0.66 ± 0.63	6.2 ± 2.7
Pb	C	68 ± 5	6.0 ± 3.4	59 ± 15	126 ± 20	72 ± 15
	V_d	0.26 ± 0.14	0.31 ± 0.15	0.29 ± 0.10	0.25 ± 0.09	0.12 ± 0.04
	Dry flux	5.7 ± 3.0	0.60 ± 0.44	5.5 ± 2.3	10.1 ± 3.9	2.7 ± 1.1
Zn	C	61 ± 7	2.0 ± 1.2	76 ± 21	160 ± 40	81 ± 16
	V_d	0.56 ± 0.27	0.21 ± 0.09	0.38 ± 0.13	0.14 ± 0.04	0.48 ± 0.09
	Dry flux	10.9 ± 5.5	0.13 ± 0.09	9.3 ± 4.0	7.1 ± 2.7	12.4 ± 3.4
			Cd	Cu	Pb	Zn
Total dry fluxes (weighted):			0.16 ± 0.11	1.58 ± 0.67	5.08 ± 1.25	7.94 ± 2.00

but consistently lower (36% on the average). This difference might be related to the fact that Baeyens *et al.* (1990) measured at a fixed location, whereas our measurements covered a distance of approximately 110 km from the Goeree platform in several directions, away from the continent.

Wet deposition

The resulting precipitation scavenging rates of 3.3×10^{-6}, 3.7×10^{-6}, 2.3×10^{-6} and $3.6 \times 10^{-6}\,s^{-1}$ for Cd, Cu, Pb and Zn, respectively are within the variation range given by Van Aalst (1988) of 2×10^{-6}–$6 \times 10^{-6}\,s^{-1}$. As for dry deposition, particles with diameters larger than 4 μm contribute enormously (more than 98%) to the total wet deposition rate. The wet deposition rates, for five different wind sectors, obtained for the Southern Bight of the North Sea are shown in Table 5. As is seen from this table, wind sectors east/northeast, south/southeast and local account for most of the wet deposition of Pb and Zn, respectively. As for dry deposition, wind sectors associated with continental air masses dominate the heavy metal deposition. As far as the wet fluxes of Cd and Cu are concerned, wind sectors west/southwest and south/southeast are predominant.

Table 6 lists the wet deposition fluxes from this work, compared with results reported by other authors. It is necessary to mention that the measurements of Peirson *et al.* (1973) were carried out at a gas platform, and those of Dedeurwaerder *et al.* (1982) and Baeyens *et al.* (1990) at the West-Hinder station, while Cambray *et al.* (1979) and Paris Commission (PARCOM, 1989) performed their sampling at coastal stations. The precipitation intensities for all these works ranged between 260 and 796 mm yr^{-1}. Last, but not least, it has to be pointed out that some of the authors base their results on the dissolved phase of the collected material. It is seen from this table that there is an enormous spread in the results of wet flux estimates. However, the good agreement between the outcomes of Cambray *et al.* (1979), Dedeurwaerder *et al.* (1982), Baeyens *et al.* (1990) and this work is striking for Pb. The lowest estimates are those reported by PARCOM (1989).

Total deposition

Table 7 shows the dry, wet and total fluxes to the Southern Bight of the North Sea. One can determine from this that, on average, 69% of the total deposition for the four elements of interest is accounted for by wet deposition. However, it is here where we lack most of the information needed to assess the real importance of wet deposition. Table 8 shows a comparison of the total atmospheric flux estimated for the Southern Bight, with that of other marine areas. The flux values for the tropical North Pacific are based on direct measurements. For all elements, the deposition fluxes show relatively high values for the Southern Bight of the North Sea, while the reported value for Pb for the New York Bight is very high. However, this value dates from 1976. Based on the figures given in Table 7, and given the total surface area for the Southern Bight of the North Sea of 160,000 km^2 (Cambray *et al.*, 1975), the total input (in ton yr^{-1}) is shown in Table 9, and compared with other pathways extracted from the report on the Quality Status of the North Sea (1987). It is seen from this table that 55, 24, 40 and 22% of the total are attributed to the atmospheric input for Cd, Cu, Pb and Zn, respectively. It is also seen that for Cu the atmospheric input is similar to that of rivers. However, these results correspond only to the soluble fraction, and the reported solubilities in sea water, which depend on the particle size and pH value, are:

Table 4. Dry deposition fluxes ($kg\,m^{-2}\,yr^{-1}$) compared with those reported by other authors

Reference	Cd	Cu	Pb	Zn
Cambray *et al.* (1975)	—	<30	24	420
Dedeurwaerder *et al.* (1982)	0.04	0.7	4.5	3.5
Baeyens *et al.* (1990)	0.19	3.5	7.5	13
This work	0.16	1.6	5.1	7.9

Table 5. Wet deposition fluxes ($kg\,km^{-2}\,yr^{-1}$) to the Southern Bight of the North Sea, divided in five different wind sectors

Wind sector	Cd	Cu	Pb	Zn
West/southwest	0.165	1.13	1.26	3.01
North/northwest	0.016	0.11	0.76	0.12
East/northeast	0.083	0.20	2.95	6.27
South/southeast	0.122	0.23	2.56	5.84
Local	0.044	1.79	1.14	4.52
Total	0.4	3.5	8.7	20

Table 6. Wet deposition flux estimates compared with those reported by other authors

Reference	Cd	Cu	Pb	Zn
Peirson *et al.* (1973)	4.2	21	49	53
Cambray *et al.* (1979)	—	11	11	31
Dedeurwaerder *et al.* (1982)	1.6	25	9	140
PARCOM (1989)	0.2	0.8	1.1	4.5
Baeyens *et al.* (1990)	2.9	25	7	170
This work	0.4	3.5	8.7	20

Table 7. Dry, wet and total deposition fluxes ($kg\,km^{-2}\,yr^{-1}$) to the Southern Bight of the North Sea

Type of deposition	Cd	Cu	Pb	Zn
Dry	0.16	1.6	5.1	7.9
Wet	0.43	3.5	8.7	20
Total	0.59	5.1	13.8	28

Table 8. Total flux (kg km^{-2} yr^{-1}) into the Southern Bight of the North Sea compared with values from other marine areas

Total flux	Cd	Cu	Pb	Zn
New York Bight (1)	0.3	—	39	14
Baltic Sea (2)	0.16	—	11	—
Baltic Sea (3)	0.14	2.9	2.4	11
W. Mediterranean (4)	0.13	0.96	10.5	11
W. Mediterranean (3)	1	4.2	29	34
S. Atlantic Bight (5)	0.09	2.2	6.6	7.5
Bermuda (6)	0.04	0.3	10	0.75
Bermuda (7)	0.09	1	12	1.76
North Atlantic (2)	0.05	—	3.1	—
Trop. N. Atlantic (8)	0.05	0.2	3.1	1.3
Trop. N. Pacific (9)	0.003	0.09	0.07	0.67
North Sea (2)	0.5	—	17	—
North Sea (3)	0.3	2.7	14	14
This work	0.59	5.1	13.8	28

References: (1) Duce *et al.* (1976a), (2) GESAMP-IMO/FAO/UNESCO/ WMO/WHO/IAEA/UN/UNEP (1985), (3) GESAMP-IMO/-FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP (1989), (4) Arnold *et al.* (1982), (5) Windom (1981), (6) Duce *et al.* (1976b), (7) Jickells *et al.* (1984), (8) Buat-Ménard and Chesselet (1979), (9) Arimoto *et al.* (1985).

Table 9. Total input of Cd, Cu, Pb and Zn (in ton yr^{-1}) to the Southern Bight of the North Sea, compared with other pathways

Pathway	Cd	Cu	Pb	Zn
Rivers	39	970	768	5587
Discharges	16	243	144	1176
Dumping	23	1265	2407	8759
Atmosphere	94	806	2200	4432
Total	172	3284	5519	19,954

Table 10. Comparison of our results for the total input (ton yr^{-1}) to the North Sea with model outputs reported by other authors

Reference	Cd	Cu	Pb	Zn
Van Jaarsveld *et al.* (1986)	11	100	2000	940
Krell and Roeckner (1988)	11	—	1200	—
Graßl *et al.* (1989)	—	—	2300	—
Warmenhoven *et al.* (1989)	15	110	1900	930
This work	158	1348	3678	7409

81–84% (Hodge *et al.*, 1978); 15–86% (Hodge *et al.*, 1978; Moore *et al.*, 1984; Maring and Duce, 1989); 13–90% (Hodge *et al.*, 1978; Maring, 1985); 24–76% (Hodge *et al.*, 1978; Crecelius, 1980) for Cd, Cu, Pb and Zn, respectively. The large spreading of the solubility values appearing in the literature is evident. Moreover, the direct dumping of waste will soon decrease due to recent EC legislation, and hence the relative contribution of the atmospheric input will increase. It should also be borne in mind that the heavy metal load of rivers is, to some extent, due to leaching of atmospherically deposited pollutants from land. The very important role of atmospheric deposition to the heavy metal pollution of the North Sea is thus evident.

Comparison with modeled inputs

A comparison of our results with modeled inputs for the North Sea is shown in Table 10. In general, the four models agree very well, which can be expected since the source-emission data are similar in all of them. There are more marked differences between our results and those from the models, particularly for Cu, Cd and Zn, where the modeled outcomes represent 8, 10 and 13% of our estimates, respectively; whereas for Pb this difference is of 50%.

These discrepancies can be related to several reasons, namely, the aerosol size distribution used in these models varies significantly from ours. Indeed, in our calculations aerosols had sizes ranging from 0.09 to 23 μm (aed), with a significant heavy metal fraction (25–50%) in the range >4 μm (aed). The particle size dependence used in other models has already been discussed. On the other hand, none of these models takes into account particle growth due to high relative humidities. It has to be taken into account that our values have been estimated assuming that the aerosol concentrations for the whole North Sea are approximately 50% of those from the Southern Bight.

RECOMMENDATIONS FOR FUTURE RESEARCH

It is therefore essential that further research should be devoted toward: (i) a thorough and ample characterization of the large atmospheric particulate matter,

specially on their heavy metal content; (ii) the determination of solubility as a function of particle size and chemical speciation; (iii) a better knowledge on the temporal distribution of precipitation events for the North Sea area; and (iv) the determination of the functional relationship between height and precipitation intensity.

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