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The atmospheric input of nitrogen species to the North Sea

By ANDREW R. RENDELL[1], CHRISTOPHER J. OTTLEY[2], TIMOTHY D. JICKELLS[1] and ROY M. HARRISON[3], [1]*School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK*; [2]*Department of Environmental Science, University of Lancaster, Lancaster, LA1 4YQ, UK*; [3]*School of Biological Sciences, University of Birmingham, Birmingham, B15 2TT, UK*

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ABSTRACT

An assessment of atmospheric inputs of nitrogen to the southern North Sea (south of 56° N) has been made following a series of research cruises between August 1988 and October 1989, during which wet and dry sampling for aerosol and gaseous species was undertaken. Wet and dry deposition appear to contribute approximately equally to total deposition, yielding fluxes of 126×10^3 t N a^{-1} and 102×10^3 t N a^{-1}, respectively. A tentative assessment for the northern North Sea has been made based on extrapolation from data generated here and from coastal sites. When combined with fluxes calculated for the southern area, the total atmospheric deposition of nitrogen to the whole North Sea is estimated to be 412×10^3 t a^{-1}. In terms of gross nitrogen inputs to the North Sea, the contribution from the atmosphere is relatively minor, the budget being dominated by the influence of the North Atlantic inflow. However, it does represent at least 26% of the terrestrial input. Furthermore, the effects of both seasonality in inputs and remoteness from estuarine influence suggest that during the growing season, when primary production in the North Sea is often nutrient limited, the atmosphere may provide the dominant source of nitrogen in stratified areas away from the coast, and at a time when the long-term trend in European emissions of NH_3 and NO_x to the atmosphere is upward.

1. Introduction

Algal primary production in marine waters is controlled by both the supply of nutrients (mainly nitrogen, phosphorus and silicon) and other factors such as temperature and light availability. In coastal waters, external sources of nutrients become very important and include direct discharges, estuarine plumes and the atmosphere. Increases in nutrient inputs to the North Sea estimated from riverine concentrations have been well documented in recent years (e.g., van Bennekom and Salomons, 1981, for the Rhine, the river with the largest discharge to the North Sea), but the importance of the atmosphere as a source of nutrients, particularly to the open North Sea during the growing season, is to date poorly known. Work undertaken in this laboratory has demonstrated that atmospheric inputs of phosphorus and silicon to the North Sea are minor, probably because of their limited natural and anthropogenic atmospheric emissions. By contrast, global and regional nitrogen cycles have been significantly perturbed, greatly enhancing atmospheric nitrogen deposition, particularly since the gas phase chemistry of nitrogen allows efficient atmospheric emission and transport (Brimblecombe and Stedman, 1982; Duce et al., 1991; Galloway et al., 1985).

Best estimates, based on extrapolation from a single coastal site, have suggested that, on an annual basis, the atmospheric input of nitrogen to the North Sea amounts to 40% of the input from estuaries (QSR, 1987), but no direct assessments have been made. Wet deposition, in particular, could well be important in areas remote from estuarine influence, through providing a pulse of nutrients to the photic zone, and by enhancing water column stability. Such inputs could increase primary production and possibly cause nuisance algal blooms.

The visible, economic and environmental impact in recent years of algal blooms and eutrophication has given cause for concern that

the frequency, intensity and duration of such conditions in the North Sea may have been increasing in response to rising anthropogenic inputs of nutrients. The North Sea is naturally subject to conditions which encourage rapid algal growth, and as such it may be particularly sensitive to additional nutrient inputs (Brockmann et al., 1988). During the growing season, blooms can occur at any time through disruption of stratification, at frontal zones, or in coastal areas, where nutrients become available to phytoplankton in the photic zone. Otherwise, and particularly away from the coast, phytoplankton growth after the initial spring bloom will be largely controlled by nutrient regeneration processes (Brockmann et al., 1988) and perhaps inputs from the atmosphere.

Here, we report results from the first long-term study of atmospheric inputs to the southern North Sea conducted at sea and including both wet and dry deposition of aerosol and gaseous species. Attempts are also made to extend the flux estimates to the whole North Sea. These flux estimates are compared to other major inputs in order to assess the significance of the atmospheric input.

1.1. Sources and fates of some nitrogen species in the atmosphere

The dominant species of nitrogen relevant to the present study are the gases HNO_3 and NH_3, and the aerosol species NH_4^+ and NO_3^-. Atmospheric ammonia sources are predominantly associated with livestock wastes, with lesser contributions from fertilizer production and application (Buijsman et al., 1987). Ammonia is the primary neutralising agent for acidic species present in the atmosphere, and a substantial fraction of the upward ammonia flux is neutralised in this way (ApSimon et al., 1987; Asman and Janssen, 1987). Ammonium sulphates are usually the most abundant ammonium salts in the atmosphere, and once formed they are relatively involatile, contrasting with ammonium chloride and ammonium nitrate which are both dissociable in the reverse of their formation reactions:

$$NH_4Cl\ (\text{aerosol}) \rightleftharpoons NH_3\ (\text{gas}) + HCl\ (\text{gas})$$

$$NH_4NO_3\ (\text{aerosol}) \rightleftharpoons NH_3\ (\text{gas}) + HNO_3\ (\text{gas})$$

Over the North Sea, remoteness from sources and efficient dry deposition deplete HNO_3, HCl and NH_3, resulting in disequilibrium and gradual dissociation of ammonium chloride and ammonium nitrate (Ottley and Harrison, 1992).

The precursors of HNO_3 in the atmosphere are the oxides of nitrogen NO and NO_2. High-temperature ($>1000°C$) combustion processes promote the oxidation of atmospheric molecular nitrogen to nitric oxide (NO) which, in most ambient conditions, is rapidly converted to nitrogen dioxide (NO_2) in the presence of ozone (Elsom, 1987; Brimblecombe, 1986; Altshuller, 1956). During daylight hours, the formation of nitric acid from the oxidation of NO_2 by the OH radical limits the atmospheric lifetime of NO_2 to approximately one day. This implies that the generation of HNO_3 will occur relatively close to the emission source of NO (Finlayson-Pitts and Pitts, 1986).

Over the North Sea, the reaction of atmospheric sulphuric and nitric acids on sea-salt aerosols can displace hydrochloric acid and generate sodium sulphate and sodium nitrate coatings on the aerosols (Bruynseels et al., 1988). This effect is most pronounced on the aerosol size fraction presenting the greatest surface area to atmospheric acids. For the North Sea, this appears to be the 8–20 μm particle size range (Ottley and Harrison, 1992). Due to its low volatility under atmospheric conditions, the formation of sodium nitrate may then be considered an effective chemical sink for atmospheric nitric acid.

Both dry and wet deposition are important processes by which the nitrogen species discussed here are removed from the atmosphere. For marine areas, dry deposition of gases is controlled by factors including chemical reactivity, gas solubility, the concentration gradient across the air-sea interface, and removal in the aqueous phase (e.g., biological uptake). Important parameters controlling the dry deposition of particles include atmospheric concentration, particle size, wind speed, and scavenging of material by sea-spray (Slinn and Slinn, 1980; Williams, 1982). Removal of gases and aerosols by wet deposition may be from both in-cloud scavenging and below-cloud washout. For gaseous species, the rain-drop concentration is strongly influenced by equilibrium processes operating between the rain-drop and the surrounding air.

In addition to the inorganic nitrogen species so far discussed, attempts were made to determine

the concentration of dissolved organic nitrogen (DON) in rain. The relative importance of DON in a study concerned with assessing atmospheric nutrient inputs to the North Sea lies with its potential for biological uptake, which is somewhat uncertain, though some of the organic pool in marine waters is thought to be labile (Jackson and Williams, 1985). The sources of atmospheric organic nitrogen are similarly uncertain, and may be marine, terrestrial and anthropogenic. However, the production of amine nitrogen is known to be associated with metabolism and the degradation of living organisms (Gorzelska and Galloway, 1990, and references therein), and as such, this group of organic nitrogen compounds, at least, will probably have both marine and terrestrial sources.

2. Sampling

Sampling was undertaken aboard RRS Challenger for two weeks each month between August 1988 and October 1989 as part of the

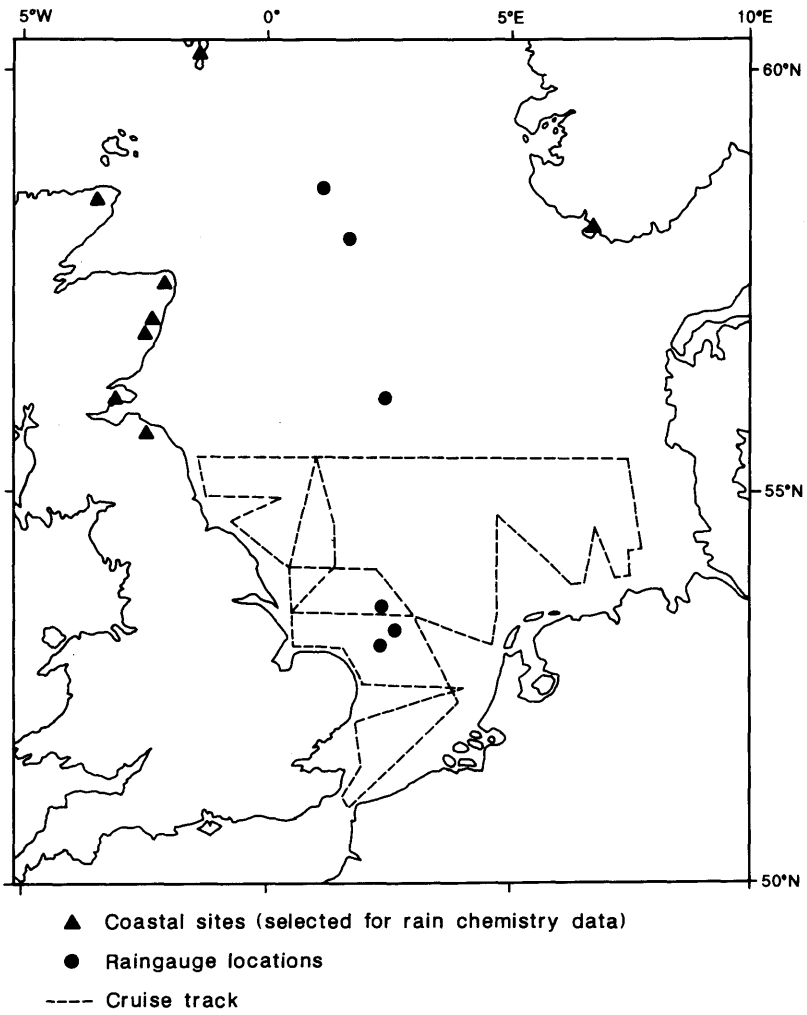

Fig. 1. The North Sea, showing the cruise track, the locations of the raingauges, and the sites selected for rain chemistry data.

NERC-funded North Sea Project. Each two week cruise nominally followed the same pre-defined cruise track, deviations only resulting from adverse weather conditions or time restraints. This allowed for good spatial and temporal coverage of the southern North Sea area up to 55°30′N (Fig. 1).

The equipment used to sample aerosol and gaseous species has been described in detail elsewhere (Ottley and Harrison, 1992, and references therein). Briefly, 3-stage filter packs, comprising an arrangement of Teflon™, nylon and phosphoric acid impregnated Whatman™ 41 filters, were deployed inverted above the ship's bow deck at a height of approximately 10 m above sea level. These were operational between February and October 1989. On a later cruise in May 1990, a May "Ultimate" cascade impactor (May, 1975) located nearby and operating isokinetically at 20 l min^{-1} (Vawda et al., 1989), generated d_{50} aerosol size fractions of 20, 8, 4, 2, 1 and 0.5 μm, supplemented by a 0.5 μm Teflon™ back-up filter. All sampling was only undertaken during suitable weather conditions and when the relative wind direction on board was such that there was minimal risk of shipborne contamination (particularly from the smoke stack).

Rain was collected in 280 mm (internal diameter) polypropylene funnels fitted with 500 ml low-density polyethylene bottles. These assemblages were deployed in pairs; one suitably prepared for the determination of trace metal species, involving a rigorous acid-washing routine (results to be presented elsewhere), and the other, cleaned using a 5% solution of Decon™ 90, followed by thorough rinsing in high-purity deionised water, for the determination of major ions. Collecting rain at sea poses very special problems. There is a tendency for it to be associated with bad weather and therefore the avoidance of excessive sea-spray can be difficult. The ship itself also provides potential sources of contamination, particularly from the smoke stack and the rigging. To reduce these to a minimum, collectors were deployed in exposed sites above the port and starboard bridge wings, and forward of the ship's funnels. Rain was then collected on an event basis (i.e., collectors were opened and closed manually immediately preceding and following a rain event), during reasonable weather conditions, and on the windward side when the relative wind direction on board was favourable (Galloway et al., 1983).

Sample processing on board employed standard clean techniques and the use of a class 100 laminar flow hood in the ship's laboratories. Filter samples were refrigerated and analysed within one week of arriving back at the base laboratory. Rain samples were immediately deep-frozen at −15°C and stored frozen whilst awaiting analysis.

3. Analysis

Following desorption, filter nitrate and nitric acid were determined by ion chromatography (Dionex 2000i/SP) while analyses for ammonia and ammonium employed a fluorescence technique (Ottley and Harrison, 1992; Rapsomanikis et al., 1988).

Rain samples were analysed for nitrate by ion chromatography (Dionex 4000i), nitrite using a sulfanilamide-NEDA colorimetric method, and ammonium using a phenol-hypochlorite colorimetric method (Parsons et al., 1984). DON was determined indirectly on un-filtered samples using a photo-oxidation (UV) method similar to that employed by Walsh (1989). The DON concentration was defined as the difference between the total dissolved inorganic nitrogen fraction (nitrate, nitrite and ammonium) before and after irradiation. It is not possible to be certain that all relevant species of organic nitrogen are measured by this technique, though the study by Walsh (1989) suggests that it is likely.

Analytical detection limits (defined as three standard deviations on replicate determinations of the blank) are listed in Table 1.

Table 1. *Analytical detection limits (defined as three standard deviations on replicate determinations of the blank)*

	Particulates (nmol m^{-3})	Gaseous species (nmol m^{-3})	Rain (μM)
HNO_3		0.11	
NO_3^-	0.05		0.16
NO_2^-			<0.01
NH_3		0.86	
NH_4^+	1.89		0.52

4. Results

A total of 70 filter-pack samples and 70 rain samples were collected during the cruise programme. Of the rain samples, 11 were excluded from the analyses due to either insufficient volume or unacceptable sea spray contamination (defined as a sodium concentration equal to or greater than 10% that of seawater). A further 5 samples were only of sufficient volume to analyse for nitrate. Attempts to assess DON concentrations were made on the 33 samples of the largest volumes. Tables 2, 3 detail the results of the analyses.

The need for a large data set in order to derive meaningful average concentrations is illustrated by the observed ranges in concentration for all the species reported here, which sometimes span more than two orders of magnitude. This spatial and temporal variability is primarily a function of regional and seasonal variation in source strength (e.g., ApSimon et al., 1987) coupled with the influence of various meteorological factors (e.g., Lindberg, 1982). For example, air masses arriving in the North Sea, having passed over the intensively farmed and industrial regions of southern Britain or Europe, will typically exhibit greater concentrations of anthropogenic species than would air masses arriving from the north (Ottley and Harrison, 1992; Chester and Bradshaw, 1991; Yaaqub et al., 1991). The chemical character of such air masses is further affected during their passage by dispersal processes and the frequency, intensity and duration of precipitation events, which also show a relationship to air mass trajectory (e.g., Yaaqub et al., 1991).

The analytical uncertainty associated with the filter analyses was less than 5% of the determined concentrations. Of greater potential significance are possible uncertainties introduced with the choice of sampling technique. Ammonium salt volatilization from the Teflon™ filter within the filter pack may yield enhanced levels of HNO_3 on the nylon filter and NH_3 on the Whatman™ 41 filter. Likewise, NH_3 may be neutralised by previously collected acids upon the nylon filter. However, during the cruise programme, low temperatures and high humidities together with the low concentrations of volatile ammonium salts present in the North Sea atmosphere (Ottley and Harrison, 1992) makes this source of uncertainty negligible. Work in coastal regions (Schwickowski et al., 1988) and terrestrial sites (Harrison and Kitto, 1990) suggest that gaseous species may be overestimated by around 10–15% by this volatilisation process. In the case of ammonia collection on the nylon filter, this may be corrected by summing the ammonia concentration obtained by both the nylon and Whatman™ impregnated filters to give total atmospheric ammonia, possibly incurring the small error detailed above. The interference from reaction of gaseous HNO_3 with particulate NaCl on the Teflon™ filter is potentially more important. However, the data for HNO_3, HCl and aerosol chloride loss reported by Ottley and Harrison (1992) indicate that very little artefact conversion of NaCl to HCl can be occurring by this mechanism, and that the filter pack data reliably represent the true atmospheric composition. This artefact is also unlikely to occur in the impactor where contact between gases and collected particles is less intimate; indeed, the particulate nitrate size distribution shows little on the first impactor stage. The blank contribution to each sample was generally minimal and only became important where the air masses sampled were northerly in origin. In this case, the blank contribution may be up to 10% of the determined filter concentrations.

Table 2. *Results of the analyses for gaseous and aerosol species*

	Arithmetic mean (μmol m^{-3})	Range (μmol m^{-3})	Standard deviation (μmol 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	bd–147.6	21.8
NH_4^+	92.2	bd–933.2	128.9

bd: below detection.

Table 3. *Results of rainwater analyses*

	Volume-weighted mean (μM)	Range (μM)	Mean blank (μM)	Analytical uncertainty (1sd)
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[a)]	1.2– 14.4[a)]	0.3	±3.6 μM[a)]

[a)] Computed using positive values for DON only, see text.

Full procedural blanks performed on the rain sampling equipment gave concentrations for NO_3^- and NH_4^+ which were on average less than 10% of the sample concentrations. However, blanks were only significant for clean samples of small volume. Accounting for the associated blank in all samples makes a trivial contribution to the volume weighted mean, having an overall effect of less than 2%. The blanks for both NO_3^- and NH_4^+ are therefore subsequently ignored.

Likewise, the DON blank is insignificant when compared to the mean analytical uncertainty, and is therefore hereinafter disregarded. Since DON was determined as the difference between total dissolved inorganic nitrogen before and after irradiation, the associated analytical uncertainty will be controlled by the propagation of errors arising from the contributing analyses. Consequently its size will be a function of total dissolved inorganic nitrogen rather than DON concentration. It is therefore more meaningful to express the mean analytical uncertainty as a concentration rather than a percentage.

With such large uncertainties and the relatively small contribution DON makes to the total dissolved nitrogen concentration, a number of negative values for DON might be expected. However, in 5 samples DON is more negative than can be explained by considering the associated uncertainties (assuming zero DON and a 99% confidence interval). The reason for this is uncertain, but it is not thought to be a problem of contamination or to arise from applying the analytical technique. The photo-reduction of NO_3^- to NO_2^- in seawater at rates of around 5% per day has been reported by Zafiriou and True (1979b), with possible further reduction of NO_2^- to NO (Zafiriou and True, 1979a). Assuming that organic material may sometimes be present in rain at levels sufficient to enhance these photochemical reactions (Spokes, 1991), this process, which would probably be much faster under a UV lamp, might explain the large dissolved nitrogen deficit observed for a few samples post-irradiation.

Clearly, this method for determining DON in rainwater needs, at best, refining, if it is appropriate at all. But it may at least have indicated the importance of DON relative to other dissolved nitrogen species in North Sea rain. Rain samples collected in the eastern Atlantic and analysed in this laboratory for DON using the same method do not show the same tendency for occasional high negative DON concentrations, and results suggest that the mean DON concentration reported here (determined from the 22 samples showing positive values) may be slightly under-estimated (assuming a common source). However, it is possible that the computed DON concentrations may include particulate organic nitrogen and some unreactive dissolved inorganic nitrogen, such as ammonium adsorbed on particles, which can be released during irradiation (Walsh, 1989).

The uncertainty in both the DON results and the extent to which DON is labile means that the inclusion of DON in subsequent budget calculations must be tentative. However, it makes a relatively small contribution and so its inclusion is unlikely to compromise any conclusions reached.

Nitrite in North Sea rain was found to be of relatively minor importance, with a mean concentration of less than 0.1 μM. Its contribution in budget calculations is therefore subsequently ignored.

5. Discussion

5.1. *Dry deposition*

The dry deposition flux, F_D ($\mu g\ m^{-2}\ s^{-1}$), of material to a surface can be calculated from its atmospheric concentration, C_a ($\mu g\ m^{-3}$), and deposition velocity, V_d ($m\ s^{-1}$), such that

$$F_D = V_d C_a.$$

The deposition velocity for aerosols is controlled largely by the particle size distribution and meteorological factors. A mass weighting technique is recognised as the best interpretation of the dry deposition velocity from atmospheric concentrations and the particle size distribution (Arimoto et al., 1985; Baeyens et al., 1990; Dulac et al., 1989), from which it may be demonstrated that the largest aerosol particles may dominate the dry deposition flux despite their minor contribution to total atmospheric mass. The sampling equipment used in this investigation, as described in Ottley and Harrison (1992), has excellent collection characteristics for the large aerosol up to 50 μm, thus minimising the errors incurred due to poor aspiration efficiency. Using the model of Slinn and Slinn (1980) and a mass weighting technique

Table 4. *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 × 10⁵ km²) (10³ 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, see text.

(Ottley and Harrison, 1992), nitrate and ammonium have dry deposition velocities of 0.63 cm s^{-1} and 0.21 cm s^{-1}, respectively. By far the largest errors are likely to arise from the use of theoretically-derived values of V_d as a function of size, as experimental validation is extremely difficult.

For gaseous species, the model of Hicks and Liss (1976) suggests that for readily water-soluble gases such as HNO_3 and NH_3 the transfer velocity at the air-sea interface is a function of wind speed. At the 10 m reference height used in this study, the transfer velocity is 0.13% of the wind speed for HNO_3, and 0.14% of the wind speed for NH_3. The modal wind speed for the North Sea is Beaufort force 3, or approximately 5 m s^{-1} (van Aalst et al., 1983), generating transfer velocities for HNO_3 of 0.65 cm s^{-1}, and for NH_3, 0.70 cm s^{-1} (Ottley and Harrison, 1992).

For each cruise, individual determinations of the aerosol and gaseous species were assigned to 1° latitude by 1° longitude grid squares according to sampling location. The grid square data was averaged to produce a spatial pattern for the sampling area (Ottley and Harrison, 1992). Deposition fluxes were then derived for each square, which were then summed to produce dry deposition fluxes to the entire southern North Sea (defined as the area south of 56° N). Table 4 details the results. The figure for ammonia should be considered an upper limit, as there is some doubt as to the direction of the ammonia flux in the marine atmosphere. Ammonia is generated in biologically productive waters and may pass into the atmosphere if the atmospheric partial pressure is low. This process has been demonstrated in the remote marine environment (Quinn et al., 1988) but there is uncertainty as to its importance in regions heavily influenced by terrestrial and anthropogenic emissions.

5.2. *Wet deposition*

The wet deposition flux, F_w (g m^{-2} a^{-1}) of a species is similarly the product of its concentration in precipitation, C_P (mg l^{-1} = g m^{-3}), and the precipitation rate, P (m a^{-1}), that is

$$F_w = PC_P.$$

Until now, the precipitation rate for the North Sea has been very poorly constrained, creating a large uncertainty in flux calculations. Estimates have tended to use either model predictions (e.g., Peterson et al., 1989) or extrapolation from measurements made either on a single gas platform off the north Norfolk coast (Cambray et al., 1975), or on a light ship in the southern bight (Baeyens et al., 1990). In order to improve on these estimates, six aerodynamic semi-automatic raingauges (type ARG100, Environmental Measurements Ltd) have been located on oil and gas platforms in the British sector of the North Sea (Fig. 1). Although there have been problems of adequacy in aerial coverage, exposure and reliability, the measurements appear to provide a more reasonable basis for estimating North Sea rainfall than was formerly possible. For the first year of operation, which was contemporaneous with the cruise programme, data from the platform raingauges have been used, together with coastal data, to derive an estimate of southern North Sea rainfall for that period, determined to be 400 mm a^{-1}.

The computed wet deposition fluxes are detailed in Table 4. Both dry and wet deposition appear to contribute approximately equally to the total atmospheric flux suggesting that the efficiency of wet removal processes is matched by the high surface reactivity of certain nitrogen species. However, this conclusion is not supported by estimates of nitrogen deposition to the global

ocean, where wet deposition dominates the atmospheric flux (Duce et al., 1991), which suggests that dry deposition is relatively more important close to emission sources.

5.3. *A comparison of nitrogen inputs to the southern North Sea*

The relative importance of the atmospheric input of nitrogen to the southern North Sea is illustrated in Table 5, which compares inputs from all known major sources. Consideration of gross nitrogen inputs suggests that the contribution from the atmosphere is relatively minor. However, the nature of the North Sea circulation (Nelissen and Stefels, 1988; Reid et al., 1988) means that the central southern North Sea is somewhat isolated from the influence of the North Atlantic inflow, the English Channel and river run-off. Here, therefore, the atmospheric input of nitrogen is of greater significance. The importance of the atmosphere can be further appreciated by considering the effects of seasonality. The nitrogen inputs from rivers (Edwards, 1973), and probably the North Atlantic and English Channel, are at a minimum during the summer months, whereas the atmospheric input is probably at a maximum. European emissions of NO_x to the atmosphere are not strongly seasonal but nevertheless peak in late winter (DOE, 1990; EMEP/MSCW, 1987). However, ammonia emissions are clearly at a maximum during the summer months (ApSimon et al., 1987). It is possible, therefore, that during late spring and summer, when algal primary production in the North Sea appears to be nutrient limited (Hydes and Edmunds, 1989), the dominant source of nitrogen in open, stratified areas will be from the atmosphere.

Table 5. *Nitrogen inputs to the southern North Sea*

	Nitrogen input (10^3 t a^{-1})	(%)
North Atlantic inflow	767[a)]	27
English Channel	705[a)]	25
run-off	1000[a)]	36
atmosphere	228	8
direct discharges and dumping	114[a)]	4

[a)] Nelissen and Stefels 1988, and references therein. (The figure for the atmosphere is derived from this study).

5.4. *Inputs of nitrogen to the northern North Sea*

Unlike the situation in the south, no direct assessment of atmospheric inputs of nitrogen to the northern North Sea has been made in this study. It was therefore necessary to adopt an indirect approach, which will obviously be subject to greater uncertainty.

Dry deposition was estimated by assuming the atmospheric concentration of nitrogen species over the northern North Sea to be half that observed on the northerly east–west track during the cruise programme, as suggested by the models of Asman and Janssen (1987) for ammonia and ammonium, and Peterson et al. (1989) for metallic species. It was also assumed that the particle size distributions in the north are similar to those in the south (Ottley and Harrison, 1992).

Wet deposition was estimated by using available data from remote northern coastal sites (Table 6, Fig. 1). This shows remarkable uniformity, and was therefore simply averaged to provide a concentration estimate. Any anticipated reduction in species concentration in rain with distance from the coast (and therefore sources) due to atmospheric dispersal or deposition processes, is assumed to be offset by a reduction in rainfall, which would provide less of an atmospheric cleansing and sample dilution effect. This assumption is broadly supported in the southern North Sea where the mean concentration of total nitrogen in rain is similar to that observed at coastal sites of eastern Britain (DOE, 1990), despite reduced rainfall at sea.

Table 6. *Volume-weighted mean concentrations of nitrate and ammonium in rain at northern North Sea remote coastal sites*

	Rain (mm)	NO_3^- (μM)	NH_4^+ (μM)	Period
Skreadalen, Norway[2,3]	2194	17	21	1978–1986
Hill of Shurton[2]	1365	27	21	1986–1988
Achanarras[2]	753	20	22	1986–1988
Peterhead[1]	876	29	25	1981–1985
Aberdeen[4]	—	32	16	1987–1988
Glen Dye[2]	1067	32	28	1986–1988
Loch Levan[2]	781	25	28	1986–1988
Whiteadder[1,2]	713	31	34	1981–1988
Mean		27	24	

[1]DOE 1987; [2]DOE 1990; [3]EMEP; [4]Balls 1989.

Table 7. *Nitrogen inputs to the northern North Sea (defined as the area north of 56 °N, calculated from Davies 1982 to be 2.9 × 10⁵ km²)*

	Nitrogen input (10^3 t a^{-1})	(%)
North Atlantic inflow	7000[a)]	96
run-off	73[a)]	1
atmosphere dry	39	3
atmosphere wet	145	
direct discharges and dumping	15[a)]	<1

[a)] Nelissen and Stefels 1988, and references therein.

Northern North Sea rainfall, estimated in a similar way to the estimate derived for the south, was determined to be 700 mm a^{-1}.

Table 7 provides a comparison of nitrogen inputs to the northern North Sea.

The North Atlantic inflow is clearly the overwhelmingly dominant source of nitrogen to the northern North Sea but, as in the southern situation, it is likely to have less of an impact away from the British coast, and during the summer months. Therefore, the atmospheric input, the dominant terrestrial source of nitrogen to the northern North Sea, may well be more significant than gross inputs suggest, and especially in central, nutrient-limited areas during the growing season.

6. Conclusions

Results from the first long-term direct assessment of atmospheric nitrogen inputs to the southern North Sea are combined in Table 8 with an estimate for the northern area, and compared with inputs from other known major sources to provide a budget for the whole North Sea.

Table 8. *Nitrogen inputs to the whole North Sea*

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

[a)] Nelissen and Stefels 1988, and references therein.

The figure for the atmosphere is in close agreement with the assessment made for the North Sea Ministers' Conference (QSR, 1987) which was inferred from land measurements made in south Norway. In terms of gross inputs, the nitrogen budget is dominated by the North Atlantic inflow. However, this estimate is subject to considerable uncertainty; and while the atmospheric input constitutes a minor component in terms of gross inputs, it represents 26% of the terrestrial input. This figure is likely to be a lower limit since inputs estimated from riverine concentrations may be subject to significant reduction due to estuarine processing (e.g., Billen, 1988; Jordan et al., 1991). Furthermore, mean annual inputs hide variations with season and region which create conditions in open North Sea areas where the atmosphere may provide the most significant input of nitrogen during the growing season.

Large areas of the North Sea are particularly sensitive to conditions which promote low oxygen concentrations below the thermocline. An increase in nutrient loading to the nutrient-poor euphotic zone will increase the probability of oxygen depletion and therefore the risk of mass mortality of benthic and pelagic organisms and fish (Brockmann et al., 1988).

In recent years, much attention has been focussed on estuarine nutrient inputs and their impact on the North Sea in terms of eutrophication. However this study has demonstrated that the role of the atmosphere in this regard cannot be over-looked, especially since emissions of nitrogen compounds to the atmosphere have dramatically increased in recent years. Emissions of ammonia have risen by 50% over Europe since 1950, and more than doubled in the Netherlands (ApSimon et al., 1987). Meanwhile, there has been a five-fold increase in NO_x emissions over the same period, although most of that increase occurred prior to around 1980, with some levelling off since then (Pacyna et al., 1991).

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