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Atmospheric Concentrations and Deposition of Heavy Metals over the North Sea: A Literature Review

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Abstract. A literature review of the atmospheric concentration rates and dry and wet deposition fluxes of particulate Cd, Cr, Cu, Pb and Zn to the North Sea and adjacent areas is given. The results of direct measurements of dry and wet deposition fluxes are compared to indirect estimates and to modelling values. This work points out the large uncertainties in results of different studies on atmospheric input of trace elements into the North Sea. The current knowledge about the dependence of the deposition velocity upon the particle size and about the processes controlling wet deposition fluxes, and the quality and completeness of the emission data are still inadequate for describing the environmental cycle and impact of heavy metals in the North Sea.

Key words: Heavy metals, concentration, deposition, North Sea, troposphere.

1. Introduction

At present, there is much discussion on the sources and abatement policies of pollution to the sea. Atmospheric transport and deposition of pollutants over long distances have received much attention, particularly in connection with the acid rain problem, the formation of photochemical oxidants and ozone, and the global climatic effects. It is only relatively recently that it has become possible to estimate the amounts of material entering the oceans via the atmosphere. Though the pollution of the oceans is not a new phenomenon, the question of how important a role the atmosphere plays in this was addressed only a decade ago (NAS, 1978). As the calculations have become less crude, the atmospheric route seems to have gained in importance relative to the other paths, like those borne by rivers and direct discharges.

Still, quantitative data on heavy metal emissions, their concentration levels in air and their accumulation and transfer in the North Sea ecosystem have not been systematically gathered and intercompared hitherto. There are various sources which emit trace metals into the atmosphere, i.e. man-made pollution, aerosol formation from sea-spray, volcanic activity, vegetation and soil erosion. The concentrations of anthropogenic pollutants in the atmosphere are mainly due to the volatility of these elements at the high temperatures of fossil fuel combustion, and many other high-temperature industrial processes, particularly the extraction of non-ferrous metals

TABLE I. Comparison of the 1982 survey of trace element emission by Pacyna (1987) with national emission data (tons y^{-1}) for countries bordering the North Sea

Country	Cd	As	Pb	Zn	Reference
U.K.	31	117	8610	2230	Pacyna, 1987
	14	315	7590	–	Hutton and Symon, 1986
Belgium	12	85	2100	700	Pacyna, 1987
	22	–	2380	1090	Van Jaarsveld *et al.*, 1986
The Netherlands	5.5	34	2200	290	Pacyna, 1987
	3.8	–	–	–	Kendall *et al.*, 1985
Germany	80	350	5560	6660	Pacyna, 1987
	79*	500	7590	10000	*Schladot and Nürnberg, 1982 Braun *et al.*, 1984
Denmark	6.3	7	650	130	Pacyna, 1987
	5	–	–	–	Murkherje, 1986
Sweden	16	183	1053	426	Pacyna, 1987
	12	130	950	1200	Naturvardsverket, 1982
Norway	2.1	41	730	120	Pacyna, 1987
	1.7–2.7	–	–	–	Naturvardsverket, 1982

from sulphides. Among other industrial sources, waste incineration is becoming increasingly important, particularly in Western Europe, because of the emissions of Cd, Pb and other trace elements and a need to incinerate increasing amounts of wastes. A first preliminary review of the atmospheric emissions of various trace elements from anthropogenic sources in Europe, for 1979/1980, was provided by Pacyna (1983). The earlier surveys were concerned with either a single metal (van Enk, 1980; Hutton, 1982) or certain types of emission sources, e.g. fossil fuel combustion. As such, they were very valuable for control strategies, but less applicable for modelling of the long-range transport of air pollutants and their migration. The survey of Pacyna has more recently been updated and improved. In Table I, the estimates of Pacyna (1987) of trace element emissions from all sources in countries bordering the North Sea are compared with the countries' own estimates. The former estimates are based on emission factors, calculated separately for each of the countries, on statistics on the consumption of raw materials and on the production of various industrial goods in 1982.

2. Data on Trace Metal Concentrations in Air

There is quite a detailed data base of concentration measurements for trace metals in aerosols over the European regional seas (GESAMP, 1989). Table II gives an overview of literature values for the particulate Cd, Cr, Cu, Pb and Zn concentrations in the marine troposphere over the North Sea and adjacent areas. The data set covers a relatively long time period, of about 20 years. The oldest data, supplied by Peirson *et al.* (1973), Kretzschmar and Cosemans (1979) and Van Aalst *et al.* (1983) (who give a list of concentrations measured between 1974 and 1981 at coastal stations in Great Britain, Belgium and The Netherlands), are generally higher than the other reported values in Table II. The less accurate collection procedures and the precision of measurements in those days may be one reason, but these values were also obtained from coastal or even inland measurements, i.e. closer to the emission sources. Van Daalen (1991) measured the concentrations over the province of South-Holland in the Netherlands and although his sampling sites were not very far removed from the North Sea coast, his data show clearly high concentrations. The rest of the coastal values in Table II seem to agree very well with the exception of the Belgian ones from Ostende, due to very high concentrations measured in the continental air masses (factor 2 to 5 higher compared to the values for the eastern and western air-masses). Although not explicitly North Sea coastal measurements, the data collected by Flament *et al.* (1987) at the French coast in the Channel and those reported by Schneider (1987) in the Kiel Bight offer a good basis for intercomparison of results.

In contrast with measurements performed at coastal stations around the North Sea, much less data are available for samples taken on the North Sea itself. Results from the West Hinder light-ship station (51°23′ N, 2°21′ W) located off the Belgian coast were reported by Baeyens and Dedeurwaerder (1991), Dedeurwaerder (1988) and ATMOS (1984). The West-Hinder results are generally higher than comparable ones for the southern North Sea. One possible explanation is that ship West-Hinder is only separated from the coastline by a relatively small distance and is located at a very dense traffic channel (100 ships per day) on the North Sea. Values reported by Ottley and Harrison (1993) are broadly comparable to previously published values for metal concentrations in the North Sea atmosphere. The aircraft-measured values (Injuk *et al.*, 1992) agree well with those of cruises with the R/V Belgica (Otten *et al.*, 1989). Values reported by Otten *et al.* (1989), predominantly based on measurements done in the northern part of the North Sea, during north-westerly winds, can be considered as background values for the North Sea area. A concentration gradient from the southern North Sea (high concentrations) to the northern part (low concentrations) is observed.

Under the Paris Convention, an international commission (PARCOM-ATMOS) has been established to assess the state of the marine environment and formulate the policy to eliminate or reduce existing pollution. With regard to atmospheric pollution, a dual approach has been proposed: A monitoring programme at a num-

TABLE II. Measured airborne concentrations over the North Sea and adjacent areas in ng m^{-3} (s- or n-preceding an area means southern or northern, respectively)

Area	Period	Cd	Cr	Cu	Pb	Zn	Remarks	References
United Kingdom (coast)	'72	<4–<18	1.0–14	<1–55	35–380	64–415	range for 7 sites	Peirson *et al.* (1973)
United Kingdom (coast)	'75	4–6	–	13–15	20–120	15–300	range for 2 sites	Cawse (1974)
The Netherlands (coast)	'84–'88	0.3–2	1.7–14	3.7–23	36–178	18–200	–	van Daalen (1991)
North Sea (coast)	'72–'81	0.5–2.5	0.5–5	<5–25	20–200	10–100	–	van Aalst *et al.* (1983)
The Netherlands (coast)	'87	0.8	–	5.5	45	59	Hage	Cambray *et al.* (1975)
The Netherlands (coast)	'84–'85	0.7	1.3	3.3	39	40	Pellworm	Steiger (1991)
The Netherlands (coast)	'83	0.6	1.6	3.0	41	30	Tange	Kemp (1984)
Belgium (coast)	'72–'77	8	–	19	278	300	Ostende	Kretzschmar and Cosemans (1979)
Belgium (coast)	'81–'84	3.4	–	12.8	77	174	–	ATMOS (1984)
Norway (coast)	'78–'79	0.3	1	7	19	–	–	Pacyna *et al.* (1984)
Norway (coast)	'85–'86	0.14	1.1	1.6	18	15	Birkenes	Amundsen *et al.* (1992)
England (coast)	'87–'88	1.1	–	–	34	41	–	Yaaqub *et al.* (1991)
England (coast)	'72–'73	–	7.0	–	168	155	Leiston	Cambray *et al.* (1975)
German Bight	'86	1.9	1.9	4.7	52.6	46	island	Kersten *et al.* (1991)
Kiel Bight	'81–'83	–	–	40	53	57	lighthouse	Schneider (1987)
East Channel	'87	3	–	20	56	100	–	Flament *et al.* (1987)
North Sea	'86–'90	1.6	1.5	3.5	20.2	38	Helgoland	Kriews (1992)
North Sea	'87	0.9	–	3.9	28.5	42	FPN	Steiger (1991)
North Sea	'71–'73	–	4.8	–	155	161	Gasplatform	Cambray *et al.* (1975)
North Sea	'88–'89	1.4	–	11	55	67	flights	Injuk *et al.* (1992)
North Sea	'88–'89	1.3	–	6.9	29	75	cruise	Ottley and Harrison (1993)
North Sea	'84–'88	–	–	11	39	54	cruise	Otten *et al.* (1989)
sNorth Sea	'81–'84	2.9	–	9	104	94	West-Hinder	ATMOS (1984)
sNorth Sea	'84–'85	0.7	–	3	39	41	–	Stoeßel (1987)
sNorth Sea	'80–'85	4	–	17	150	150	West-Hinder	Dedeurwaerder (1988)
sNorth Sea	'84–'88	–	–	17	62	86	cruise	Otten *et al.* (1989)
sNorth Sea	'80–'85	2.8	–	14.7	96	67	West-Hinder & cruises	Baeyens and Dedeurwaerder (1991)
nNorth Sea	'72–'73	–	1.4	20	21	32	Collafirth	Cambray *et al.* (1975)
nNorth Sea	'84–'88	–	–	2	2	2	cruise	Otten *et al.* (1989)
North Sea	'91	0.2	2.0	1.9	4.5	30	Gullfaks 'C'	Dannecker *et al.* (1992)

ber of coastal stations and a modelling programme for which an emission database is being set up. The monitoring programme of PARCOM-ATMOS includes measuring concentrations in precipitation of Pb, Cd, Cu, Zn, Cr, Hg, Ni, NH_4^+ and NO_3^- and some of these species in air. In Tables III and IV, the basic description of the stations monitoring heavy metals in air and in precipitation and annual mean aerosol concentration values are given. From the summarized results in Table IV, it is obvious that only data from the Belgian stations (B1 and B2b) are not comparable with the others, due to high values for Cu, Ni, Pb and Zn. But these results agree well with reported ones for the same region by Kretzschmar and Cosemans (1979), indicating a high level of pollution for this region, or unrepresentative sampling. In Figure 1, the North Sea area with the stations which take part in the PARCOM-ATMOS monitoring program is given.

3. The Atmospheric Input of Trace Elements to the North Sea

For many years, research on pollution of the North Sea marine environment has focused on the most obvious inputs, those borne by rivers and direct discharges of wastes. In the work of Goldberg (1973) and Cambray *et al.* (1975), a first indication can be found that the atmospheric input might also be a significant contributor of trace elements to the North Sea. The first major studies of the deposition of heavy metals from the atmosphere started in the United Kingdom in the beginning of the 1970's (Cawse, 1974). The concentrations of some 40 elements were determined in dry and wet deposition at seven non-urban sites, while the water soluble and insoluble fractions of the total deposition were analyzed separately. At the same time, analyses of the deposition of heavy metals were made in Norway (Breekke, 1976), in the USA (Andren *et al.*, 1975; Feely *et al.*, 1976) and in the FRG (Ruppert, 1975). The routine monitoring of trace elements in precipitation began in Sweden in 1983 (Ross, 1987) with the aim to determine the atmospheric wet deposition of Cd, Cu, Fe, Mn, Pb and Zn.

Van Aalst *et al.* (1983) employed a simple model to assess the long-term average concentrations of various elements in the sea, and to determine the atmospheric input of a large group of contaminants into the North Sea. They have compared their results with information on the other inputs into the North Sea and concluded that atmospheric deposition was a relatively important source of contamination with Cu, Pb, Ni and Zn, and to a lesser extent with Cd and Cr. A first international attempt to estimate the input of various elements to the sea by atmospheric deposition and via other pathways was made by a European group of experts on behalf of the International Council for the Exploration of the Sea (ICES, 1978).

Since trace elements are removed from the atmosphere by dry deposition (sedimentation, interception and impaction) and by wet deposition (rainout, washout), the literature overview concerning both processes is given separately below.

TABLE III. Coastal measuring stations participating in Paris Commission Comprehensive Atmospheric Monitoring Programme (CAMP)

Number country	Name	Latitude longitude	Elevation	Distance from the sea	Parameters measured
B1 Belgium	Houtem	51°01′ N 2°35′ E	sea level	9 km	Pb, Zn in air
B2b Belgium	Bredene	51°14′ N 2°57′ E	≪ 10 m	2 km	Cu, Ni, Pb, Zn in air
B3a Belgium	Brugge	51°15′ N 3°11′ E	≪ 10 m	8 km	Cd, Cu, Pb, Zn in precipitation
GB1 Great Britain	East Ruston	52°48′ N 1°28′ E	5 m	8 km	Cd, Cr, Cu, Ni, Pb, Zn in air Cd, As, Cr, Cu, Ni, Pb, Zn in precipitation
GB2 Great Britain	Staxton Wold	54°11′ N 0°26′ W	170 m	10 km	Cd, Cr, Cu, Ni, Pb, Zn in air Cd, As, Cr, Cu, Ni, Pb, Zn in precipitation
GB3 Great Britain	Banchory	57°5′ N 2°32′ W	120 m	26.5 km	Cd, Cr, Cu, Ni, Pb, Zn in air Cd, As, Cr, Cu, Ni, Pb, Zn in precipitation
DK1 Denmark	Ulborg	56°17′ N 8°26′ E	40 m	20 km	Cd, As, Cr, Cu, Ni, Pb, Zn in air Cd, Cu, Pb, Zn in precipitation
D1 Germany	Westerland	54°53′ N 8°19′ E	5 m	2 km	Cd, Cu, Pb in air Cd, As, Cr, Cu, Ni, Pb, Zn in precipitation
NL3 The Netherlands	Kollumerwaard	53°20′ N 6°16′ E	0–5 m	10 km	Cd, As, Pb, Zn in air Cd, Cu, Ni, Pb, Zn in precipitation
NL2 The Netherlands	Leiduin	52°20′ N 4°35′ E	0–5 m	6.3 km	Cd, Cr, Cu, Ni, Pb, Zn in precipitation
N1 Norway	Birkenes	58°23′ N 8°15′ E	190 m	20 km	Cd, Pb, Zn in precipitation
N3 Norway	Lista	58°06′ N 6°34′ E	13 m	–	Cd, Cr, Cu, Ni, Pb, Zn in precipitation

TABLE IV. An overview of the data submitted to PARCOM-ATMOS as regards elemental concentrations (ng m^{-3}) in aerosols for 1988, 1989, 1990 and 1991, measured at 'CAMP' stations (ATMOS, 1990; ATMOS, 1991; ATMOS, 1992)

Station	Period	Cd	As	Cr	Cu	Ni	Pb	Zn
B1	'90	–	–	–	–	–	104	351
B2b	'89	–	–	–	–	–	112	150
	'91	–	–	–	23	15	86	222
DK1	'88	0.3	1.6	2.3	1.2	1.9	19.2	23.7
	'89	0.3	–	1.0	2.29	1.66	21.8	25.8
	'90	–	–	1.48	1.6	1.7	17	24
	'91	–	–	2.5	2.3	2	17	23
D1	'88	0.4	–	–	3.4	–	23.3	–
	'89	0.42	–	–	2.69	–	20.4	–
	'90	0.30	–	–	3.10	–	17.3	–
	'91	0.36	–	–	1.5	–	18	–
NL3	'90	0.33	0.78	–	–	–	27	52
	'91	0.4	1.48	–	–	–	30.2	51
GB1	'88	0.5	–	0.7	3.7	2.0	35.4	27.7
	'89	0.43	–	0.82	3.85	2.30	31.3	27.5
	'90	0.33	–	0.65	2.77	1.75	21	23
	'91	0.66	–	0.72	3.36	3.27	26.1	73.9
GB2	'88	0.5	–	1.2	4.6	3.1	22.3	111.3
	'89	0.64	–	1.33	3.62	2.5	27.2	59
	'91	1.9	–	0.79	3.06	2.36	17	50.7
GB3	'88	0.1	–	0.2	0.9	0.5	7.9	8.3
	'89	0.12	–	0.31	1.24	0.74	7.6	7.3
	'90	0.13	–	1.19	1.97	2.60	6.8	16.2
	'91	0.12	–	0.3	1.58	0.81	7.02	10.5

3.1. DRY DEPOSITION FLUXES TO THE NORTH SEA

Dry deposition of particles to the sea surface is the sum of all physical removal processes that take place when there is no form of precipitation (rain, snow or hail), such as gravitational settling, turbulent diffusion, Brownian diffusion or impaction. In general terms it can be stated that small particles (< 0.1 μm) are removed mainly by Brownian diffusion and large particles (> 10 μm) by gravitational settling. In the intermediate size range, impaction and interception are important. The loss of particles to the sea surface is frequently described in terms of a dry deposition velocity, which is the ratio between the deposition rate per unit area, and the ambient concentration. The dry deposition velocity of particles is strongly dependent on particle size, wind velocity and surface characteristics. Both theoretical considera-

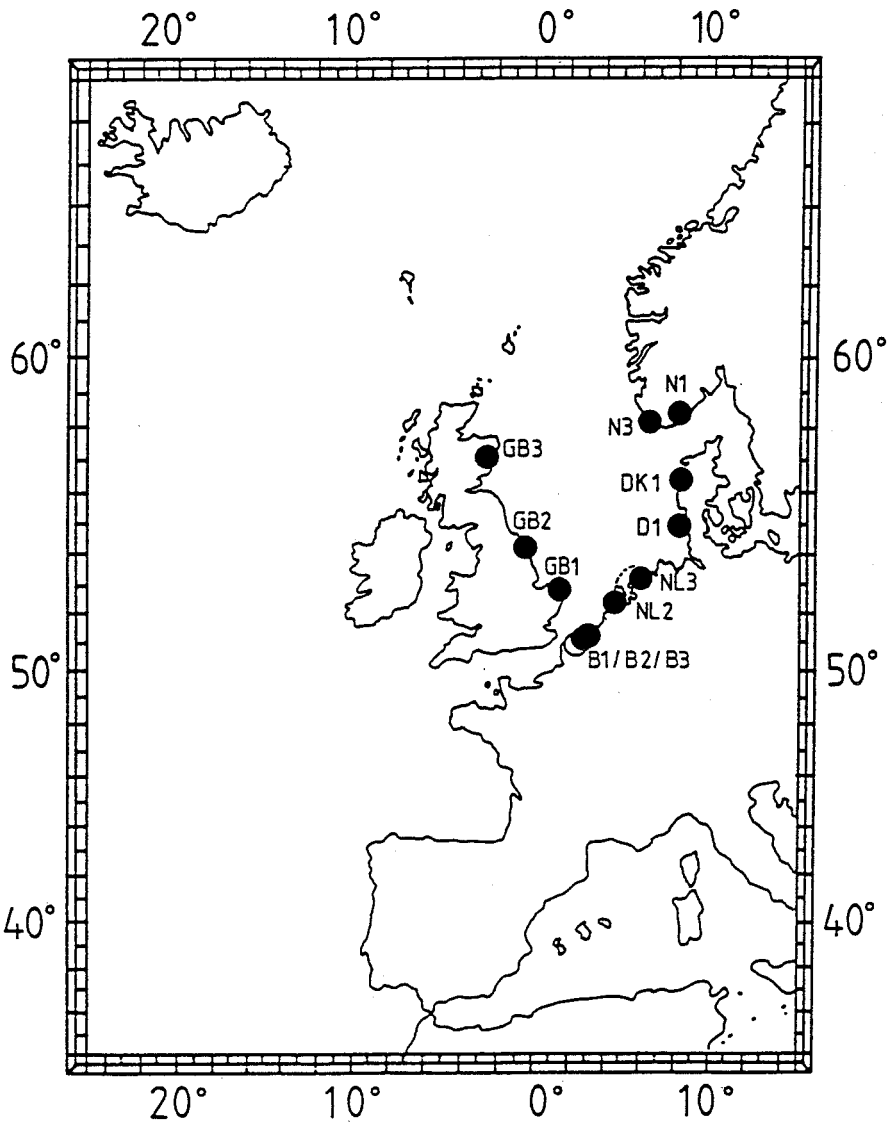

Fig. 1. The North Sea area with the stations which take part in the PARCOM Comprehensive Atmospheric Monitoring Programme (CAMP) – so called 'Central North Sea Stations'.

tions and field experiments show that the deposition velocity is small for particles with aerodynamic diameter less than 1 μm, typically of the order of 0.1 cm s^{-1}, while for the large particles it reaches a value of a few cm s^{-1}.

Transport fluxes across the air-sea interface can be determined by theoretical or semi-empirical relations (Sehmel and Hodgson, 1978; Slinn and Slinn, 1980; Williams, 1982; Friedlander *et al.*, 1986; Main and Friedlander, 1990). Dry depo-

sition velocities can also be evaluated by direct measurements of actual dry fluxes and particle concentrations in the air. Although the performance characteristics of air sampling equipment is quite well known, the properties of dry deposition collectors, as well as the structure of the laminar boundary layer above the collector and the collection efficiency still remain uncertain. It is still not clear how comparable the deposition to the surrogate surface is with the deposition to the natural sea surface. Another practical limitation, in case the deposited mass is measured, is that the results are strongly affected by the deposition of only a few large particles. Since the gravitational settling velocity is roughly proportional to the square of the particle diameter and the particle mass is proportional to the cube of the particle diameter, the deposited mass is a function of diameter to the 5th power. As a first approximation, a single 10 μm particle will therefore contribute as much to the total deposited mass as 100,000 particles of 1 μm. This makes direct measurements of the dry deposition velocity extremely difficult.

Only a few experimentalists have tried to measure directly the dry deposition of trace metals to the North Sea. Cambray *et al.* (1975) used a Whatman 541 cellulose filter, which was placed on a gas platform (53°5′ N, 2°21′ E). Samples were collected on a monthly basis. The high values found were explained by the authors as due to the possible contamination by resuspended sea water or by the platform itself.

Baeyens *et al.* (1990) measured dry deposition fluxes in a direct way with vasilinated plexiglass plates, in 14-days exposed intervals. Sampling was carried out throughout one year, at the West-Hinder lightvessel and during several cruises on the North Sea with the R/V Mechelen and the R/V Belgica. The collector plates were used horizontally and vertically. Directly measured dry deposition values were compared with the fluxes calculated by the adopted model of Slinn and Slinn (1980) and from a large set of *in situ* measured particle size distributions and their elemental concentrations. Despite the large uncertainties on the calculated dry deposition fluxes, results generally agree fairly well for both methods. The collection surfaces provide higher values, except for Mn and K, while the largest difference between both methods was observed for Pb (by a factor of 2.3).

Estimated dry deposition fluxes at the west coast of Sweden by Selin *et al.* (1992) were derived from trace element concentrations in the air in the winter of 1990 and from experimentally obtained deposition velocities.

Aircraft-based aerosol sampling in the lower troposphere was performed between September 1988 and October 1989 (Rojas *et al.*, 1993), above the Southern Bight of the North Sea. The dry deposition fluxes of Cd, Cu, Pb and Zn were calculated from size-differentiated atmospheric concentrations as a function of wind direction and dry deposition velocities obtained with the Slinn and Slinn model.

The dry deposition fluxes reported by Kriews (1992) are based on arithmetic mean values of atmospheric elemental concentrations, measured at Helgoland while 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 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.

3.2. WET DEPOSITION FLUXES TO THE NORTH SEA

Wet deposition is the combination of rainout (in-cloud scavenging of particles) and washout (below-cloud scavenging of particles). Capture of particles by cloud droplets does not automatically lead to removal of the particles from the atmosphere, since cloud droplets may evaporate on their way to the earth's surface. This merely results in redistribution of the aerosol.

The amount of micropollutants which is deposited to the oceans over a certain period of time can be determined either directly or indirectly (Struyf and Van Grieken, 1993). In the direct way the wet atmospheric fluxes are determined by collecting rainwater in rain collectors over a certain period of time and measuring the concentrations of the substances involved. For particles, the annual wet flux F_w can be calculated with the following formula:

$$F_w = \sum_i C_i P_i,$$

or the flux F_w is the sum over all individual rain events i of the product of the concentrations in rainwater (C_i) times the amount of precipitation per unit area and time (P_i). The above equation is usually approximated as follows:

$$F_w = \overline{C} P,$$

where $\overline{C}$ is the average rainwater concentration and P the yearly precipitation rate. However, there are some major difficulties arising from determination of the wet deposition to the sea surface directly. Practically, collection of atmospheric material by rain water samplers should be avoided during dry periods (Ruijgrok *et al.*, 1990), (54°10′ N, 7°53′ E) in the period from 1986–1990, and deposition velocities following from the Slinn and Slinn model.

Atmospheric fluxes reported by ATMOS (1992) are based on mean aerosol concentration values measured at all the CAMP stations monitoring heavy metals in air during '88, '89, '90 and '91 and dry deposition velocities of 0.1 cm s^{-1} (Table V). However, the latter value is far from being generally accepted.

Estimated dry deposition fluxes by Ottley and Harrison (1993) are based upon data collected on 10 research cruises in 1988–89. A cascade impactor designed to collect efficiently size segregated aerosols, has produced detailed size distributions from which mass weighted deposition velocities were derived, followed by dry deposition flux estimates.

As seen in Table VI, published dry deposition fluxes of heavy metals to the North Sea show significant variations. In Table VII the dry deposition velocities,

TABLE V. The annual mean aerosol concentration (ng m^{-3}) and estimated dry deposition fluxes (kg km^{-2} y^{-1}) based on measurements at 'CAMP' stations (ATMOS, 1992)

Period	Param.	Cd	As	Cr	Cu	Ni	Pb	Zn
'88	conc.	0.36	1.6	1.1	2.76	1.87	21.6	42.7
	flux	0.01	0.05	0.04	0.09	0.06	0.73	1.45
'89	conc.	0.38	–	0.87	2.7	1.8	21.6	29.9
	flux	0.01	–	0.03	0.09	0.06	0.68	0.95
'90	conc.	0.27	0.78	1.1	2.4	2.0	32.2	93.2
	flux	0.01	0.03	0.03	0.07	0.06	1.0	3.0
'91	conc.	0.58	1.14	1.24	5.09	4.01	25.5	62.2
	flux	0.02	0.04	0.04	0.16	0.13	0.80	1.96

used by different authors for estimation of the dry deposition fluxes above the North Sea, are given. Considering the complex interaction of processes involved in particle deposition it is, perhaps, not surprising that inconsistencies have been evident in the reported research. Some of these inconsistencies are likely to indicate a real variability in environmental influences since an important number of factors influence the dry deposition processes. Meteorological data such as friction velocity, the aerodynamic surface roughness and the atmospheric stability are related to the deposition of particles. Humidity gradients and rainfall characteristics all affect the deposition of particles too. Furthermore, pollutant properties which vary with temperature, humidity and electrostatic gradients at the sea surface will result in a variation of the deposition characteristics of particles.

The main subject of discrepancy in the results concerning dry deposition velocities is due to the size distribution of the collected aerosols. Indeed, Van Aalst (1988) states that dry deposition velocities might vary in the range between 0.1 to 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 sea salt 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 VIII 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 (Rojas *et al.*, 1993). It is seen from this table that 98% of the measured dry deposition velocity for Cd is accounted for by particles larger than 4 μm so wet-only samplers need to be used. Additional problems include sea-spray and contamination or deterioration of the samples prior to or during analysis by material sampling and handling, particularly if one deals with trace amounts (Ross, 1984; Buijsman *et al.*, 1991). Also, the statistical relevance

TABLE VI. Dry deposition fluxes (kg km^{-2} y^{-1}) to the North Sea – comparison of the literature data

	Cambray *et al.* (1975) Gas-platform	Stoßel (1987) Pellworm	Bayens *et al.* (1990) West-Hinder & ship		Selin *et al.* (1992) Sweden-west coast	Rojas *et al.* (1993) aircraft	ATMOS (1991) CAMP-stations	Kriews (1992) Helgo-land	Ottley and Harrison (1993) North Sea
			model	exp.					
S	–	–	–	–	275	–	–	–	–
Cr	–	–	–	–	–	–	0.04	0.34	–
Mn	6.8	–	3.5	3.0	–	–	–	1.68	–
Fe	290	155	82	180	–	–	–	76	–
Ni	–	–	–	–	0.5	–	0.13	0.23	–
Cu	30	1.1	2.8	3.5	–	1.9	0.16	0.29	0.7
Zn	420	6.8	6.2	13	1.9	10.3	1.96	3.69	4.9
As	–	–	–	–	–	–	0.04	0.11	–
Pb	24	4.3	3.3	7.5	0.4	4.23	0.80	1.06	0.7
Cd	–	0.3	–	–	–	0.28	0.02	–	0.06

TABLE VII. Dry deposition velocities (cm s^{-1}), used by different authors for estimation of dry deposition fluxes

	Van Jaarsveld and Onderlinden (1986)	Krell and Roeckner (1988)	Dulac *et al.* (1989)	Baeyens *et al.* (1990)	Selin *et al.* (1992)	Rojas *et al.* (1993)	ATMOS (1992)	Kriews (1992)	Ottley and Harrison (1993)
S	–	–	–	–	1.0	–	–	–	–
Cr	–	–	–	–	–	–	0.1	0.69	–
Mn	–	–	–	0.49	–	–	–	0.75	–
Fe	–	–	–	0.56	–	–	–	1.0	0.30
Ni	–	–	–	–	1.3	–	0.1	0.28	–
Cu	0.22	–	–	0.53	–	0.48	0.1	0.26	0.44
Zn	0.22	–	–	0.41	0.34	0.35	0.1	0.31	0.30
As	–	–	–	–	–	–	0.1	0.19	–
Pb	0.22	0.2	0.04	1.35	0.14	0.25	0.1	0.17	0.13
Cd	0.22	0.2	0.05	0.53	–	0.39	0.1	–	0.24

TABLE VIII. Relative contribution of the particle size classes in the determination of dry deposition fluxes for the Southern Bight of the North Sea (Rojas *et al.*, 1993)

Contribution to the dry deposition in %				
Diameter (μm)	Cd	Cu	Pb	Zn
1–2	1.1	1.5	1.1	0.4
2–4	0.4	3.1	1.4	1.7
4–8	2.2	6.3	14	11
8–16	50	5.7	39	27
>16	46	83	43	59

of such direct measurements is doubtful. Firstly, precipitation is a discontinuous process and secondly, there is a natural variability of the concentrations of trace substances in precipitation. This means that a large number of rain events must be covered before meaningful average wet fluxes can be obtained, which is expensive and time-consuming. Also, these measurements are very much determined by the sampling location and time, which is problematic if one wants to investigate the deposition over a larger area and over a considerable period of time (Smith, 1991). For this reason, indirect approaches are often preferred. The limited amount of directly measured data is then used to check the results of these indirect approaches. For indirect measurements, the wet deposition flux of material to the ocean surface can be written as:

$$F_w = WPC_a,$$

where C_a is the concentration of the substance in air, P is the yearly precipitation rate and W is the washout ratio – also called scavenging ratio – which is the ratio of the concentration of a substance in rainwater to the concentration of the same substance in air (both concentrations measured in the same volume units, e.g. μg m^{-3}).

This equation can be modified in a number of ways. Some authors for instance, add the density of air ρ as an extra factor (GESAMP, 1989):

$$F_w = WPC_a\rho^{-1}.$$

In this case the resulting washout ratios are temperature and pressure dependent and about a factor of 1200–1300 smaller. An alternative method to calculate the wet flux is the use of scavenging rates. This subject was extensively described by Slinn (1983).

3.2.1. *Data on Precipitation*

The existing estimates of surface precipitation (rain, snow, hail, ...) over the seas and oceans are based on a very limited data set. A serious problem with the

measurement of precipitation, both on the ground and aloft, is its great variability in time and space. Moreover, the total amount of rainfall at any location can be a combination of a small number of very intense showers (of convective origin) together with comparatively extended periods of light rainfall from stratiform clouds. The overall contributions of these two kinds of precipitation are often comparable (Browning, 1990). Even for a relatively small area such as the North Sea, an accurate value for annual average rainfall is not available at present. It is, however, generally recognized that less rain falls over sea than over land (see e.g. Cambray *et al.*, 1979; Baeyens *et al.*, 1990). By measurements on a gas platform, the rainfall there was observed to be about 55% of that at land-based stations at similar latitude on either side of the North Sea (Cambray *et al.*, 1975). Taking this observation into account, a mean rainfall value of 438 mm per year was calculated for the North Sea on the basis of measurements of seventeen stations situated on adjacent land. This value was seen as a kind of 'standard' value. However, this value was adjusted to 475 mm annually on the basis of measurements at seven stations surrounding the North Sea (Cambray *et al.*, 1979). Van Aalst *et al.* (1983) disagree with Cambray's value, claiming that the difference between the amount of precipitation on land and at sea is lower than assumed before. Baeyens *et al.* (1990) measured the yearly precipitation volume at the West-Hinder light vessel; the mean value, based on a period of two years, amounts to 430 mm per year. They also indicated that, in general, there is less precipitation above the sea. They found an average ratio West-Hinder/De Blankaert (a Belgian coastal station) of 0.72 and a ratio of 0.60 for West-Hinder/all Belgian meteorological stations. Krell and Roeckner (1988) used a model to simulate the atmospheric input of Pb and Cd into the North Sea, and used yet another annual precipitation rate, namely 558 mm.

According to Balls (1989), the uncertainty in the amount of rainfall is the most important single error source in flux estimations. It is obvious that more reliable values are urgently needed in order to be able to calculate more accurate wet deposition fluxes. In the future, space-based techniques for measuring global rainfall will provide us with data with a good resolution and accuracy. Radars and/or radiometers, installed on satellites, will be able to measure the instantaneous intensity of the rain or hail that is falling, from which an estimation can be made of how much rain has fallen in a particular area over a certain amount of time, and all of this will happen on a routine basis (Bowler, 1990; Kedem *et al.*, 1990; Scofield, 1991).

3.2.2. *Concentrations in Precipitation*

In Table IX an overview of data concerning measured precipitation concentrations over the North Sea and adjacent areas is given. It is obvious that the Swedish concentrations measured by Ross (1987 and 1990) are lower than those reported for The Netherlands (van Jaarsveld and Onderlinden, 1986; van Daalen, 1991).

The coastal values listed by van Aalst *et al.* (1983) show rather large variations, probably because they were obtained by different operators using other sampling methods at different sites and over other time intervals. However, the lowest values of these ranges agree very well with the concentrations measured at the North Sea coasts of Norway (Pacyna *et al.*, 1984; S & TWG, 1987) and in Scotland (Balls, 1989). Ross (1987) observed that the concentrations in southern Sweden were higher and that the wet deposition fluxes were higher than the Swedish anthropogenic emissions, so a long range transport of the pollutants was postulated. Clearly, the southern North Sea concentration values included in Table IX are very high compared to the other values. The inconsistency of those mentioned in the GESAMP report (1989) is ascribed to sampling problems (e.g. not all measurements were wet-only) and difficult analysis associated with this kind of measurements. The concentration values reported for the rainwater collected at the West-Hinder station and during several cruises at the Southern Bight (Dedeurwaerder *et al.*, 1985; Baeyens *et al.*, 1990) are very high compared to other values, although the sampling was done only when precipitation occurred and precautions were taken to avoid contamination. The results of the ATMOS report (1984) point out that the heavy metal concentrations in rainwater above the sea are higher than above land. Cambray (1975) thought that this so-called 'maritime effect' was caused by bubble bursting processes, which bring aerosols coming from an enriched sea surface layer into the atmosphere. However, Balls (1989) concluded on the basis of measurements of the enrichment factor in surface water that this process is not a significant contributor to the 'maritime effect'. Possible alternative processes are thought to be enhanced solubility of the metals above the sea due to ageing of the aerosols emitted by land based sources (ATMOS, 1984).

Trace metal concentrations in precipitation collected from 'CAMP' stations, around the North Sea (Table X) are quite variable from year to year, probably due to orographic effects. Also, they show much less consistency, undoubtedly because of the greater sampling and analytical problems associated with such measurements.

3.2.3. *Estimated Wet Deposition Fluxes to the North Sea*

As explained above the wet flux of trace metals can be estimated either directly or indirectly. In Table XI wet and total fluxes to the North Sea and its coasts are given. The results will depend on the area considered to constitute the North Sea and the value used for the annual precipitation rate are included, as well as on the method used (direct or indirect measurement).

It is very difficult to compare any data in the Table XI, because the authors used different rainfall rates and methods, and because both total fluxes and wet fluxes are listed. The estimated fluxes to the coast of southern Norway (S & TWG, 1987) and of Scotland (Balls, 1989) are reported to be lower than the other coastal values. And for the North Sea itself, the West-Hinder values are either relatively

TABLE IX. Measured precipitation concentrations ($\mu g\ l^{-1}$) over the North Sea and adjacent areas (s- preceding an area means southern)

Area	Period	Cd	Cr	Cu	Pb	Zn	Remarks	References
The Netherlands (coast)	'82–'83	0.26–0.36	0.21–0.8	1.8–4.9	8.9–20	18–32	bulk	van Jaarsveld and Onderdelinden (1986)
The Netherlands (coast)	'86–'88	0.5–0.9	1.4–1.8	6.7–8.0	13–20	21–31	wet-only	van Daalen (1991)
Sweden (coast)	'84–'85	0.033–0.15	–	0.46–1.5	2–9	4.2–16	bulk	Ross (1987)
Sweden (coast)	'87–'88	0.04–0.12	0.06–0.16	0.85–2.32	1.84–3.75	4.1–10.2	wet-only	Ross (1990)
North Sea (coast)	'72–'81	0.3–1.2	0.2–4	4–30	10–35	20–160	literature range	van Aalst *et al.* (1983)
Norway (coast)	'78–'79	0.27	–	–	11	15	weekly bulk	Pacyna *et al.* (1984)
Norway (coast)	'80–'84	0.37	–	–	7.1	9.2	–	S & TWG (1987)
Scotland (coast)	'87–'88	0.68	–	2.3	4	13	wet-only	Balls (1989)
sNorth Sea	'81	3	–	39.5	13	194	wet-only	Dedeurwaerder *et al.* (1985)
sNorth Sea	'74–'85	0.5–9.5	–	2.5–77	10–29	26–490	literature range	GESAMP (1989)
sNorth Sea	'84–'87	10	–	77	29	500	wet-only	Baeyens *et al.* (1990)
German Bight (platform)	'88–'91	0.26	1.88	17.8	12	275	wet-only	Schulz (1993)

TABLE X. An overview of the data submitted to ATMOS as regards elemental concentrations ($\mu g\ l^{-1}$) in precipitation for 1988, 1989, 1990 and 1991, measured at 'CAMP' stations

Station	Period	Cd	As	Cr	Cu	Ni	Pb	Zn
B3A	'91	0.1	–	–	1.26	–	2.7	8.16
DK1	'88	0.08	–	–	1.4	–	4.2	12.1
	'89	0.10	0.45	0.46	1.1	0.45	3.93	15.58
	'90	0.10	–	0.28	0.99	0.50	2.73	9.10
	'91	–	–	0.17	1.42	0.35	2.72	1350
D1	'89	0.25	0.21	0.52	2.89	3.34	4.24	11.39
	'90	0.15	0.31	0.49	1.05	0.71	2.43	11.47
NL2	'88	0.19	–	–	2.9	–	6.4	–
	'89	0.12	–	–	2.62	0.35	10.18	14.95
	'90	0.16	–	–	2.45	–	5.91	11.26
	'91	0.16	–	0.40	2.97	0.51	6.41	14.52
NL3	'90	0.16	–	–	2.53	–	2.78	12.56
	'91	0.13	–	–	3.36	0.77	6.84	13.82
GB1	'88	0.28	–	–	3	–	8.7	16.1
	'89	0.23	0.78	1.93	4.65	1.42	7.67	25.08
	'90	0.40	0.70	0.75	2.00	1.46	4.93	16.8
	'91	0.16	0.42	0.50	6.50	1.70	7.70	18.70
GB2	'88	0.58	–	–	6.5	–	22.7	46.1
	'89	0.57	1.11	1.68	7.85	3.28	22.79	61.33
	'90	0.36	1.10	1.04	3.52	2.66	10.65	33.45
	'91	0.46	1.18	0.90	7.60	5.50	19.00	49.50
GB3	'88	0.20	–	–	2.4	–	7.5	8.3
	'89	0.13	0.59	0.68	3.06	1.31	5.25	9.66
	'90	0.13	–	0.25	1.94	0.74	3.04	8.98
	'91	0.14	0.26	0.30	4.30	0.70	4.00	8.10
N1	'88	0.11	–	–	–	–	7.4	14.1
	'89	0.11	–	–	–	–	5.45	11.43
N3	'91	0.06	–	0.60	2.50	0.10	7.00	14.20

high (Baeyens *et al.* 1990) or very low (Dedeurwaerder *et al.*, 1985). Baeyens *et al.* (1990) reported that the wet flux to the North Sea is clearly higher than that at a Belgian coastal station. It should be noted that the input values reported by Rojas *et al.* (1993) are based on sampling flights and that they were calculated using scavenging rates.

As far as wet fluxes are concerned, the uncertainties are far from being known. The theoretical approach to wet deposition is rather crude in the sense that the

TABLE XI. Total (dry + wet) or wet flux to the North Sea in kg km^{-2} y^{-1} (s- preceding an area means southern)

Area	Rain [mm y^{-1}]	Cd	Cr	Cu	Pb	Zn	Method	Remarks	References
Coastal stations	438	–	1.4	10.5	11	31	direct	wet	Cambray *et al.* (1979)
Coastal stations	778–1028	0.3–1.4	–	6.1–16.2	5.6–13.5	20.6–55.6	direct	total	Flament *et al.* (1984)
Coastal stations	–	0.09–1.7	0.58	0.8–27	5.1–14	9.3–156	–	total	PARCOM (1987)
Scotland (coast)	–	0.39	–	1.3	2.3	7.6	direct	wet	Balls (1989)
sNorway (coast)	1399	0.48	–	–	9.2	12	direct	total	S & TWG (1987)
Dutch Continental Shelf	–	0.06–0.11	0.15–0.30	0.28–0.55	4.8–9.6	2.4–4.8	–	total	S & TWG (1987)
North Sea	680	0.1–0.5	–	1–4.4	4–23	5–23	indirect	total	GESAMP (1989)
North Sea	430	2.9	–	25	7	170	direct	wet (dissolved)	Bayens *et al.* (1990)
North Sea	500	0.35	–	2.68	6.5	15.1	indirect	total	Rojas *et al.* (1993)
sNorth Sea	–	1.6	–	24.9	9.4	143	–	wet	ATMOS (1984)
Southern Bight	458	0.0002	–	0.0026	0.0014	0.015	direct	total	Dedeurwaerder *et al.* (1985)
Southern Bight	500	0.43	–	2.5	8.8	19.7	indirect	wet	Rojas *et al.* (1993)
Southern Bight	500	0.71	–	5.36	12.9	30.2	indirect	total	Rojas *et al.* (1993)
German Bight	677	–	0.43	1	5.7	4.3	indirect	wet	Kriews (1992)
German Bight	–	0.34	0.95	14.4	9.2	–	direct	wet	Schulz (1993)
Sweden (west coast)	–	–	–	3	2.6	9	direct	total	Selin *et al.* (1992)

mechanisms by which atmospheric particulate matter is scavenged by rain, are not yet fully understood. For indirect estimations of the wet flux, the washout ratio used in the calculations is of considerable importance. In Table XII some relatively recent values for trace metals are listed. They are again, very difficult to compare. The values used in the GESAMP (1989) report and by Rojas *et al.* (1993) are 'best estimates' based on published washout ratios for trace metals above the North Sea. In the ATMOS report (1984), it is stated that values for Cu, Zn and Cd above the sea are up to 5 times larger than above land.

To assess the environmental effect of the atmospheric input of heavy metals into the North Sea, it is important to know whether a distinction can be made between the amount of a certain trace metal that reaches the surface of the earth in a dissolved or in a particulate form. For instance, dissolved metals are much more readily available to be incorporated by organisms. Flament *et al.* (1984) investigated the metal distribution over the solid and liquid phases in rain at some French coastal sites. They found the following percentages of dissolved material: Pb (21–31%), Cd (53–78%), Cu (63–94%) and Zn (68–87%). Losno *et al.* (1988) observed that Zn partitioning is governed by adsorption/desorption processes on existing particles, which are pH dependent. Nevertheless, Colin *et al.* (1990) state that the nature of the particles is also important. Jickells *et al.* (1992) conclude that the solubility of an element is the result of the complex interplay of several factors and cannot be simply assigned to one factor such as pH.

3.3. TOTAL DEPOSITION FLUXES TO THE NORTH SEA

The total amount of heavy metals deposited to the North Sea (5.25×10^5 km^2) as reported by several authors, is given in Table XIII. The atmospheric flux reported in the ATMOS (1984) report is significantly higher than the other values, except for Pb. The range calculated by van Aalst *et al.* (1983) is also relatively high but the other total flux values agree fairly well. They were assessed at totally different points in time, with other methods and concentration measurements to start from (coastal precipitation vs. airborne concentrations), and even the area taken into consideration was different. The annual estimation of atmospheric fluxes reported by ATMOS are based on measurements during '88, '89, '90 and '91 at the so-called 'Central North Sea stations', but taking into account concentration gradients from land to sea due to removal processes or due to dilution. For each station a bulk gradient correction factor (defined as the ratio of the average deposition at a certain station to the average deposition over the total North Sea area) was derived from model calculations developed by RIVM (van Jaarsveld *et al.*, 1986; van Jaarsveld *et al.*, 1991). It is evident that, for a number of elements, the estimated depositions reported for '91 (ATMOS, 1992) are higher than those calculated for '90 (ATMOS, 1991). The estimated increases in Pb (30%) and Cu (40%) are due to high concentrations at UK stations.

TABLE XII. Washout ratios for trace metals

Cd	Cr	Cu	Pb	Zn	Remarks	References
125–500	150	140–751	76–169	179–1000	literature range	Schroeder *et al.* (1987)
–	–	–	–	1226	value measured	Jaffrezo and Colin (1988)
200–1000	–	200–1000	200–1000	200–1000	range used	GESAMP (1989)
150	–	150	150	150	value used	Rojas *et al.* (1993)
–	200–1280	60–3800	20–1350	280–11500	value measured (snow)	Cadle *et al.* (1990)

TABLE XIII. Total (dry + wet) atmospheric input of trace metals into the North Sea, in tons y^{-1}

Rain [mm y^{-1}]	Cd	Cr	Cu	Pb	As	Zn	Method	References
–	–	740	5600	5800	460	1600	indirect	Cambray *et al.* (1979)
685	110–430	70–1400	1400–10000	3600–13000	220–720	7200–58000	direct	van Aalst *et al.* (1983)
–	–	100–530	380–1600	1800–6400	150–510	3900–12000	indirect	Stößel
–	45–240	300–900	400–1600	2600–7400	40–120	4900–11000	direct	PARCOM (1987)
–	900	–	13542	7367	–	77566	–	ATMOS (1984)
500	47	205	620	1900	95	4600	indirect	ATMOS (1990)
520	32	88	321	958	95	2740	indirect	ATMOS (1991)
650	27	94	610	1241	83	3099	indirect	ATMOS (1992)
680	50–250	–	500–2300	2300–12000	130–580	2700–12000	indirect	GESAMP (1989)
600	158	–	1348	3670	–	7409	indirect	Injuk *et al.* (1992)
677	–	–	–	3500	160	–	indirect	Dannecker *et al.* (1992)
677	–	530	5100	3200	160	–	direct	Dannecker *et al.* (1994)
677	–	400	670	3500	160	4200	indirect	Kriews (1992)

If deposition to the total North Sea area is estimated from observations at coastal stations, one has to deal with the problem of how representative those observations are for larger areas, with respect to both precipitation amounts and measured concentrations. The first problem can be solved reasonably by using a precipitation which varies from year to year, i.e. by taking a precipitation amount which is 70% of the median precipitation of all the coastal stations. The second problem can be solved only when knowledge about atmospheric residence times is included in the method. A combined method based on observations and model calculations can therefore be expected to give the most realistic results.

As far as the relative importance of dry and wet deposition goes, most authors seem to agree on the fact that, for the trace metals, the wet flux is more important than the dry flux, except perhaps for Pb, where they may be of the same magnitude. However, on the extent of this difference, opinions vary very widely (Galloway *et al.*, 1982; ATMOS, 1984; Schroeder *et al.*, 1987; GESAMP, 1989; Martin *et al.*, 1989; Baeyens *et al.*, 1990; Remoudaki *et al.*, 1991). Martin *et al.* (1989) remark that the ratio of wet to dry deposition is controlled by many meteorological factors and also by the distance between the sampling site and the emission source (see also Migon *et al.*, 1991; Remoudaki *et al.*, 1991).

Whenever the deposition of micropollutants to a water surface is estimated, attention should be paid to the reverse fluxes (from the water to the atmosphere) as well. According to the ATMOS report (1984), for which the heavy metal content in the sea surface microlayer was determined, the maximum water-to-air fluxes are at least 30 times smaller than the total input fluxes. The authors of the GESAMP (1989) report state that, although the atmospheric concentrations of trace metals associated with large (resuspended) sea salt particles constitute only a minor fraction of the total atmospheric concentration, this fraction may well account for a significant part of the gross dry deposition flux. This complicates the assessment of the 'real' deposition fluxes to the sea.

3.4. DEPOSITION FLUXES BASED ON MODEL CALCULATIONS

An alternative way of determining the deposition of micropollutants from the atmosphere to the sea involves atmospheric transport models. Basically, one uses emission data for a certain source area (e.g. Europe) in combination with a long range transport model (which requires a number of input data) to simulate the dispersion and deposition of a substance for a determined receptor area (e.g. the North Sea). Model calculations can provide independent estimates for atmospheric inputs which can be compared to input estimates from measurements. Moreover, the calculations may indicate the spatial variation of the deposition, and allow the evaluation of the representativeness of measurements at coastal stations. In this section the results of calculations performed using relatively recent models, which have been applied to the calculation of the total deposition of heavy metals to

the North Sea, will be discussed and compared to the values obtained from field measurements.

3.4.1. *Literature Data on the Deposition Fluxes Based on Model Calculations*

In the 1980's, van Aalst *et al.* (1983) employed a simple model to compare the long-term (ca. 1 year) average concentrations of various elements, and wet and dry deposition for an area of 1000×1000 km^2 of the North Sea. The total air concentrations at the receptor site were calculated as the sum of the contributions from the different emission areas (the 'cells' of the emission grid) weighted by the probability that the air masses would be carried down from that emission cell. Based on the mass-median diameters, a value of 0.1 to 1 cms^{-1} for the deposition velocities was used. The results showed good agreement between measurements and calculations. The data from this and other works (PARCOM, 1985) were reviewed by van Aalst and Pacyna (PARCOM, 1986) in order to assess the atmospheric inputs of trace elements to the North Sea.

A more advanced 3-dimensional trajectory model based on the Monte Carlo method has been employed to estimate the long range transport and deposition of Pb to the North Sea (Krell *et al.*, 1986). The emission data used were the numbers from Pacyna (1985). In 1988, Krell and Roeckner used a more sophisticated trajectory model to estimate the dry and wet deposition of Pb and Cd into the North Sea, via a long range transport model using gridded data of the respective anthropogenic emissions in Europe and the relevant meteorological data. The authors considered aerosols only in the size range from 0.2 to 1 μm and a deposition velocity of 0.2 cm s^{-1} was used for all heavy metals. This model is particularly designed for episode studies. The model of Graßl *et al.* (1989) is very similar to the model of Krell and Roeckner.

The total annual atmospheric input of Pb to the North Sea was determined for all the months of 1980 to be ca. 1440 tons by Petersen (1987). A relatively large contribution on the order of 50% was estimated for the UK. The Netherlands, France and Germany contributed about 12% each, Belgium 5%, Sweden 1.5%, Denmark 1% and Norway even less. However, conclusions from this work should be taken with caution. The results are based only on a one year period, which shows a significant month-to-month variability of the deposition. More recently the same author estimated the annual input of Pb to be 2300 tons (Petersen *et al.*, 1988).

The TREND model was developed at the Dutch National Institute of Public Health and Environmental Protection in order to calculate long term averaged concentrations and depositions (van Jaarsveld *et al.*, 1986). It is a statistical long-range version of the Gaussian plume model, what means that the dispersion from a source is assumed to follow the prevailing wind direction and wind speed within a sector of 30% in the horizontal plane. The vertical dispersion is limited by the earth surface and the top of a mixing layer. Due to wet and dry deposition and chemical reactions, atmospheric concentrations decrease during the transport; this

process is also taken into account. The model assumes homogeneous climatology and boundary characteristics over whole Europe. The occurring meteorological situations are grouped in a limited number of classes and the calculations are carried out separately for 5 size classes from < 0.95 μm to > 20 μm particles, each of which has its own deposition characteristics. For all heavy metals a deposition velocity of 0.22 cms^{-1} was implemented. This model has been applied successfully to a period of a month, but even shorter periods yielded reasonable results.

The model of Warmenhoven *et al.* (1989) is, in fact, an elaborated version of the van Jaarsveld model, but instead of applying it to trace metals solely, a number of organic compounds like PAHs, PCBs, pesticides, etc. were also taken into consideration. The model assumes the same meteorology, surface characteristics and mass-averaged deposition velocities over the whole surface area.

The main problem concerning model based calculations is in estimating the emissions. Though, for some countries, there were explicit data on emissions of pollutants, generally the annual emissions from all countries have been estimated on the basis of industrial and agricultural activities within the countries. All the models used similar emission data as input to their model.

The total atmospheric input of some pollutants into the North Sea given by the above models is listed in Table XIV. Included is also the 'best' estimate defined as the value obtained when emissions are multiplied with the average ratio of measured/modelled air concentration. It can be seen that there is a general agreement between the results of the different models. Taking into account that all models use more or less the same emission data, this agreement confirms the idea that the influence of the different model assumptions is not very large, at least not in the case of the total deposition into the North Sea.

For the reported trace elements, the model values are consistently lower than the values obtained from field measurement data in Table XIII. Krell and Roeckner (1988) claim that this discrepancy can be explained as follows: the extrapolation of coastal measurements, on which most deposition estimates up until 1988 were based, cannot be justified, because there is no reason to believe that the high precipitation intensities/volumes measured along the southern and western coasts are representative for the whole of the North Sea. The authors find a strong argument in the life-time of clouds which is not more than a few hours for the precipitating one: in this way, most of the pollutant material is likely to be washed out within about 100 km from the coast. Their model simulations (and those by van Jaarsveld *et al.* (1986)) reveal a substantial decrease of the deposition across the southern and western coasts. Van Jaarsveld *et al.* (1986) state that the discrepancy might partly be due to less accurate sampling and analysis of rainwater as well.

3.4.2. *Validation of the Models*

Van Jaarsveld *et al.* (1986) note that there are some assumptions inherent to their model, which do not agree very well with reality. For instance, it is not correct to

TABLE XIV. Comparison of the total deposition (tons y^{-1}) to the North Sea calculated with different models

Reference	Cd	Cr	Cu	Pb	Zn	As
Earlier estimates reviewed in PARCOM (1985)	110–430	70–1400	1400–10000	3600–13000	7200–58000	220–720
PARCOM (1986)	14	70	130	2600	1200	42
Van Jaarsveld *et al.* (1986)	11	58	100	2000	940	–
Petersen (1987)	–	–	–	1440	–	–
Petersen *et al.* (1988)	–	–	–	2300	–	–
Krell and Roeckner (1988)	11	–	–	1200	–	–
Graßl *et al.* (1989)	–	–	–	2300	–	–
Warmenhoven *et al.* (1989)	15	72	110	1900	930	–
Van Jaarsveld (1991)	10	–	–	960	600	–
ATMOS (1990) – 'best' estimates (model/measurements)	13	–	–	870	1800	–

assume that transport and dispersion over sea are analogous to those over land. The stability over sea is mainly determined by the temperature difference between the air and the seawater, and shows hardly any diurnal variation. Also, in the coastal zone complicated transition phenomena occur, which are not accounted for in the model. However, the authors do not think that a more realistic model would yield largely different results.

Krell and Roeckner (1988) had difficulties in validating their model because of the lack of comparison material for the North Sea. Therefore, they were obliged to simulate air and precipitation concentrations at certain sites and for certain periods (e.g. a month) for which measurements were made, and their results agreed fairly well with the measured values.

Warmenhoven *et al.* (1989) estimate that the results concerning the heavy metal deposition are the most reliable ones. In general, the validity of this model is mainly governed by the quality of the emission data and the choice of the emission grid (because some materials are so stable in the atmosphere, that a much larger emission area should be taken into consideration). As a result of this, the real deposition of these elements should be higher than predicted by the model. Finally, the assumption that the North Sea is a well-mixed tank, without any inflow or outflow except from rivers (and the atmosphere), has an influence on the deposition estimates. In this concept it would be more realistic to include the dynamics of the North Sea in the model.

4. Relative Contribution of Atmospheric Deposition of Trace Metals to the Total Input into the North Sea

Apart from atmospheric pollution, the North Sea is subject to a number of other sources of pollution as well: e.g. input via rivers, direct discharges from industries into the estuaries, dumping of industrial wastes and drainage of sewage (van Aalst *et al.*, 1983). It is very difficult to evaluate the relative importance of the various input sources as most input estimates are subject to considerable uncertainty arising from analytical and sampling problems. Moreover, the actual quantity of pollutants entering the North Sea varies from year to year, depending on factors like natural variations in river flows and water exchange with adjacent sea areas, economic variations (industrial expansion and reorganization, large strikes), changing legislation (emission and dumping restrictions), atmospheric conditions (wind flow patterns, rainfall intensity) and unforeseen circumstances (accidents).

Although, in a number of publications, estimates of the non-atmospheric input are given (e.g. Cambray *et al.*, 1979; van Aalst *et al.*, 1983; ATMOS, 1984), we chose to use the recent data as given by Warmenhoven *et al.* (1989). They use the figures reported during the Second International Conference on the Protection of the North Sea in 1987, which are based on information obtained from the countries concerned. For the contaminants which are not included in the report of the Conference, the total fluxes are estimated on the basis of data on the total

TABLE XV. Relative contribution of atmospheric deposition to the total loading of the North Sea, in percent

Element	Atmospheric-measured ATMOS (1992)	Atmospheric-modelled Warmenhoven *et al.* (1989)
Cd	22	14
Cr	2	2
Cu	18	4
Pb	26	35
Zn	15	5

loading through the Rhine and the Meuse (Folkertsma, 1989). This author points out, however, that the values calculated in this way can only serve as in indication of the order of magnitude. Also, the contamination and natural heavy metal load of the water entering the North Sea from the English Channel, the Baltic Sea and the North Atlantic is not included in the estimates. And the river catchment areas are also subject to atmospheric deposition (Warmenhoven *et al.*, 1989). According to Warmenhoven *et al.*, 1989, the yearly estimates for non-atmospheric deposition of metals in tonnes are: 95 (Cd), 4000 (Cr), 2800 (Cu), 3500 (Pb) and 1700 (Zn). By comparing the non-atmospheric input to the atmospheric input fluxes discussed earlier, it is possible to get an idea of the relative importance of both pathways for the input of pollutants to the North Sea. In Table XV, the non-atmospheric values are compared with the measured and modeled atmospheric data. We used the values calculated by the model of Warmenhoven *et al.* (1989) and flux values reported by ATMOS (1992). The most important pathway for each compound seems the same for measurements and model. Based on this data, non-atmospheric input is more important for all the elements. GESAMP (1989) notes that, for particulate trace elements, the major source is usually the rivers. However, particulate riverine material is likely to be deposited close to the source regions, while atmospheric input can more easily occur in remote oceanic areas. Still according to the GESAMP report, the global atmospheric and riverine inputs are comparable for dissolved Cu, while for Zn and Cd atmospheric inputs appear to dominate. The atmospheric input of Pb is expected to decrease over the next decade, due to the growing use of unleaded gasoline. Martin *et al.* (1989) state that the atmospheric input to the Mediterranean Sea is predominant over the river input, either dissolved or particulate. For organic contaminants as well, the riverine flux may influence only the nearshore areas, while atmospheric input is supposed to have a much wider impact over regional seas (GESAMP, 1989).

However, it must be emphasized that the accuracy of the estimations of both the atmospheric and non-atmospheric input sources is still very poor.

5. Conclusions

From this literature review several important gaps in the knowledge of the atmospheric deposition to the North Sea have become apparent.

For aerosols, the presently available concentration data need to be improved by more accurate determinations of the size distribution of airborne particulate matter since this is directly controlling the deposition rates. The dependence of the deposition velocity upon the particle size requires further investigation and better knowledge of the kinetic parameters as deposition/transfer velocity.

It is obvious that current knowledge about the wet deposition of trace elements to the North Sea is insufficient. For the trace metals, which were dealt with in this review, a number of specific problems like the lack of accurate washout ratios for the North Sea area or the contribution of resuspension from the sea surface to the observed pollutant concentrations still have to be solved. Reported washout or scavenging ratios for a particular element vary substantially. Part of the problem is in the method by which scavenging ratios are determined; usually they are computed from rain and air concentrations measured on samples that were not collected contemporary. Therefore, it is absolutely necessary to work out a 'global' measurement strategy for the North Sea area which would include precipitation and air sampling, preferably simultaneously at a large number of sites (ship cruises, islands, platforms, coastal stations) and over a considerable period of time, in order to be able to calculate the scavenging rates from really paired rain and air samples. The considerable expansion of the geographical coverage of rain sampling programmes should eliminate the uncertainties on the temporal distributions of precipitations events for the North Sea area.

The results of different studies on the atmospheric input of trace elements into the North Sea are still indicating large uncertainties. A combined model and monitoring approach seems to be most useful for the determination of atmospheric fluxes to large surface waters. Model studies give much lower values than the studies based on measurements. The major uncertainty in model studies is the quality and completeness of the emission data and the different size distributions used in the models. Furthermore, none of the models takes into account particle growth due to high relative humidities. Emission estimates for Cd and Zn currently in use are most probably too low. Cd emissions in 1982–1989 over a whole region, should be at least 30% higher. For Zn, the general underestimating is at least a factor of 3. Therefore, research on emission processes and identification of unknown emission categories is urgently needed for heavy metals (Van Jaarsveld, 1991).

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Integrated stratigraphy and sedimentology of the Late Ypresian Egem Member sands (Yd) (Southern Bight North Sea Basin, Belgium)

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With 7 figures and 5 tables in the text

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Abstract: In the Belgian Basin, the overall regressive conditions at the end of the Early Eocene Ypresian stage are superimposed by several minor but distinct transgressive pulses. Biostratigraphic resolution was in general too poor to unravel the vertical succession of the sandy glauconitic deposits spanning the Early to Middle Eocene boundary. High sediment supply and a rapidly changing deltaic depositional environment created strong lateral facies shifts which resulted in several stratotypes of local importance.

In this paper an attempt is made to decode these lateral and vertical facies variations in the Late Ypresian Egem Member sands. Lithology-related characteristics (like geotechnical data and geophysical well log parameters for onshore sediments together with offshore seismic data) enable the reconstruction of a general vertical succession of lithological Egem Member sands subunits. This model seems valid in the regional context of the Southern Bight of the North Sea Basin: its sequence stratigraphical framework was tested through correlation feedback to outcrops and boreholes, and its sediment facies architecture was interpreted in terms of relative sea level fluctuations.

Zusammenfassung: Im Belgischen Becken werden die überwiegend regressiven Bedingungen am Ende der untereozänen ypresischen Stufe durch einzelne kleinere transgressive Phasen überlagert. Die biostratigraphische Auflösung war hierbei im allgemeinen nicht ausreichend, um die vertikale Abfolge der sandigen, glaukonitreichen Ablagerungen an der Grenze vom Unter- zum Mitteleozän zu entschlüsseln. Hohe Sedimentationsraten und schnell wechselnde Ablagerungsbedingungen innerhalb des Deltamilieus führten zur Ausbildung deutlicher lateraler Faziesänderungen. Hierauf beruht die Entstehung einer Vielzahl Stratotypen von lokaler Bedeutung.