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The atmospheric distributions of trace metals, trace organics and nitrogen species over the North Sea

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A 15 month survey was carried out into the distributions of trace metals, trace organics and nitrogen species in particulate and rainwater samples collected from the atmosphere over the southern North Sea. This is the first time a comprehensive and reliable data-set of this kind has been obtained for a coastal region from collections made at sea.

Trace metals. There is a south–north decrease in the emission of trace metals to the atmosphere from the land masses surrounding the North Sea. ‘End-member’ aerosol trace metal concentrations have been identified for the three major source regions; i.e. continental Europe, U.K. and the open-sea, and indicate that, in general, aerosols from air masses which have crossed continental Europe are richer in some trace metals (e.g. Zn and Pb) than those from air masses which have crossed the U.K. There are short-term variations in the concentrations of trace metals in aerosols over the North Sea; however, on an integrated long-term basis the concentrations reflect land-based source emission strengths, and increase towards the south of the region. There is also pronounced short term variability in the concentrations of trace metals in rainwaters collected over the North Sea, but separate contributions from marine, crustal and anthropogenic sources can be identified. Atmospheric fluxes contribute substantially to the total inputs of trace metals to the North Sea, with both ‘wet’ and ‘dry’ deposition processes being important.

Particulate trace organics. The distributions of three main hydrocarbon classes were studied; i.e. saturated hydrocarbons (n-alkanes), PAH (polynuclear aromatic hydrocarbons) and UCM (uncharacterized complex material). Carbon preference indices of n-alkanes suggest that terrestrial sources dominate, with marine sources being insignificant. In terms of air mass origins, trace organic concentrations are ranked in the order: continental Europe > U.K. > open sea.

In terms of air mass origins, the concentrations of trace organics and some trace metals (e.g. Zn and Pb) are higher in aerosols having a continental European than U.K. source. However, on the basis of predominant air mass trajectories over the survey period, the major source of both trace organics and trace metals to the North Sea atmosphere was air which had recently crossed over the U.K.

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Nitrogen species. Compared to the North Atlantic sea water inflow, the atmosphere is a minor source of nitrogen species to the North Sea. However, atmospheric nitrogen inputs constitute at least 25% of the terrestrial inputs, and may provide the dominant source of nitrogen in stratified areas of the North Sea remote from riverine inputs. 'Wet' deposition processes dominate the total nitrogen flux to the sea surface, but 'dry' deposition of gaseous and particulate species contributes significantly.

1. Introduction

The North Sea is surrounded by some of the most industrialized nations in the world and considerable concern has arisen over the extent to which it is polluted by several classes of contaminants. These contaminants can be transported to the North Sea by a variety of routes, but in recent years it has been suggested that the atmospheric pathway can dominate the inputs of some contaminants (Cambray *et al*. 1975). To investigate this, a cooperative study was carried out to establish the atmospheric concentrations and sea surface fluxes of trace metals, trace organics and nitrogen species over the southern North Sea. The study involved research groups at the Universities of Liverpool (UL), Essex (UE) and East Anglia (UAE). Aerosol and rainwater samples were collected on board the RRS *Challenger* over a 15 month period (August 1988 to October 1989) at various locations along the ship's track; this is illustrated in figure 1, together with the locations of several land stations at which atmospheric samples have been collected around the North Sea. In addition, rainwater samples were taken at Mannington Hall, a site on the U.K. east coast, over approximately the same period of time as the *Challenger* samples were collected.

2. Trace metals

(*a*) *Trace metals in aerosols*

Particulate trace metals in the North Sea atmosphere were determined by the UL group (98 samples) and the UE group (91 samples), using collection techniques which have been described in Chester & Bradshaw (1991) and Ottley & Harrison (1992*a*), respectively. A summary of the data obtained by the two groups for the concentrations of particulate trace metals over the southern North Sea is given in table 1, together with a selection of data reported by other workers for the atmosphere of the North Sea and the surrounding land regions at the collection sites illustrated in figure 1. From table 1 it can be seen that for those metals which are common to the studies carried out by both groups, the mean concentrations agree well; with the exception of Zn, which is higher by a factor of *ca*. 2 for the UE relative to the UL data-set; the reason for this is not known.

Data obtained by the UL group included a wide range of trace metals and it is of interest to compare their findings with those obtained for the long-term collections carried out at Hemsby (U.K. east coast) and Helgoland. On the basis of the arithmetic mean data, the concentrations of the trace metals which were common to three studies are remarkably similar. Thus, the concentration ranges for the three data sets are; Fe (201–353 ng m^{-3} of air), Ni (2.6–3.8 ng m^{-3} of air), Zn (33–41 ng m^{-3} of air) and Pb (29–34.5 ng m^{-3} of air). It would appear, therefore, that a reasonable

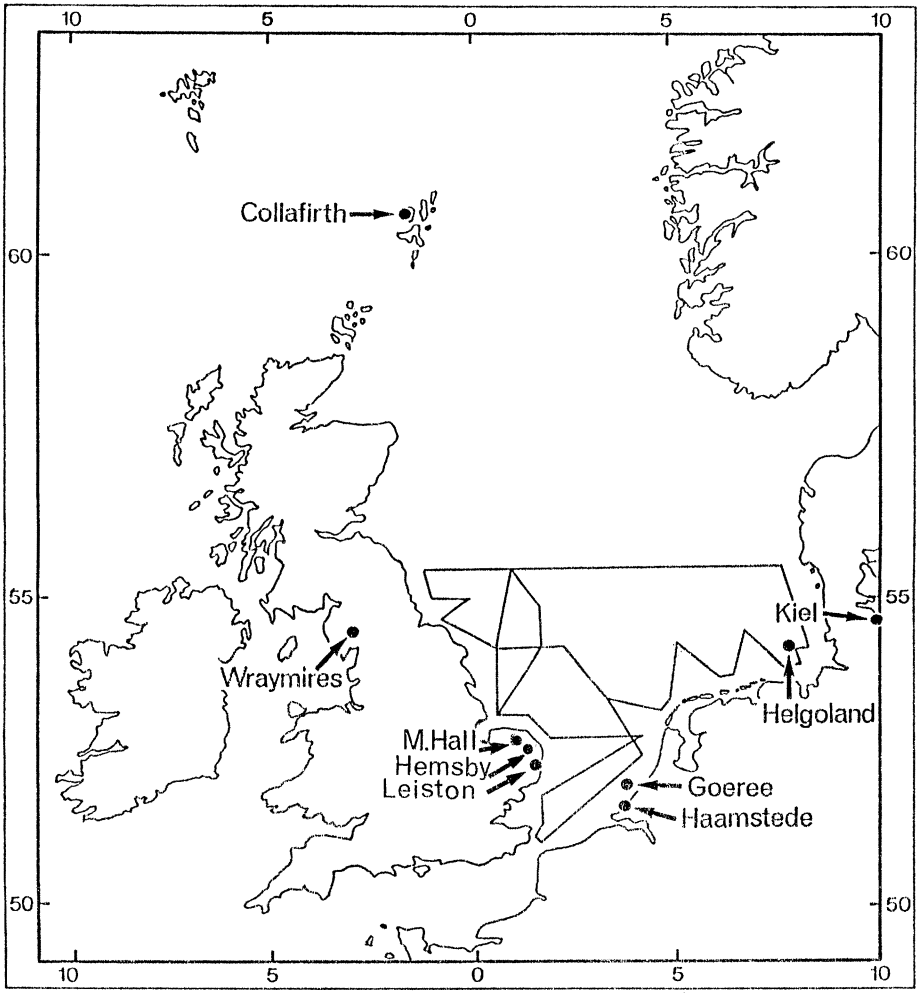

Figure 1. Locations at which aerosol and rainwater samples have been collected from the atmosphere over, and around, the North Sea, M. Hall in the Mannington site. The aeroplane collections listed in table 1 extended for 100 km seaward from the Goeree platform. The solid black line indicates the track over which samples were collected from on board the RRS *Challenger*. After Chester & Bradshaw (1991).

estimate is now available for the concentrations of some trace metals in the North Sea atmosphere. However, the mean bulk aerosol concentration is perturbed by variations in the geographical distributions of the aerosols. For example, there is a north–south increase in the atmospheric concentrations of some trace metals at land stations around the North Sea which, in general, follows variations in the metal source strengths on the land areas (van Aalst *et al.* 1982). Chester & Bradshaw (1991) and Ottley & Harrison (1992*a*) used air mass back trajectories to demonstrate that this north–south increase in emission strengths from the surrounding land masses imposes a control on the concentrations of particulate trace metals in the air masses which cross the source regions, and they were able to identify a number of ‘end-member’ aerosols on the basis of their average trace metal concentrations. Data for these ‘end-member’ aerosols are given in table 2, together with those identified by

Table 1. *Particulate atmospheric trace metal concentrations over the North Sea and surrounding areas*

(Concentration units; ng m^{-3} of air. Positions of the sampling locations are given in figure 1.)

	surrounding land area						North Sea		present study arithmetic mean	
element	Collafirth[a]	Wraymires 1972–73[b]	Keil Bight[c]	Leiston 1972–73[b]	Haamstede[d]	Hemsby[e]	aeroplane collection[f]	Helgoland[g]	A[h]	B[i]
Al	—	120.5	394	235	—	—	—	210	294.5	197[j]
Fe	54	175	369	335	—	216	160	201	353	184[j]
Mn	—	10.5	15	21	—	10	—	7.2	14.5	—
Ni	< 3.7	4.5	4.0	5.3	22	2.7	—	2.6	3.8	—
Cr	0.7	2.0	2.9	5.65	7.5	—	—	1.7	4.7	—
Co	—	0.14	—	0.375	—	—	—	0.24	0.25	—
Cu	20	< 6	7.7	< 10	22	—	7.8	3.9	6.3	6.9
Zn	15	60	57	137.5	130	41	69	33	41	74.5
Pb	21	64	53	127.5	190	34	33	29	34.5	29
Cd	—	—	—	—	2.5	1.1	0.83	1.4	—	1.25
Na	—	—	—	—	—	—	—	4790	—	3805
K	—	—	—	—	—	—	—	306	—	1239
Ca	—	—	—	—	—	—	—	418	—	467
Mg	—	—	—	—	—	—	—	559	—	401

[a] Cambray *et al.* (1975); [b] Cawse (1974); [c] Schneider (1987); [d] Diederen & Guichert (1981); [e] Yaaqub *et al.* (1991); [f] Otten *et al.* (1989); [g] Kersten *et al.* (1988); [h] A, Chester & Bradshaw (1991); [i] B, Ottley & Harrison (1992*a*); [j] Al and Fe are underestimated by more than 50% due to incomplete analytical recovery and sampler inlet characteristics.

Table 2. *Trace metal concentrations associated with 'end-member' aerosols transported to the North Sea atmosphere from different sources*

(Concentration units: ng m^{-3} of air. UK, United Kingdom; EU, continental Europe; OS, open sea.)

	Bradshaw (1992)			Ottley & Harrison (1992*a*)			Yaaqub *et al.* (1991)		
element	UK	EU	OS	UK[a]	EU	OS	UK	EU[b]	OS
Al	300	440	84	145–221[c]	283[c]	156[c]	—	—	—
Fe	304	657	116.5	145–211[c]	208[c]	156[c]	186	371	133
Mn	13	25	3.6	—	—	—	8.5	19.5	7.0
Ni	3.7	4.8	0.97	—	—	—	—	—	—
Co	0.24	0.31	0.12	—	—	—	—	—	—
Cr	3.8	10	1.3	—	—	—	—	—	—
Cu	5.3	11	1.8	1.7–8.2	11	1.8	—	—	—
Zn	31	83	7.7	40–75.5	174	3.5	33	76	28
Pb	28	68	4.8	9.8–32.5	63	24	31	48	20
Cd	—	—	—	1.05–1.45	2.02	0.73	1.1	1.4	0.75

[a] Values for England and Scotland sectors; data for Scotland listed first.

[b] Values averaged for west and east Europe.

[c] Al and Fe are underestimated by at least 50 % due to incomplete analytical recovery and sampler inlet characteristics.

Yaaqub *et al.* (1991), and it can be seen that there is a generally good agreement between the three data-sets and that, in general, air masses which have crossed continental Europe are richer in some trace metals (e.g. Zn and Pb) than those which have crossed the U.K. However, on the basis of predominant air mass trajectories, the major source of the trace metals during the survey period was air which had crossed the U.K.

Chester & Bradshaw (1991) showed that, on a short-term basis, air masses from all sources can be transported to almost any region of the North Sea, and that as a result of this it is the origin of an air mass, and not the location at which it is sampled, which constrains the short-term particulate trace metal concentrations in the North Sea atmosphere. Over longer periods, however, the short-term variations are smoothed out and a north–south increase in trace metal concentrations becomes apparent; i.e. the source strength emission signal is preserved. For example, Ottley & Harrison (1992*a*) demonstrated that there is a northeast–southwest increasing concentration gradient for particulate trace metals in the North Sea atmosphere, upon which is superimposed a decrease in concentration towards the centre of the North Sea basin; this is illustrated for Pb in figure 2.

(*b*) *Trace metals in rainwaters*

Trace metals in rainwaters were determined by the UEA group for samples collected on board RRS *Challenger* (61 samples for major ions, 35 for trace metals) and at the Mannington Hall site (80 samples for both major ions and trace metals). The analytical procedure used measured the total trace concentrations (Jickells *et al.* 1992*a*); for the anthropogenic metals (e.g. Cu, Pb, Zn, see below) most of the total concentration in rainwater is dissolved, but for crustal metals (e.g.; Al, Fe – see below) only *ca.* 10–20 % of the total concentrations are in the dissolved state (Jickells *et al.* 1992*b*). Average trace metal concentrations in the rainwaters are listed in table

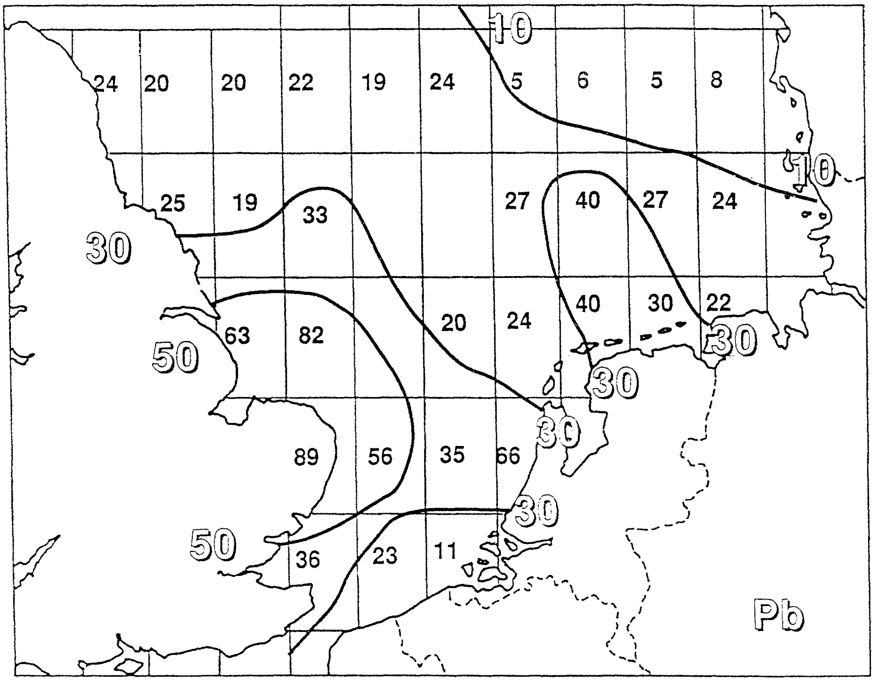

Figure 2. Spatial distribution of particulate Pb concentrations in the North Sea atmosphere on a 1° by 1° resolution grid. Data in ng m^{-3} of air, averaged over the total collection period. From Ottley & Harrison (1992*b*).

Table 3. *Trace metal concentrations in rainwaters over the North Sea and surrounding areas*

(Concentration units: µg l^{-1}; volume weighted means.)

				present study	
element	N.E. coast Scotland[a]	Belgian coast[b]	N coast Germany[c]	*Challenger*; North Sea	Mannington Hall; E coast England
Al	—	—	—	21	56
Fe	88	159	18	31	17
Mn	3.8	9.5	4.2	3.6	2.7
Ba	—	—	—	0.96	4.1
V	—	—	1.7	—	1.6
Cu	2.3	39	1.7	0.98	4.0
Zn	13	194	25	7.6	2.9
Pb	4.0	13	6.4	3.5	4.1
Cd	0.68	3	0.48	0.08	0.25
Sb	—	—	0.38	0.12	—
Sn	—	—	0.52	0.34	—

[a] Balls (1989); [b] Dedeurwaerder *et al.* (1983); [c] Stossel (1987).

3, together with other data for the North Sea region. In general, the *Challenger* and Mannington Hall data-sets agree reasonably well, and the differences that are found may be related to several factors which could include the following; (*a*) a bias resulting from the smaller number of samples in the shipboard data-set as a consequence of the severe constraints on rainwater sampling at sea, (*b*) higher concentrations of some species collected closer to their sources (e.g. higher Al concentrations at the Mannington Hall site), (*c*) natural variability in concentrations, and (*d*) analytical differences. However, the generally good agreement between the two data-sets, and that reported by Stossel (1987) for a coastal site fringing the central southern North Sea, suggests that the data for some coastal sites can be considered to be representative of local marine conditions. The higher trace metal values reported by Dedeurwaerder *et al*. (1985) for rainwater samples collected in the Southern Bight of the North Sea may imply that there is a north–south increasing concentration gradient in rainwaters similar to that found for aerosols; however, Balls (1989) reported data for a coastal site in north east Scotland which are similar to those reported here for the southern North Sea, suggesting that a marked gradient may not exist.

On the basis of enrichment factor and inter-element relationship data for both the *Challenger* and the Mannington Hall sites, it appears that Al and Fe have predominantly crustal sources in the rainwaters and that anthropogenic sources dominate the inputs of the other metals; in addition, there may be a secondary marine source for Mn (Rendell, 1992). There may, however, be an important difference between the two data-sets; i.e. in the *Challenger* rainwaters an inverse relationship was found between the concentrations of most of the trace metals and sample volume, implying that rain is very efficient at cleansing the atmosphere and that most of the metals are washed out in the few millimetres of rain with subsequent rain diluting the samples. In the Mannington samples such a relationship is only clearly evident for V and Al. This may have been the result of the factors (*a*)–(*d*) outlined above, or it may imply that different scavenging processes occur over the open North Sea relative to the coastal site.

(*c*) *Atmospheric trace metal fluxes to the North Sea*

Trace metals are removed from the atmosphere by a combination of ‘dry’ (i.e. not involving an atmospheric aqueous phase) and ‘wet’ (precipitation scavenging) processes.

(i) For the ‘dry’ deposition flux, Ottley & Harrison (1992*a*) used cascade impactor data to provide information on the mass size distributions and mass weighted dry deposition velocities for a series of trace metals in the North Sea aerosol. After making allowance for the sea surface recycling of trace metals, i.e. those which do not make a net contribution to the air to sea flux (for details – see Ottley & Harrison 1992*a*), the authors calculated the dry flux of trace metals to the surface of the North Sea on a 1° by 1° grid pattern. They demonstrated the importance of ‘large particles’ (i.e. those with mass median diameters greater than 20 μm) on the overall dry deposition flux, and their flux data for the total North Sea (i.e. northern and southern sections) are given in table 4*a*. Following the approach adopted by van Aalst *et al*. (1982), Bradshaw (1991) used the mean data reported by Chester & Bradshaw (1992) to make a first-order estimate of the dry deposition of trace metals to the whole North Sea, and the data are also given in table 4*a*. A selection of ‘dry’ trace metal deposition fluxes to the North Sea surface reported by other workers is included in table 4*a*, and from these various data it can be seen that there is a wide range in the magnitudes of the estimated fluxes. Those found in the present investigation are generally much lower than those reported by other workers. One reason for this is that many previous workers have extrapolated data for single sites

Table 4. *Fluxes of trace metals to the North Sea*

(Units: t a^{-1})

(*a*) Atmospheric 'dry' deposition fluxes

element	Cawse (1974)	Baeyens *et al.* (1990)	Stobel (1987)	Van Aalst *et al.* (1092)	present study A[a]	present study B[b]
Al	22050–220500	56000	—	—	61955	7300[c]
Fe	24675–194250	43400	8200	—	49236	9510[c]
Mn	578–7350	—	—	—	844	—
Ni	< 1600–2600	—	—	16–800	869	—
Cr	< 42–1323	—	—	8–800	277	—
Cu	< 500–9000	1480	570	< 800–4000	873	350
Zn	1500–35000	3290	3600	1600–16000	2386	2640
Pb	< 3000–9384	1750	2280	330–3300	1354	370
Cd	—	196	148	8–400	—	33

(*b*) Atmospheric 'wet' deposition fluxes

(All fluxes have been scaled to the same area basis.)

element	Stossel (1987)	Krell & Roeckmer (1987)[d]	Baeyens *et al.* (1990)[e]	present study
Al	—	—	31720	4085
Fe	28500	—	31200	6235
Mn	1300	—	3120	710
Cu	437	—	13000	194
Zn	4784	—	8840	1505
Pb	1768	1508	3640	688
Cd	83	13.5	1508	15
Sb	68	—	—	23.5
Sn	—	—	—	66.5
Ba	1196	—	—	189

(*c*) Comparison of trace metal fluxes to the North Sea

element	atmospheric fluxes present work[b] 'dry'	atmospheric fluxes present work[b] 'wet'	fluvial fluxes[g]	discharges and dumping[g]
Ni	869	—	240–270	903
Cr	277	—	590–630	3382
Cu	350–873	194	1290–1330	1580
Zn	2386–2640	1505	7360–7370	9850
Pb	370–1354	688	920–980	2470
Cd	33	16	46–52	43

[a] Bradshaw (1992); [b] Ottley & Harrison (1992*a*); [c] Al and Fe are underestimated by more than 50% due to incomplete analytical recovery and sampler inlet characteristics; [d] Model estimate; [e] Derived from data from Southern Bight of the North Sea; [f] Data from table 3*a*, *b*; [g] Data from North Sea Quality Status Report (DOE 1987).

to the whole North Sea. In contrast, Ottley & Harrison (1992) took account of actual spatial distributions in their calculations, and although Bradshaw (1991) extrapolated mean data to the whole North Sea, the data were collected over large regions of the sea itself. Despite the fact that the 'dry' flux estimates given in the present paper are lower than past estimates, they are still equivalent to substantial fractions of the land-derived inputs; see table 4*c*.

(ii) The 'wet' deposition flux. 'Wet' trace metal deposition fluxes to the southern North Sea have been estimated by using the *Challenger* rainwater data-set, which was collected at sea, and the rainfall estimate given by Rendell *et al.* (1992) and have been extrapolated to the whole North Sea by using the scaling factor applied to the 'wet' deposition of nitrogen (Rendell *et al.* 1992). The 'wet' trace metal flux data are listed in table 4*b*, and the 'dry' and 'wet' flux data are summarized in table 4*c*, together with those arising from other sources. A number of important points emerge from these data comparisons.

(*a*) The atmospheric fluxes estimated from the present study are generally considerably lower than those reported previously in the literature.

(*b*) Only for Pb does the 'wet' flux exceed the lower value of the 'dry' flux range, and for the other trace metals even the lower 'dry' flux estimates exceed those for the 'wet' fluxes, which is not in agreement with earlier flux data for the North Sea reported by several other workers (van Aalst *et al.* 1982). Further, this dominance of 'dry' deposition is also in contrast to data for atmospheric trace metal fluxes both to open ocean areas (Duce *et al.* 1991) and to several other coastal seas such as the Western Mediterranean (Chester *et al.* 1990).

(*c*) In general, the atmospheric fluxes are the same order of magnitude as those arising from fluvial transport and from dumping and direct discharges (see table 4*c*), thus highlighting the importance of the atmosphere as a route for the transfer of trace metals to the North Sea.

3. Trace organics

Ninety-eight samples of particulate aerosols for the determination of trace organics were collected by the UL group from the North Sea atmosphere in parallel, with those collected for trace metal determinations. The samples were analysed for their saturated hydrocarbon (mainly *n*-alkanes), polycyclic aromatic hydrocarbon (PAH) and uncharacterized complex mixture (UCM) contents; the collection and analytical details have been described by Preston & Merrett (1991). These authors reported that the most abundant trace organic component of the aerosols was the UCM which, on average, made up *ca.* 76% of the components analysed. *N*-alkanes were second in abundance (*ca.* 17% of the total), with the PAH fraction making up the remainder (*ca.* 7% of the total). However, the range of concentrations within the sample set was considerable; the standard deviations for each component being between two and three times the arithmetic mean, and the geometric means being around one order of magnitude less than the corresponding arithmetic means.

On the basis of air mass back trajectories, 55 samples in the set could be divided into three classes according to the source regions crossed before sampling; these were Class A (U.K. origin, 36 samples), Class B (Continental European origin, 13 samples) and Class C (open-sea origin, 6 samples). The mean data for each of the classes are given in table 5, from which it can be seen that the arithmetic mean concentrations of all components can be ranked in the order: Class B > Class A > Class C. However, on the basis of the predominant air mass trajectories the major source for the three classes of trace organics was air which had recently crossed the U.K.; a similar situation to that for the trace metals Zn and Pb. Within Classes A and B, the

Table 5. *Trace organic concentration data* (ng m^{-3} *of air*) *for the three North Sea air-mass sources* (Data from Preston & Merrett (1991). nd, not detected.)

	arithmetic mean	geometric mean	range	s.d.
Class A U.K. origin ($n = 36$)				
n-alkanes	7.6	1.02	nd–63.9	15.4
UCM	41.6	3.35	nd–339.0	91.5
PAH	3.91	0.61	nd–48.2	8.75
Class B continental Europe origin ($n = 13$)				
n-alkanes	13.4	1.19	nd–144.7	39.6
UCM	72.3	3.52	nd–858.2	236.2
PAH	9.54	1.31	0.01–67.5	19.8
Class C open sea origin ($n = 6$)				
n-alkanes	5.43	0.84	nd–21.9	8.3
UCM	11.99	3.04	1.6–31.6	14.1
PAH	0.196	0.11	nd–0.34	0.14

concentration ratios of UCM : n-alkane : PAH are generally similar at 10.6 : 1.9 : 1.0 and 7.6 : 1.4 : 1.1, respectively. The samples in Class C, however, exhibit a markedly different ratio signature of 61.1 : 27.7 : 1.0, reflecting a significantly reduced PAH component. This could indicate that there is a selective removal of PAH-rich particles during transit over the open-sea; a result which has consequences for flux model calculations. Alternatively, it could simply reflect a relatively weak terrestrial source of PAH to the air masses which have crossed the open-ocean. For example, carbon preference indices for the n-alkane components indicate that the source of organic material to the marine aerosols sampled is mainly terrestrial, and that marine sources appear to exert only a weak influence on the concentrations of the n-alkanes in the North Sea atmosphere.

There is a seasonal variability in the concentrations of the particulate trace organics, and all components show a winter maximum. The most probable reason for this is an increase in the combustion of fossil fuels in the winter months on the surrounding land masses. The n-alkanes also have a second maximum in summer, when plant debris, which contributes n-alkane plant waxes, is more readily available for transport in the atmosphere.

A comparison was made between the trace organic and trace metal data-sets. The results were reported in Preston *et al.* (1992); (fig. 3), and showed that although correlations were not found between either the n-alkane and trace metal, or the UCM and trace metal, data-sets, significant correlations were found between the concentrations of PAH and the following trace metals (correlation coefficients at the $> 99\,\%$ level in parenthesis); Pb (0.50), Cu (0.32), Zn (0.38), Ni (0.42) and Cd (0.48). The link between PAH and Pb is of particular interest because the two components have a common source in leaded petrol. The relationship between PAH and Pb found in aerosols over the North Sea during the period August 1988 to October 1989 can be expressed as

$$[\text{total PAH}] = 0.152\,[\text{Pb}] - 0.71.$$

Leaded petrol is clearly not the only source for either the Pb or the PAH; for example, combustion products of other fossil fuels (e.g. diesel) are richer in PAH than

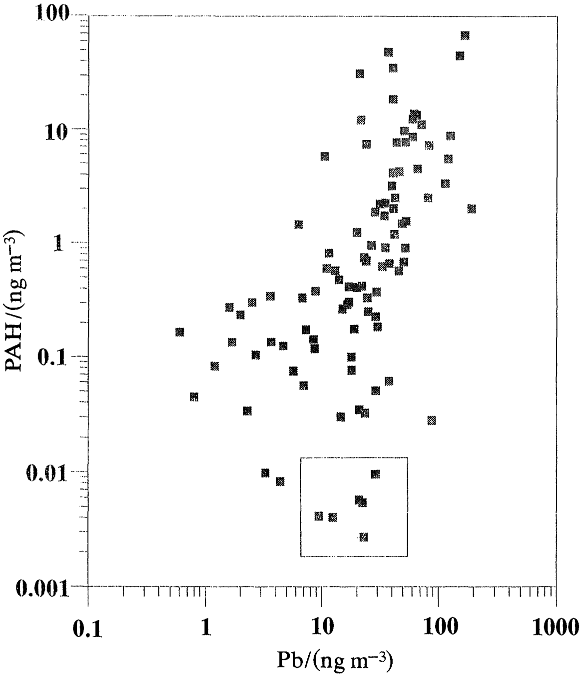

Figure 3. The relationship between total PAH and Pb in North Sea aerosols. Values in the box are possibly rain affected $r = 0.5$. After Preston *et al.* (1992).

those derived from petrol. However, Preston *et al.* (1992) suggested that changes in the relationship may be a useful indicator for the assessment of the future impact of changes in the patterns of fossil fuel on marine systems.

4. Nitrogen species and nutrients

Ottley & Harrison (1992*b*) provided data on the spatial distribution and particle size of some inorganic nitrogen, sulphur and chlorine species over the North Sea. The spatial distribution patterns showed a remarkable consistency, with the highest concentrations being found around the coast in the southern sectors of the sea where the industrial and agricultural activity is highest. The authors also investigated the chemical transformations of the aerosols and gases, and their interactions with the sea salt aerosol. Their conclusions may be summarized as follows. (i) Aerosol chloride loss is greatest over the more polluted regions of the North Sea; (ii) the concentration products of NH_3 with HNO_3 and HCl appear to be insufficient to sustain the existence of NH_4NO_3 and NH_4Cl; (iii) nitrate is associated primarily with larger particles as surface coatings on the marine aerosol.

A total of 70 filter-pack aerosol samples were analysed for nitrate, nitric acid, ammonia and ammonium, and 59 rainwater samples were analysed for nitrate, nitrite, ammonium and dissolved organic nitrogen (DON) by the UE and UEA groups. The techniques used, and the data obtained have been described by Rendell *et al.* (1992). The data-set reported by these authors represents the first year-long assessment of atmospheric nitrogen inputs to the southern North Sea based on samples collected at sea. There is considerable spatial and temporal variability in the concentration ranges for both the aerosol (table 6*a*) and the rainwater (table 6*b*)

Table 6. *Nitrogen species in the North Sea atmosphere*

(*a*) Results of the analyses for gaseous and aerosol species; nd, not detected.

	arithmetic mean nmol m^{-3}	range nmol m^{-3}	s.d./(nmol m^{-3})
HNO_3	34.9	1.0–363.1	60.8
NO_3^-	55.0	3.5–562.9	74.5
NH_3	21.8	nd–147.6	21.8
NH_4^+	92.2	nd–933.2	128.9

(*b*) Results of rainwater analyses

	volume-weighted mean/µM	range/µM	mean blank/µM	analytical uncertainty (1 s.d.)
NO_3^-	54.7	5.0–335.3	2.8	±3
NH_4^+	37.1	1.3–516.9	1.0	±5
DON	6.3	1.2–14.4	0.3	±3.6 *µ*M

(*c*) Atmospheric deposition of nitrogen species to the southern North Sea (defined as the area south of 56° N, calculated from Davies (1982) to be 2.3 ± 10^5 km^2; units; 10^3 t(N) a^{-1}.

	HNO_3–N	NO_3^-–N	NH_3–N[a]	NH_4^+–N	DON–N	total N
dry deposition	20.0	44.7	14.9	22.2	—	101.8
wet deposition	—	70.5	—	47.8	8.1	126.4
total deposition	20.0	115.2	14.9	70.0	8.1	228.2

[a] Upper limit value for NH_3.

(*d*) Nitrogen inputs to the whole North Sea

	nitrogen input (10^3 t(N) a^{-1})	(%)
North Atlantic inflow	7000[a]	75
English Channel	705[a]	8
run-off	1073[a]	12
atmosphere	412[b]	4
direct discharges and dumping	129[a]	1

[a] Nelissen & Stefels (1988) and references therein.
[b] Present study.

samples, which can span more than two order of magnitude. An assessment was made of the 'dry' and 'wet' deposition of nitrogen species to the southern North Sea. For 'dry' deposition the concentrations of aerosol and gaseous species were obtained for 1° latitude × 1° longitude grid squares. Fluxes were derived for each square, and these were summed to provide flux data for the southern North Sea. In many earlier studies, estimates of the 'wet' deposition flux used either model predictions, or data extrapolated from a few localities, to determine the amount of precipitation. In contrast, Rendell *et al.* (1991) used a precipitation estimate based on actual rainwater collections made on a series of oil and gas platforms in the North Sea. These were combined with the concentrations of the nitrogen species determined from the shipboard-collected rainwater samples to make an estimate of the 'wet' fluxes.

Data for both the 'wet' and 'dry' atmospheric deposition fluxes of the nitrogen species to the southern North Sea are summarized in table 6*c*. It can be seen from this table that although 'wet' deposition exceeds 'dry' deposition the two fluxes are of the same order of magnitude, suggesting that the efficiency of the 'wet' removal processes in matched by the high surface reactivity of some nitrogen species, and that oxidized and reduced forms of nitrogen are of approximately equal importance. Nitrogen inputs to the northern North Sea were also estimated, using an indirect assessment, and the total-N input to the whole North Sea is compared to that from other sources in table 6*d*. It is apparent from this table that in terms of gross inputs, the nitrogen budget is dominated by the North Atlantic inflow (75% of the total). However, the atmospheric input makes up *ca*. 25% of the terrestrial inputs; a figure which may be higher when estuarine processes are taken into account. Furthermore, the mean annual inputs disguise spatial and temporal variations, and the effects of seasonality and remoteness from estuarine influence suggest that during the growing season, when primary production in the North Sea can be nutrient-limited, the atmosphere may provide the dominant external source of nitrogen in stratified areas remote from the coasts.

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Discussion

G. E. Millward (*University of Plymouth, U.K.*). What fraction of the trace metals in the North Sea atmospheric aerosol are soluble in seawater? I note that the distributions for lead in atmospheric aerosols were compared to dissolved lead in the water. What is the atmospheric contribution to the dissolved phase in seawater?

R. Chester. Preliminary experimental data reveal that *ca.* 60% of the total Pb in the North Sea aerosol is soluble in sea water following deposition to the sea surface via the ‘dry’ mode. Assuming that the total Pb in North Sea rainwater is in a soluble form (see text) a recalculation of the data in table 4*c* indicates that the dissolved Pb flux to the North Sea lies in the range *ca.* 900–1500 t a^{-1}; this may be compared to the total fluxes from fluvial inputs (*ca.* 920–980 t a^{-1}) and discharges and dumping (2470 t a^{-1}).

J. H. Simpson (*University College of North Wales, U.K.*). The pie diagram for nitrate inputs to the North Sea illustrated in the presentation showed a dominant contribution of *ca.* 75% of the total nitrate budget from the Atlantic inflow. On what basis was this value estimated, and is it relevant to the nutrient balance in the southern North Sea? I take it that the other budget contributions are now reasonably well known.

D. J. Hydes (*Institute of Oceanographic Sciences, Wormley, U.K.*). The issue of the magnitude of the Atlantic nutrient input to the North Sea is clearly controversial and worthy of further study. The data of Nelissen & Stefels do serve to illustrate the potential importance of this Atlantic flux; however, the large uncertainties in the values must be recognized.