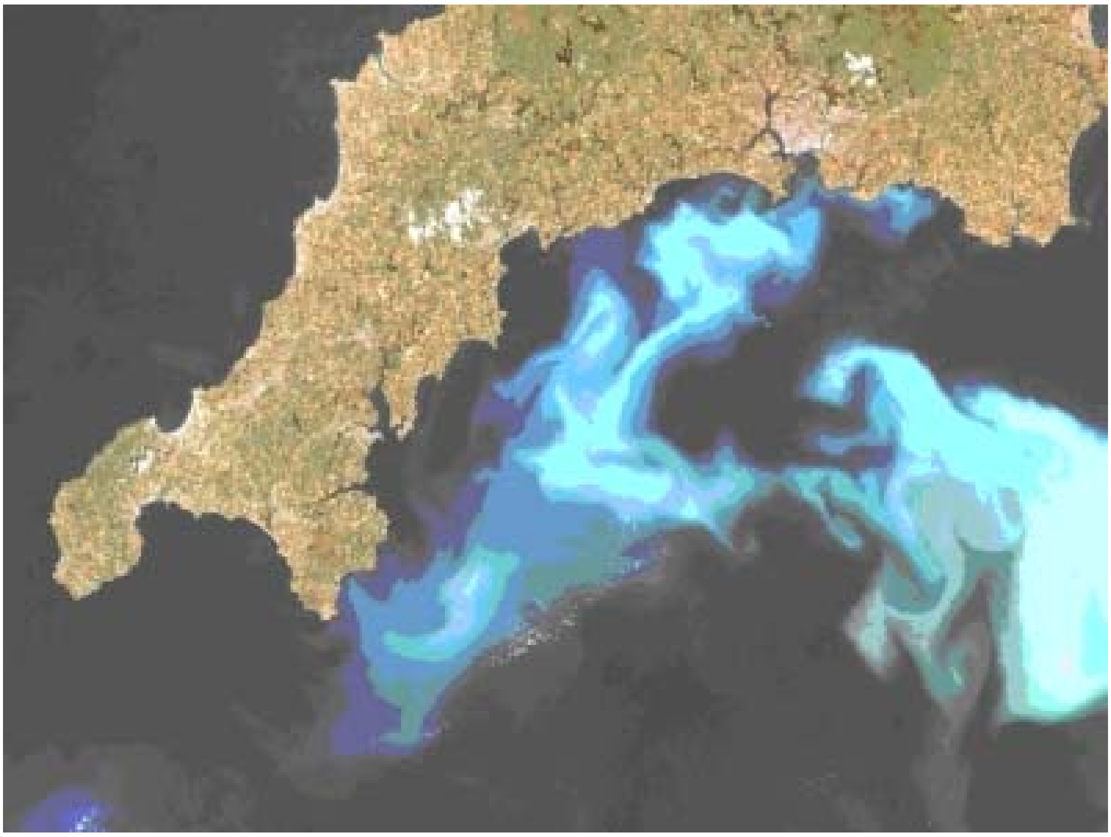
Air pollution and the eutrophication and acidification of European Seas

- Discussion Paper -



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European Topic Centre
on Air and Climate Change

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Front page picture

Satellite image of a coccolithophore bloom off southwest England. The milky whiteness of the waters is caused by the calcite liths or platelets made by the microscopic calcifying marine algal coccolithophore, Emiliania huxleyi, by extracting the calcium carbonate from the seawater. Millions of years ago, blooms like this shed their liths which fell to the seabed and in time created massive chalky deposits like the White Cliffs of Dover.
Courtesy Peter Millar, Plymouth Marine Laboratory.

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About this report

Air Pollution and the eutrophication and acidification of European Seas

Keywords: climate change, air pollution, integration, , impacts, adaptation, scenarios, Europe, acidification, eutrophication, seas, oceans, CO_2, Nitrogen

Carbon dioxide is most usually viewed as a climate gas and an atmospheric emission. In a similar way, anthropogenically released nitrogen gases in the atmosphere have been tackled as air pollution issues, even where the consequences might occur on terrestrial or freshwater environments. This report views these gases rather as pollutants. Considering Europe's marine environment the report discusses the possible scale of influence of these pollutants on marine biogeochemistry and ecological status. These two pollutants are linked through the carbon and nitrogen cycles.

The consequences of each pollutant may be profound. The potential rate of acidification of Europe's marine waters may be rapid, and may encourage a re-evaluation of desirable climate policies towards the more stringent end.Atmospheric nitrogen alone may be capable of bringing about a change in trophic status of some marine areas. Policies for reduction of nitrogen inputs to European seas may wish to more directly address atmospheric flows. More broadly, policies may wish to address the concept of a duty of care towards marine areas which risk falling outside national territorial considerations.

This report is intended as a Discussion Document, to stimulate further consideration of these issues. The analyses it provides are acknowledged as being preliminary and coarse, in order simply to provide a first measure of possible scale.

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1. Introduction

Attention to carbon dioxide is primarily directed towards its role in climate change. Atmospheric nitrogen is viewed in a little wider perspective as a regional to hemispheric pollutant, with a direct role in atmospheric ozone chemistry, in terrestrial acidification, in eutrophication, and with a role as a climate gas. Both have their principal anthropogenic source in combustion and energy production.

Yet, in addition to its climatic role, carbon dioxide has a polluting effect of its own. As atmospheric CO_2 levels rise marine uptake results in their acidification, with a range of possible ecological consequences. Atmospheric nitrogen also has potential ecological effects through its fertilizing effect, and the atmosphere is a major pathway for reactive anthropogenic nitrogen reaching marine waters. Interacting effects upon the food chain and nitrogen and carbon cycling are inevitable. When their potential re-release to the atmosphere as climate gases is considered, these pollutants are thus intricately linked in air quality, air pollution and climate change.

This discussion paper addresses the following objective:

> *With respect to eutrophication and acidification as a consequence of air pollution, the intention is to improve the Topic Centre's attention upon ecological impacts of air pollution, to explore the links with climate change factors, to explore the potential inclusion of the topic in the SoE2010 report, and to support the EEA in evaluating the status of the European Seas, and the associated policy framework…*

Elements to be covered include:

- Changes in marine nitrogen deposition
- Changing marine acidity and associated ecology
- European seas as sources or sinks of CO_2 and N
- Influences of future emissions policies for CO_2 and N

  Other points:
  - Europe is a continent characterized by proximity to the marine environment and by several enclosed/semi-enclosed regional seas
  - CO_2/N in the marine environment is a particular regional dimension in Europe to aspects of co-influences of air pollution and climate change
  - What are trends in acidifying/eutrophying effects?
  - What are the sub-regional/local differences?
  - Socio-economic and policy implications?

2. Nitrogen and CO_2 in marine systems

2.1. CO_2 and marine acidification

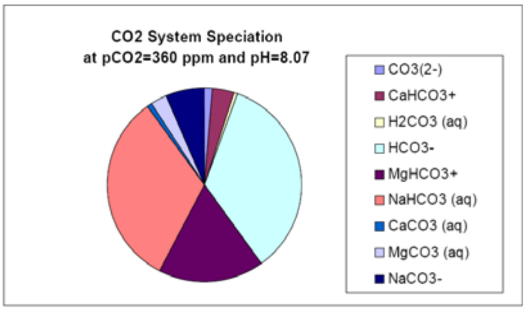
Ocean acidification is the lowering of pH in the oceans as a result of increasing uptake of atmospheric carbon dioxide (Wood et al, 2008). Over the past 200 years, the oceans have absorbed ~127 ± 18 billion metric tons of carbon as CO_2 from the atmosphere, or about one-third to 40% of the anthropogenic carbon emissions released (Sabine and Feely, 2007). This uptake slows the rise in atmospheric CO_2 considerably, thus alleviating climate change caused by anthropogenic greenhouse gas emissions (Zeebe et. Al., 2008). But it also alters ocean chemistry, with potentially serious consequences for marine life (Caldeira and Wickett, 2003). This problems got recently more recognition (IPCC, 2007) when the IPCC Fourth Assessment Report in 2007 included ocean acidification for the first time, stating, "The progressive acidification of oceans due to increasing atmospheric carbon dioxide is expected to have negative impacts on marine shell-forming organisms (e.g., corals) and their dependent species (very high confidence)".

Textbox 1: The carbonate chemistry in sea water

The main chemical reaction equations that regulate carbonate in sea water are shown in Equations (1–7) below (Ichikawa, 2007):

(1) Dissolved CO2(aq .) in equilibrium with atmospheric CO2 :
$CO2 \leftrightarrow CO2\ (aq.)$ A_o= -8.5 kJ.mol^{-1}
(2) Neutralization reaction:
$H^+ + OH^- \leftrightarrow H_2O$ A_o= 79.9 kJ.mol^{-1}
(3) CO2(aq.) nucleophilic reaction:
$CO_2(aq.) + OH^- \leftrightarrow HCO_3^-$ A_o= 43.7 kJ.mol^{-1}
(4) Calcium carbonate formation/dissolution reaction or acid dissociation:
$HCO_3^- + Ca^{2+} \leftrightarrow CaCO_3 + H^+$ A_o=11.7 kJ.mol^{-1}
(5) First acid dissociation equilibrium:
$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$ A_o=44.7 kJ.mol^{-1}
(6) Second acid dissociation reaction:
$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$ A_o=59.5 kJ.mol^{-1}
(7) Calcium carbonate formation/dissolution equilibrium:
$CO_3^{2-} + Ca^{2+} \leftrightarrow CaCO_3$ A_o=47.4 kJ.mol^{-1}

The above given reactions of CO2 with seawater reduces the availability of carbonate ions that are necessary for calcium carbonate (CaCO3) skeleton and shell formation for marine organisms The extent to which the organisms are affected depends largely on the $CaCO_3$ saturation state (W), which is the product of the concentrations of Ca^{2+} and $CO_3{}^{2-}$ divided by the apparent stoichiometric solubility product for either aragonite or calcite:



$$Warag = [Ca^{2+}][\ CO_3{}^{2-}]/K'_{sparag} \qquad (1)$$
$$Wcal\ = [Ca^{2+}][\ CO_3{}^{2-}]/]/K'_{spcal} \qquad (2)$$

where the calcium concentration is estimated from the salinity, and the carbonate ion concentration is calculated from the dissolved inorganic carbon (DIC) and total alkalinity (TA) measurements . In regions where Warag or Wcal is > 1.0, the formation of shells and skeletons is favored. Below a value of 1.0, the water is corrosive and dissolution of pure aragonite and unprotected aragonite shells will begin to occur (Feely et al, 1988).

Oceanic uptake of anthropogenic CO_2 leads to a decrease in seawater pH and thus lowers the saturation state for carbonate minerals such as calcite and aragonite ($CaCO_3$), see textbox 1. This process, is expected to have detrimental consequences, for a variety of marine organisms (Raven et al, 2005, O. Hoegh-Guldberg et al, 2007). For example, a decline in carbonate saturation state will affect the stability and likely production rates of CaCO3 minerals, which are the building blocks of coral reefs and form the shells and skeletons of other marine calcifying species. If future increases in seawater acidity affect calcification in coral reefs, such that erosion outweighs accretion, then the reefs could lose structural stability, with further negative implications for reef communities and for shore protection (O. Hoegh-Guldberg et al, 2007). Reduced calcification in shellfish such as oysters and mussels would impact worldwide commercial aquaculture production (Gazeau et al, 2007). Effects of ocean acidification on non calcifying organisms such as viruses and bacteria are largely unknown, as are potential consequences for marine food webs. Independent of climatic considerations, carbon emissions must be reduced to avoid these consequences.

Textbox 2: Coccolithophores, pteropods and calcium carbonate formation

Research into water column processes has primarily focused on those organisms, which calcify (see figure 1). This group includes the coccolithophorids, foraminfera and pteropods. Emiliania Huxleyi is numerically the most abundant coccolithophore in the ocean and became prominent during glacial periods of enhanced ocean productivity (ICES, 2007). It is a major sink of Carbon. However while Coccolithophores form an important part of the carbon cycle they do not constitute a significant food source. In the Barents Sea pteropods which do calcify are a significant food source for herring. Herring are an important part of the ecosystem and are a significant food source for fish such as cod, for marine mammals and sea birds.

Figure: (left) Beachy Head, The result of many thousands of years of coccolithophore formation; ." Online Photograph. Encyclopædia Britanica" ; (right) Reduction in calcium carbonate production for an Emilian Huxleyi bloom under present and future scenarios. Delille et al., 2005.

As the saturation of aragonite (which constitutes most of the shell) becomes below 1 then the shell will corrode. As early as 2040 there can already be notable effects on sea butterflies (pteropods) in northern waters (ICES 2007). When saturation is <1 it will cost the organisms more to maintain its skeleton and impose a sub-lethal metabolic cost rather than cause sudden death as is the case with some present deep water cold corals. However while aragonite will dissolve particulate inorganic production due primarily to calcite production is likely to still occur in the future however at a reduced rate compared to the present day.

An organism can be affected by ocean acidification in two ways; firstly through reduced pH and secondly through increased CO_2 (hypercapnia). Here we use the term ocean acidification to include both. Different species and groups of marine animals vary in their ability to cope with, and compensate for, hypercapnia and lowered pH (e.g. Portner et al. 2004, 2005) with implications for marine trophic interactions. Species with calcium carbonate skeletons, such as molluscs, crustaceans and echinoderms, are particularly susceptible to ocean acidification. As pH decreases, so too does carbonate availability that has led some authors to conclude that ocean acidification will result in reduced rates of calcification, see textbox 2 (e.g. Gattuso et al. 1999) and shell dissolution (e.g. Feely et al. 2004) for all calcified organisms, as well as metabolic depression resulting in reduced growth (e.g. Michaelidis et al. 2005). Echinoderm skeletons are composed of magnesium calcite that is particularly susceptible to dissolution as ocean pH decreases (Shirayama & Thornton 2005)

Compared with pre industrial levels, average surface ocean pH has already decreased by ~0.1 units (Raven et al, 2005, Caldeira & Wickett 2003). Seawater pH currently ranges between 7.8 and 8.2. Estimates of future atmospheric and oceanic CO_2 concentrations, based on the Intergovernmental Panel on Climate Change (IPCC) CO_2 emission scenarios and general circulation models, indicate that atmospheric CO_2 concentrations could exceed 500 ppm by the middle of this century, and 800 ppm near the end of the century. This increase would result in a decrease in surface-water pH of ~0.4 by the end of the century, and a corresponding 50% decrease in carbonate ion concentration (Orr et al, 2005, Solomon et al, 2007, Caldeira & Wickett 2003). While the magnitude of impact will vary with depth (Caldeira & Wickett 2003), latitude (Orr et al. 2005) and habitat, the effects of ocean acidification on seawater chemistry will affect all marine organisms.

Recent studies have shown that in many regions of the ocean, the aragonite saturation horizon (see footnote[1]) approach the surface up to 40 to 200 m as a direct consequence of the uptake of anthropogenic CO_2 (Feely et al, 2004, Orr et al, 2005, Caldeira and Wickett, 2005). It is shallowest in the north eastern Pacific Ocean, only 100 to 300 m from the ocean surface, allowing for the transport of under saturated waters onto the continental shelf during periods of upwelling (Feely et.al 2008).

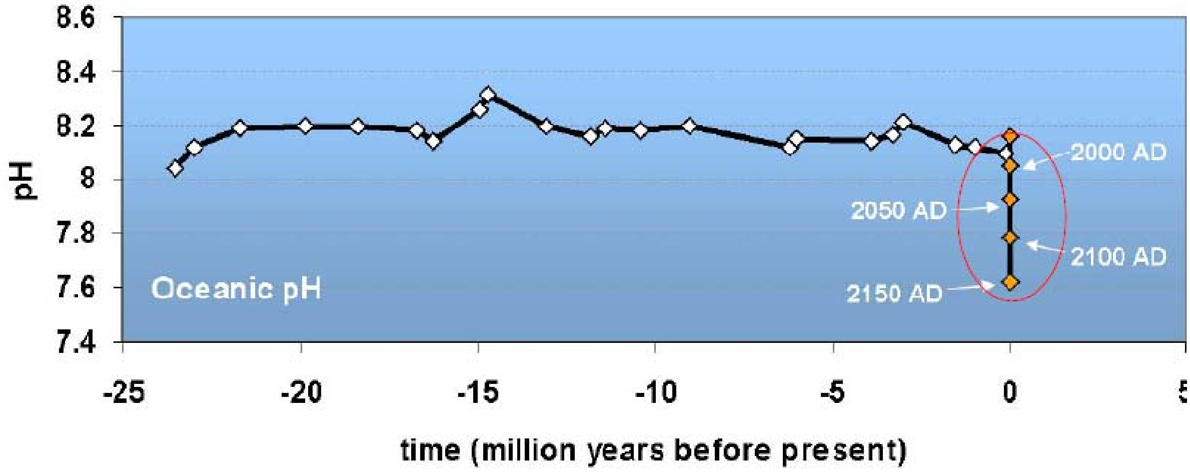


Figure 2.1: Changes in pH over the last 25 million years (source: Turley, 2008b, Pearson and Palmer, 2000)

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[1] There is a critical concentration of carbonate ions in seawater (the saturation concentration) below which $CaCO_3$ will start to dissolve. Because $CaCO_3$ solubility increases with decreasing temperature and increasing pressure, the critical concentration occurs at a depth, the ‘saturation horizon’, below which seawater is undersaturated and CaCO3 will tend to dissolve and above which seawater is super-saturated and $CaCO_3$ will tend to be preserved. Because the CaCO3 mineral calcite is less soluble than the form aragonite, the aragonite saturation horizon is shallower. Because added CO2 decreases the carbonate ion concentration, the saturation horizons will become shallower with increasing releases of human derived CO_2 to the atmosphere.

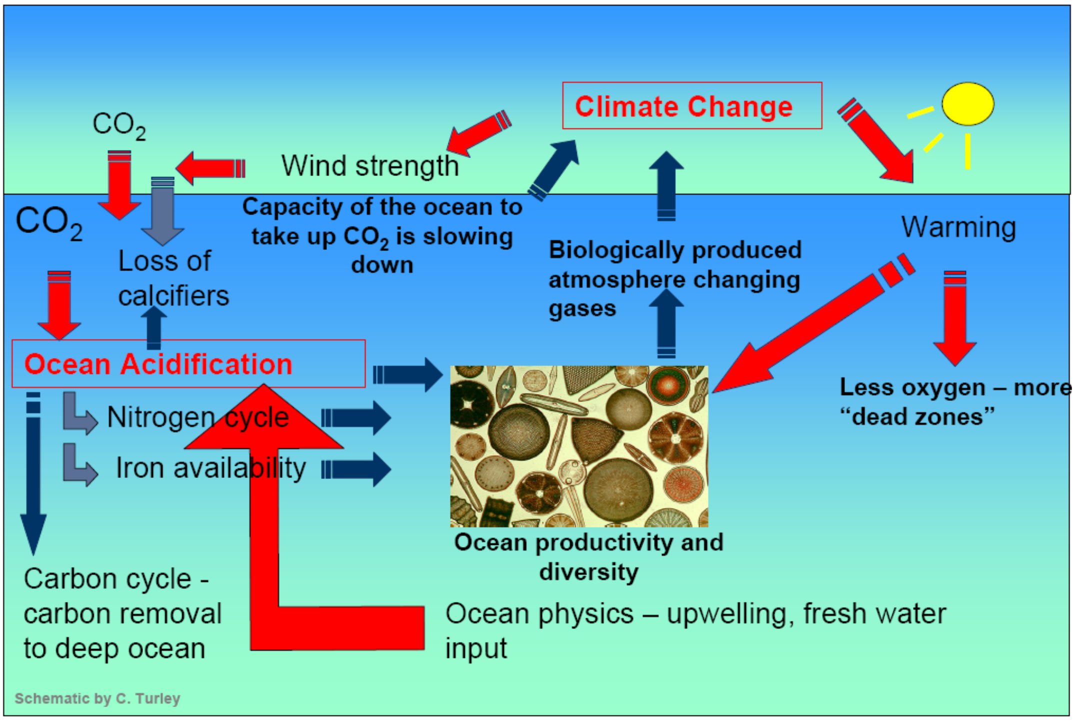


Figure 2.2: Schematic representation of the interactions between ocean acidification and Climate (source Carol Turley Plymouth Marine Laboratory, 2008b)

2.2. Nitrogen and marine eutrophication

Nitrogen is a nutrient, used deliberately on land as a fertilizer. Concern about its marine deposition from the atmosphere arises from the potential consequence of this fertilizing effect in marine waters. Nitrogen supply can enhance primary production, which is the conversion of light energy to stored energy as simple sugar. This photosynthesis relies on the availability of basic minerals such as nitrogen, and the subsequent use of energy to then construct complex organic compounds such as proteins and pigments requires nitrogen.

The basic state where low nutrient supply imposes limitation to productivity is termed oligotrophy. Whilst molecular nitrogen N_2 is universal, the high energy requirement to break the N-N bond means that few organisms can fix molecular N_2, and most organisms must assimilate reactive forms of nitrogen. These are principally oxidised and reduced forms (nitrate and ammonia/um) although organic forms (about which less is known) can be important. The initial creation and then cycling of reactive forms occurs through fixation of molecular nitrogen, enzymatic conversion to reactive form, consumption and decomposition with ammonification of organic compounds, and subsequent nitrification with oxygen to nitrite and nitrate. Three of the principal reactions are given in textbox 3, including the denitrification back to molecular nitrogen. This occurs typically slower than fixation, and so there is a tendency towards away from oligotrophy towards nutrient sufficiency. During cycling, nitrate is commonly held to be responsible for most "new" primary production in the oceans, with ammonia/um responsible for "regenerated" primary production. Over a season, winter dissolved mineral socks may accumulate to be consumed by phytoplankton growth in spring and summer until limiting levels of minerals are once again reached. Growth above this level is eutrophication. Commonly the term is used to refer to this biogeochemical response to over enrichment from an external anthropogenic source, and it is this sense it is used here. A typical sequence of events would see enhanced phytoplankton growth until disturbance of ecological systems occurs. Increased algae growth with increased sedimentation, reduced light availability, potential falling diversity, shift in species composition, algal blooms often with mucus production, proliferation of opportunist macroalgae, and potential adverse impact on fish and shellfish production. Increase in decaying plant matter will enhance water column oxygen depletion, the effects of which may be exaggerated if salinity and temperature differences in the water column lead to stratification. In severe cases such hypoxia creates a dead zone, bringing organism deaths, an alteration to food web dynamics, and ultimately ecosystem collapse. One of the world best known cases of hypoxic sea areas is in Europe - the Black Sea (Selman et al., 2008). This declined from 26 commercially viable fish species in the 1960s to five in the 1980's, and at one stage was the largest dead zone in the world. The long term biological and social implications of increased nitrogen fluxes in coastal waters are not fully understood. However, it is clear that eutrophication means reduced capability for coastal ecosystems to support services such as tourism, fishing, and shellfish.

TEXTBOX 3: Processes in nitrogen cycling

Photosynthetic primary production	$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$
Ammonification	$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$
Denitrification	$NO_3- \rightarrow NO_2- \rightarrow N_2O \rightarrow N_2$

These processes play a part both in natural cycling and in eutrophication. For example, increased scale of ammonification/nitrification reduced oxygen levels and increases CO2 concentrations and ultimately produces hypoxia of deep water. The consequence can be to harm larval survival, and ultimately produce loss of the benthic community

Such changes can occur in particular as a consequence of excess nitrogen and phosphorus supply. With the atmospheric supply of phosphorus being negligible, from an atmospheric perspective eutrophication is a nitrogen issue. Awareness, however, has been relatively recent. The series of International Conferences on Protection of the North Sea did not until the third in 1990 specify "atmospheric inputs as a source of contamination" as a topic for attention, and then gave no special attention to nitrogen. The lack of understanding was summed up by GESAMP (1991) "probably less is known about the atmospheric input of nitrogen species to our estuaries and near-shore waters than any other transport paths". Recognition of the potential influence came in EEA (1995) with acknowledgement that "eutrophication by airborne nitrogen loads is now appreciated….. in the central parts of the North Sea aerial transport is more important than riverine transport".

During these years the first estimates were made of the concentrations of reactive nitrogen which may equate to trophic status in marine waters, with most attention focusing on the North, Norwegian and Baltic Seas. One such collation is reproduced in table 2.1. This suggests that the estimated influences of concentrations of reactive nitrogen are regionally specific. Whilst the exact values appropriate for each category are open to discussion, the point made is that once a concentration can be described above and below which changes occur, and which can be reached by anthropogenic disturbance, budgeting could determine the loading necessary to exceed the criteria. In this sense there is similarity with the critical load approach used for terrestrial ecosystems.

As much as 65% of Europe's Atlantic coast show signs of eutrophication (OSPAR, 2003), and with atmospheric depositions of nitrogen being greatest nearer to the coast the role played by atmospheric deposition is a valid issue. Distant waters are also affected. With the influence of riverine inputs of nitrogen decreasing rapidly with distance from the shore whilst atmospheric deposition continues to the distant oceans, atmospheric nitrogen may a significant source of external nitrogen for open seas in Europe.

Table 2.1: Estimated water quality criteria for European Seas. (Concentrations as $\mu g\ N\ l^{-1}$. Dating from when awareness of the issue grew).

Norwegian coastal waters summer[a]	Close to background	Moderate influence	Clear influence	Severe effect
NO_x-N range	<12	12-23	24-65	>65
NH_x-N range	<19	20-50	50-200	>200
Norwegian coastal waters winter[a]				
NO_x-N range	<90	90-125	125-225	>225
NH_x-N range	<33	33-75	75-155	>155

North Sea winter[b]	north	Mid/Channel	Kattegat	German Bight
NO_x-N typical	<170	<100	50-210	280
NO_3-NO_2-NH_4 – N typical[c]		140		

Baltic Sea summer[a]	oligotrophic	mesotrophic	eutrophic	Hypertrophic
NO_x-N range	<10	10-30	30-50	>50

Adriatic Sea[d]				
NO_x-N typical	<7	21	70	110
NH_x-N typical	<7	14	>14	>28

a) Hessen et al 1992 b) North Sea Task Force 1993 c) EEA (1995) d) GESAMP 1990

An indicator for eutrophication risk in coastal waters has commonly been the change in riverine inputs of nitrogen (e.g. Bouwman et al, 2005). An example of this in practice has been the decline in riverine fertilizer inputs to the Balck Sea which accompanied economic collapse in the 1990s and the resulting steady recovery from its eutrophic status. Yet in Europe this approach is no longer entirely satisfying. Many waters have an elevated trophic status already, or are eutrophic. Whilst riverine inputs of nitrogen are expected to decline by as much as 20% in the next 3 decades (Bouwman et al, 2005), atmospheric inputs of inorganic reactive oxidised and reduced nitrogen have been stable in recent years, and are not anticipated to undergo strong decline. They can also be large, e.g. at present over 30% of total nitrogen inputs in both the North Sea (OSPAR, 2000) and the Baltic Sea (HELCOM, 2008). Moreover, on a global scale atmospheric reactive nitrogen input is growing to the point where it is rapidly approaching, and by 2030 may achieve, global oceanic estimates for N_2 fixation (Duce et al., 2008). When it is considered that in addition to this inorganic nitrogen input, relatively unstudied soluble organic nitrogen components in the atmosphere may represent a third of total atmospheric nitrogen loading (Spokes and Jickells, 2005), then the atmosphere may be moving towards being the principal route for direct nitrogen input to European seas. Indeed, the increase in anthropogenic atmospheric reactive inorganic nitrogen means atmospheric deposition is rising to the point where it may exceed natural N_2 fixation in the oceans (see section 2.2). An indicator of eutrophication risk based on riverine supply would clearly be deficient in such circumstances.

2.3. Linkages between marine acidification and eutrophication

The increase in anthropogenic atmospheric reactive inorganic nitrogen means deposition is rising to the point where it may exceed natural N_2 fixation in the oceans (see section 2.2).However, this picture is complicated by the effect of rising CO_2 content and acidity. Barcelos e Ramos *et al* (2007) have shown that the principal nitrogen fixing cyanobacteria, Trichodesmium, reacts to rising CO_2 seawater content by increased fixation. This leads to increased N:P ratios and increased C:P ratios, and the increase in bioavailable nitrogen in N-limited systems can enhance phosphorus use, which can push systems towards phosphorus limitation. The nutritional value of primary produced organic matter may also be altered. Any impact on efficiency of bacterial degradation and zooplankton reproduction could cascade on the pelagic food web. From a climate perspective, however, the effect may be one of negative feedback. Increased N_2 fixation would increase oceanic carbon sequestration.

Nutrient speciation is itself impacted by the pH of the seawater. The proportions af ammonia to ammonium are sensitive to small variations in pH (Zeebe and Wolf-Gladrow, 2001). Nitrification rates are reduced by both declining pH and by disappearance of ammonia from the substrate, such that ratios of ammonium to nitrate may increase (Huesemann et al, 2002).

The changes in balance between nitrogen forms which may occur in the North Sea up to the year 2100 with rising seawater CO_2 has been investigated by Blackford and Gilbert (2007). They predict a +10% difference in the ratio between nitrate and total inorganic nitrogen (nitrate + ammonium) in the open southern North Sea. The changes in coastal waters may be less due to masking by riverine inputs. Other studies have indicated a 20% decrease in pelagic nitrification (Orr et al, 2005). A reduction in nitrification and nitrate could mean a reduction in denitrification in the substrate, with decreased volatile nitrogen emissions, and increased eutrophication. With the North Sea already being eutrophic, the additional impact of this may be small. Much of Europe’s marine waters are also eutrophic, but such an effect could slow current recovery in some areas.

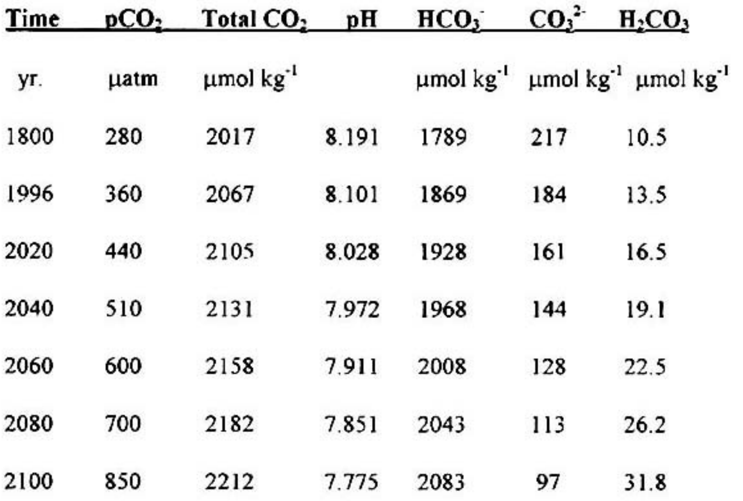
3. Emissions of CO_2 and nitrogen, and their transfer to the seas

3.1. Carbon dioxide emissions and CO_2 transfer to the oceans

The surface ocean constitutes the gateway for CO2 into the ocean's interior, with the air-sea pCO2 difference (ΔpCO2) being the thermodynamic driving force for surface gas exchange. Analysis of the raw observations at the Bermuda Atlantic Time-series Study station (BATS) [Bates, 2001] indicates that the surface water pCO2 has risen faster than the atmospheric pCO2, but if the data are seasonally detrended, surface water and atmospheric pCO2 appear to rise at more comparable rates.

Theoretical, laboratory, and modeling studies suggest that the buffer capacity of the seawater inorganic carbon system, reflected in the Revelle factor, decreases under high-CO2 conditions: Seawater equilibrated with high-pCO2 air holds less additional dissolved inorganic carbon (DIC) for the same size change in pCO2, constituting a positive feedback on the atmospheric buildup of anthropogenic CO2 [Revelle and Suess, 1957; Sarmiento et al., 1995]. The key variables that will determine the extent of future seawater chemistry changes—and therefore the impact on marine life—is the magnitude and time scale of the anthropogenic carbon release.

Table 3.1: The evolving chemistry of surface sea water under "Business as Usual" water (ICES, 2007)



Time	pCO_2	Total CO_2	pH	HCO_3^-	CO_3^{2-}	H_2CO_3
yr.	µatm	µmol kg^{-1}		µmol kg^{-1}	µmol kg^{-1}	µmol kg^{-1}
1800	280	2017	8.191	1789	217	10.5
1996	360	2067	8.101	1869	184	13.5
2020	440	2105	8.028	1928	161	16.5
2040	510	2131	7.972	1968	144	19.1
2060	600	2158	7.911	2008	128	22.5
2080	700	2182	7.851	2043	113	26.2
2100	850	2212	7.775	2083	97	31.8

For specific CO_2 emission scenarios, changes in atmospheric CO_2, surface ocean pH, and carbonate mineral saturation state have been calculated with different carbon cycle models (Caldeira and Wickett, 2003, Orr et al , 2005, Montenegro et al, 2007, Zeebe et al, 2008). In contrast to atmospheric climate model calculations, ocean chemistry projections are largely model-independent on a time scale of a few centuries, mainly because the chemistry of CO_2 in seawater is well known (Zeebe and Wolf-Gladrow, 2001) and changes in surface ocean carbonate chemistry closely track changes in atmospheric CO_2. Predicted changes in surface ocean pH for given total emissions and release time of anthropogenic carbon are thus similar among different types of models over the next few centuries, see i.e. table 3.1 (Caldeira and Wickett, 2003, Orr et al , 2005, Montenegro et al, 2007, Zachos et al, 2008)].

Projected changes in ocean carbonate chemistry should serve as a guideline for policy protocols that identify CO_2 emission targets to reduce the effects of human-made ocean acidification. For example, to avoid a surface ocean pH decline by more than 0.2 units (U.S. Environmental Protection Agency, 1976), total emission targets would have to range from ~700 Pg C over 200 years (average reduction

50% compared to current levels) to ~1200 Pg C over 1000 years (average reduction of 85% compared to current levels), see figure 3.1.

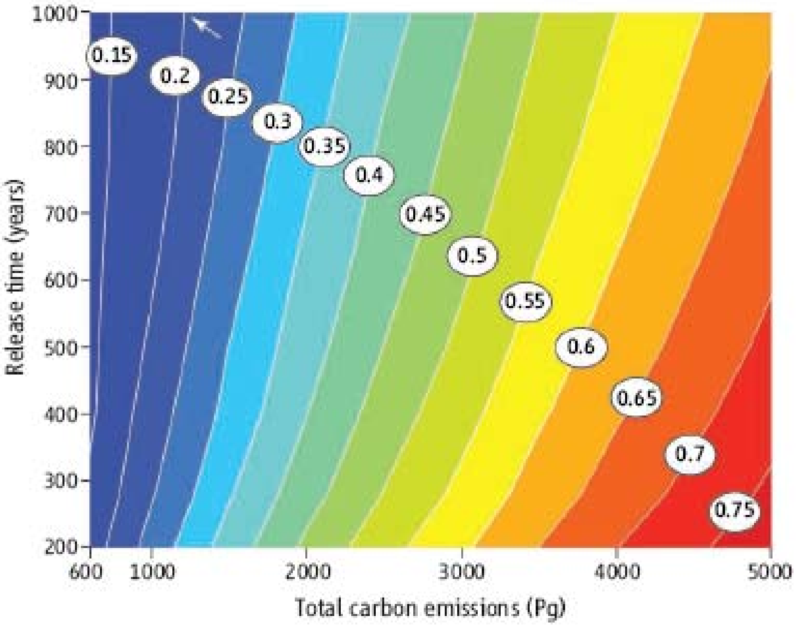


Figure 3.1: Surface ocean pH decline. The white contour lines illustrate the expected maximum pH decrease of average surface ocean waters (in pH units) as a function of total anthropogenic CO_2 emissions (Pg) and release time (in years). For example, if humans release a total of 1500 Pg C over 200 years (stabilizing at current emission levels), surface ocean pH will drop by about 0.35-0.4 units., source Zeebe et al, 2008

Cumulative global anthropogenic CO_2 emissions over the period 1850-2008 already released 340 Pg C (1240 Pg CO_2) to the atmosphere (see also figure 3.2), with Europe (40%) and N-America (32%) as the main contributors.

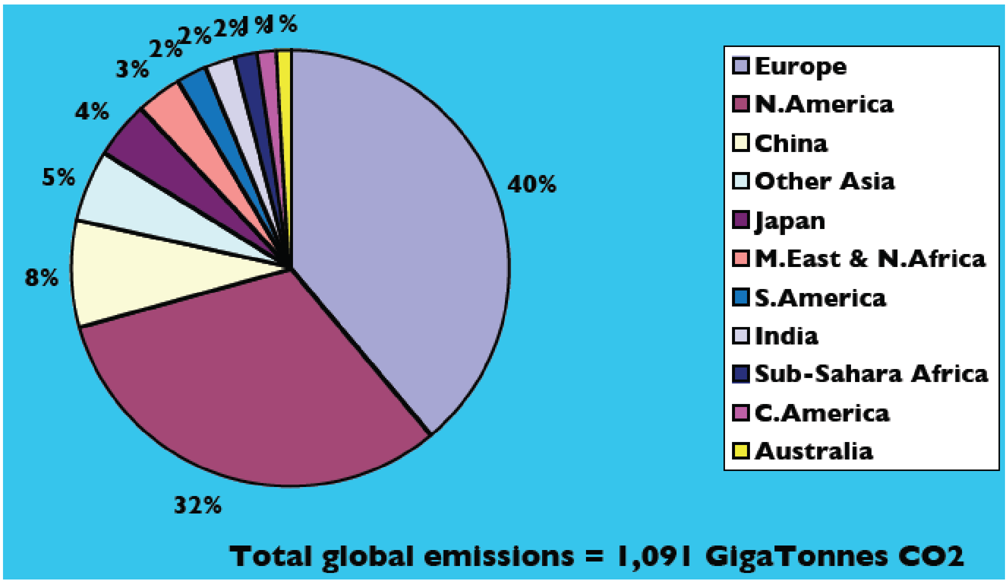


Figure 3.2: Cumulative Global CO2 Emissions 1850 – 2003 (80% from the developed world), source WRI, 2009

At current emission levels the 700 Pg limit (to comply with the USA-EPA standard) would already be reached by 2057. In table 3.2 the global cumulative CO_2 for the 4 IPCC SRES scenarios and some current mitigation scenarios are given. The table clearly shows that limiting the ocean acidification to a drop op 0.2 Ph points would require a considerable effort, the increase in CO_2 concentration should be limited to approximately 400 ppm, a value only considered in the most stringent mitigation options. (IPCC, 2007).

If emissions can be reduced after the year 2050 and capped at 1500 Pg C, surface ocean pH would decline by ~0.35 units relative to pre industrial levels. The aragonite saturation state in the warm surface ocean would drop from ~3.5 to ~2.1 under this scenario. Substantial reductions in coral calcification have been reported over this range (Raven et al , 2005, Hoegh-Guldberg et al , 2007, Kleypas et al., 1999).

Table 3.2: Cumulative global CO2 emissions for various baseline and mitigation scenarios (IPCC, 2001, 2007).

	Cumulative global CO_2 emissions (Pg)			CO_2-CO_{2eq} concentration 2100 (ppm CO_{2eq})
	1850-2050	1850-2100	1850-2200[1]	
SRES A1-C/F	920	2400	5800	970-1300
SRES A2	770	1900	5000	850-1200
SRES A1-B	1100	1900	3300	710-1000
SRES B2	930	1600	3000	620-820
SRES B1	820	1200	1700	540-680
550 PPM stabilization		850	1000	450-550
510 PPM stabilization		700	780	410-510
450 PPM stabilization		580	600	350-450

[1] Own calculation, assuming constant CO_2 emissions after 2100

3.2. Nitrogen emissions and transfer to the oceans

Whilst global emissions of nitrogen do have a relevance, the predominant influence upon European seas will come from sources close at hand. With a transport distance for reactive nitrogen of typically a few hundred to a couple of thousand kilometres, nitrogen is a regional scale pollutant, and not a global pollutant in the style of CO2. Past and expended trends of nitrogen emission in Europe are thus most relevant to questions around marine eutrophication from atmospheric nitrogen in Europe.

The most recent official reports from Europe suggest that emissions of reactive nitrogen in Europe do appear to have fallen somewhat since 1990. For the 27 countries of the European Union, oxidised nitrogen emissions are estimated to have fallen by 35% (EEA, 2008a) whilst ammonia emissions have fallen by 22%. Emissions of oxidised and of reduced reactive forms contribute approximately equally to nitrogen loading in the atmosphere. Reported oxidised nitrogen emissions in Europe of over 11000Gg (1Gg = 1kT) in 2006 means ca. 3300 Gg NOx-N, which is equal to the nitrogen content of the reported 4000Gg of ammonia emissions. With 40% of oxidised nitrogen coming from vehicle emissions, but over 90% of ammonia emissions arising from agriculture, it appears that the latter is the principal source of nitrogen in Europe. More specifically, manure management dominates as a source activity, this representing around 70% of agricultural emissions. These estimates confirm earlier assessments (e.g. EEA, 2007) in which agriculture was estimated to be the largest source of eutrophying air pollutants (44% of the total), with road transport in second place at 22%.

Due to some extent to a greater increase in vehicular transport than anticipated, it seems as though there will be difficulty for some European countries to reach 2010 emission targets, especially for oxidised nitrogen. Compared to 1990, emissions were to planned fall by more than half by 2010. At present, 13 of 27 Member States report that they expect to miss these targets (EEA, 2008b), with two also missing ammonia reduction targets. As a whole, NO_x emissions for the EU-27 as a whole are expected to be 9% over the aggregated Member States (Annex 1) ceiling values, and 20% above stricter (Annex II) ceilings for 2010. Given differences in the degree of achievement, some Member States will miss targets by as much as 50%.

Globally, atmospheric transport and deposition of reactive nitrogen has become the dominant distribution mechanism for anthropogenic nitrogen (Galloway et al., 2008). Nevertheless, direct deposition of nitrogen to the marine surface in a densely populated and economically active region such as Europe, especially given the intimacy of the marine and terrestrial environments, is dominated by regional scale flows. The particular wet or dry mechanism of atmospheric delivery is important to determining the actual levels of supply, as is the precise oxidised or reduced form of that reactive nitrogen. The greater solubility of ammonia will encourage both its dry deposition to the sea surface, and its uptake in cloud water. Emissions of NO_x, however, are far less soluble at first, such that deposition in the immediate vicinity of emissions will be less. Chemical conversion to particulate nitrate will also restrict dry deposition. Whilst also true for ammonium, the overall effect is for reduced nitrate deposition near emission sources, and extended deposition thereafter, but for rapid deposition of reduced nitrogen nearer source areas and a lesser proportion depositing over an extended distance.

One consequence of this is that the source areas for nitrogen arriving at the sea surface vary for oxidised and for reduced nitrogen. Examining the Baltic, Barrett (2006) found that this source region 'footprint' for reduced nitrogen was found to mean that the first 50% of depositions originated in the immediate couple of hundred kilometres of the coastal zone, whilst for oxidised nitrogen the first 50% of supply originated from a footprint extending across the UK, into Austria, and even as far as Turkey.

An indication of the significance of European emissions for direct marine depositions in Europe can be gained from the EMEP atmospheric modelling work (e.g. EMEP 2008). This suggests that as much as a third of any countries emissions of oxidised nitrogen will be deposited in the seas, and up to around a quarter of reduced nitrogen. With over 75% of oxidised nitrogen and over 90% of reduced nitrogen emissions from many countries being redeposited in the European area, whilst long range transboundary flows are not irrelevant to the seas in Europe, it is the regional emissions which dominate the picture.

Direct deposition to the sea surface is not the only mechanism delivering atmospheric nitrogen to the European seas. Of that deposited to the land surface a proportion will not be retained, but will be transported by hydrological flows to coastal waters. Thus, a proportion of the inputs defined as "riverine" may actually be considered as another consequence of air pollution. It is matter of perspective whether or not to include this contribution in discussion of atmospheric pollution on the marine environment. In this initial discussion report we have chosen not to do, whilst reminding that changes in atmospheric nitrogen loading will have an influence particularly on coastal waters out over that described in this report.

4. Carbon dioxide uptake and acidification in European seas

4.1. Introduction

The[2] North Atlantic Ocean [Takahashi et al., 1997] and its coastal [Thomas et al., 2004] and shelf areas [Frankignoulle and Borges, 2001] play a key role in absorbing CO_2 from the atmosphere. The latter areas are thought to act as continental shelf pumps for CO_2 [Tsunogai et al., 1999; Thomas et al., 2004; Borges et al., 2005] supplementing substantially the CO_2 uptake by the open oceans. A pilot study in the North Sea, carried out in 2001/2002 with seasonal resolution, provided fundamental insight into the continental shelf pump mechanism and strength of the CO_2 uptake in coastal seas [Thomas et al., 2004, 2005a, 2005b; Bozec et al., 2005, 2006]. Chemical and biological activity, which are high in the surface of the world ocean and notably so in its shallower extensions [Wollast, 1998] such as the North Sea, partly mediate CO_2 uptake and introduce both positive and negative feedbacks with anthropogenic CO_2 uptake. For example, elevated CO2 levels decrease benthic and pelagic calcification and increase CaCO3 dissolution in sediments, both of which act to damp the growth of atmospheric CO2 (Riebesell et al. 2000, Delille et al., 2005; Orr et al., 2005.)

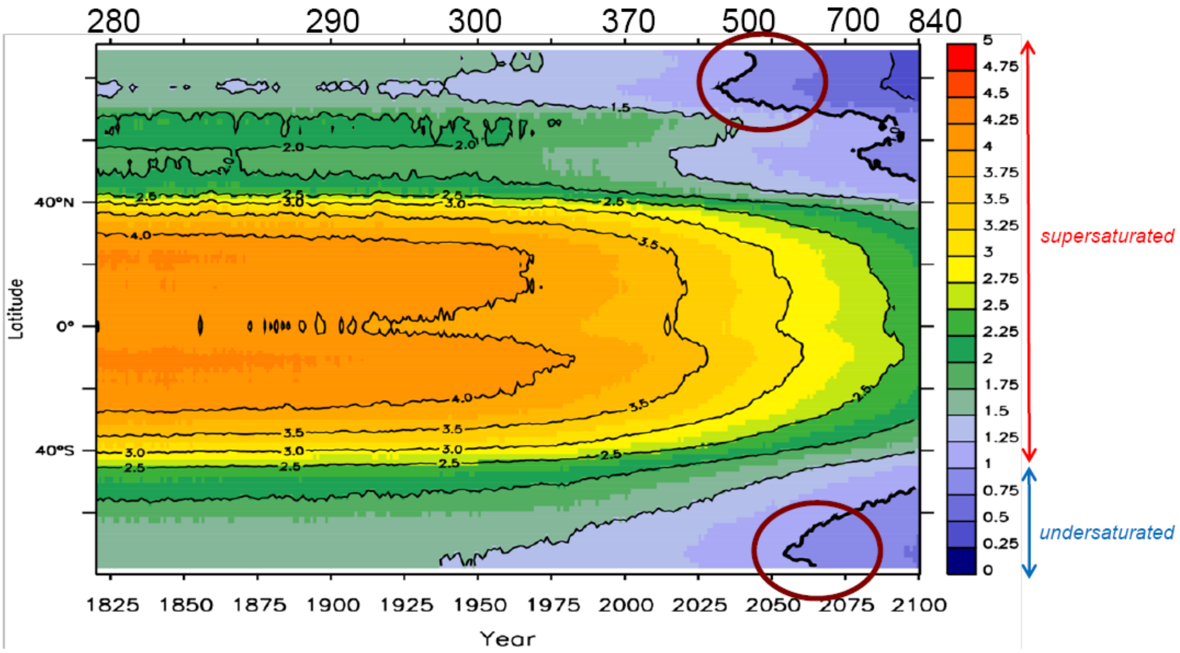


Figure 4.1: Projected surface aragonite saturation state (ΩA), source: Plattner, 2008; Steinach et al, 2008):

The observed decline in the air-sea p CO_2 difference in the northern North Atlantic could arise from a variety of biological, chemical, and physical factors and may reflect either natural interannual to decadal variability [e.g., Le Quere et al., 2000], the longer-term secular trend due to anthropogenic CO_2 transience, or some or both (Thomas et al, 2007).

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[2] Revised text from Thomas et al, 2007

4.2. Atlantic Ocean

Figure 4.4 presents the results of the model calculations of the revelle factor for the North Atlantic for 2004. The model (Thomas et al, 2007) included:

- A global ocean carbon model, to estimate the long-term trends of surface water p CO_2 and the Revelle factor over the North Atlantic
- A model for the biogeochemical cycling of C, O, N, P, Fe, and Si and AT and four phytoplankton functional groups (diazotrophs, diatoms, picoplankton, nanoplankton, and coccolithophores)
- A ecosystem module [Moore et al., 2004].

The evolution of atmospheric CO_2 with time from 1820 to 2004 is prescribed using ice core and atmospheric observations.

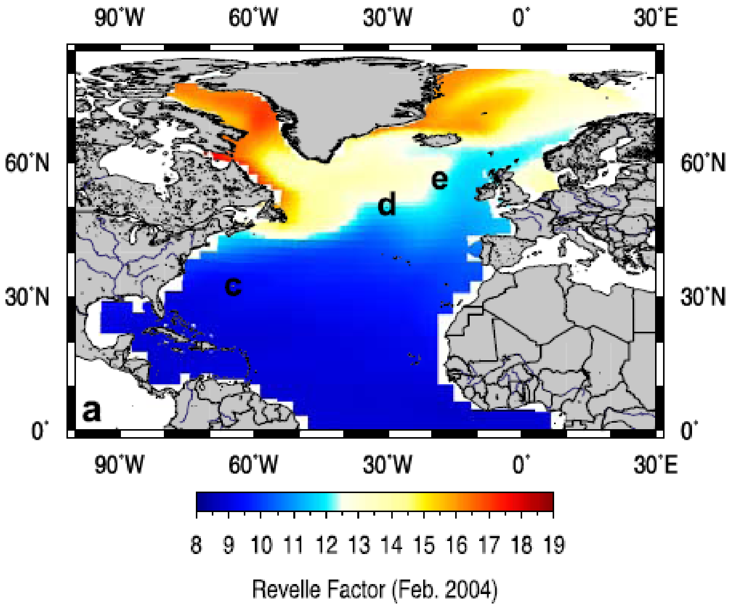

Figure 4.4: Simulations of the CO2 system in the North Atlantic Ocean. (a) Simulated Revelle factor in the North Atlantic Ocean in February, 2004. The month of February has been chosen as a biologically inactive period., source: Thomas et al, 2007

4.3. Baltic Sea

Parts of the Baltic Sea are lightly undersaturated with respect to carbonate in winter and is likely the largest water body at the globe to experience seasonal surface under-saturation. The explanation can be found in lower carbonate (/5) and calcium concentration (/4) in the sea water compared to the North Atlantic at same latitude (Tyrrell et al, 2008) and the low temperature of the water (*7),:

$$\Omega = [CO3\ 2-][Ca2+]/\ K^{*}_{sp}$$

at Sal = 7, T = 0°C;

- ~5-fold lower $[CO_3^{2-}]$
- ~4-fold lower $[Ca^{2+}]$ at Sal = 7, T = 0°C
- ~7-fold lower K^{*}_{sp} (5 * 4 / 7)

≈ 3-fold lower Ω in Baltic compared to standard calculation at S=42 and T=16

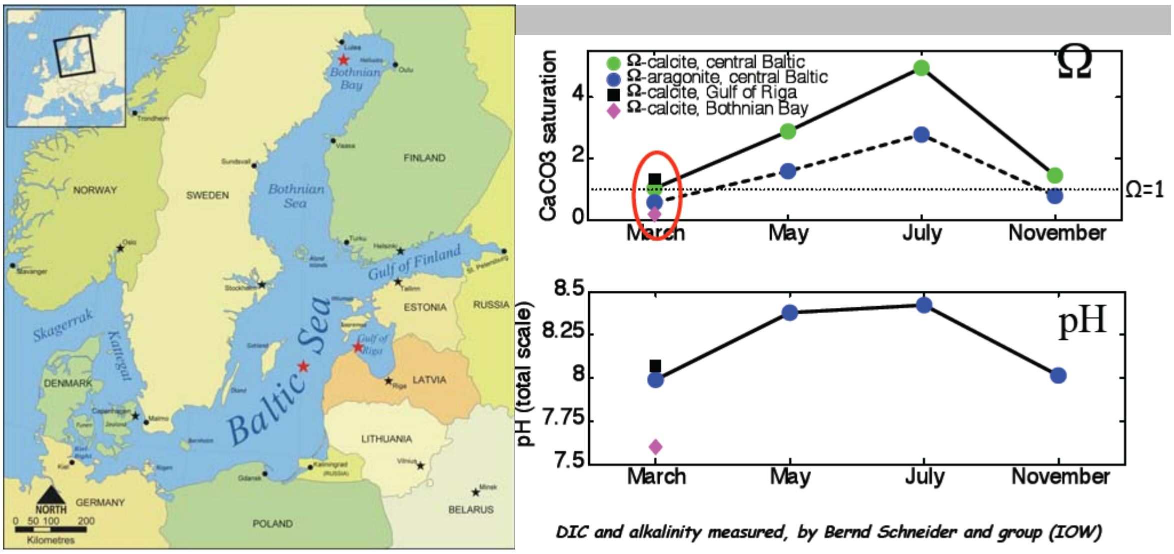

Figure 4.5: Low Saturation States in Baltic Sea, Central Baltic under saturated in winter, even though pH not esp. low. Source: Tyrrell et al, 2008.

Already in 1976 (Alexandersson, 1976) Alexandersson noted that “In the near future, atmospheric carbon dioxide from the combustion of fossil fuels may cause the surface layers of the ocean to become generally under saturated with calcium carbonate. The hypothetic sedimentary effects of such an event are here discussed in the light of studies in the Skagerrak Bay, North Sea. In this area, near shore sediments in the depth range 0–40 m are affected by present-day carbonate dissolution. Not surprisingly, evidence of inorganic carbonate precipitation is absent. Stages in the dissolution process are microscopic etch patterns on calcareous grains, partially dissolved grains, and finally structural breakdown and complete dissolution of skeletal elements. Mineral phases affected are calcite, aragonite, and a spectrum of magnesium calcites. Dissolution is quantitatively unimportant in living calcareous organisms, but preservation of shells and skeletons as fossils is much impeded. A future change towards similar conditions in all the world's shelf seas would certainly mean an end to the typical warm-sea carbonate sedimentation as it is known today on the Bahama Banks and in other supersaturated regions.”

4.4. North Sea

The[3] North Sea consists of a shallower southern region showing classical characteristics of shelf seas, while the deeper, central and northern regions clearly represent oceanic conditions [Thomas et al., 2005b]. The flushing time for North Atlantic Ocean water circulating through the North Sea is on the order of 1 year [Lenhart et al., 1995], and seasonal stratification partly mimics open ocean conditions. Still, winter convection usually reaches the bottom, allowing anthropogenic CO_2 to penetrate the entire water column of the North Sea. The combination of ocean conditions in a relatively shallow, well-ventilated (on annual timescales) system accentuates temporal changes of the CO_2 system relative to the open ocean subpolar Atlantic at the same latitude where the anthropogenic CO_2 signal is spread over the vertical by deep convection. Approximately 75% of the uptake of atmospheric CO2 by the North Sea occurs between February and summer [Thomas et al., 2004, 2005b], counteracting the effects of the biological DIC drawdown in the surface waters. By late summer the water column mean DIC is thus dominated by seasonal organic matter degradation in the subsurface layer.

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[3] Revised text from Thomas et al, 2007

During (Thomas et al, 2007) two campaigns (2001, 2005) the entire North Sea has been sampled by an adapted grid of 90 identical stations during both years, resulting in high resolution data sets for assessing the temporal changes between 2001 and 2005. From the data (see table 4.1) two important North Sea specific relationships could be derived:

$$A_T\left[\mu\text{mol kg}^{-1}\right] = 1949.6 + S(10.34)[\pm 23]$$
$$\Delta\text{DIC}_{\text{sol}}\left[\mu\text{mol kg}^{-1}\right] = S(3.53348) - T[^\circ\text{C}]8.10648 + 7.08289.$$

The Revelle (see Revelle, 1957) factor $(\Delta pCO_2/pCO_2)/(dDIC/DIC)$ in table 4.1was calculated using standard thermodynamic relationships. The data shows that the atmospheric pressure increased by 11 matm between 2001 and 2005 (Table 4.1), which is similar to the atmospheric CO_2 pressure rise recorded at the nearby Norwegian Sea.

The North Sea–wide averages Revelle factor increased from 10.6 in 2001 to 11.1 in 2005. The water column mean DICnorm increased over almost all of the North Sea (average 11 mM), with highest values up to 34 mM in the shallower, central and southern regions. This net water column DIC storage amounts to on average 1.1 mol C m^{-2}, or approximately 0.25 mol C m^{-2} yr^{-1}, and complements the still evident CO_2 transfer from the atmosphere into the Atlantic Ocean by the North Sea's continental shelf pump.

The increase of the mean DICnorm in the southern region can be ascribed to a DIC increase of the waters imported from the Atlantic Ocean because of anthropogenic uptake and constitutes one mechanism for the rise of the p CO_2 in supersaturated waters. Moreover, the supersaturation in the southern region reflects in part summer seasonal warming, yet the surface water undersaturation during winter and spring [Thomas et al., 2004, 2005b] also permits CO_2 uptake there.

Table 4.1: Results from two North Sea measurements campaigns (2001, 2005) , source: Thomas et al, 2007

	Atmospheric pCO_2, μatm	Surface Temperature, °C	Surface Water pCO_2, μatm	ΔpCO_2, μatm	Surface Water pCO_2 at $T = 16^\circ C$, μatm	ΔpCO_2 at $T = 16^\circ C$, μatm	Surface DIC, μM	Normalized Surface DIC, μM
Entire North Sea								
2001	359	16.3 ± 1.2	327 ± 43	−31.2 ± 42	323 ± 36	−35.7 ± 37	2089 ± 36	2091 ± 41
2005	370	15.0 ± 1.4	349 ± 34	−20.0 ± 34	366 ± 29	−4.1 ± 31	2109 ± 27	2103 ± 27
Northern North Sea (North of 54°N)								
2001	359	16.0 ± 1.2	311 ± 33	−47.2 ± 33	311 ± 28	−48.5 ± 28	2079 ± 35	2080 ± 40
2005	370	14.8 ± 1.3	342 ± 27	−27.3 ± 27	361 ± 26	−8.0 ± 29	2107 ± 27	2099 ± 25
Southern North Sea (South of 54°N)								
2001	359	16.9 ± 1.0	378 ± 25	18.6 ± 25	366 ± 26	4.2 ± 29	2121 ± 11	2128 ± 17
2005	370	16.7 ± 0.8	405 ± 30	36.2 ± 30	403 ± 29	25.4 ± 34	2135 ± 6	2138 ± 9

	Water Column Mean DIC, μM	Normalized Water Column Mean DIC, μM	Change of DIC_{norm} Water Column Inventory, mol DIC m^{-2}	Water Column Mean AOU, μM	Water Column Mean A_T, μM	Revelle factor (Normalized)
Entire North Sea						
2001	2153 ± 22	2106 ± 22		19.7 ± 9.9	2371 ± 13	10.1 ± 0.36
2005	2166 ± 21	2117 ± 16	+1.1 ± 1.2	18.9 ± 10.4	2375 ± 11	10.7 ± 0.33
Northern North Sea (North of 54°N)						
2001	2160 ± 19	2101 ± 21		22.9 ± 7.9	2372 ± 13	10.0 ± 0.29
2005	2169 ± 19	2114 ± 15	+1.2 ± 1.3	20.9 ± 8.9	2376 ± 10	10.6 ± 0.29
Southern North Sea (South of 54°N)						
2001	2127 ± 8	2125 ± 16		6.1 ± 4.1	2368 ± 17	10.5 ± 0.34
2005	2137 ± 8	2140 ± 10	+0.1 ± 0.3	0.8 ± 3.7	2367 ± 13	11.1 ± 0.34

[a] The standard deviation reveals spatial variability of the averages which indicate general trends of the parameters between 2001 and 2005. The Revelle factor has been calculated from the station data (Figure 1) rather than from the basin-wide or regional averages. The atmospheric observations are in excellent agreement with observations from Ocean Station M (66°N, 2°E) (CO_2 Time Series data are available at http://www.esrl.noaa.gov/gmd/ccgg/carbontracker/tseries.php?type=mr). The water column mean concentrations are computed from the water column inventory divided by the water column depth.

Ocean Station M in the NOAA/CMDL atmospheric monitoring network4.

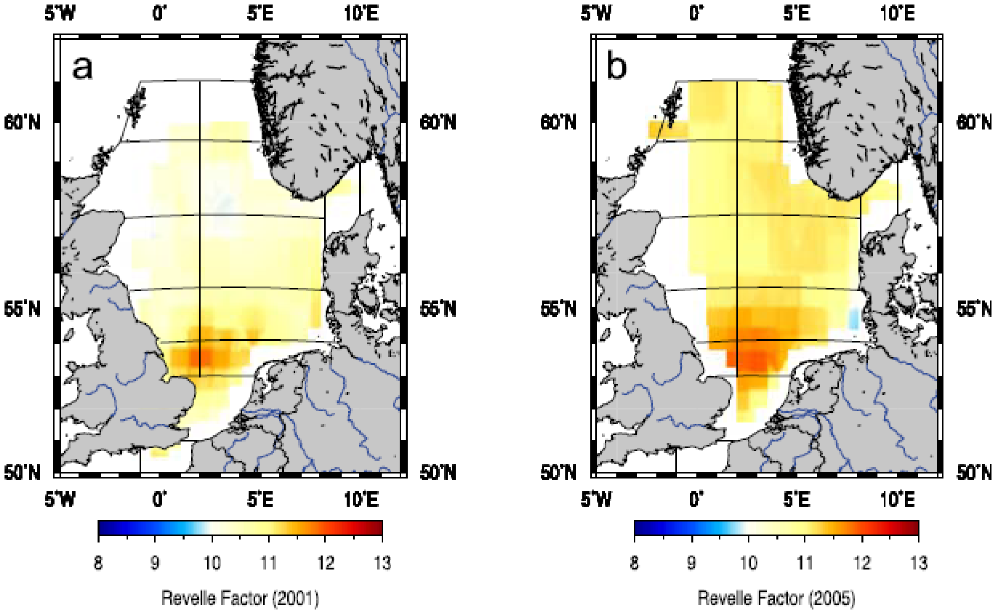

Figure 4.2: Revelle factor and its changes in the North Sea. The Revelle factor, computed from the observed data, is shown for 2001 (Figure 4.2 left) and 2005 (Figure 4.2 right), source: Thomas et al, 2007

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[4] (CO_2 Time Series, 2006, available at http:// www.esrl.noaa.gov/gmd/ccgg/carbontracker/tseries. php?type=mr).

5. Nitrogen inputs to the European seas

5.1. Rates of nitrogen deposition

Table 4.1 presents a summary of current estimates for rates of nitrogen deposition from the atmosphere to the sea areas of Europe. These estimates are expressed in milligrammes of nitrogen per square metre, as this unit can be compared with biological demand and production rates, and provides a metric which allows comparison between different sea areas. Values have been rounded to the nearest 50mg N m^{-2} yr^{-1}, and sources are listed. These represent both observed and modelled estimates, and are presented to indicate either an approximate value, or an indication of the range of estimates that exist in literature. These values include both depositions to open waters, and depositions at the coast.

Table 5. Estimates of atmospheric deposition of nitrogen to European marine waters. Units: mg N m^{-2} yr^{-1}

Sea area	Total N deposition *mg N m^{-2} yr^{-1}*	source
Arctic seas	50- 100	1,7
North Sea	600-1050	1,5, 6, 7
Celtic seas	500	1
Bay of Biscay	400	1
N.E. Atlantic	50-100	1,7
Baltic Sea (whole)	600	2, 3, 5
Gulf of Bothnia	300	3
Baltic Proper	1000	2,3
Kattegat	750-1300	2,3
Mediterranean	450	4,5
w. Mediterranean	400	4 ,8
Adriatic Sea	900	4
Black Sea	400-650	4,5

Sources: 1. Van Pul et al (2009); 2. HELCOM (1997b); 3. HELCOM (2008); 4. MAP (1994); 5. EMEP (2008); 6. OSPAR (2000); 7. SFT (2008); 8. Martin et al (1989)

Whilst there is naturally a clear interannual variability, it is notable that most of the estimates in Table 5.1 lie approximately within a factor of 2-3. This suggests limited uncertainty. Further evidence is found in Dentener et al (2006), where intercomparisons between 23 different atmospheric transport model estimates suggested a variance in deposition fluxes of up to 30%.

The question is what this means for nutrient limitation to primary production. Nitrogen demand varies through the season and geographically according to environmental conditions, and hence no simple factor can transfer the values in table 5.1 into a measure of biological effect. A first order approximation, however, can be obtained from crude assumptions. With annual deposition rates as given in table 5.1, mixing in the immediate surface layer down to 50m, N_2 fixation of 500mg N m^{-2} , and a riverine input of 2000 mg N m^{-2} the estimated contribution of atmospheric nitrogen can be compared with the water quality criteria for trophic state given in table 2.1. The assumptions amount to a fixed and riverine N supply of 50µg N l^{-1}. These very preliminary estimates are given in table 5.2.

Table 5.2: First order coarse approximation of the influence of atmospheric nitrogen deposition upon seawater concentrations and on trophic state. 'Nedded to hange category' means changing from oligotrohic to mesotrophic, to eutrophic, or to hypertrophic, or from moderate to clear to severe influence. See table 2.1 for categories.

Sea area	**Atmospheric N concentration in seawater** μg ***N*** l^{-1}	**Proportion of demand**	**Proportion of available reactive nitrogen %**
N.E. Atlantic/Arctic seas	1- 2	10% of background	2-4
North Sea/ Biscay/Celtic seas	10-21	50%+ of that needed to change category	20-42
Baltic Proper	20-26	100% of that needed to change category	12-52
Mediterranean	9		18
Adriatic Sea	18	~50%+ of that needed to change category	36
Black Sea	8-13		16-26

5.2. Temporal aspects

5.2.1. *Long term changes*

Figure 5.1 presents the temporal changes in deposition that have occurred between 1990 and 2006 as observed by the monitoring programmes reporting data to OSPAR for the North Sea, and HELCOM for the Baltic Sea. Each annual value presents the average annual deposition rate per sq.metre across all stations. This suggests for the North Sea that decrease has not been marked, and that for the Baltic a sharp decrease has levelled out since the mid 1990s. Rates of deposition at coastal sites in the Baltic are notably below those for the North Sea coast.

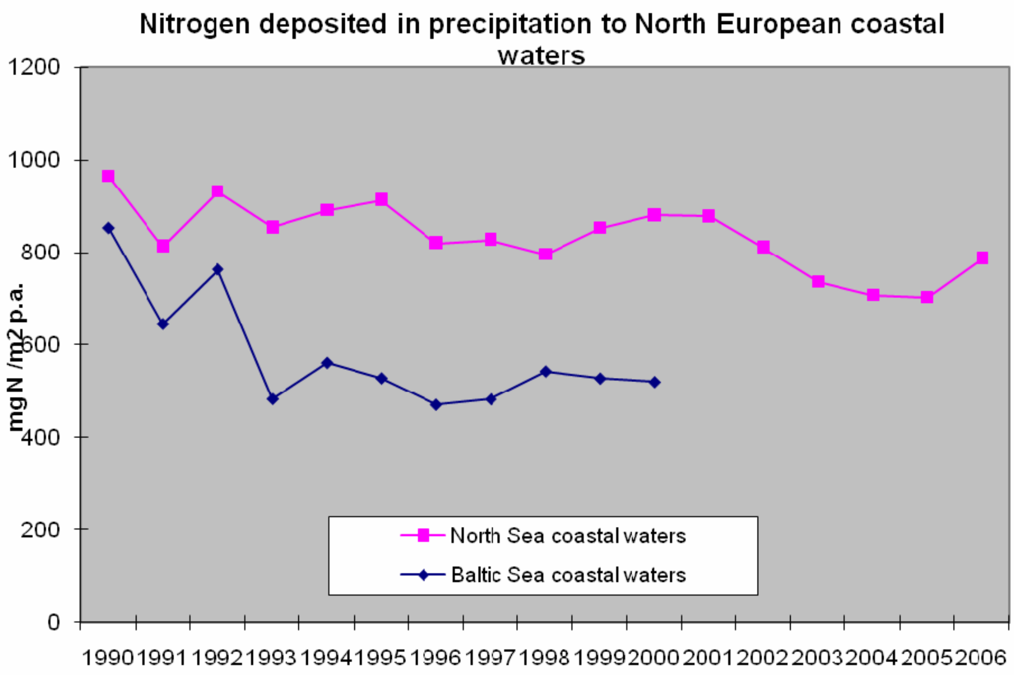

Figure 5.1: Rates of deposition of total reactive inorganic nitrogen to the North and Baltic Sea coastal waters, 1990-2006. Source: OSPAR and HELCOM observation data.

The lack of clear temporal trends in recent years confirms the findings of the OSPAR assessment panel (van Pul et al, 2009). Reviewing available evidence, only 2 observing stations had a statistically significant upward trend of up to 68% in depositions of oxidised nitrogen between 1998 and 2006, three stations a statistically significant downward trend of up to 21%, and 12 stations showing no trend. Reduced nitrogen similarly showed most stations with no trend. Modelling results give a similar picture (Figures 5.2 and 5.3), although estimate a significant downward trend in oxidised nitrogen of 17%. Overall, this would seem to indicate but at in the best case very limited change over the last decade, during which period international policies for abatement of atmospheric nitrogen emissions have been in place. This finding also supports the view expressed by the OSPAR commission, that 'atmospheric deposition of nitrogen is variable and no significant trend can be seen [1990-1996]' (OSPAR 2000), and the view of the HELCOM commission that 'no significant trends can be recognized in nitrogen depositions to sub-basins of the Baltic Sea in the Period 1995–2006' (HELCOM, 2008).

5.2.2. Short term variability

The significance of short term variability is in the potential for atmospheric deposition to have immediate, albeit temporary, influence on productivity. Such an influence may occur as a consequence of cyclonic, and hence episodic, events. Spokes and Jickells (2005) provided examples of the extremes of low level dry deposit of nitrogen compared with high intensity storms. For air masses which had spent several days over the ocean, daily rates of dry deposition of nitrogen equivalent to around 70mg m^{-2} yr^{-1} were observed for the North Eat Atlantic (note that similar levels are estimated as the actual year round rate in N.E. Atlantic and Arctic waters - Table 4.1). This was estimated to supply <0.2% of biological nitrate uptake at the time. In contrast, one storm event in the Kattegat was measured supplying nitrogen at rates equivalent to over 1300mg N m^{-2} yr-^{1}, or 13% of local demand at that time in May. The same rate of supply off during a single May month off western Ireland was found to contribute 30% of the standing stock of surface water inorganic nitrogen. Still larger, Spokes et al. (1993) recorded an event in the southern North Sea which dposited nitrogen for a short period at a rate equivalent to over 4000mg N m^{-2} yr^{-1}, although due to high biological demand at this time (august), this still represented around 15% of nitrogen requirement. Inevitably time of year and location will play a role in determining the significance of short term events. During summer months when river flows are lower, atmospheric inputs may represent a greater share, although higher biological demand may render them of lesser biological significance.

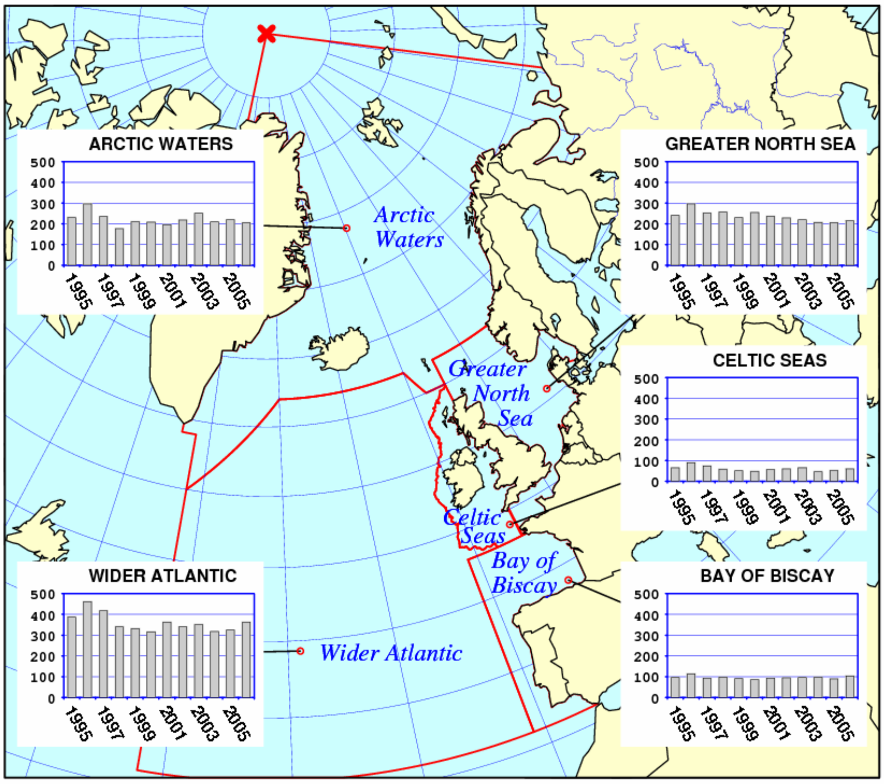

Figure 5.2: Time series of modeled annual oxidized nitrogen deposition in the OSPAR Regions. Units are in kt N a-1. Source: van Pul et al 2009

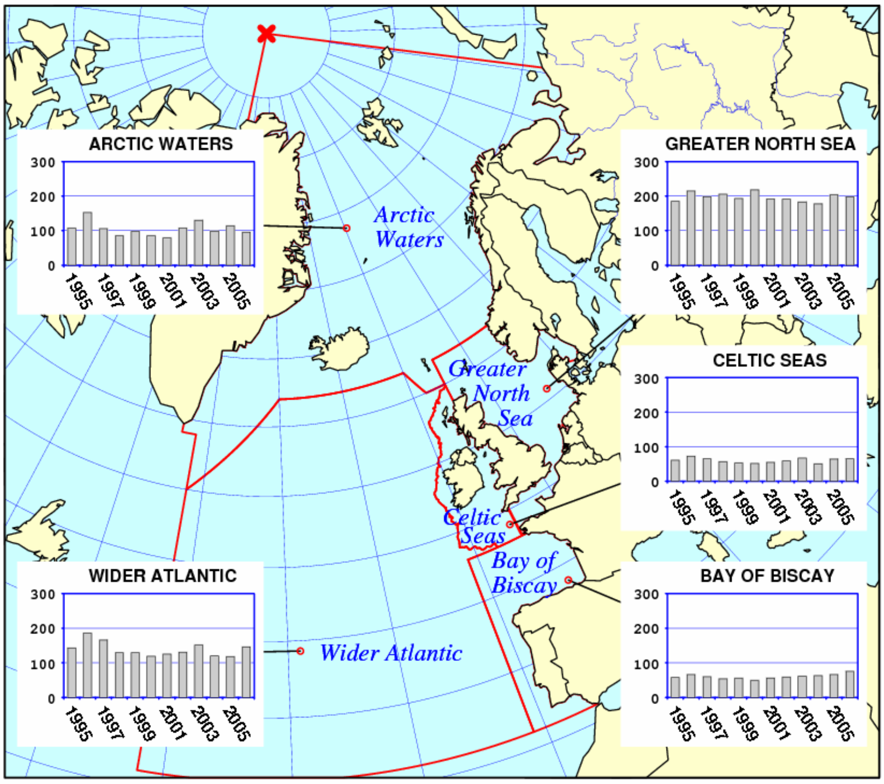

Figure 5.3: Time series of modelled annual reduced nitrogen deposition in the OSPAR Regions. Units are in kt N a-1. Source: van Pul et al 2009

5.3. Atmosphere *.v.* rivers as sources of land-based nitrogen

Establishing the relative significance of riverine as compared to atmospheric sources of inorganic nitrogen is to determine the significance of each of these pathways in delivering land-based nitrogen to the seas. The OSPAR QSR (2000) and HELCOM (1996, 1997a, 1997b and 2004) give estimated inputs of nitrogen from rivers, direct discharge and the atmosphere. For the Westrern Mediterranean values given by Martin et al (1989) are used. The percentages of total nitrogen entering these seas (the total encompassing riverine, direct discharge, and atmospheric) which are contributed by atmospheric deposition are given in table 5.2.

In future, this proportion is expected to increase on a word scale (e.g. Duce *et al*. 2008). Increasing industrial activity around the globe together with rising standards of living can be expected to mean greater atmospheric emissions of nitrogen. In Europe this increase may be less strong, but is still expected. Whilst Europe has seen some success in decoupling growth and polluting emissions, the anticipated decline in riverine inputs is greater than may be anticipated in atmospheric emissions.

As has been mentioned before, the contribution of atmospheric nitrogen to riverine inputs should not be forgotten. Deposition of nitrogen to the land surface will only be partly retained, with the remainder passing through hydrological systems to coastal waters. It is a matter of perspective as to where to allocate this nitrogen supply. Only for purposes of initiating discussion is this aspect not considered further in this discussion report.

Table 5.2: Proportions of total nitrogen inputs derived from the atmosphere.

North Sea	35%
Baltic Sea	31%
W. Mediterranean	47%

6. Considering the significance of anthropogenic atmospheric CO_2 and nitrogen for ocean acidification and eutrophication

A[5] number of national and international reports have brought the issue of ocean acidification to the attention of policy makers in the UK, Europe, US and wider including those dealing with climate change (e.g. UNFCCC and IPCC), marine conservation (e.g. WWF, GECC and IWC) and the protection of our seas (e.g. OSPAR and The London Convention). This has contributed to the rising recognition of this issue by governments, agencies and NGOs as well as the climate change and energy communities and the general public. Ocean acidification has the potential for a massive impact on future climate change mitigation/adaptation strategies (Turley, 2008). Some difficult questions may need to be faced, such as “what is dangerous pH change?” and what does it mean for aquatic/atmospheric CO_2 concentration and subsequent for the global anthropogenic emission targets. For a while the possible influence of atmospheric nitrogen on eutrophic state has been noted, and international organisations, such as HELCOM and OSPAR, have assembled estimates of rates of nitrogen supply. The precise influence on tropic status, however, has been rarely addressed. The two issues become directly linked through the interactions of carbon and nitrogen uptake in marine production. As one changes, there will be implications for the other. Europe’s marine environment is intimately linked with the terrestrial, both physically and economically. Below are some important key points which summarize the current knowledge and its main policy implications:

- Much of the scientific and public focus on anthropogenic carbon dioxide (CO_2) emissions has been on climate impacts. Emission targets have been suggested based primarily on arguments for preventing climate from shifting significantly from its preindustrial state. However, recent studies underline a second major impact of carbon emissions: ocean acidification. Over the past 200 years, the oceans have taken up ~40% of the anthropogenic CO_2 emissions. This uptake slows the rise in atmospheric CO_2 considerably, thus alleviating climate change caused by anthropogenic greenhouse gas emissions. But it also alters ocean chemistry, with potentially serious consequences for marine life (Caldeira and Wickett, 2003).
- The response of different organisms is expected to be inhomogeneous (Langer et al, 2006), current evidence suggests that large and rapid changes in ocean pH will have adverse effects on a number of marine organisms. Yet, environmental standards for tolerable pH changes have not been updated in decades. For example, the seawater quality criteria of the U.S. Environmental Protection Agency date back to 1976 and state that for marine aquatic life, pH should not be changed by more than 0.2 units outside of the normally occurring range (U.S. Environmental Protection Agency, 1976). These standards must be re evaluated based on the latest research on pH effects on marine organisms.
- Once new ranges of tolerable pH are adopted, CO_2 emission targets must be established to meet those requirements in terms of future seawater chemistry changes. Projected changes in ocean carbonate chemistry should serve as a guideline for policy protocols that identify CO_2 emission targets to reduce the effects of human-made ocean acidification. For example, to avoid a surface ocean pH decline by more than 0.2 units (U.S. Environmental Protection Agency, 1976), global cumulative CO_2 should not exceed 700 Pg C, between 1850 and today (2008) cumulative emissions are estimated at 320 Pg C, all 4 IPCC baseline (A1-B2, no climate change policy) exceed this target already by 2050. Avoidance of this target by 2100

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[5] Introduction text based on Turley, 2008

requires CO_2 concentration to stay below 400 PPM, a value only reached in the most stringent mitigation scenarios.

- Field observations demonstrate a significant recent decline in the buffering capacity of the inorganic carbonate system (increasing Revelle factor) in surface waters in the North Sea due to the uptake of anthropogenic CO2. This effect, predicted by thermodynamic calculations as far back as the 1950s [Revelle and Suess, 1957; Sarmiento et al., 1992], sets up a negative feedback that decreases the ability of the surface ocean to take up additional anthropogenic CO2. Simple idealized calculations suggest that the reduced buffer feedback could explain about 10–30% of the observed declines in the air-sea $DpCO_2$ and net local CO_2 uptake flux in the North Sea.
- Aragonite and calcite saturation horizons ($\Omega=1$) are rising at about 1-2 m yr-1 and could reach the surface ocean as early as 2020 in the Arctic Ocean.
- Surface ocean undersaturation with regard to aragonite is projected to occur within years to decades (Arctic, Southern Ocean, coastal systems?), but is subject to large uncertainties.
- Greatest effects of reactive nitrogen deposition will be felt in waters seasonally or normally depleted in surface nitrogen. Using the conservative marker for areas so affected of <7μM means that the North Sea, Baltic Sea, Mediterranean Sea and Black Sea are all open to seasonal impacts from atmospheric nitrogen.
- The atmosphere is a source of nitrogen but not of phosphorus, and anthropogenic perturbation of nitrogen flows is far greater than of phosphorus. Atmospheric deposition of nitrogen has potential to shift N:P balance, thereby exacerbate P limitation of N_2 fixation, alter species composition and productivity, and alter removal of carbon to deep water.
- Accounting only for atmospheric nitrogen which is directly deposited to the sea surface, current rates of deposition in the Baltic may already be sufficient on their own to push trophic status into a higher category than otherwise would be the case. In the north and Adriatic Seas such direct depositions alone are likely to be at least 50% of that needed to cause change in trophic status. The scale of nitrogen deposition to terrestrial surfaces with consequent runoff and transfer to coastal waters would reasonably be expected to significantly increase the effect in coastal waters.
- Past transnational air pollution policies in Europe have been defined as transboundary – concerned with the impacts of emission in one territory upon another territory. The open marine areas may be considered to have fallen outside strict legal definitions through their common status. With the global perspective engendered by concern over climate it may be desirable to recognise a duty of care in policy negotiation which transcends concepts of national territory.

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