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Atmospheric input of inorganic nitrogen species to the Kiel Bight

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ABSTRACT: The atmospheric input of inorganic nitrogen species to the Kiel Bight (south-west Baltic Sea) is characterized. This characterization is based on marine precipitation samples collected at Kiel Lighthouse in weekly intervals during a whole year, using wet-only and bulk-sample methods. The temporal patterns of nitrate and ammonium concentrations are highly variable, with less variability during summer. Maximum concentrations were found in winter. The annual precipitation weighted mean concentrations are 124 $\mu mol \cdot dm^{-3}$ for nitrate and 172 $\mu mol \cdot dm^{-3}$ for ammonium. Nitrite concentrations were low, its contribution to wet deposition being thus negligible (on average only 0.3 % of the wet deposition of nitrate plus ammonium). Dry deposition represents approximately one third of the total input of airborne nitrogen species. Wet and dry deposition represent an annual input of around 5000 tons of nitrogen to the Kiel Bight (2571 km^2), being a significant contribution to its total nitrogen content (5900 tons in winter). The hypothesis of a triggering effect of intense nitrogen wet deposition pulses for summer phytoplankton blooms is raised and a possible relationship of phytoplankton patchiness with these deposition patterns to the sea is suggested.

INTRODUCTION

Very little importance was given in the past to the atmospheric input of nitrogen species to the sea. As reviewed by Prado-Fiedler (1988), the relevant nitrogen species carried down by rainfall and dry deposition are nitrate and ammonium ions, both formed by tropospheric reactions from nitrogen oxides and ammonia, respectively. The earliest paper pointing out the relevance of this kind of atmospheric deposition was that of Menzel & Spaeth (1962). They presented evidence that a large fraction of the ammonia occurring in surface waters near Bermuda was contributed by rainfall. In the meantime, a number of papers dealing with deposition of nitrogen species to the ocean have been published elsewhere (see Duce, 1986, for a review). Moreover, it has been recently shown in the North Carolina coastal region that nitrogen-enriched rainfall leads to significant enhancement of marine primary production (Paerl, 1985). The atmospheric input of nitrogen species may therefore account for a sizeable contribution to nutrient levels in the sea. This contribution should be taken into consideration, as it can produce long-term modifications in the patterns and magnitude of primary production and even lead to eutrophication.

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Today, eutrophication is not merely a problem of restricted local interest, but one affecting large areas having limited water exchange with the open ocean, such as the coastal waters of the Eastern United States, the Eastern part of the North Sea and the Baltic among others (IOC, 1988). The importance of eutrophication of the Baltic and more specifically of the Kiel Bight is well recognized, since it is suspected to be the triggering factor for the episodes of intense oxygen depletion observed in the summers of 1981 to 1983 (Gerlach, 1984). The Kiel Bight is the south-west section of the Baltic Sea and forms part of a transit region between the Baltic and the Kattegat, being a relatively isolated and shallow water body surrounded by a series of islands and the Jutland Peninsula. As defined by Babenerd & Gerlach (1986), it comprises an area of 2571 km^2.

On the one hand, the nitrogen load contributed to the Kiel Bight via rivers and land-based discharges is relatively well known (Gerlach, 1986). On the other hand, the knowledge of the load stemming from the atmosphere is poor. Because of the lack of direct measurements of atmospheric nitrogen deposition to the marine area, only estimates by means of extrapolation of land-based wet deposition data have been made (Gerlach, 1984; Babenerd & Zeitzschel, 1985; Gerlach, 1986). The representativeness of land data, when extrapolated to the marine receptor, is still a matter of discussion. In this paper, the annual atmospheric input of inorganic nitrogen species to the Kiel Bight is characterized. This characterization is based on deposition measurements carried out at sea on a weekly basis during a whole year.

MATERIAL AND METHODS

Wet-only precipitation and bulk deposition samples were collected on a weekly basis at the Kiel Lighthouse, which is situated on an artificial concrete island in the Kiel Bight, some 20 km north-east of Kiel. This sampling site, being easily accessible by motorboat during most of the year, allows realistic marine deposition data to be frequently obtained for this part of the Baltic.

An appropriate sampler for wet-only deposition was constructed and operated. The detailed characteristics of this sampler can be found in Prado-Fiedler (1988). The sampler has a PTFE funnel with a collecting area of 109 cm^2. Bulk deposition was collected in a PTFE bottle connected to a funnel similar to that of the wet-only sampler, having a collecting area of 113 cm^2. Both samplers were mounted on the rail of the uppermost platform of the Kiel Lighthouse (30 m above sea level).

Samples were analysed for ammonium and nitrate within 5 hours after retrieval. Aliquots of 1.50 to 3.00 cm^3 and of 0.50 to 3.00 cm^3 (depending on precipitation height) were taken for ammonium and nitrate determinations respectively. Rainfall was also analysed for nitrite during part of the study, if enough sample volume was available. Nitrate was determined by ion chromatography and conductivity detection. Ammonium was measured colorimetrically as ammonia with the indophenol-blue method, adding citrate as indicated by Koroleff (1976), with some minor modifications necessary to cope with the higher concentrations present in rainwater as compared to seawater (for which the original method was developed). Nitrite was determined colorimetrically using the method given by Grasshoff (1983). Each determination was made in triplicate except for nitrite, where, in most cases, no duplicates could be made because of insufficient sample volume. Standard errors of the determinations were $\pm$ 5 % for nitrate and $\pm$ 10 % for

ammonium. The detailed methodology for the different analyses performed is given by Prado-Fiedler (1988).

Wet deposition was computed for each sample as the product of the measured precipitation height multiplied by the concentration of the component of interest. Dry deposition was estimated as the difference between bulk deposition and wet only deposition.

RESULTS

The time-series plots of nitrate and ammonium concentrations in rainwater are presented in Figures 1 and 2. Their most outstanding feature is the highly variable temporal pattern of both concentrations. The difference between the observed maximum and minimum concentrations is as great as a factor 70 for nitrate and a factor 87 for ammonium. This high variability is expressed numerically in Table 1, where the mean, standard deviation and range for nitrate and ammonium concentrations are given. The variability tends to be smaller during summer, with almost constant values for nitrate in June. The maximum nitrate and ammonium concentrations were found in winter. Only 18 determinations of the nitrite concentration in rainwater were carried out due to the large volume of sample required for that purpose. The measured concentrations of nitrite

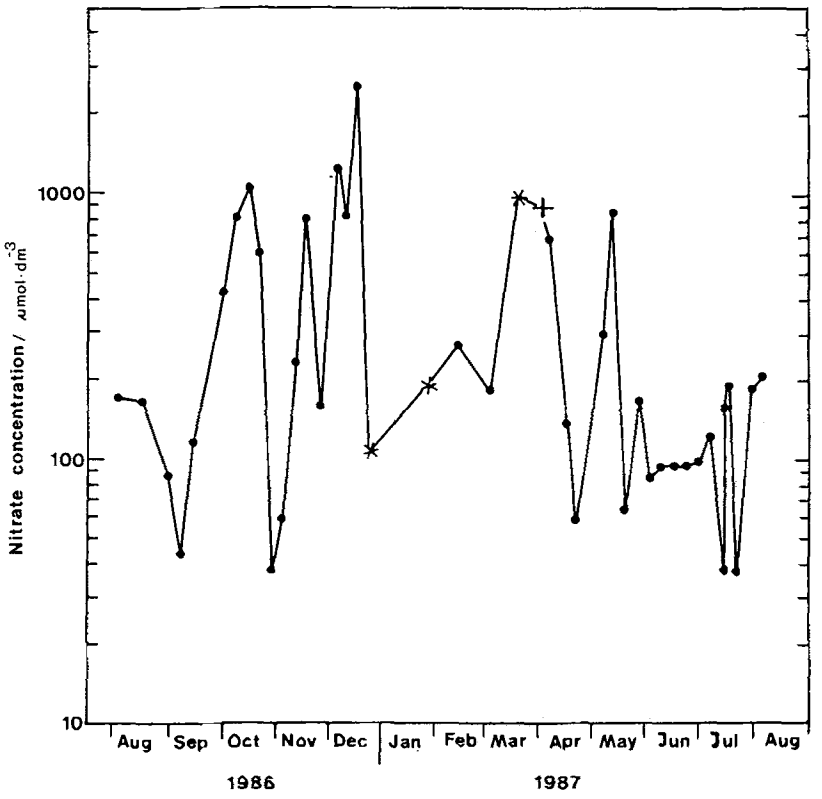

Fig. 1. Time-series plot of the nitrate concentration in precipitation. • rain; * snow; + sleet

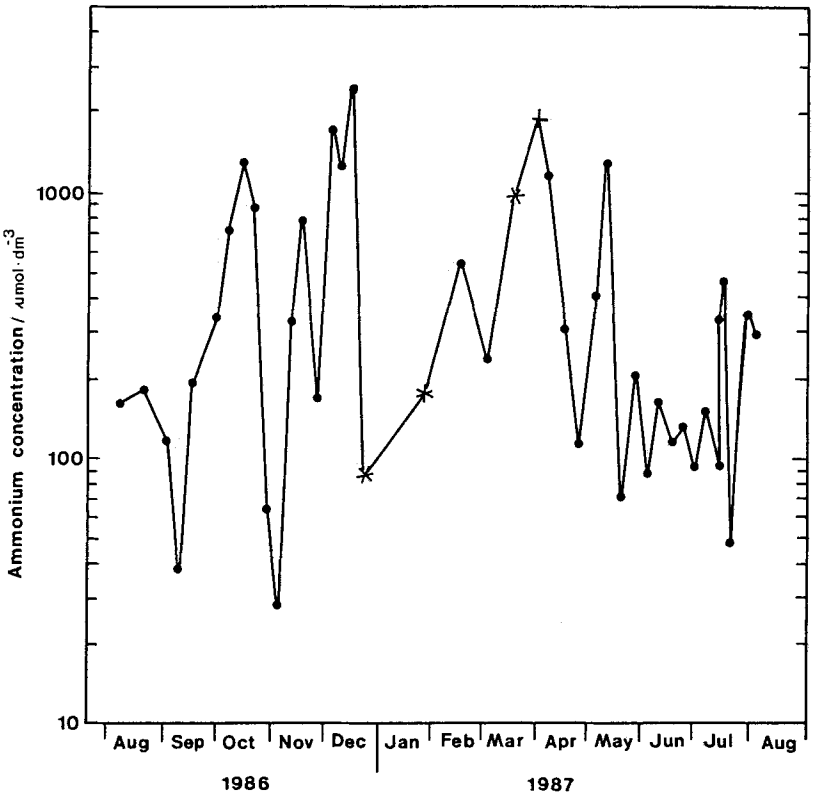

Fig. 2. Time-series plot of the ammonium concentration in precipitation. • rain; * snow; + sleet

Table 1. Statistical summary of nitrate and ammonium concentrations in precipitation (wet-only) collected between July 1986 and August 1987 at Kiel Lighthouse (54° 30'N, 10° 16.5'E)

		Arithmetic mean	Std. dev.	Range	Annual precipitation weighted mean
Nitrate	(μmol · dm^{-3})	376	489	36.6–2588	124
Ammonium	(μmol · dm^{-3})	485	568	27.8–2416	172

were very low, ranging from 0.27 to 1.50 μmol · dm^{-3} with a mean of 0.77 μmol · dm^{-3} and a standard deviation of 0.48 μmol · dm^{-3}.

The weekly wet deposition of nitrate and ammonium are shown in Figures 3 and 4. Wet deposition of both components showed an even greater variability than those exhibited by concentration, reaching a difference of up to a factor 120 between maximum and minimum values. This high variability appears as irregular pulses in the time series-plots. Nevertheless, an oscillatory trend in the deposition pattern can be identified, as shown by moving averages computed over each N = 5 consecutive responses of the time series (see Figures 3 and 4). An increase in the deposition values occurs towards winter

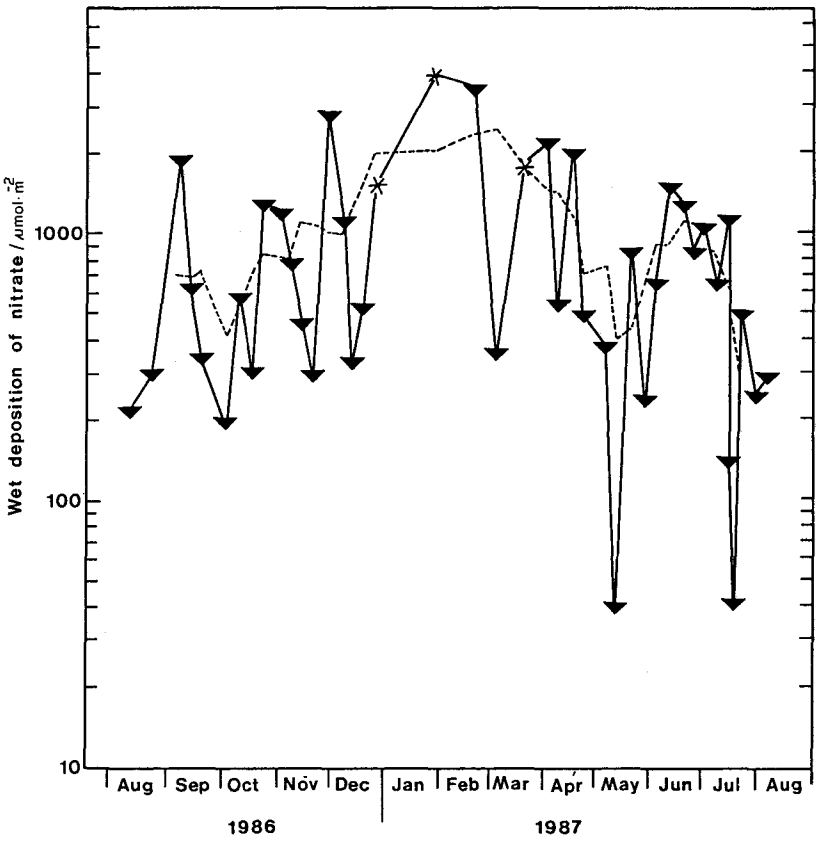

Fig. 3. Time-series plot of the wet deposition of nitrate. The dashed line shows the running average for the deposition values (see text). * snow

with a peak in February–March, followed by a decrease towards spring. A second less intense rise is found towards summer, peaking by end June. The lowest deposition values are found in May and September. Due to its very low concentration, nitrite contribution to wet deposition of nitrogen species is negligible. It represents at most 1.2 % of the total wet deposition of nitrate plus ammonium, being normally less than 0.5 %. The average of 18 determinations is 0.3 %.

The annual wet-only deposition of nitrate and ammonium at Kiel Lighthouse is given in Table 2. These estimates result from the sum of the weekly deposition measured during a whole year. In the case of nitrite the result of the 18 samples are extrapolated to a year. Dry deposition of nitrate and ammonium represent 32 % and 34 %, respectively, of their corresponding total input (wet and dry) at Kiel Lighthouse. Estimates of the weekly dry deposition of nitrogen species ranged from 3 % to 70 % of the total input (nitrate plus ammonium). This variability results from the differences in precipitation height between samples. Estimates of the annual dry deposition of nitrate and ammonium are presented in Table 3. These estimates were calculated by extrapolation of the measurements carried out between February and August 1987.

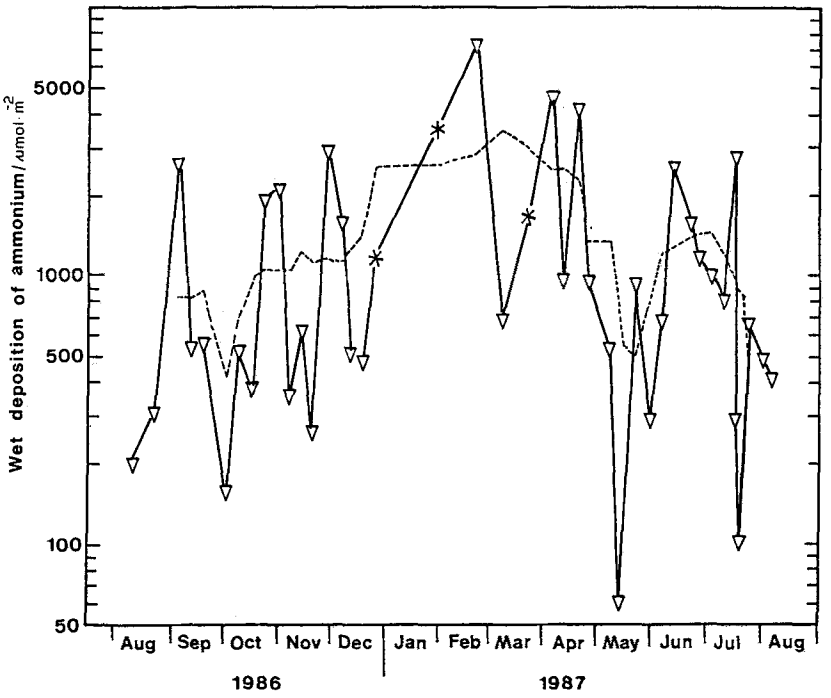

Fig. 4. Time-series plot of the wet deposition of ammonium. The dashed line shows the running average for the deposition values (see text). * snow

Table 2. Annual wet-only deposition of nitrogen species at Kiel Lighthouse (54°30'N, 10°16.5'E). Given as mmol · $m^{-2}a^{-1}$

Species	NO_3^-	NH_4^+	NO_2^-	Total
Flux	40	56	0.3	96

Table 3. Annual dry deposition of nitrogen species at Kiel Lighthouse (54°30'N, 10°16.5'E). Given as mmol · $m^{-2}a^{-1}$

Species	NO_3^-	NH_4^+	Total
Flux	16	28	44

Table 4 presents the estimated data on the atmospheric input of nitrogen species to the Kiel Bight. These estimates were calculated assuming that the annual inputs (wet and dry deposition) measured at the Kiel Lighthouse are representative for the whole Kiel Bight. The calculations were done by multiplying the area of the Kiel Bight stated by Babenerd & Gerlach (1986), i.e. 2571 km^2, by the deposition values for each nitrogen species as given in Tables 2 and 3.

Table 4. Total annual input of atmospheric nitrogen species to the Kiel Bight. Given in tons of nitrogen per year

Species	Wet	Dry	Total
Nitrate	1434	574	2008
Ammonium	2000	1020	3020
Nitrite	10	–	10
Total	3444	1594	5038

DISCUSSION

A great temporal variability of nitrate and ammonium concentrations in rainwater is a consequence of the many random variables associated with precipitation events. Since wet deposition depends on precipitation amount besides concentration in rainwater, the temporal variability of the nitrogen species deposition should be greater than that of concentration.

The higher concentrations of nitrogen species found in precipitation during the winter months can be explained by the occurrence of a combination of meteorologic factors. A stable stratification of the underlying air is characteristic under winter synoptic conditions. This stucture will lead to elevated concentrations during air stagnation. This effect may be enhanced by increased emissions during wintertime. This will be the case of NO_x emissions, since roughly one third originates from power plants and house heating (BMI, 1984). Particulate ammonium and nitrate formation also originate from oil-fired plants (Forrest et al., 1979). The particulate ammonium content in advected air masses during wintertime in the Vienna basin has been observed to rise in a similar way as the sulphate component, being in phase with the particulate nitrate (Ober et al., 1987).

Moreover, the occurrence of low precipitation amounts, as observed in the first part of December 1986 and during March 1987, leads to an increase of the reservoir of nitrogen species available for scavenging (in and below cloud) in the troposphere. This leads to higher concentrations in precipitation.

Following this, the lower and also more uniform concentrations of nitrate and ammonium in rain throughout the summer may be due to reduced emmission rates as well as to a combination of meteorological parameters which are the occurrence of sustained and more intense rainfall and of turbulent mixing that prevents the existence of stable air stratification.

The molar ratio of $NH_4^+ : NO_3^-$ of each precipitation event differs from 1 : 1, being usually – but not always – greater than one. The observed range for these ratios was 0.46 to 2.50. This high variability and the lack of a consistent trend of the ratios (i.e. always greater or smaller than 1) does not allow the estimation of the ammonium deposition by using an average molar ratio and the measured nitrate deposition or vice versa.

Estimates of the atmospheric deposition to the Baltic are sparse consisting in extrapolations from land based stations. Rodhe et al. (1980) give a mean estimate of 400 000 tons/year of nitrogen for the deposition over the whole Baltic; this is equivalent to 70 mmol $\cdot$ $m^{-2}a^{-1}$. Söderlund (1987) points to a similar figure, giving also an estimate for

the different subbasins of the Baltic Sea. His estimate for wet deposition of nitrogen to the Belt Sea (including the Kiel Bight as a part of it) is 1.6 $g \cdot m^{-2}a^{-1}$ of N (i.e. 114 $mmol \cdot m^{-2}a^{-1}$). The lower wet deposition value for the whole Baltic as given by Rodhe et al. (1980) is a necessary consequence of the lower annual amounts of precipitation in the northern parts of the Baltic, as compared to its southern parts. The only estimate available for the Kiel Bight alone is given by Gerlach (1986); his value of 5000 tons N/ year (equivalent to 143 $mmol \cdot m^{-2}a^{-1}$) is based on wet deposition data measured in land stations of Schleswig-Holstein and Denmark.

The measurements carried out during a whole year at Kiel Lighthouse point out that a flux of 5038 tons N/year would characterize the atmospheric input of fixed nitrogen species to the Kiel Bight. The similarity with the estimate given by Gerlach (1986) is only coincidence, since the present study considers also the contribution of dry deposition. When considering only the wet deposition fraction, a figure of 3444 tons of N/year results. This lower value, equivalent to a flux of 96 $mmol \cdot m^{-2-1}$, shows clearly the overestimation resulting from the extrapolation of land based data for wet deposition. The estimate given by Söderlund (1987) may therefore also be up to 20 % too high.

Since the precipitation amount is of overwhelming importance, it is worth knowing whether the sampled year is representative of the average normal conditions in that respect. There are no official precipitation data available for Kiel Lighthouse. The nearest meteorological station for which long records are available is Strande, located south-west of Kiel Lighthouse, at the mouth of the Kiel Fjord. The available information for Strande (Monatlicher Witterungsbericht) shows that the period ranging from July 1986 to August 1987 (sampling at Kiel Lighthouse) had a precipitation excess of 13 % compared to the normal. Data for Schleswig (next nearest meteorological station with long records) show also a similar value of 7 % precipitation excess. Therefore, if this small excess also occurred at Kiel Lighthouse,the estimate given by this study for the wet deposition of nitrogen species to the Kiel Bight may be about 10 % greater than that expected for normal precipitation conditions.

A direct comparison of the absolute amount of precipitation measured at Kiel Lighthouse with data of Strande for the same period shows clearly that less rain falls at sea. The official data for Strande (717 mm) represent more than twice the precipitation measured at Kiel Lighthouse (321 mm). These values are equivalent to a daily precipitation of 2.0 and 0.9 $mm \cdot d^{-1}$, respectively. A similar decrease of precipitation height at sea has been found in deposition measurements of heavy metals to the Kiel Bight using a Buoy system. A three-year average for summer gives a value of 1.1 $mm \cdot d^{-1}$ (Dr. B. Schneider, pers. comm.), which is comparable with the measurements at Kiel Lighthouse.

Dry deposition as estimated here represents almost a third of the total flux of airborne nitrogen species to the Kiel Bight. This estimate is based on the dry deposition of the particulate phase only, since samplers of PTFE material do not absorb HNO_3 (Dasch, 1985). The underestimation resulting from sampling only particulate dry deposition may be of minor significance in the case of ammonia, since marine air and surface seawater seem to be not greatly out of equilibrium with respect to ammonia (Ayers & Gras, 1980; Liss, 1983; Ayers et al., 1984). A different picture can be expected for nitric acid. The model calculations of Levine & Schwartz (1982) suggest that dry deposition and precipitation scavenging are of comparable importance as sink processes for nitric acid vapour. Söderlund (1987), on the basis of literature cited therein, assumes that 40 % of the total

airborne nitrates are in the form of nitric acid over the Baltic Sea. By using this proportion of the yearly average of the measured concentration of total nitrate in air at Kiel Lighthouse ($0.4–9.7 \cdot 10^{-2}$ $\mu mol \cdot m^{-3}$) and assuming a value of 0.01 $m \cdot s^{-1}$ for the total transfer velocity of HNO_3 (Söderlund, 1987), an estimate of up to 12 $mmol \cdot m^{-2}a^{-1}$ results for the dry deposition of nitric acid gas. This figure represents an increment of 27 % of the estimate given in Table 3 for the total dry deposition of nitrogen species. This estimate may be too high if the effective average total transfer velocity for HNO_3 is lower than the maximum value assumed here.

When the discussed factors are taken into account, by reducing the wet deposition burden to that expected for a "normal" year and increasing the estimate for the dry deposited nitrate, a rounded figure of 5000 tons N/year holds for the total input of airborne fixed nitrogen to the Kiel Bight. If this flux is compared with the content of nitrogen of the Kiel Bight in winter (5900 tons; Gerlach, 1986), a residence time of 1.2 years results. This time is comparable to the turnover time for water in the Kiel Bight (1.3 years as calculated from the data given in Gerlach, 1986). Thus, the deposition of fixed nitrogen from the atmosphere represents a significant contribution to the total nitrogen budget of the Kiel Bight.

An interesting fact is the summer rise in the deposition values originating from heavy rainfall (see Figs 3 and 4). By summer, nutrients in the surface layer of the Kiel Bight have been used up by the spring bloom of phytoplankton, and a stable water stratification prevents nutrients rising from the deep layer to renew the nutrient level in the surface layer; the input of water stemming from the Baltic is also weak and its reduced nutrient level lacks importance (Gerlach, 1986). The additional atmospheric input of fixed nitrogen via wet deposition could therefore be a triggering factor for summer blooms of phytoplankton. This is especially true if it is also considered that the wet deposition of atmospherically derived nitrogen species is of episodic nature, in form of short-term pulses. For example, the precipitation registered during the week between 2nd and 9th June 1987 was equivalent to an input of 148 tons of nitrogen, which is a considerable quantity.

Bearing in mind that rain does not fall uniformly along a front system and that marine rains are also usually associated with showers having a typical horizontal cross section of 500 m to 5 km, the intense episodic input of nitrogen species concentrated in a relatively small area may contribute to the formation of a patch of phytoplankton. Hence, the origin of phytoplankton patchiness may be related to the characteristic pattern of precipitation over the sea.

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