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The atmospheric impact on fluxes of nitrogen, POPs and energy in the German Bight

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Summary

The external forcing of the German Bight system is largely due to the atmosphere. Energy fluxes that drive mixing processes and biological productivity, as well as atmospheric nutrient inputs outside the Elbe estuary, are important factors for biomass production. This study is based on the KUSTOS experiments focusing on air-sea exchange with intensive observations of a) radiative fluxes at the surface of the drifting water body; b) atmospheric surface layer parameters determining the mixing conditions in the planetary boundary layer; c) the speciation of atmospheric nitrogen compounds; d) and changes in aerosol and gas composition during transport over sea. These episodic data were complemented by a) synoptic data analysis of water and air temperature, wind, pressure and water vapour pressure over the sea; b) corresponding oceanic data on heat advection and mixed layer depth from an oceanic model driven by observations in the atmosphere; c) computations of the highly variable heat and radiative fluxes with the mesoscale atmospheric model METRAS; d) long-term atmospheric deposition measurements of nutrients in the German Bight; e) investigations of the atmospheric processes responsible for the formation of coarse particulate nitrate by means of a new aerosol submodel in the METRAS transport model. We present detailed seasonal or annual budgets for fluxes of heat, momentum, nitrate, ammonium, persistent organic pollutants. The atmospheric fluxes of heat and chemical matter are compared with load and fluxes in the water column in order to identify when and where the atmospheric impact is relevant and detectable. Spatial and temporal variability is discussed for the fluxes of heat, momentum and nitrogen. From the budgets we identify categories of potential atmospheric impact. Apart from the category "no atmospheric impact" valid e.g. for Cr, As, Ni and phosphate, we identify 4 others: 1) "atmosphere driven": short term, local dominant impact for heat and momentum; 2) "episodic atmospheric impact": long term, local and dominant impact with large fluxes involved for radiation, PCB, Pb; 3) "persistent atmospheric pollutant": long term dominant but regionally indifferent impact for α- and γ-HCH; 4) "steadily perturbing the marine ecosystem": long term, widespread impact superimposed on the dynamic system driven by marine biology for nitrate, ammonium.

Der Einfluss der Atmosphäre auf die Stickstoff-, POP- und Energieumsätze in der Deutschen Bucht (Zusammenfassung)

Die Atmosphäre ist ein wichtiger externer Antrieb für das System Deutsche Bucht. Der Austausch von Impuls und Wärme bestimmt wesentlich die Mischungsvorgänge im Meer und daran gekoppelt die biologische Produktivität, während atmosphärische Nährstoffeinträge insbesondere außerhalb der Elbfahne die Biomasse-Produktion beeinflussen können. Vorgestellt werden Ergebnisse bezüglich des Einflusses von Wärme, Strahlung, Impuls, Stickstoffverbindungen und persistenten organischen Schadstoffen auf die Bilanz dieser Parameter in der Deutschen Bucht. Dazu werden Messungen der KUSTOS-Intensiv-Meßkampagnen sowie langjährige Meßreihen, aber auch Modellergebnisse des Atmosphärenmodells METRAS und des ozeanographischen Deutsche-Bucht - Modells herangezogen. Im Vergleich zeigt sich, daß der Einfluß der Atmosphäre für die Parameter Impuls und Wärme lokal und auf kurzen Zeitskalen zu beschreiben ist. Von eher episodischer Bedeutung sind die atmosphärischen Einträge von Stoffen wie etwa PCB oder Pb und die Strahlungsflüsse. Wegen der langen Verweildauer im System muß für Stoffe wie α- und γ-HCH, aber auch Nitrat und Ammonium, von einer ständigen, über lange Zeit wirkenden, aber regional indifferenten Belastung ausgegangen werden. Die Rolle der atmosphärischen Stickstoffeinträge ist durch ihre Überlagerung über die schnellen biologischen Umsetzungen im Meer nur als eine kleine, wenn auch ständige Störung des marinen Ökosystems zu beschreiben, deren Auswirkungen nicht ausreichend bekannt sind.

1 Introduction

In order to understand the German Bight marine system it is necessary to determine its external forcing. The exchange of matter and energy at the boundaries of the system plays a central role. We seek here an improved understanding of the atmospheric impact on air-sea exchange fluxes. While different atmospheric processes affect the fluxes at the air-sea-interface indirectly, the direct impact of atmospheric fluxes on the mass budgets and the functioning of the marine system is often of higher interest.

By comparing parameters as different as turbulent heat flux and wet nitrogen deposition, we will try to identify basic principles of atmospheric impact on fluxes and, in turn, on the biogeochemical processes in the marine system. With the aim of identifying important links between the atmospheric and the oceanic system we also take a look at the spatial and temporal scales of intensive air-sea interaction processes. The results of measurements and model simulations reported here will be used to understand why and when and to what extent the atmosphere triggers air-sea-exchange fluxes. Considering the limited experimental resources available in the KUSTOS project, the more universal approach of this study, as outlined above, necessitates incorporation of other published work as well. However, where appropriate, this work presents results on air-sea exchange during the central experiments of KUSTOS to further elucidate the system conditions described elsewhere in this volume.

The atmospheric studies within KUSTOS comprised experiments and modelling of nitrogen, acting as major and micronutrients because of their significance for marine productivity. Wet and dry deposition from the atmosphere contributes significantly to the input of natural and anthropogenic substances into the North Sea and is especially important in the open sea because the influence of river discharge decreases with distance from the coast. The Quality Status Report (ANDERSEN et al. [1996]) for the North Sea concluded that the input of nitrate and ammonium via the atmosphere for the entire shelf sea comprised 30 % of the total input. Therefore, quantification of the atmospheric nitrogen fluxes represents an essential input term for German Bight ecosystem analysis and modelling. There is evidence that micronutrient trace elements, especially Fe, Mn, Zn and Cu, enter the North Sea to a considerable extent via the atmospheric pathways (SCHULZ [1993]). The determination of these fluxes is a prerequisite for studying the biogeochemistry of trace elements in the water column and interpreting their distribution pattern in the different compartments of the system.

Fluxes of energy and momentum drive the oceanic circulation and control most of the heat budget. It is well known that the solar radiative influx as well as the heat exchange by evaporation, turbulent sensible heat flux and outgoing longwave radiation dominate the local heating and cooling rates of surface seawater. To allow for a better characterisation, information is needed on scales of years to hours. Several studies of the mean North Sea climate have already been published (e.g. H. J. BULLIG AND P. BINTIG [1954]; H. MARKGRAF, AND P. BINTIG [1956]; R. HÖHN [1971]; C. G. KOREVAAR [1990]). However, no comprehensive monthly, homogeneous, high spatial resolution climatology is available for the North Sea today. In most cases the spatial resolution is coarse, only selected months are shown and the results have not been checked for consistency by numerical models. In the German Bight, the Wadden Sea may provide an extra source/sink of heat, mainly because of tidal changes in the eulitoral area. Heat is stored or released by the mud-flats in a way differing considerably from that of seawater. Wind, temperature and humidity are also determined to a large extent by the regionally variable, mesoscale meteorological phenomena. These considerations led to the development of a model combination to improve the simulation of the interaction on different scales. Measurements analysed and interpolated using the analysis model of LUTHARDT [1985, 1987] have been used to derive a detailed climatology dataset (hereafter abbreviated CD) as well as to supply the basic atmospheric forcing to the Deutsche Bucht model, an oceanographic model developed at the Institute of Oceanography at the University of Hamburg (POHLMANN

[1991]; NITZ [1998]; DICK et al. [this volume]). Hourly tide and sea surface temperature data from the oceanographic model were then used to drive the atmospheric mesoscale model METRAS, which has been developed at the Meteorological Institute of the University of Hamburg (SCHLÜNZEN [1990]; SCHLÜNZEN et al. [1996]). Using this model, energy balance components at the land and sea surfaces as well as the deposition of nitrogen compounds into the North Sea can be calculated in high resolution. The fluxes of momentum and heat were used to provide the fine resolution forcing fields for the oceanographic Deutsche Bucht Model. The forcing data at the lateral open boundaries were supplied by the North Sea model (POHLMANN [1991]), which provides information about the tidal forces and the far field effects.

A general problem in assessing the overall impact of the atmosphere on fluxes at the air-sea-interface is the difficulty of measuring, modeling and extrapolating a highly variable system. Air masses may cross the inner German Bight within hours and weather conditions change dramatically from season to season but may also differ from hour to hour. Precipitation may be a very local phenomenon, and the calculation of a meaningful mean necessitates measurements over several years.

Since we are interested in a link between atmospheric fluxes and processes in the marine system, emphasis will also be put on a selected number of other relevant quantities. These are nitrogen deposition, in both its reduced and oxidised form as has been described above.

2 Results

2.1 Radiation, heat and momentum fluxes

2.1.1 Measured radiative fluxes during the KUSTOS central experiment

Radiation and surface temperatures were measured aboard the research vessel during the campaigns to provide input data for oceanic calculations and as a validation tool for the concurrent modelling. Solar radiation is partially absorbed and transformed into thermal energy at the sea surface. Thermal energy may be redistributed within the mixed layer of the ocean or may lead to latent and sensible heat fluxes into the atmospheric boundary layer. Table 1 shows the measured mean radiative fluxes for the three experiments.

The mean net radiational heating has been positive in all three experiments. Especially in spring and summer, sea surface waters warmed up by day due to incoming radiation, which was not compensated by energy loss during the night. The winter experiment showed a considerably smaller amount of downward terrestrial radiation due to the variations of low clouds and water vapour. Usually the air temperature during winter days is below that of seawater. However, due to ice cover during the winter experiment 1996, the ocean had cooled the atmosphere, and the advection of warmer air led to fog formation.

	KUSTOS 94 Summer	KUSTOS 95 Spring	KUSTOS 96 Winter
Net solar radiation flux	222 ± 68	228 ± 107	75 ± 79
Downward terrestrial radiation flux	343 ± 16	321 ± 23	260 ± 28
Upward terrestrial radiation flux	–401 ± 4	–351 ± 9	–301 ± 2
Net radiation flux	149 ± 42	181 ± 76	31 ± 19

Table 1: Mean radiative fluxes and their standard deviations [W/m^2] during the KUSTOS central experiments measured aboard the research vessel in the German Bight. Terrestrial radiation fluxes correspond to that part of the radiation spectrum which is emitted by the earth surface.

2.1.2 Seasonal and annual radiation and heat budget

Routine meteorological data from 1981–1990 (from the CD) were used to compute mean sensible and latent heat fluxes for the German Bight. The mean annual cycle in the German Bight of the most relevant parameters, air and water temperature as well as humidity are shown in Figure 1. The resulting heat fluxes show a strong dependence on the seasons. This is a complex result of the changing solar energy input and transfer velocities of sensible heat, momentum and water vapour. Latent heat fluxes are generally larger and have a larger amplitude than sensible heat fluxes, because they are affected not only by air-sea gradients of temperature but also by relative humidity. The highest fluxes appear in autumn, when high winds and an unstable marine boundary layer produce large heat and large negative momentum fluxes.

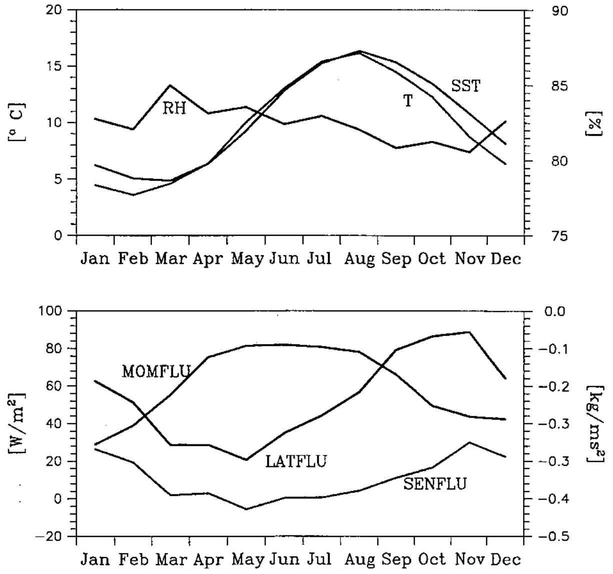

Fig. 1: Mean annual cycle during 1981–1990 of relative humidity (RH in %), air temperature (*T*), sea surface temperature (*SST*), momentum flux (*MOMFLU* in kg/ms^2), latent heat flux (*LTFLU*) and sensible heat flux (*SENFLU*) in the German Bight.

The climatology data have been combined to calculate a summer and winter heat budget individually (Figure 2). The budgeting box dimensions are defined in SÜNDERMANN et al. [this volume]. The difference in the heat content of water masses has been computed against a reference temperature of 0°C. Seasonal longwave and shortwave radiation fluxes were taken from BECKER [1981]. Ocean advective heat fluxes were derived in two ways. Firstly, we used a crude method combining net seawater flow rate data for the German Bight as given by PULS et al. [this volume] and the temperature gradient in the German Bight, which indicates whether the German Bight is a sink or a source of heat to the atmosphere. In winter, we find in the CD a temperature decrease of –0.73 °C/84 km between the chosen western and eastern grid points. In summer, this situation is reversed and seawater temperature rises by +0.37 °C/84 km in the eastern part of the German Bight. North to south gradients are smaller in both seasons. For these we find in winter from south to north –0.36 °C/126 km and in summer +0.26 °C/126 km. German Bight water masses are thus heated in summer while passing by. In winter, warm water is advected into the area by currents and heats up the atmosphere (see Figure 2 for the resulting heat fluxes in each season). This calculation gives a net heat inflow of +0.20 10^{19} J in the winter season and a loss of –0.07 10^{19} J in summer. In a second attempt to estimate the heat budget, we average the hourly heat flux data in the North Sea model (POHLMANN [1991]) for the years 82–96 at the borders of our budgeting box. This provides a more precise estimate because it integrates the fluxes spatially and in time. The result, especially in summer, is 50 % different from what we have calculated above. Net fluxes increase in winter up to +0.25 10^{19} J and in summer up to –0.13 10^{19} J.

For comparison, we provide a simple estimate of advective heat fluxes in the atmosphere. It is based on the climatology data (CD), which show – from west to east – an air temperature difference of –0.78 °C during the winter months and +0.22 °C during summer. The volume of air advected is computed using the mean wind velocity and an atmospheric mixing layer extending up to a pressure level of 850 hPa. From these values we derive the net advective heat flux by atmospheric transport. Because of rapid air mass fluctuations this kind of cal-

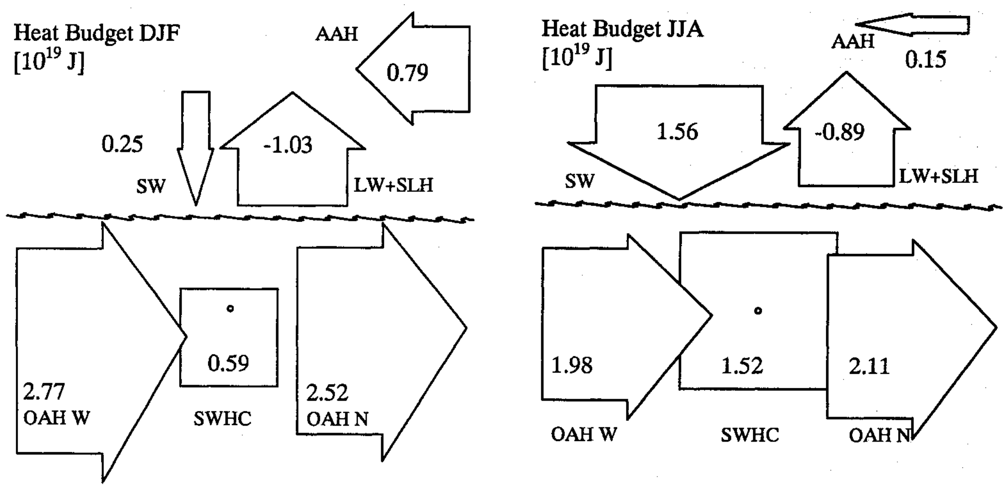

Fig. 2: Heat budget for the German Bight in the winter (December to February DJF) and summer seasons (June to August JJA) derived from Climatology Data and North Sea Model for Ocean heat fluxes (SWHC: Seawater heat content of German Bight water masses; OAHW+N: Heat advected by ocean currents through western box border and Northern box border; AAH: Atmospheric advected heat; SW: Shortwave incoming radiation; LW+SLH: Loss of heat due to longwave radiation, sensible and latent heat fluxes).

culation is more questionable than in the case of oceanic currents. More suitable would be an integration of such fluxes with a climate model. However, since the contribution is rather high in winter, one should put more emphasis on this component in future studies.

An interpretation of the heat content versus the heat fluxes is difficult because the heat content is a relative number. However, the relatively small net amount of heat which is advected by water masses indicates that warming and cooling in the German Bight is mainly controlled locally by the gain and loss processes of radiation and heat exchange at the air-sea-interface. Both in winter and in summer, the atmosphere is the single most important factor for any heat change of the seawater. The threefold increase of heat content in summer corresponds to a mean annual amplitude of seawater temperature of 12 °C (minimum in February/March 4.2 °C, maximum in August 16.2 °C) for the German Bight in the years 1981–1990.

The largest seasonal changes in the budget are linked to solar shortwave energy input. Solar angle but also cloud cover dominate its variability. The limited solar energy input in winter creates a situation where heat can rapidly be removed due to the large latent heat fluxes associated with unstable atmospheric conditions and higher wind speeds. Cooling rates in winter thus are much higher than in summer. Although advection becomes more important in winter, it cannot compensate the reduced solar input.

Since we find that the heat budget is controlled on a local scale, any variability of the radiation and heat fluxes will control the temperature in the upper water layer with a small time delay. It is therefore of interest to analyse the variance of these fluxes. We computed the standard deviation of the fluxes on different temporal scales. Table 2 contains the standard deviation for different data ensembles. The climatology data have been taken from the 12 inner German Bight grid points of the analysis model used to produce the CD to retrieve a meaningful average.

The smallest variability is found between the 10 grid points used in the analysis model, but also when comparing the different years. The small areal variability may be due to the coarse grid resolution of the analysis modell. However, we believe it reflects the rather homogenous sea surface conditions which do not favour the buildup of significant long-term gradients in such a small area.

	Standard Deviation			
	Momentum Flux	Sensible Flux	Latent Flux	Temperature
	[kg m^{-1} s^{-2}]	[W m^{-2}]	[W m^{-2}]	[°C]
Total Variability in CD (N=1440)	0.093	15.3	24.8	4.36
Areal Variability in CD between inner German Bight grid points (N=12)	0.020	1.7	4.8	0.34
Interannual variability CD all year (N=10)	0.015	2.0	3.1	0.66
Variance between mean month 81–90 (N=12)	0.067	10.7	20.4	4.24
Variance between mean season 81–90 (N=4)	0.059	9.7	19.7	3.88
Interannual variability between DJF (N=360)	0.102	18.4	16.6	1.75
Interannual variability between MAM (N=360)	0.059	8.9	12.4	2.39
Interannual variability between JJA (N=360)	0.029	3.7	14.9	1.64
Interannual variability between SON (N=360)	0.077	11.1	16.3	2.10
KUSTOS METRAS simulation 1995	0.096	22.5	43.7	

Table 2: Variability of heat and momentum fluxes and seawater temperature in the German Bight from the Climatology Data CD (1981–1990; 144 months from 10 grid points) and from all hourly METRAS Data during the simulation period in 1995.

The interannual variability of annual averages is less important than that of a given season. The overall seasonal cycle makes up most of the total variability for all evaluated parameters with the exception of that of latent heat fluxes. For both momentum and sensible heat fluxes the interannual variability is remarkably largest for the winter season. This is an indicator that these fluxes are closely coupled to each other.

The METRAS simulation shows that latent heat fluxes have a predominantly short term variability. This is in accordance with the finding in the CD that the interannual variability between seasons does not vary between one season and another. Also the seawater temperature variations are of interest, since they reflect the integral of all heat and radiation fluxes acting at the air-sea interface. While the seasonal amplitude is large, it is of interest to see that the interannual variability for the spring season is largest. It seems that the rapid warming in spring differs substantially from year to year. One could imagine that this variability triggers the onset of the spring bloom. It was shown earlier that the onset of the phytoplankton bloom is linked to wind induced mixing of the surface ocean (DICKSON et al. [1988]).

2.1.3 The impact of the fluxes of radiation and heat on the sea during the second KUSTOS central experiment in spring 1995

The results of the model chain from the analysis model to the oceanographic model and finally to the atmospheric model METRAS and back to the oceanographic model allow an investigation of the variability of the energy fluxes and of the atmospheric influence on water temperature, water currents and salinity content with a high temporal and spatial resolution. Due to the iterative procedure it is possible to investigate the interaction between the atmospheric and oceanographic components in detail. Moreover, the impact of the fine resolution meteorological forcing data on the advective transports of heat in the German Bight can be studied (DICK et al. [this volume]).

Figure 3 shows the time series of the area-averaged METRAS model results for the shortwave radiation balance and the net energy flux between the sea and the atmosphere. The latter is called ocean heat flux hereafter.

The shortwave radiation balance equals the sum of incoming solar radiation and the outgoing shortwave radiation, which is reflected at the soil or sea surface. The reflectivity or albedo of a water surface is strongly dependent on the angle of incidence of the sun. With a high solar elevation and cloudless sky only about 4 % of the incident solar radiation will be reflected, whereas the solar radiation will be reflected almost completely, if the sun is only a few degrees above the horizon. Consequently the shortwave radiation balance describes that part of the solar radiation which penetrates into the sea and will be absorbed in a water layer whose thickness depends on the content of particles and living organisms. Therefore, the shortwave radiation flux into the sea leads to a warming of a rather thin water layer under turbid conditions. The solar radiation penetrating into the seawater plays an essential role with regard to photosynthetic processes in the water column (RADACH AND MOLL [1993]; DOERFFER et al. [submitted]; RICK et al. [submitted]).

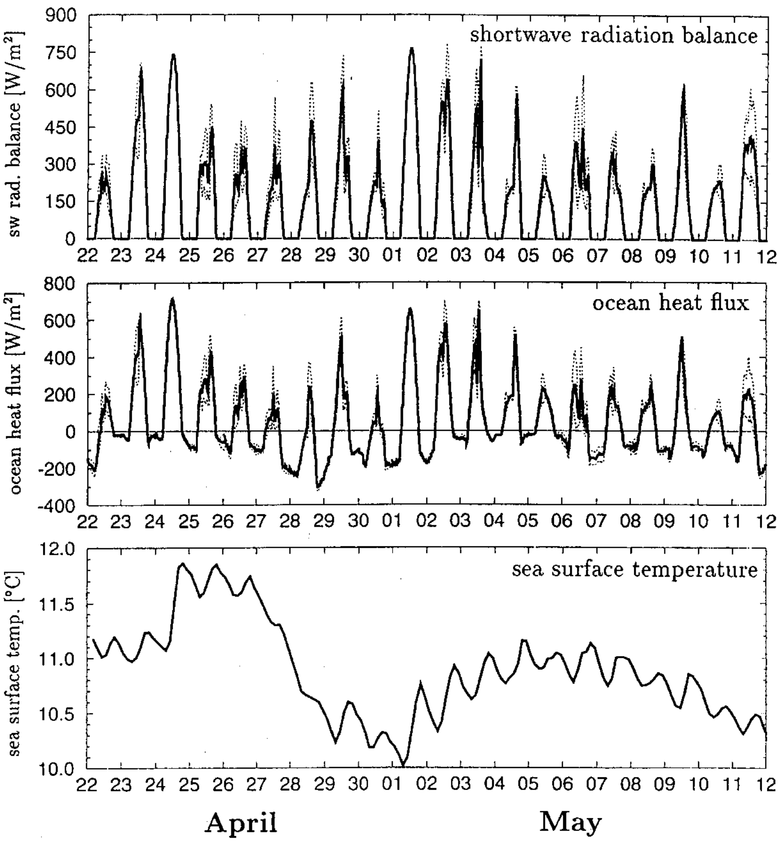

Fig. 3: Time series of the area-averaged METRAS model results for the shortwave radiation balance (a) and the ocean heat flux (b). The dotted lines present the area standard deviation. Also shown is the water temperature of the upper 5 m-layer, averaged over the whole KUSTOS area with respect to time (c).

As can be seen in Figure 3a the shortwave radiation balance is very different from one day to the next. The incoming solar radiation is strongly dependent on the degree of cloudiness, which is characterised by a high spatial and temporal variability. Only on some days with a low cloud cover (24th April and 1st May) is the spatial variability of the shortwave radiation balance very low. On overcast days the shortwave radiation balance is only about 1/3 of the values reached on cloudless days.

The ocean heat flux shown in Figure 3b is calculated as the sum of net radiation flux, sensible and latent heat fluxes. The daily course of the ocean heat flux is largely dominated by the net shortwave radiation flux. The net longwave radiation flux, which contributes to an energy loss of the ocean, is strongly dependent on the cloud cover, too, whereas the fluxes of sensible and latent heat (not shown here) are mainly dominated by the wind velocity and the temperature and moisture difference between the sea surface and the adjacent atmospheric layer.

Figure 3c shows the water temperature of the upper 5 m-layer averaged over the whole KUSTOS area as computed by the oceanographic model. The diurnal variability is obvious, which shows that the input of heat energy is dominated by the shortwave radiation. Advective processes are neglible when we average over the area. High values of shortwave radiation, as on 24 April and on 1 May lead to a considerable increase in sea surface temperature. The day-to-day variation is governed by the composite ocean heat flux and leads to the temperature decrease in the middle and at the end of the episode. The response of the sea surface temperature to the variable energy input from interaction with the atmosphere is very fast and direct. The contribution of changes in vertical mixing efficiency, possibly forced by river run off, could not be determined in our study.

Because of the high heat capacity of water and turbulent mixing in the ocean the temporal changes of the seawater temperature are damped compared to the temperature development in the atmosphere. Hence fluctuations in the sensible and latent heat fluxes are mostly governed by changes in the temperature of the advected air masses. Consequently the turbulent fluxes show firstly a daily variation in the proximity of the coastlines (see Figure 4) due to the advection of heated air in the daytime and cooled air during the night from the land surfaces and secondly an irregular variation resulting from synoptic advection. The last mentioned phenomenon can be seen in Figure 3 on 27 to 29 April, when cold air was advected by strong northerly winds over the warmer sea surface and the high energy loss of the sea due to sensible heat exchange and evaporation overcompensates the energy gain from the shortwave radiation absorption, if the daily means are considered. Nevertheless, despite this extreme event the contribution of the shortwave radiation to the ocean heat flux remained the main factor of the energy balance components controlling the energy exchange between the sea and the atmosphere during the second KUSTOS central experiment (see Table 3).

		Mean	Standard deviation
Momentum flux	[kg/(cm²)]	–0.110	0.096
Shortware net radiation flux	[W/m²]	152.2	192.1
Longware net radiation flux		–41.6	20.7
Net radiation flux		110.6	186.3
Sensible heat flux		9.3	22.5
Latent heat flux		53.9	43.7
Ocean heat flux		47.5	203.2

Table 3: Energy balance components averaged over the German Bight area from the METRAS model output over the time period 22 April 1995 00 CET until 11 May 1995 24 CET.

As can be seen in Figure 4 concerning the sensible heat flux, the time-averaged turbulent fluxes show strong gradients near the coast, especially during night time. The reason for the enhanced sensible heat flux along the North Frisian Wadden Sea at night is the advection of colder air from the land surfaces to the much warmer coastal waters and strong heating of this air. During daytime, with the temperature of the advected air remaining only slightly lower than the sea surface temperature, the sensible heat flux along the North Frisian coast was less developed than over the sea regions far away from the land surfaces. Like the sensible heat flux, also the latent heat flux increases strongly near the North Frisian coast at night due to the instable stratification of the atmospheric surface layer, while hardly any evaporation occurs during the day. Summarising these phenomena and taking into account a higher longwave radiative cooling of the coastal sea due to the relatively warm water, a zone with marked energy loss extending along the North Frisian coast was simulated during the night hours of the second KUSTOS experiment (not shown). During daytime, the spatial distribution of the ocean heat flux is dominated by an increase in the shortwave radiation balance from north-west to south-east due to the spatial distribution of the time-averaged cloud cover.

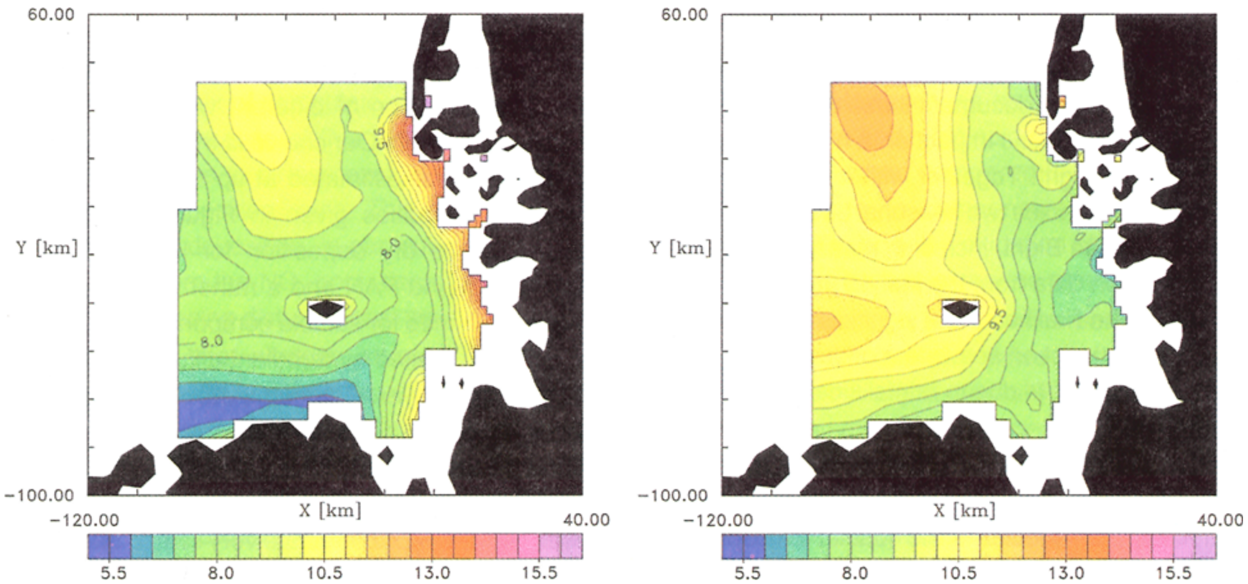

Fig. 4: Time-averaged turbulent sensible heat flux fields in the budget area German Bight for the period 22.4.–11.5.95, night time values left and daytime values right [W/m^2].

These diurnal variations of the heat fluxes through the sea surface lead to a pronounced diurnal cycle also in the water column. During the day the stability of the water column increases causing a shallow diurnal thermocline, whereas at night the water column is destabilised which generates penetrative convection.

The influence of river run-off on the heat balance of the German Bight is relatively weak. The temperature differences in conjunction with the released water masses are too small to effect noticeable changes in the heat content of the German Bight.

2.2 Nitrogen fluxes

The air-sea-exchange flux of nitrogen in the German Bight has recently been shown to contribute significantly to a nitrogen budget for the whole region (BEDDIG et al. [1997]). At the same time, it has often been pointed out that the riverine input and the internal cycling of nitrogen is dominating the nitrogen fluxes in near coastal waters, especially when the region of interest is close to an important estuary like that of the Elbe (BROCKMANN et al. [this volume; T. HYDROGR. Z.et al. submitted]). However, it is of interest to explore the conditions, spatial relation to estuarine influences and times at which atmospheric fluxes become important for any local nitrogen budget. For coastal management purposes it would also be of interest to include a discussion on the role of atmospheric nitrogen deposition in the Elbe drainage area, contributing to the nitrogen load of the German Bight. This is an aspect which we had not investigated because of difficult problems with regard to retention and wash-out of nitrogen in the terrestrial ecosystems.

In the first section we report data collected with respect to atmospheric concentrations of nitrogen species in the German Bight and the implications for the current understanding of the relevant chemical processes and spatial patterns of air-sea exchange of nitrogen. The importance of coarse nitrate formation in the coastal atmosphere was the motivation for both a closer look at the data and for an episode simulation, where offshore blowing air underwent heterogeneous atmospheric transformation processes upon interaction with sea salt aerosol. We assess here the importance of dry deposition of different nitrogen species. Total deposition data collected in our long-term study in the German Bight are used to investigate to what extent wet deposition events dominate the atmospheric nitrogen flux. Therefore we also document these data to discuss finally the atmospheric impact on a nitrogen budget in the German Bight. Together with internal, advective and riverine N-fluxes two seasonal budgets are set up for the German Bight, including measured sea water concentration data from the last 15 years. Finally we examined the likelihood of a significant short term atmospheric impact on seawater concentrations of ammonium and nitrate due to rainfalls carrying large nutrient loads.

2.2.1 Nitrogen species in the coastal atmosphere

The atmospheric nitrogen flux itself is composed of several nitrogen species. While $NO+NO_2$ (NO_x) and NH_3 are the principal emitted species of anthropogenic origin, transformation and transport processes produce a suite of nitrogen species. These species have different removal properties, depending on water solubility, molecular diffusivity and inertial properties in the case of particulate nitrogen. It should be noted that only species with both high abundance and large atmospheric deposition velocities are expected to dominate the atmospheric flux into the sea.

The ambient air concentrations in the German Bight of the relevant nitrogen species as measured during the three KUSTOS central experiments (each 2–3 weeks) in Westerhever/Eiderstedt (54° 22' N 8° 38' E) and aboard the research vessels Alkor and Heincke (50–70 km offshore, see SÜNDERMANN [this volume for map]) are shown in Figure 5. We have averaged 12-hourly data for the purpose of providing an average composition of the atmospheric nitrogen pool for the German Bight (for methods and details of sampling see PLATE AND SCHULZ [1997]; BEHLEN [1996] and PLATE [2000]). It can bee seen that a considerable amount of nitrogen is still in the form of NO_x which are the precursors of nitrate and other oxidised nitrogen species. However, also ammonia is a dominant species, whose source is the intensively farmed northern German lowlands (PLATE et al. [1995]).

In Figure 5 we present an estimate of the mean dry deposition of the different species. The choice of an average dry deposition velocity is difficult without a model integration of different wind regimes and sea surface states. Our choice is therefore associated with an error estimated at up to 50 %. The dry deposition velocities given in Figure 5 range between neglible dry deposition for insoluble gases such as NO and PAN and a rather high deposition velocity of 1 cm/s for soluble components, where the deposition is limited by turbulent diffusion in the marine boundary layer. Coarse nitrate was assumed to have even higher deposition velocities due to the additionally acting process of sedimentation. Though present at high concentrations, the anthropogenic gases NO and NO_2 contribute very little to the air-sea flux. It is important to note that NO_x thus will be transported farther out to the North Sea because NO_x deposition velocities are small. Their role is to form a pool, which is slowly oxidised during transport over sea. This is responsible for the input of nitrate also in those marine areas which are remote from the coast. The NO_x oxidation products nitric acid and nitrate are soluble in sea spray droplets and rainwater and form the main body of the nitrate deposition flux. The particulate aerosol fraction on particles having a diameter > 1 µm is the product of the reaction of sea salt with nitric acid. In the deposition estimate this fraction appears due to the high settling velocity of large particles.

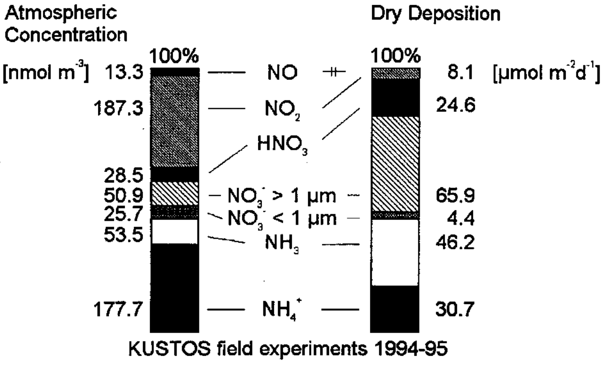

Fig. 5: Mean partitioning for all three KUSTOS campaigns of nitrogen among major gaseous (NO, NO_2, NH_3) and particulate species (NH_4^+): 0.2, NH_3 – < 1 µm: 1.5, HNO_3: 1.0, NO_2: 0.05, NO: 0.01, PAN, HNO_2, N_2O_5: 0.01).

Reduced nitrogen (NH_x) fluxes are almost as large as those of nitrate, which was confirmed in our bulk deposition measurements (see below). However, the precursor of particulate ammonium is soluble ammonia. Because of this solubility there is no surface resistance to air-sea exchange, and we can expect high deposition rates. This implies that reduced nitrogen deposition, in particular compared to that derived from the NO_x-pool, decreases substantially with increasing distance from the coast.

It appears that nitrogen air-sea fluxes should have a fundamentally different spatial structure from riverine inputs. Effective atmospheric dispersion processes and atmospheric chemistry processes differ from the relatively slow ocean transports starting from a localised river estuary and large influences of marine biological and geochemical cycles. Since ambient air concentrations should reflect the spatial structure of air-sea fluxes, one of our interests was to compare coastal concentrations with those observed on a research vessel in the German Bight, measured in a Lagrangian sampling constellation. Operating two stations in quasi-connected flow has not been done so far for such a long overall sampling time. Our measurements during the three KUSTOS campaigns are summarised in Table 4 and were grouped according to onshore and offshore air mass transport conditions. About 30 % of the sampling cases were excluded because winds blew parallel to the shoreline.

The largest decrease between the coastal station and the open sea site (about 50–100 km offshore) was observed for gaseous ammonia during offshore winds. This reflects a rapid loss of highly soluble ammonia from surface level, either by dilution with upper air or by deposition. Dilution is likely to be an important factor, since ammonia sources at the ground are close to the coastal measurement site, which favour a pronounced vertical profile over land, to be dispersed over sea. In the opposite transport direction, it seems that ammonia is emitted from the Wadden Sea area (PLATE et al. [1995]). If emission really takes place, the net flux of ammonia in the near-shore coastal waters is difficult to assess, since recycling of ammonia is taking place in these areas. An integration over a longer period would be needed as has been done by ASMAN et al. [1994].

On the other hand, particulate ammonium and nitrate as well as nitric acid concentrations do not differ much between the research vessel position and the coast. However, as has been pointed out above, the nitrate and nitric acid dry deposition fluxes are not small when compared to ammonia. This requires a source to compensate for deposition losses. This is the ongoing oxidation of the NO_x-pool to nitric acid in the coastal marine atmosphere.

Another indication of a balance between deposition and production of oxidised nitrogen compounds is the similarity of the $NaNO_3$ concentrations at the coast and offshore, especially in offshore flow conditions. The reactivity of nitric acid is responsible for the dramatic change in sea salt composition in the anthropogenically influenced coastal aerosol, as compared to that of natural seawater. By reaction with nitric acid, sea salt is depleted in chloride and the ratio of Cl/Na decreases (see Table 4). On average 22–33 % of the sea salt particle mass is transformed to sodium nitrate (see Fig. 6). One would expect this process to lead to a more pronounced increase in $NaNO_3$ concentration in offshore winds. However, it seems that already in Westerhever aged sea salt arrives from the Baltic Sea – or in case of curved trajectories marine air from the North Sea and Atlantic Ocean. This is transformed at more than 30 %. As the air in such offshore wind conditions is transported farther out to the sea, sodium concentrations increase, but much less those of $NaNO_3$ and HNO_3.

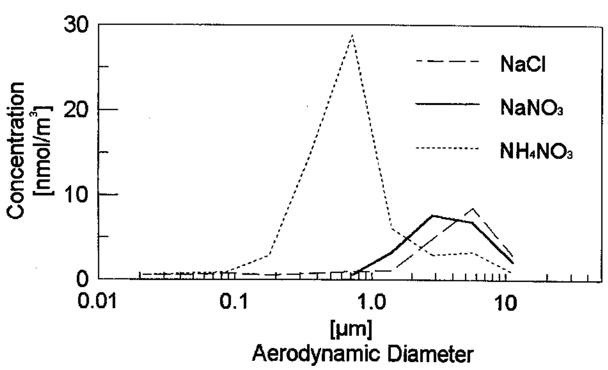

Fig. 6: Mean size distribution of sea salt and nitrogen containing particles, calculated from 14 measurements (during 422 hours) with a low pressure impactor (BERNER, LPI 25–14) on the research vessel during the KUSTOS central experiments in 1994–95.

		Onshore winds NW-SW ⇒		Offshore winds SE-NEO ⇐	
		R/V Heincke / R/V Alkor 213 hours	Coastal station Westerhever 239 hours	*R/V Heincke / R/V Alkor* 245 hours	Coastal station Westerhever 234 hours
		Atmospheric concentrations			
$NH_{3\ (gaseous)}$	[nmol m^{-3}]	20	130	62	320
$NH_4^+{}_{(particulate)}$		194	234	149	195
$NO_3^-{}_{(particulate)}$		120	105	94	100
$HNO_{3\ (gaseous)}$		29	49	26	23
$Na^+{}_{(particulate)}$		78	40	43	19
		Transformation of sea salt to sodium nitrate			
Cl^-/Na^+ (in Seawater: 1.17)		0.84	0.84	0.76	0.78
Transformed sea salt.	[%]	28	22	30	33
$NaNO_3$	[nmol m^{-3}]	29	12	16	12

Table 4: Averaged atmospheric concentrations of measured nitrogen compounds and sodium in the German Bight for selected cases, grouped according to transport conditions from all three KUSTOS campaigns. Gaseous and particulate species were measured with a denuder difference method.

Our data is not sufficient to conclude at what distance from the coast nitrate deposition would decrease because of a decreasing nitrogen oxide pool. During onshore and offshore blowing winds we find similar amounts of nitrate and nitric acid. Onshore transport conditions – influenced by southwesterly winds – transport polluted air from Great Britain and South West Europe across the sea over long distances. The slightly higher particulate nitrate concentrations we have observed at sea – both during offshore and onshore conditions – might even indicate an offshore deposition maximum at some distance . Since the average air concentrations differ little between our two sites in the open sea and at the coast, and since dry and wet deposition is to a large extent proportional to air concentrations, we have to conclude that nitrate deposition on a seasonal or annual basis is spatially rather homogeneous throughout the German Bight.

2.2.2 Mesoscale simulation of an offshore transport situation

The observed interaction of aerosol and gas species and the importance of the sea salt reaction was the motivation for the development of the aerosol model SEMA (see for a detailed description von Salzen [1997], von Salzen and Schlünzen, [1999a]). The model was also incorporated into the 3D mesoscale model METRAS to simulate an offshore transport situation in the German Bight during the KUSTOS central experiment (1.5.95). In contrast to many other periods during the experiment, this day was characterised by fairly constant easterly winds. The day can be used to study the transformations of continental air arriving in the coastal atmosphere. Such transport conditions simplify the definition of border conditions for a mesoscale model, which cannot be run for too long periods because of computer time limitations. To initialise the simulation, aerosol and trace gas samples collected on board R/V *Heincke* and at Westerhever on April 30, 1995 were used. Radiosonde data at R/V *Heincke* were used for the initialisation of the meteorological fields.

The model simulates the modification of the aerosol size distribution with four size classes (0.0625 – 16 µm) along with its composition and the reaction of the nitrogen oxides, including 73 gas- phase reactions of inorganic and organic compounds, based on diurnally varying surface emissions of SO2, NO, NO2, CH4, CO and VOCs (NIEMEIER [1997]). Ocean emissions of NH_3 were computed according to ASMAN et al. [1994] and land emissions following TUOVINEN et al. [1994]. The submodel SEMA includes the condensation and evaporation of sulphuric acid, nitric acid, ammonia and water vapour in contact with the particulate aerosol phase. The novelty is the computation of the diffusion-limited formation of secondary sea salt species. The thermodynamical approach used in the model applies activity coefficients to the highly concentrated aerosol particles. The replacement of chloride by nitrate seems to be well represented by the model (VON SALZEN AND SCHLÜNZEN [1999b]). A comparison with the measurement of the aerosol size distribution (12:00–23:00) on the same day at the research vessel position shows a chloride replacement of 29 %, while the simulation predicts 32 %. However, the simulation underpredicts both nitric acid (–60 %) and nitrate (–25 %) concentrations at sea, which is probably caused by too small cross-boundary emission fluxes of precursor substances (NO_x, VOC...).

The simulation enables the flux dominating the transfer of nitrogen into and within the marine boundary layer to be investigated. To compute relevant fluxes of reactive nitrogen species in the coastal atmosphere, a marine boundary layer box of 105 m height as subdomain of the model domain is defined, extending seaward from the coastline (see Figure 7). The height corresponds roughly to the marine boundary layer height derived from the radiosonde data at R/V *Heincke* during this day aboard R/V *Heincke*. Figure 7 also shows the sea salt concentration distribution as it evolves during offshore winds. A steep vertical gradient of sea salt aerosol evolves with sea salt aerosol slowly dispersing upwards. The vertical distribution of the simulated sea salt suggests that the subdomain was chosen sufficiently high to study the transformations during the simulation period. The results also show that sea salt produced over the Baltic Sea may contribute significantly to the concentrations observed over land and at the coast. The vertical nitric acid distribution shows very low concentrations at the open sea location and a maximum at 70 m. The reason for these vertical gradients is the limited vertical exchange in a stable marine boundary layer.

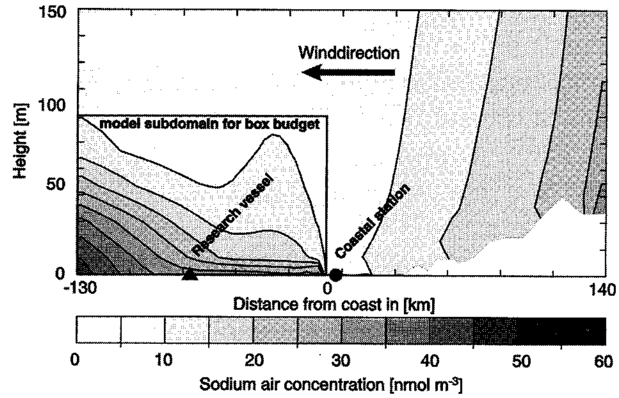

Fig. 7: Horizontal cross-section of vertical distribution of NaCl concentration as simulated by the 3D-SEMA/METRAS model.

For three important nitrogen species we present fluxes associated with horizontal and vertical advection, sedimentation, vertical diffusion and deposition for the 24-hour period of 1 May 1995 (Fig. 8). Horizontal advection represents by far the largest flux term. The imbalance in the advection transport processes especially for fine nitrate is due to an overall decrease in concentration during the simulation period as a consequence of the small cross boundary fluxes at the eastern border. The longevity of the fine nitrate species prevents that other processes become important. Chemical transformation processes are summarized in Figure 9. It shows that new production of fine nitrate amounts to only 2 %/hour of the present particulate fine nitrate, while 5 %/hour of coarse nitrate and 7 %/hour of HNO_3 are produced within the subdomain.

However, we are most interested in a comparison of chemical transformations with vertical fluxes of nitric acid and coarse nitrate, because both reflect the intensity of air-sea-interaction. It appears that a substantial portion of nitric acid (12 %/h) enters the box through its top surface by advection and diffusion. This is due to a constant nitric acid source from oxidation of the NO_x-pool in the mixed layer, which extended up to a height of 1500 m over land. Within the box, production of HNO_3 (7.4 %/h) is slightly smaller than loss due to formation of fine nitrate (–7.4 %/h) and coarse nitrate (–3.5 %/h). The vertical gradient is maintained by considerable dry deposition at the surface (–6.2 %/h). The HNO_3 dry

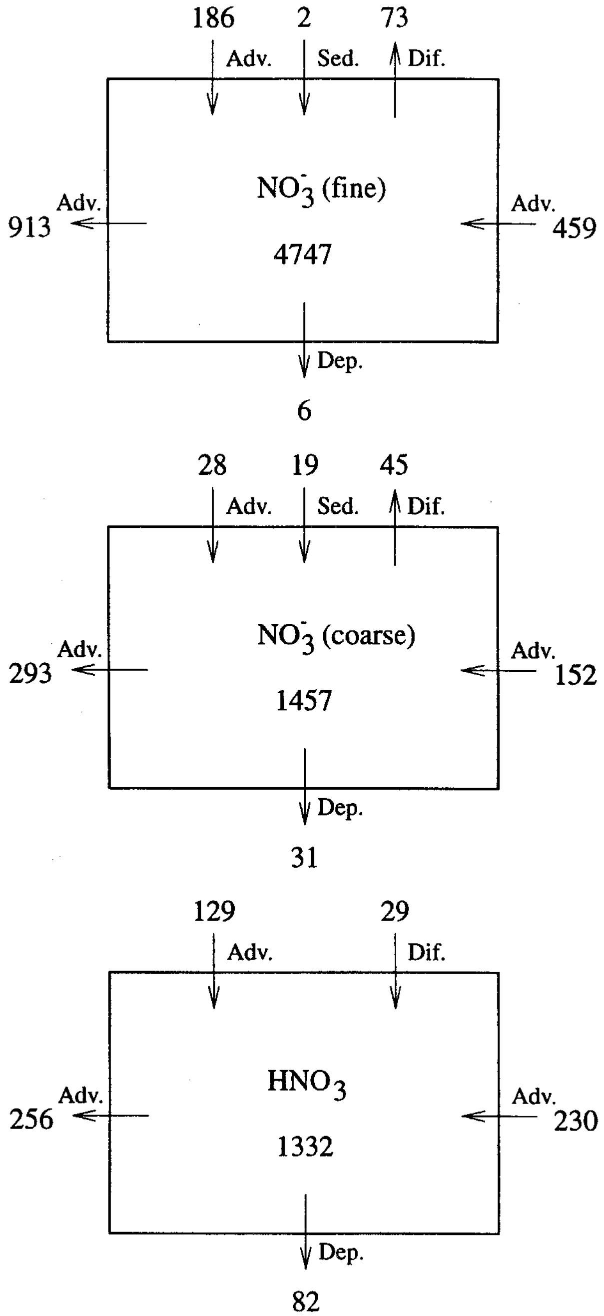

Fig. 8: Calculated budget for marine boundary layer box up to 150 m for 1 May 1995, including horizontal and vertical advection (Adv), sedimentation (Sed), turbulent diffusion (Dif) and dry deposition fluxes (Dep) for fine nitrate (< 1 µm Dp), coarse nitrate (> 1 µm) and nitric acid. Numbers represent the fluxes [Mole/hour], respectively mean load per day in the subdomain [Mole].

deposition flux is computed to be three times higher than that of coarse nitrate and roughly as much as is produced within the boundary layer from NO_x. The vertical fluxes alone would account for an increase in HNO_3 concentration by 6.5 % per 3-hour air mass travel time. Such travel time would correspond to a wind of 7 m/s and the distance between the ship and the research vessel (~70 km). It is interesting to note that we observed a small concentration increase in our measurements in offshore winds also when averaging over a longer period (see Table 4).

Because coarse nitrate is produced in the marine boundary layer, the fluxes of this component are rather balanced at the top of the subdomain (0.1 %/h). The production of coarse nitrate is the largest term in the subdomain. But only 40 % of the coarse nitrate produced in the box is deposited. The rest is transported further out. The increase in concentration would amount to 10.3 % per 3 hours travel, a little more than for nitric acid. This agrees well with the difference in the concentration of $NaNO_3$ measured between Westerhever and the research vessel site (Table 4), even though it was small. However, it should

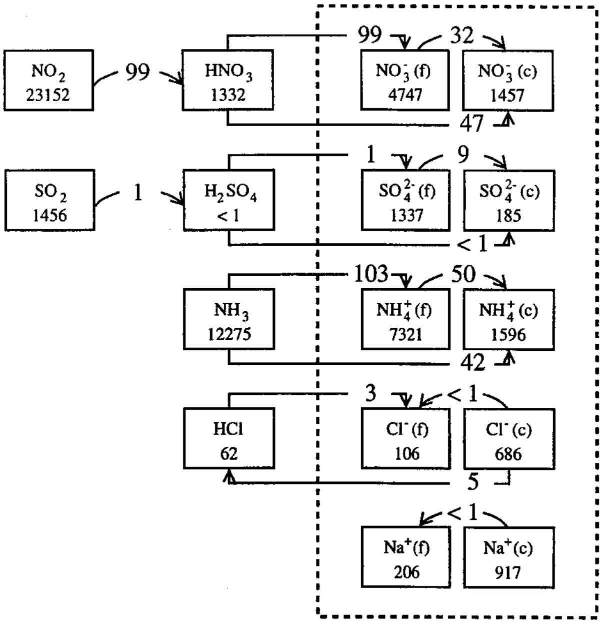

Fig. 9: Simulated physico-chemical transformation within the marine boundary layer box for 1 May 1995 [Mole/hour].

be noted that we had relatively low sea salt concentrations on that day, and the formation of coarse nitrate would then be of minor importance compared to that of nitric acid as well as the dry deposition flux of coarse nitrate.

The simulation confirms that the deposition flux may be rather homogeneous in the German Bight due to small horizontal concentration gradients, which is confirmed by the deposition calculation in the model for that particular day. An important finding is the prediction that the deposition of nitric acid is more important than that of coarse nitrate, at least with offshore winds. It is not clear whether this can be generalised, since a one-day simulation is not representative.

2.2.3 Long term measurements of the atmospheric nitrogen input

The episodic studies of ambient air concentrations during the KUSTOS central experiments are not strictly representative to allow an assessment of the atmospheric input of nitrogen species to the sea. Wet deposition forms the dominant portion of the atmospheric flux, being of a highly stochastic nature, even though there are intermediate dry episodes of several weeks duration.

Therefore, to derive a seasonal budget for the German Bight, we use our weekly atmospheric deposition measurements in Westerhever/Eiderstedt and on the research platform "Nordsee" 54° 42' N 7° 10' E, in the open North Sea 70 km west of the island of Sylt. The seasonal fluxes of nitrogen have been summarised in Figure 10 from a time series compiled in 6 years from 1989 to 1995. The small yearly cycle is slightly enhanced at sea both for nitrate and ammonium. Possibly, higher wind speeds, higher sea salt loading and more rain at sea during the winter season contribute to this effect. Compared to the fluxes in the water column throughout the year this cycle is of minor importance.

The differences between the two stations and the errors involved at a windy station like the research platform are discussed in detail by REBERS [1997]. Despite uncertainties due to wind effects we can conclude that nitrate and ammonium deposition rates, and their ratio, differ at the coastal and open sea stations. On average we find almost the same ammonium deposition flux for the research platform FPN (Nov. 1988–March 1993: 74 mmol m^{-2} a^{-1}) and the coastal station Westerhever WHV (July 1989–July 1996: 77 mmol m^{-2} a^{-1}) although ammonia air-sea-fluxes decrease over sea due to dispersion and deposition of land derived ammonia. However, nitrate deposition at sea is significantly enhanced (FPN: 126 mmol m^{-2} a^{-1} ; WHV 53 mmol m^{-2} a^{-1}). This increased nitrate offshore deposition as well as the increase in the ratio of nitrate to ammonium is not a result of higher rain amounts in the offshore sampling units (FPN: 589 mm/a; WHV: 612 mm/a). Both findings can be explained by the enhanced deposition velocity of coarse nitrate, formed by the sea salt reaction discussed above. As has been discussed above, nitrate is constantly produced from the NO_x pool in the atmosphere. As has been concluded above, we expect to find a deposition maximum for nitrate at some distance off the coast . Also, with the single deposition measurement site we are not able to identify the region where this maximum would be.

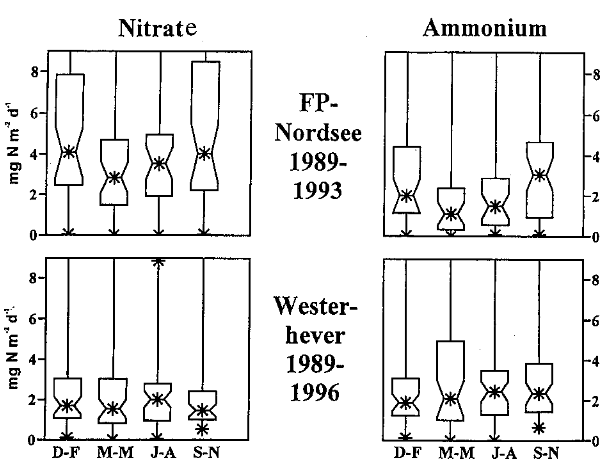

Fig. 10: Summary of weekly deposition measurements grouped for winter (December–February), spring (March–May), summer (June–August), autumn (September–October). Each box shows median value (star), 25 and 75 percentiles (lower and upper box boundaries), and the confidence range for the median (95 % level) as notch.

A similar study was performed for the Southern North Sea. A combination of aerosol measurements and wet-only sampling during cruises of the NERC North Sea project yielded a total nitrogen input of 70 mmol m^{-2} a^{-1} (OTTLEY AND HARRISON [1992], RENDELL et al. [1993]). We cannot exclude that this smaller deposition estimate is reflecting real regional differences. An increase in volume weighted rain concentrations of nitrate between a coastal site (1,2 mg/l) and the open sea samples (3,2 mg/l) was observed by KANE et al. [1994], in accordance with our findings of an increase in nitrate deposition in the open North Sea.

2.2.4 Seasonal nitrogen budgets for the German Bight

For an overall assessment of the nitrogen fluxes for the German Bight we have compiled two seasonal budgets (Fig 11). For this purpose seawater concentrations were averaged from cruises in the German Bight between 1984 and 1996 using data from the database of the group Brockmann. Values were taken from a water depth < 20 m. Because of a change in analysing frequency and intensity in the course of the years, data are not strictly consistent with respect to the partitioning of species in the water column. Each number in Figure 11 thus comprises the concentration average for the nitrogen species extrapolated to a water body of 10000 km^2 and 20 m depth. Advective fluxes in the ocean were derived using concentrations averaged in two regions around the western and northern boundaries of the German Bight budgeting box as defined above for the heat fluxes. These two bands, where data were taken, extended about ±60km around the western boundary at 6.3°E and around the northern boundary at 55° N. As a result 200–2000 individual measurements went into the averaging procedure. The concentrations were then multiplied with the mean advective water flux through the boundary as provided by the ocean model. Primary productivity is a substantial source of internal cycling of nitrogen. To illustrate the relation to external fluxes we used the data given by RICK et al. [submitted] as classified there for "winter conditions" (adjusted to a seasonal budget of only three months) and for "summer high and stagnant conditions". Riverine fluxes were reported in BEDDIG et al. [1997]. The increased importance of the fluxes due to denitrification processes are discussed by VAN BEUSEKOM et al. (this volume). It is believed now that earlier estimates of dinitrification had underestimated the actual flux of N_2 and N_2O.

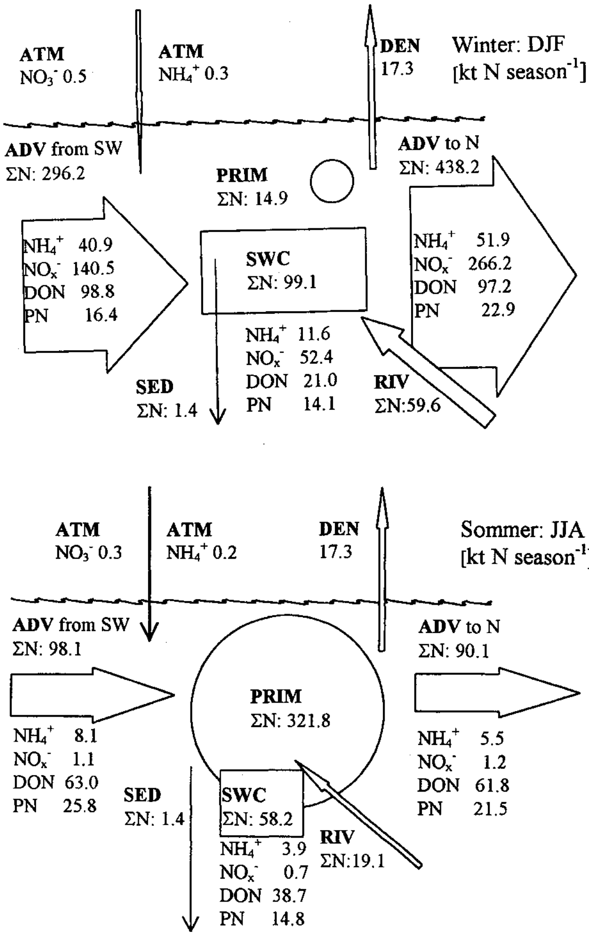

Fig. 11: Seasonal budgets of nitrogen compounds in the German Bight: Sea water content SWC, turnover associated to primary production PRIM, advection ADV; particulate sedimentation SED, denitrification DEN, atmospheric deposition ATM; riverine input RIV.

Altogether we find that the atmospheric flux is small as compared to the large turnover in the system. The large advective fluxes in the ocean (ADV from SW and to N) are almost balanced in each season. These fluxes are largest in winter, when the turnover is smallest. Winter thus is the season in which the most efficient exchange with other sea areas occurs. Both turnover and riverine input vary considerably from season to season. It is only in summer that we see an atmospheric nitrate input flux coming close to the nitrate plus nitrite content (NO_x) of sea water. Only in summer is a direct impact of the atmospheric flux on the inorganic nitrogen content possible. However, there is a large reservoir of DON and PN which is available to the biological system. The large turnover of nitrogen in the summer months cannot be based just on the small content of inorganic nitrogen compounds.

The size of the budget box also influences conclusions as to the importance of atmospheric inputs because a larger area would favour atmospheric input over riverine fluxes. Apart from the riverine inputs there is no other external input term and it is a conservative estimate that in the long term and far out at sea mainly atmospheric input is driving new production. If denitrification is a larger sink of nitrogen than previously thought (see discussion in BEDDIG et al. [1997]), then atmospheric input has only one significant counterpart as removal process. A reduction in atmospheric input would be followed by a rapid removal of nitrogen load in sea water to natural levels within a few years. The uncertainty of the status and development of the nitrogen load in areas remote from the estuarine regions probably can be linked to the uncertainty of the atmospheric input estimates.

2.2.5 Atmospheric impact of nitrogen fluxes on seawater concentrations

A direct impact of an atmospheric input event on seawater concentrations is difficult to prove experimentally. During the KUSTOS experiments only two events could be traced, which indicated some link between a wet deposition event and the surface seawater concentration (REBERS [1997]).

To investigate the possible impact of weekly atmospheric input we resorted to a statistical approach. We computed the increase in seawater concentrations which results from any of the deposition measurements of our long term measurement series, when dispersed into the upper 10 m of the sea. A rough estimate of diffusive fluxes in the water shows that a rain event is dispersed in the upper 10–20 m within a few hours, provided that it is not prevented by thermohaline stratification. The corresponding surface seawater concentrations of dissolved ammonium and nitrate have been selected from previous cruises in the years 82–95. We chose outer German Bight values northwest of 54° N and 8° E for the months April to September, taken at depths between 1–13 m. Figure 12 shows the frequency distribution for both data sets.

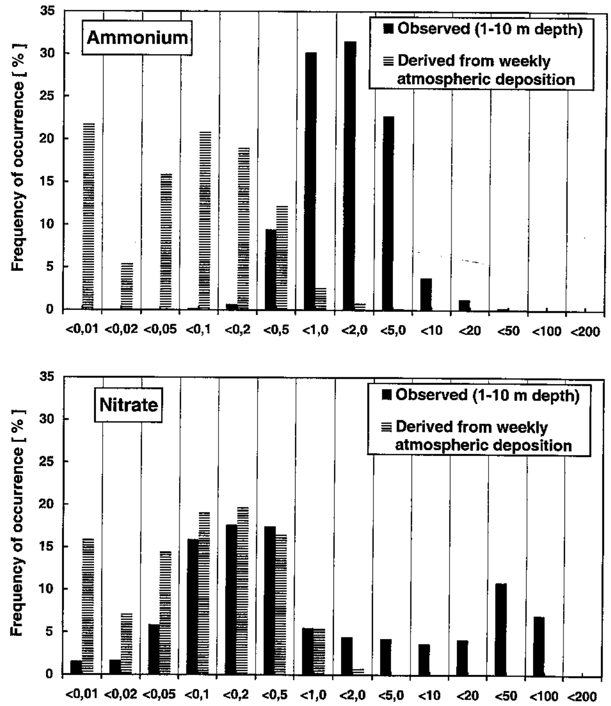

Fig. 12: Frequency distribution of measured sea water concentration (dissolved inorganic nitrate and ammonium) in the open sea areas of the German Bight as compared to what can be calculated using weekly atmospheric input data. Atmospheric input has been assumed to be mixed down to 10 m.

The overlap of the two frequency distributions is much larger for nitrate than for ammonium. This indicates that an atmospheric nitrate deposition event has a greater potential to change seawater concentration. The probability of nitrate seawater concentration doubling in this way was computed to be 29.3 %, while it is only 4 % for ammonium. (COMPUTED HOW?)

2.3 Fluxes of persistent organic pollutants

The fate of atmospheric pollutants in seawater is dramatically different depending on whether they are soluble or in the particulate phase in the water column. High solubility of a component shortens its lifetime in the atmosphere due to increased wet scavenging and prolongs the residence time in the water column. Measurements of three persistent organic substances (POPs), or classes of substance, have been chosen to demonstrate this behaviour. DIN-PCBs, bound to particulate matter, are transferred most rapidly to the sediment, while the soluble (α-HCH and (γ-HCH remain longer in seawater.

Figure 13 summarizes the available information and our own deposition measurements (GERWIG [2000]). The longevity of the persistent substances chosen implies that the advective fluxes in the ocean dominate the annual budgets. Values for the PCBs are subject to large uncertainties. Not all congeners of this substance class had been quantified in all the cited literature. Therefore we use the sum of the 6 PCB congeners 25,52,101,153,138,180 known as DIN or ICES PCB. If total PCB is reported we have divided numbers by four, as BAART et al. [1995] have suggested. Others have used a factor of five (BRORSTROEM-LUNDEN [1995]). With regard to the seawater data from THEOBALD [1998] we calculated the amount of DIN PCB by summing up PCB congeners 138 and 153 and multiplying them with a factor of 3. The factor reflects the ratios found in PCB congeners in German Bight samples (SCHULZ-BULL [1991]).

Even though it is difficult to estimate the sediment content of each of the three POPs because of sediment turbation during storms in a shallow sea and local maxima as for instance in the sedimentation area south east of Helgoland, major differences between the substances show up. DIN-PCBs dominate in the sediment (Table 5) while they do not with regard to the atmospheric input and the advective fluxes. Atmospheric fluxes of α-HCH and DIN-PCB are estimated to be of the same amount. The difference between the three substance classes is most probably reflecting their solubility and thus lifetime in the water column. However, since the sediment is memorising inputs for decades, some of the differences may also reflect changes in deposition over the years.

The budget also suggests that in addition to solubility effects a degradation process is in effect. For, α-HCH and DIN-PCB input from the river and the atmosphere create a surplus in the German Bight area and thus a net outflow. Data for γ-HCH suggest that it is more easily degraded by photo-oxidation and marine micro-organisms (HÜHNERFUSS et.al. [1997]).

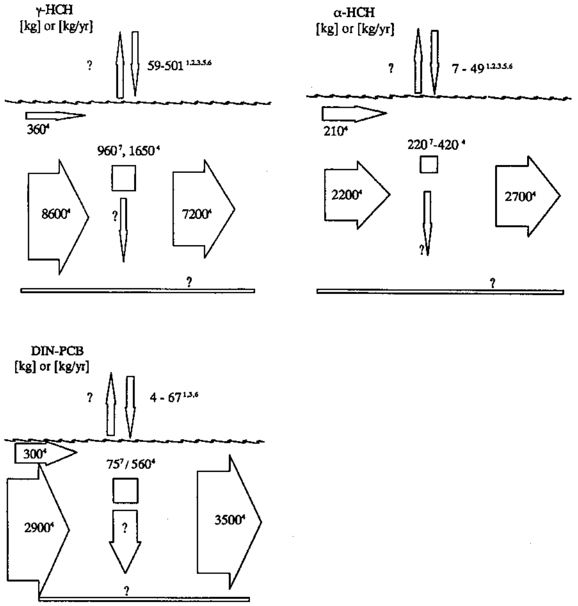

Fig. 13: Fluxes and deposits of persistent organic pollutants in the German Bight: Calculated from available data from the German Bight and nearby marine regions [[1]BRORSTRÖM-LUNDÉN (1995), [2]CLEEMANN et al. (1995), [3]this study, [4]HÜHNERFUSS et al. (1997), [5]KREUZMANN et al. (1995), [6]SELKE (1994), [7]THEOBALD (1998)] (German Bight dimensions defined for this budget: area = 24500 km^2, Volume = 550 km^3 [PULS (1994)].

		γ-HCH	α-HCH	DIN-PCB
Sediment content	[kg]	14–45	2.6–3.8	209–243
Solubility at 20 °C	[mg L^{-1}]	6.5	1	0.3 10^{-6}–160 10^{-6}

Table 5: Total German Bight content of selected persistent organic pollutants in the upper 2 cm of the sediment, based on measurements of dry weight content [LANDGRAFF, 1995]. Solubilities for HCHs are from SUNTIO et al. [1988] and for DIN PCBs from BRODSKY AND BALLSCHMITTER [1988].

Despite the shorter lifetime of γ-HCH, its large fluxes and high solubility make it an important contaminant for the marine ecosystem. Substantial amounts enter the system via the atmosphere. Recently γ-HCH has still been used in France at a yearly consumption of 1182 t [OSPARCOM [1996]]. A reason for the long-range transport of this pesticide is that it is applied by spraying procedures, involving also helicopters, and that it is volatile.

Conclusions

The most interesting common aspect when investigating the impact of the atmosphere on air-sea fluxes with respect to parameters as different as momentum and nitric acid is the importance of their specific variation in time and the consequences of this variation. In contrast, spatial variability seems to be less important.

The large seasonal amplitude of the exchange of heat dominates the sea water temperature development throughout the year. However, short term fluctuations are as large and can alter sea water temperatures much more.

Atmospheric nitrogen fluxes will contribute to long term changes of the nitrogen load, especially remote from estuarine areas, in the inner German Bight and central North Sea. Nitrate is shown to dominate the N-fluxes due to a combination of slow transformation of gaseous precursors and enhancement of deposition in the marine atmosphere upon contact with sea salt aerosol. The short term impact of wet deposition events has been assessed in a statistical way and it has been indicated that dissolved nitrate sea water concentrations in summer might contain an atmospheric input signal.

All budgets are dominated by large advective fluxes in the water due to the small area used for budgeting. For the persistent organic pollutants a consistent picture evolves, which links long residence time in the water due to high solubility to a larger dispersion in sea water. A more rapid removal of soluble substances by wet deposition does not mean that these substances are to be found only in the coastal regions.

Spatial variability of atmospheric fluxes in the German Bight seems to be of lesser importance with two exceptions. Firstly, fluctuations that do influence sea water conditions in the short term may have strictly local effects if they also vary spatially. Increased cloudiness near the coast may inhibit incoming solar radiation and hence biological productivity there. Secondly, coast-to-sea gradients of atmospheric fluxes and sea water conditions may change the role of the atmosphere for different regions, even if the spatial variability is small. An important example here is the increasing impact of the atmospheric nitrogen load with increasing distance from the coast, which is a combination of enhanced deposition at sea plus rapid removal of riverine inputs in the areas close to the estuaries. The large amount of nitrogen residing in the marine system prevents, however, that short term effects of nitrogen input are easily detectable. However, long term trends in productivity and eutrophication in the open sea areas are most likely linked directly to atmospheric inputs. The uncertainty in annual atmospheric nitrogen fluxes amounting to an order of magnitude, which we had to conclude, is thus of concern. Estimates of denitrification rates imply that the system might recover rapidly within a few years if atmospheric loads are reduced.

From the budgets we can identify categories of potential atmospheric impact. Of relevance and helpful for the identification of possible cause effect relationships are the following four categories:

1) "atmosphere driven": If the variation of a parameter in the surface water is linked immediately to atmospheric variations, then the impact of the atmosphere is beyond question and can be found from simple correlation analysis. Another important component is the possibility of reversed fluxes from the ocean to the atmosphere. The local dominant impact for heat and momentum in the German Bight is a good example;
2) "episodic atmospheric impact": If the surface ocean has just a small memory for the atmospheric impact, then atmospheric influence may be observed in the long term, but most likely for short episodes where the impact maximises. This involves large fluxes as compared to the content of the repective parameter. They occur during short episodes and might be difficult to detect (radiation during cloudless days, PCB and Pb deposition during a specific rain event);
3) "persistent atmospheric pollutant": A pollutant in general is a substance which does not belong to the natural composition. If the memory of the system is long, then the atmospheric impact of these substances is dominant in the long term but regionally indifferent (e.g. α- and γ-HCH);
4) "steadily perturbing the marine ecosystem": The most difficult category is the long term, widespread atmospheric impact, which is a consequence of a steadily perturbing forcing from fluxes at the air-sea-interface. These fluxes are superimposed on a very dynamic system and are difficult to detect, since the major fluxes of matter are driven by marine biology with large turnovers (nitrogen compounds).

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