

# **Reducing SO<sub>2</sub> and NO<sub>x</sub> emissions from Ships by a seawater scrubber**

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## List of used abbreviations

amu	atomic mass units
CCN	cloud condensation nuclei
DIN	dissolved inorganic nitrogen ( $\text{NH}_4^+$ , $\text{NO}_2^-$ , $\text{NO}_3^-$ )
DMS	Dimethyl sulphide
DON	dissolved organic nitrogen
FGD	Flue gas desulphurisation
IMO	International Maritime Organization
Mam-Pec	Computer model to generate predicted environmental concentrations
$\text{NO}_x$	stands for the different nitrogen oxides
PAH	polycyclic aromatic hydrocarbons
PON	particulate organic nitrogen
PSU	practical salinity units
SWS	seawater scrubber
VOC	volatile organic compounds

# 1 Introduction

Burning of fossil fuels contributes significantly to atmospheric pollution. For several decades concern has been expressed about the major pollutants, carbon dioxide, sulphur dioxide and nitrous oxides. Carbon dioxide is considered to be largely responsible for global warming while the latter two gases contribute amongst others to acid rain and eutrophication of terrestrial and aquatic ecosystems. For power stations a large number of technologies have been developed to reduce these emissions (see chapter 1.3), while the shipping industry has made less progress in limiting emissions. This is despite the fact that recent estimates suggest that shipping is a major factor in global S and N cycles (chapter 2.1). The reduction of atmospheric emissions by ships, with emphasis on seawater scrubber technology (flue gas desulphurisation process), is therefore the main objective of this report.

## 1.1 Air pollution

Air pollutants are substances that are introduced into the atmosphere via anthropogenic activities. Air pollution occurs as both, gaseous and particulate forms which, when present in excess, are harmful to human health, buildings and ecosystems. Four major impacts determine the classification of pollutants under the traditional policy field *Air Pollution*:

- acidification of soil and water by pollutants such as sulphur oxides and nitrogen oxides.
- damage to buildings sensitive to the same substances;
- formation of tropospheric ozone from so-called ozone precursors, e.g. volatile organic compounds, nitrogen oxides and carbon monoxide, thus indirectly affecting human and animal health and vegetation;
- direct effects on human health and ecosystems, e.g. through high atmospheric concentrations of particles and volatile organic carbon compounds (VOCs).

Although some of these compounds are also produced by natural processes, the main environmental problems result from human activities, such as burning of fossil fuels (coal, natural gas and oil). Air pollutants may be transported over considerable distances, affecting air quality, ecosystems, lakes and other surface waters, groundwater, soils and buildings also in areas remote from the pollution source. Public concern is focussed mainly on damage to forests and smog, although in Scandinavian countries emphasis is also placed on the acidification of lakes. The atmospheric pollution with sulphur dioxide and nitrous oxides is described in detail in chapters 2.1.2.2 and 2.2.1.2.

### Particulates

Particulate air pollution originates from diverse sources. One major source of primary particle emissions is fuel combustion, including mobile sources such as diesel and gasoline-powered vehicles. The relative contributions of these different sources to the particle concentration at a given site may vary significantly. Atmospheric particles consist of organic and inorganic substances and are present in liquid or solid forms. They are subdivided according to diameter: coarse particles  $>2.5 \mu\text{m}$ , fine particles  $<2.5 \mu\text{m}$ . A further distinction is to classify particles as either primary or secondary, according to their origin. Particles that are emitted directly into the atmosphere are termed primary particles, whereas secondary particles form during atmospheric reactions. The primary particles contain dust and other solid materials, which are primarily formed during combustion processes. Fine particles also include secondarily formed aerosols, smaller combustion particles and re-condensed organic and metallic

compounds with low volatility. Most secondary particulate matter occurs as sulphates and nitrates formed in reactions involving sulphur dioxide and nitrogen oxides. Shipping contributes to both, primary and secondary particles. Natural atmospheric emissions of particulates also derive from volcanic activities.

#### 1. Primary particulates:

Flue gases contain soot particles, which are produced by incomplete combustion of fossil fuels. Besides the ability of particles to serve as condensation nuclei, soot contains polycyclic aromatic hydrocarbons (PAHs), a family of semi-volatile organic pollutants encompassing compounds such as naphthalene, anthracene, pyrene, or benzo(a)pyrene. PAHs from combustion products have been identified as carcinogenic. Combustion-derived PAHs are rapidly transferred from the atmosphere to aqueous systems and accumulate in the sediment.

#### 2. Secondary particulates

Secondary particles (including sulphate and nitrate aerosols) are formed from gaseous pollutants ( $\text{SO}_2$ ,  $\text{NO}_x$ ). From the combustion of fossil fuels, ships emit sulphur dioxide and nitrous oxides. The primary air pollutants sulphur dioxide and nitrogen oxides undergo chemical transformations as they are dispersed in the atmosphere, forming sulphuric acid and nitric acid respectively, which may be deposited downwind as acid rain. Secondary particles can be transported over long distances.

### **1.2 Contribution of shipping to air pollution**

Shipping contributes to air pollution by the burning of fossil fuel. The emitted nitrous oxides ( $\text{NO}_x$ ) and sulphur oxides ( $\text{SO}_x$ ) together with particulate compounds such as soot contribute to the anthropogenic perturbation of the Earth's radiation budget (Capaldo et al., 2000). The emission of  $\text{NO}_x$  and  $\text{SO}_x$  has different consequences for the atmosphere:  $\text{NO}_x$  is involved in production of ground level ozone but it also reacts with tropospheric ozone thus aiding in the depletion of the ozone layer.  $\text{SO}_2$  is oxidised to  $\text{SO}_3$  and eventually forms sulphuric acid, which contributes to acid rain and provides cloud condensation nuclei by formation of secondary particles, thereby increasing the albedo. Owing to the reactivity of sulphur gases in the atmosphere, most anthropogenic  $\text{SO}_2$  emissions are deposited locally, therefore shipping contributes mainly to coastal air pollution.

Corbett and Fischbek (1997) give annual emissions of  $3.08 \times 10^6$  ton N and  $4,24 \times 10^6$  ton S for the global fleet accounting for 14 % (N) and 16 % (S) of emissions from all fuel combustion sources (Tab. 1). On the other hand, only 2 % of the  $6,000 \times 10^6$  ton carbon dioxide emitted annually from fossil fuel combustion are related to the operation of ships. This indicates that ship engines are among the highest pollution sources for nitrogen and sulphur gases. Various estimates for the contributions of shipping to global air pollution are presented in Tab. 1.

Tab. 1: Comparison of estimates for global exhaust gas emissions from ships.

Source	Calculation (1)	Year	C <sup>(2)</sup> [10 <sup>6</sup> t]	SO <sub>2</sub> [10 <sup>6</sup> t]	NO <sub>x</sub> [10 <sup>6</sup> t]
Isensee, 2001		1997	101*	6.4	6.0
IMO, 2000	M	1996	112	5.5	9.8
IMO, 2000	F	1996	117	5.8	10.3
Det Norske Veritas, 1999	M	1996	109	5.5	9.9
UNFCCC, 1997	?	1994	109	7.7-11.5	9.3
Corbett and Fischbeck, 1997	F	1996	-	8.5	10.1
Corbett, 1999	?	1992	123.6	8.5	10.1
mean		1994 - 1997	114.2	6,7	9,3

(1) M = model, F = fuel based calculations

(2) Calculated from CO<sub>2</sub> emissions

Emissions from shipping operations are not equally distributed over the seas. Most vessels navigate relatively near shore, following the main shipping lanes. Corbett (1999) concludes that almost 70 % of these emissions occur in a coastal zone of 400 km width. Similarly, Oftedal (1996) estimates that 74 - 83 % of all vessels are within 200 nautical miles of land at any time. Consequently, the impact of shipping on the NO<sub>x</sub> and SO<sub>2</sub> emissions is highest in the northern hemisphere, particularly along the west and east coasts of the United States, in northern Europe and the North Pacific.

### 1.2.1 Legislation:

As soon as the IMO regulation for the prevention of air pollution from ships (Marpol 73/78 Annex VI) comes into force, emissions from ship exhausts have to be reduced. Annex VI contains provisions allowing for special "SO<sub>x</sub> Emission Control Areas" to be established with a more stringent control on sulphur emissions. In these areas, the sulphur content of fuel oil used on board ships must not exceed 1.5 % m/m. Alternatively, ships must fit an exhaust gas cleaning system or use any other technical method to limit SO<sub>x</sub> emissions. Currently the Baltic Sea, the North Sea and the Channel are designated as SO<sub>x</sub> Emission Control Areas in the Protocol. It is expected that the Annex will come into force during 2004.

### 1.3 Techniques for the reduction of atmospheric emissions in power plants

The technology for the reduction of the atmospheric pollutants should be environmentally benign. Otherwise, the problem would be shifted only. There are three possibilities to reduce the SO<sub>2</sub> emissions from combustion processes: removal of sulphur or sulphur dioxide before, during or after combustion.

### **1.3.1 Techniques for the removal of sulphur from petroleum**

As after World War II production of high sulphur crude oils increased considerably and product specifications became more stringent, the oil industry was forced to develop techniques for removal of sulphur. In addition, the catalyst used in the Platforming Processes can handle only low ppm levels of sulphur. In addition, environmental considerations also forced reductions of sulphur emissions.

The major process used today is Hydrotreating or Hydrodesulphurisation, i.e. treatment of the oil with hydrogen gas obtained e.g. during catalytic reforming.

In this process sulphur compounds are removed by conversion to hydrogen sulphide ( $H_2S$ ) in the presence of a catalyst. As only sulphur is removed, high yields of liquid end products result. In addition,  $H_2S$  can be washed from the product gas stream by an amine wash.  $H_2S$  is recovered in highly concentrated form and can then be converted to elemental sulphur via the Claus-Process.

For Hydrotreating two processes are used, the liquid phase or trickle flow and the vapour phase processes for light straight-run and cracked fractions. In both cases the feedstock is mixed with hydrogen-rich make-up and recycle gas and reacted at temperatures of 300 - 380 °C. Pressures of 10 - 20 bar for naphta and kerosine and 30 - 50 bar for gasoline are applied. Under these conditions, S and N compounds are converted to hydrogen sulphide and ammonia, while a part of the aromatic compounds present will be hydrogenated.

Catalysts employed are cobalt, molybdenum or nickel finely distributed on aluminium extruders.

More recent developments include biological conversion of sulphur-containing petroleum components to elemental sulphur and sonocatalytic treatment as well as hydrogen peroxide oxidation in the presence of iron(III)complexes at low temperatures. The latter two will remove dibenzothiophenes, compounds being of particular concern to the oil industry.

### **1.3.2 Flue Gas Desulphurisation**

The removal of  $SO_2$  after the combustion process is termed Flue Gas Desulphurisation (FGD). The different FGD processes can be classified by their technologies:

#### *Limestone/Gypsum System*

The limestone FGD is to date the most widely used process. In principle, a solution of crushed limestone in water is sprayed into the flue gases. The  $SO_2$  reacts with calcium ions to form a calcium sulphite slurry. Aeration of the slurry with compressed air oxidises calcium sulphite to calcium sulphate. After removal of the water, the calcium sulphate can be disposed or used by the building trade. While the reduction of  $SO_2$  is around 90 % the process has the disadvantage that limestone has to be stored and gypsum waste in large quantities is produced.

#### *Spray Dry System*

A slurry of slaked lime is used as an alkaline sorbent. The slurry is injected into the flue gases in a fine spray. The flue gases are simultaneously cooled by the evaporation of water. The  $SO_2$  present reacts with the drying sorbent to form a solid reaction product, with no wastewater.

#### *Wellman-Lord Process*

In the Wellman-Lord process, hot flue gases are passed through a pre-scrubber where ash, hydrogen chloride, hydrogen fluoride and SO<sub>3</sub> are removed. After pre-scrubbing, the gases are then cooled and fed into an absorption tower, where the SO<sub>2</sub> reacts with a saturated sodium sulphite solution to form sodium bisulphite. The sodium bisulphite is regenerated after a drying step to sodium sulphite again. The remaining product - the released and clean SO<sub>2</sub> - may then be liquefied or converted to elemental sulphur or sulphuric acid. The sorbent is regenerated during the combustion process and is continuously recycled, but the products (sulphur compounds) have to be stored.

### *Seawater Scrubbing Process (SWS)*

#### *Experience with the FGD by seawater scrubbing process in power plants*

Probably the first large sized FGD was installed at the Battersea power plant (London Power Company) in the UK in 1930. During the power station planning approval local authorities expressed concern about the impact on the local community of the emissions of large quantities of SO<sub>x</sub> from the combustion of coal. The water of the Thames was used as the major sorbent although for a short period limestone was added. This practise was soon discontinued as it was determined that it provided no additional benefit to the scrubbing system. The Battersea power station operated in this mode for more than 50 years.

In 1972, ABB Environmental in Norway and Norsk Hydro started the development of a flue gas desulphurisation process (Flakt Hydro process) using seawater for the absorption of SO<sub>2</sub> from flue gases. The first seawater scrubber was introduced in 1988 at the Statoil refinery in Mongstad Norway (Tokerud, 1989). The *seawater scrubbing* process exploits the natural buffering capacity of seawater to absorb acidic gases instead of producing huge amounts of gypsum. After passing a dust collector, the hot flue gas enters the scrubber. The scrubber is a packed absorption tower, where the gases flow counter-current to seawater. During this process SO<sub>2</sub> is efficiently absorbed by the seawater. Air is supplied to oxidise the absorbed SO<sub>2</sub> to sulphuric acid and to saturate the seawater with oxygen. Before discharging the effluent into the sea, further seawater is added to bring the pH back to normal seawater values. The sulphate ions themselves are harmless, as they are major constituents of ordinary seawater. However, the pH of the effluent may be of concern. To reduce the sulphuric acid problem, e.g. in sensitive areas, precipitation of sulphate with limestone is possible. This system is simple and inherently reliable with low capital and operational costs. It can remove up to 99 % of SO<sub>2</sub>, with no disposal of waste to land. However, heavy metals and chlorides that are also present in the scrubbing water must be captured by use of a water treatment system, otherwise they will be released to the sea with the wash water.

The Mongstad oil refinery (Statoil) situated on the west coast of Norway installed the FGD in 1988 (Nyman and Tokerud, 1991). The effluent water from FGD is mixed with seawater and is discharged to the sea. As the Norwegian Sea is deep and well mixed, further water treatment was regarded unnecessary (Glenna and Tokerud, 1991). Powergen and partners already tested the SWS process for flue gas desulphurisation in some power plants.

#### *Summary of the FGD technologies*

Each method has both advantages and limitations related to cost, removal efficiency, operational experience and waste products produced. For ships, the lack of space is an important criterion. Space is not only needed for the FGD itself, but also for chemicals (depending on the technology) and waste products. Some control technologies affect more than one pollutant and have different impacts on environmental effects. FGD simultaneously removes SO<sub>2</sub>, NO<sub>x</sub> and particulate matter, which have impacts on



acidification, on ambient levels of SO<sub>2</sub> and primary particles and on secondary sulphate aerosols.

## **1.4 Technologies for the reduction of atmospheric emissions by ships - the seawater scrubber**

For ships the seawater scrubbing is a very suitable process, because

- no limestone has to be stored on board,
- no waste (gypsum) is produced, which has to be deposited on land,
- the seawater already contains substantial amounts of sulphate and nitrate

The DME EcoSilencer seawater scrubber removes 90-95 % of SO<sub>2</sub> and 10 - 20 % of NO<sub>x</sub>. Additionally, the SWS removes 80 % of the particulates and 10-20% of hydrocarbons. The use of cyclone technology ensures that the particulate material is retained on board ship and not included with effluent overboard seawater. The particulate sludge is then deposited ashore along with shipboard oily waste according to local environmental and safety regulations. The DME system needs no extra space, as it can be installed inside the exhaust system. Accompanying positive side effects are the reduction of engine noise and a reduction of the diesel smell.

As the conversion of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> and NO<sub>x</sub> to NO<sub>3</sub><sup>-</sup> consumes oxygen, aeration of the effluent is necessary. The DME system incorporates a high degree of recirculation, thus ensuring that sulphur oxides are given adequate time and oxygen contact to be converted to SO<sub>4</sub>. In the following calculations complete oxidation will be assumed.

The DME MES EcoSilencer works by bringing water in contact with hot exhaust gas. The exhaust gas is channelled through a concentric duct into a shallow water tank. Within the water, there are a set of mixing baffles which break up large gas flow into smaller bubbles, forcing the gas to come in contact with water, and thereby encouraging transfer of species from gas to water. The SO<sub>2</sub> in exhaust gas is relatively soluble in seawater, so this transfer happens to a very high degree. Large particles (greater than 10 micron) are also captured in the water. Very fine particles (smaller than 2.5 micron) are not effectively cleaned using this method.

Since the recirculated water is maintained at a pH of 2.0-4.0, this makes a very good medium for scrubbing of NO<sub>x</sub>. Measurements have shown up to 20% removal of NO<sub>x</sub>, and this is enhanced due to the acidity of scrubbing liquor.

Water that is removed from the scrubber is pumped through a set of large cyclones. These cyclones are designed to separate some of the heavy particles, as well as light particles in a two-stage system. Underflow from the main cyclones is concentrated again, and the underflow is fed to a settling tank for collection of soot and oil. Under normal operating conditions, this system can be run with no ongoing maintenance (such as filter backwash or media recharge), and the resulting cleaned recirculated water is maintained at a low concentration of hydrocarbons, making it safe for discharge to sea. An on-line hydrocarbon monitor is used to ensure that oil in water that may result from poor engine operation is detected and discharge valves are closed before this can be released. Under normal operation, the overboard discharge water will contain less than 4ppm of hydrocarbon. This is far less than the total oil that would reach the surface water from particle fallout in an unscrubbed plume.

### **1.4.1 Composition of the effluent**

While NO<sub>x</sub> production depends on the engine design and to some extent engine power, SO<sub>2</sub> production depends on the sulphur content of the fuel. During seawater scrubbing the SO<sub>2</sub> is finally converted to sulphuric acid and NO<sub>x</sub> to nitric acid. 95 % of the SO<sub>2</sub> is

eliminated by this technique and ca. 20 % of  $\text{NO}_x$ . The salts in the effluent are  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$ .

The seawater scrubber is fed with natural seawater, which is then added to the seawater cooling system. The dilution is typically between 5:1 and 10:1. The mixture of cooling water and buffering water is then discharged to the sea. The pH of the effluent mixture ranges from 4.8 to 6.4 depending upon dilution rate which is a function of engine operating conditions. The intention of this work is to analyse the impact of the produced ions and the low pH on marine life.

### **1.5 Questions of concern**

- ◆ Is air pollution simply converted to seawater pollution by discharging the scrubbing water directly into the surrounding waters?
- ◆ Are there differences in the effects on fully marine and brackish waters? Is there any breakpoint for salinity, at which the scrubbing water should not be discharged anymore?
- ◆ Can the produced sulphuric and nitric acids be buffered in semi-enclosed systems and brackish waters?
- ◆ Is there any oxygen deficiency in the surrounding seawater by discharging sulphuric acid?
- ◆ What are the impacts of scrubber effluent on harbour waters compared to power stations effluents
- ◆ What is the worst-case scenario?

To answer these questions, background information on global sulphur and nitrogen cycles and seawater chemistry will be provided in the following before the effects of acid discharge will be discussed.

## **2 Element cycles**

### **2.1 Sulphur**

The element sulphur occurs as crystals, granular aggregates, massive layers and powdery crusts in three different forms: amorphous, rhombic and monocline crystals. It forms as a product of volcanic activity, around volcanic craters and hot springs, but also by weathering of sulphide minerals and bacterial reduction of dissolved sulphate. Sulphur melts easily and burns producing sulphur dioxide gas.

Sulphur is an essential nutrient for plants. It is also a major element of seawater and marine sediments. In nature sulphur compounds may cycle through a series of oxidation states (-2, 0, +2, +4, +6). Therefore, sulphur compounds may act as both electron acceptors and electron donors. Bacteria of a wide range of genera gain metabolic energy from either oxidising or reducing sulphur compounds. Major forms of sulphur include sulphate and sulphide minerals, dissolved sulphate ( $\text{SO}_4^{2-}$ ), dissolved sulphide ( $\text{HS}^-$ ), and hydrogen sulphide gas ( $\text{H}_2\text{S}$ ). Organic sulphur is a component of organic compounds such as humic substances, kerogen and proteins. Sulphur in fossil fuels (mercaptans, thiophenes, mono- and polycyclic sulphur compounds) originates from these latter sources (e.g. Guadelupe et al., 1991; Thompson, 1994; Saiz-Jiminez, 1995; Sinninghe-Damsté et al., 1998).

#### **2.1.1 Sulphur: an important component of the world economy Production**

Elemental sulphur for industrial purposes is produced by oxidation of hydrogen sulphide gas or reduction of sulphur dioxide and organic sulphur. These compounds are constituents of natural gas and oil, from which they are also recovered. Of all sulphur sources, natural sulphur from open pit mining accounts for less than 1 %, nevertheless representing  $3 * 10^6$  t/yr world-wide. Most of the sulphur is recovered from natural gas and oil (CIEC, 1999). For the exploitation of deep sulphur layers the Frasch process is the most important technique: Sulphur is melted with heated water under pressure and the liquefied sulphur is then pumped to the surface with compressed air (Holleman and Wiberg, 1985).

#### **Use of sulphur**

Sulphur is an essential nutrient for the growing plant. It is present in fertilisers, usually in the sulphate form that plants can use. For example, superphosphate contains about 11 % S while ammonium sulphate, usually regarded as a nitrogenous fertiliser, contains 24 % S which is more than its nitrogen content. However, about 90 % of industrial sulphur is used in the manufacture of sulphuric acid, the most important sulphur compound. More sulphuric acid is produced than any other chemical in the world. In Western Europe in 1997 over  $19 * 10^6$  tonnes were produced, the total production world-wide being estimated at around  $150 * 10^6$  tonnes (Smith et al., 2001). It is said that the economic prosperity of a country can be assessed by its consumption of sulphuric acid. Sulphuric acid was manufactured by the lead-chamber process until the mid-1930s. This process has now been replaced by the contact process, involving the catalytic oxidation of sulphur dioxide.

Tab. 2: World production and consumption of sulphuric acid (EFMA, 2000)

	1992	1993	1994	1995	1996	1997
	10 <sup>6</sup> tonnes H <sub>2</sub> SO <sub>4</sub>					
production	145.7	132.5	137.9	148.9	151.3	155.6
consumption	147.1	132.8	138.8	150.1	153.3	157.5

## Demand for sulphuric acid

The largest single sulphuric acid consumer by far is the fertiliser industry. Sulphuric acid is used with phosphate rock in the manufacture of phosphate fertilisers while smaller amounts are used in the production of ammonium and potassium sulphate. Substantial quantities are also used as an acidic dehydrating agent in organic chemical and petro-chemical processes, as well as in oil refining. In the metal processing industry, sulphuric acid is used for pickling and descaling steel; for the extraction of copper, uranium and vanadium from ores, in the purification of non-ferrous metals and plating. In the inorganic chemical industry, it is used most notably in the production of titanium dioxide.

Further applications of sulphuric acid are wood pulping processes for paper production, some textile and fibres processes, leather tanning, the use as electrolyte in car batteries and production of detergents and pharmaceuticals. Other end uses for sulphuric acid include effluent/water treatment, production of plasticisers, dyestuffs, explosives, silicate for toothpaste, adhesives, rubbers, edible oils or lubricants and the manufacture of food acids such as citric acid and lactic acid.

Waste streams containing sulphate are generated by many industries, including mining, metallurgical, pulp and paper and petrochemical industries. By discharging these sulphate containing wastes to the rivers, all sulphate finally ends in the sea.

### 2.1.2 Sulphur emissions to atmosphere

No gaseous sulphur compound is a permanent or long-lived constituent of the atmosphere. The short residence time for sulphurous gases is a consequence of rapid oxidation: Sulphur and its gaseous compounds hydrogen sulphide (H<sub>2</sub>S) and sulphur dioxide (SO<sub>2</sub>) are oxidised to sulphur trioxide (SO<sub>3</sub>), which dissolves in water droplets of the clouds to form sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). This process is responsible for acid rain.

#### 2.1.2.1 Natural emissions of sulphur

Natural emissions of sulphur into the atmosphere from biogenic sources and from volcanoes are estimated to be around  $60 * 10^6 \text{ S yr}^{-1}$  ( $2 \times 10^{12} \text{ mol S yr}^{-1}$ ). These values range from 46 to  $124 * 10^6 \text{ S yr}^{-1}$  (Whelpdale, 1992). In addition, sea spray contributes by the release of sulphate to a large amount to sulphur emissions. This estimate is very imprecise with  $35 - 315 * 10^6 \text{ S yr}^{-1}$ , of which around 90 % cycles back into the oceans.

Finally, the biogenic production in the open sea contributes to almost half (46 %) of all natural sulphur emissions to the atmosphere (Whelpdale, 1992). Dimethyl sulphide (DMS), the main volatile sulphur species emitted by marine phytoplankton in the oceans, plays a major role in the atmospheric sulphur cycle (Lovelock et al., 1972; Nguyen et al., 1984; Andreae and Raemdonck, 1983, Bates and Cline, 1985)

In short, DMS released by marine phytoplankton enters the troposphere and is oxidised there to sulphate particles, which then act as cloud condensation nuclei (CCN) for marine clouds (Charlson et al., 1987). Both the nature of the DMS oxidation mechanism as well as the quantification of the extent to which the oxidation product H<sub>2</sub>SO<sub>4</sub> contribute to new CCN is largely unknown. Further, DMS has an indirect impact

on the acidity of rainwater. The atmospheric DMS concentration varies seasonally, dependent on phytoplankton blooms. The DMS production has been reported to be by a factor of 20 higher in the summer compared to the winter in the Southern Indian Ocean (Sciare et al., 2000).

#### **2.1.2.2 Global anthropogenic sulphur emissions**

The emission of sulphur compounds into the environment is undesirable because of their acidifying characteristics. The global anthropogenic sulphur emissions have been estimated to be in a range from 60 to  $110 \times 10^6 \text{ t S yr}^{-1}$  ( $2 - 3 \times 10^{12} \text{ mol yr}^{-1}$ ) for the years 1976 to 1985 (Moller, 1984; Hameed and Dignon, 1988). The combustion of fossil fuels accounts for 80 to 85% of the total.

#### **2.1.2.3 Particulate sulphate**

Sulphate compounds are emitted as primary, directly released and secondary particles. The sources of primary sulphate particles include open pit mines, dry lakebeds, and desert soils. Other sources of primary sulphate particles are various fuel combustion processes from both stationary and mobile sources.

Secondary sulphate particles are produced in the atmosphere when oxides of sulphur ( $\text{SO}_x$ ) are transformed into particles via physical and chemical processes. The main source of  $\text{SO}_x$  is stationary and mobile fuel combustion. The types of sources that emit  $\text{SO}_2$  are generally located in urban areas. Secondary sulphate particles formed from  $\text{SO}_2$  emissions can be transported over long distances. These transported sulphate particles can comprise a significant portion of the ambient sulphate in some rural areas.

#### **2.1.3 Deposition of sulphate and sulphuric acid**

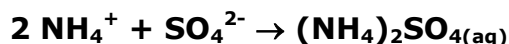
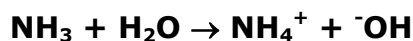
Gases in the atmosphere can reach the surface by wet and dry deposition processes. For wet deposition precipitation is the delivery mechanism to the surface. The gases can dissolve in clouds and rain drops or adsorb to frozen precipitation elements. Sulphate particles represent good condensation nuclei and may be scavenged by the clouds.

Those deposition processes, which do not involve precipitation, are collectively termed dry deposition. Sulphate can be chemically bound or adsorbed to small particles, which then reach the surface by gravitational settling (Whelpdale, 1992). The direct adsorption of  $\text{SO}_2$  to particles is still poorly understood.

Secondary particles formed through chemical reactions are typically much smaller ( $<10 \mu\text{m}$  diameter) than particles derived from physical processes ( $>100 \mu\text{m}$  diameter). The smallest particles in the atmosphere are the result of high temperature combustion and gas to aerosol conversions.

Depending on the relative humidity and the presence of other atmospheric gases like ammonia, the sulphuric acid formed will be removed directly in precipitation, or neutralised and converted to ammonium sulphate. The atmospheric conversion of sulphur dioxide to ammonium sulphate (Scheme 1) is an example of a gas to aerosol conversion process. These particles will range in molecular mass from 50 to as many as 10,000 amu.

### **Scheme 1**



Thus, particles form through complex gas phase, heterogeneous, and liquid phase reactions.

## **2.2 Nitrogen cycle**

Elemental nitrogen ( $\text{N}_2$ ) is gaseous and the major constituent of air (78.09 % Vol.). By this, 99 % of all nitrogen on earth occurs in the air. Chemically bound nitrogen can be found as nitrate, and organic bound nitrogen in e.g. proteins or nucleic acids. Pure nitrogen can be simply produced by fractionation of liquid air (Linde Process).

By its ability to have oxidation states ranging from -3 up to +6, numerous combinations with other elements are possible. The most important reaction partners are hydrogen (reduced form) and oxygen (oxidised forms). Especially ammonia is of great importance for the world economy a.o. as fertiliser (Holleman and Wiberg, 1985).

Nitrogen is also an essential nutrient for life, but only a few plants are able to use elemental nitrogen as source. A variety of different bacteria are able to oxidise or reduce nitrogen compounds to gain energy.

### **2.2.1 Emissions of nitrogen compounds to the atmosphere**

Nitrogen dioxide ( $\text{NO}_2$ ) is a reddish brown, highly reactive gas that is formed in the air through the oxidation of nitric oxide (NO). Nitrogen oxides (NOx), the term used to describe the sum of NO,  $\text{NO}_2$  and other oxides of nitrogen, plays a major role in the formation of ozone. The major sources of man-made NOx emissions are high-temperature combustion processes, such as those occurring in automobiles and power plants.

Nitrogen oxides also contribute to the formation of acid rain and to a wide range of other environmental effects, including: potential changes in the composition and competition of some species of vegetation in wetland and terrestrial systems, visibility impairment, acidification of freshwater bodies, eutrophication of estuarine and coastal waters, and increases in levels of toxins harmful to fish and other aquatic life. The consequence of eutrophication is an explosive algae growth leading to a depletion of oxygen in the water.

#### **2.2.1.1 Natural emissions of nitrogen**

Atmospheric reactions of nitrogen are much more complex than the atmospheric reactions of sulphur. Ammonia ( $\text{NH}_3$ ) is the most reduced form of nitrogen, and is

released in small quantities from anaerobic degradation of organic matter containing nitrogen. Similar to hydrogen sulphide, ammonia reacts with the hydroxyl radical to form oxidised nitrogen species. Nitrogen oxides are released to the atmosphere from both natural and anthropogenic sources. The two most common nitrogen gases released to the atmosphere from biological processes are nitrous oxide (N<sub>2</sub>O) and nitrogen dioxide (NO<sub>2</sub>).

### 2.2.1.2 Anthropogenic emissions of nitrogen

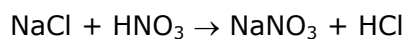
Combustion processes release mostly nitrogen oxide (NO) and nitrogen dioxide (NO<sub>2</sub>). The exact composition of nitrogen oxides emitted from combustion processes varies with temperature of the combustion process, and the nitrogen oxides from combustion are often referred to as NO<sub>x</sub> to indicate the uncertainty in chemical composition.

Like sulphur, the modern global nitrogen cycle is very different from the "Pre-industrial" nitrogen cycle. The difference is the large amount of nitrogen added to the atmosphere through combustion processes. The excess atmospheric nitrogen oxides contribute to acid rain in the same way that excess sulphur oxides do. Tab. 3 lists the important atmospheric nitrogen oxides and their oxidation states.

Tab. 3 Important Atmospheric nitrogen oxides

<b>nitrogen oxide</b>	<b>oxidation state</b>
N <sub>2</sub> O	+1
NO	+2
NO <sub>2</sub>	+4
HNO <sub>3</sub> , N <sub>2</sub> O <sub>5</sub>	+5
NO <sub>3</sub>	+6

Atmospheric nitrogen compounds are transported over long distances (Schulz et al. 1998). During transport they undergo specific physical-chemical changes (Fig. 1). NO<sub>x</sub>-compounds are typical anthropogenic precursors of oxidised nutrients like nitrate. The extremely complicated reactions within the atmosphere are described in detail by Holland (1978). For example, a dramatic change in the composition of aerosols concerning sea-salt in the coastal area has been observed by Schulz et al. (1998). This change is caused by the reaction of sodium chloride with the (anthropogenic) nitric acid. The chloride of the sea-salt is exchanged by nitrate and hydrochloric acid is formed:



By this reaction up to 55 % of the original sodium chloride in aerosols may be replaced by sodium nitrate during winds from the main land. These extremely hygroscopic aerosols are easily deposited because of their high mass.

Sodium chloride containing particles, originating from sea spray, are highly enriched in the coastal atmosphere. Contents of up to several 10 mg Cl<sup>-</sup>/m<sup>3</sup> have been determined which rapidly decrease landwards. Thus, a remarkable amount of nitrogen deposition occurs in the coastal area. Schulz et al. (1998) regard this reaction as one of the most important sinks for oxidised nitrogen compounds in the coastal marine atmosphere.



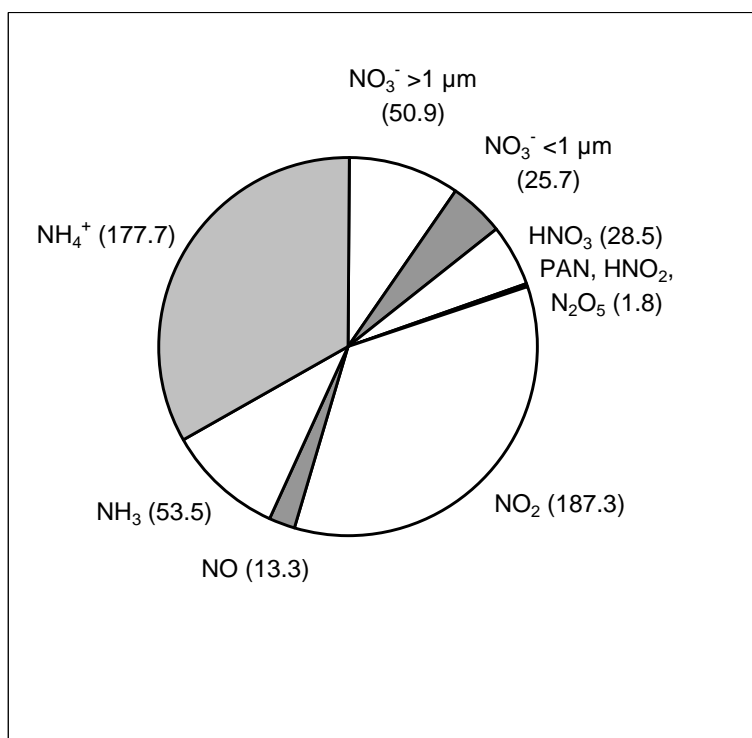


Fig. 1: Mean composition of atmospheric nitrogen compounds (nmol m<sup>-3</sup>) in the German Bight (Schulz et al., 1998), PAN: peroxyacetylNitrate.

### 3 Composition of seawater

Seawater is a steady-state system. It is a solution of salts of nearly constant composition, dissolved in variable amounts of water. There are well over 70 elements to be found in seawater but only 11 make up >99 % of the dissolved salts; all occurring as ions, i.e. electrically charged atoms or groups of atoms. These major ions behave *conservatively*. This means that they have constant ratios (Tab. 4), both to one another and to salinity, in almost all ocean waters and that they do not participate in (mostly biological) reactions to such a degree as to experience a noticeable change in concentration. This property of seawater allows the calculation of concentrations of conservative constituents from salinity data.

Tab. 4 Average sea- and freshwater compositions (internet site).

		freshwater (river)		seawater	
		mg/L	weight %	mg/L	%
sodium	Na <sup>+</sup>	7	5.83	10800	30.72
potassium	K <sup>+</sup>	2	1.67	400	1.14
magnesium	Mg <sup>2+</sup>	4	3.33	1300	3.70
calcium	Ca <sup>2+</sup>	15	12.50	410	1.17
chloride	Cl <sup>-</sup>	8	6.67	19400	55.19
bicarbonate	HCO <sub>3</sub> <sup>-</sup>	58	48.33	140	0.40
sulphate	SO <sub>4</sub> <sup>2-</sup>	12	10.00	2700	7.68
silica	SiO <sub>2</sub>	14	11.67	2	0.01

As well as major elements, there are many trace elements in seawater - e.g., manganese (Mn), lead (Pb), gold (Au), iron (Fe) and iodine (I). Most of these occur in parts per million (ppm) or parts per billion (ppb) concentrations. In contrast to the major elements, the relative abundance of trace elements are variable.

Although freshwaters display high variability in their composition the most abundant ions in river water are bicarbonate and calcium (Tab. 4). Compared to seawater, the abundance of bicarbonate is only 2.6 times less. Bicarbonate plays an important role in pH buffering (chapter 3.3).

**Non-conservative** substances dissolved in seawater are, among others, some gases (e.g. oxygen and carbon dioxide) and inorganic nutrients. These are essential for the growth of plants, including algae. Major nutrients include nitrate, phosphate, and silicate (the latter required only by silicate depositing organisms). Nutrients are usually depleted in surface waters, where plants grow, and are found in higher concentrations in deeper waters, where the plant and animal remains that sink from surface waters decay.

### 3.1 Marine sulphur cycle

The large amount of sulphate in seawater ( $2.65 \text{ g L}^{-1}$ ) derives from volcanic activities and degassing at the seafloor. Further, sulphates reach the oceans via river flows, but the concentration in seawater remains constant at around  $2.65 \text{ g L}^{-1}$ . A small part of the total sulphate load in rivers comes from the natural weathering of pyrite and gypsum. In addition, the water cycle carries recycled sulphate of marine origin. However, most of the riverine sulphate derives from human activities, e.g. mining, erosion and air pollution. Current fluxes are double those in pre-industrial times. Sulphate is conservative in oxic oceans but not in anoxic basins or within sediments. Sulphate is used by sulphate reducing bacteria to form HS or  $\text{H}_2\text{S}$ . Bacteria carry out various transformations of sulphur (Fig. 2).

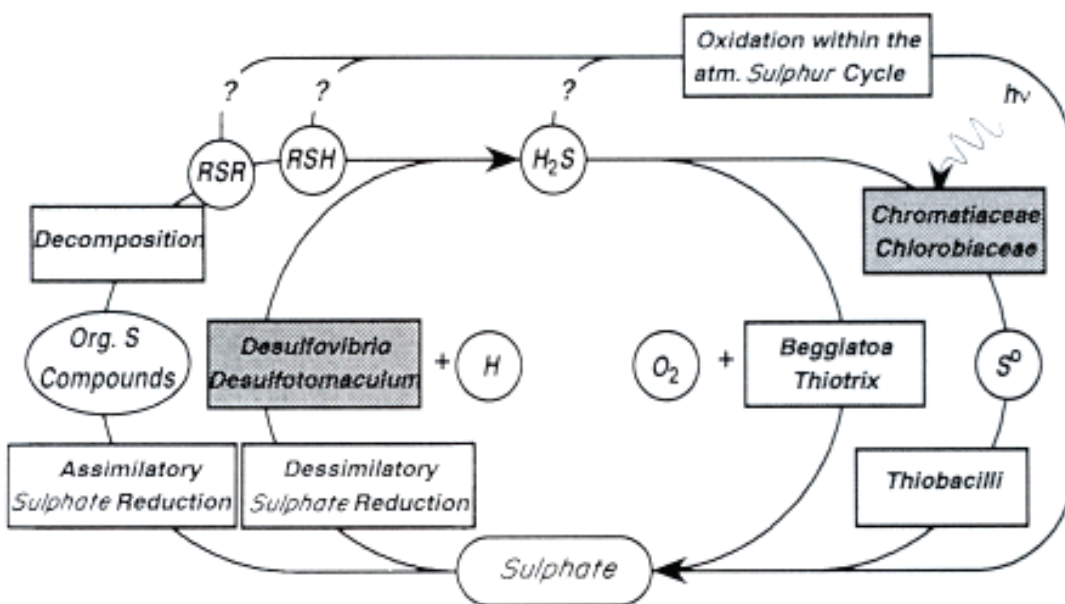
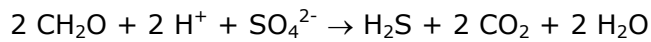


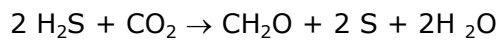
Fig. 2: Scheme of the microbiological cycle of sulphur and its possible influence on the atmosphere

1. Sulphate reduction in anaerobic environments ( $\text{CH}_2\text{O}$  represents organic matter as carbohydrates)



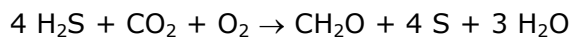
This reaction is analogous to aerobic respiration but with  $\text{SO}_4^{2-}$  rather than oxygen acting as the terminal electron acceptor in the oxidation reaction. The  $\text{H}_2\text{S}$  produced may precipitate as authigenic minerals such as greigite, mackinawite and pyrite or may be used in one of the following reactions:

2. Sulphur-based (anaerobic) photosynthesis



This reaction is probably the earliest form of photosynthesis using  $\text{H}_2\text{S}$  rather than  $\text{H}_2\text{O}$  as the hydrogen donor in the reduction of  $\text{CO}_2$ . Today it is employed by green and purple sulphur-bacteria .

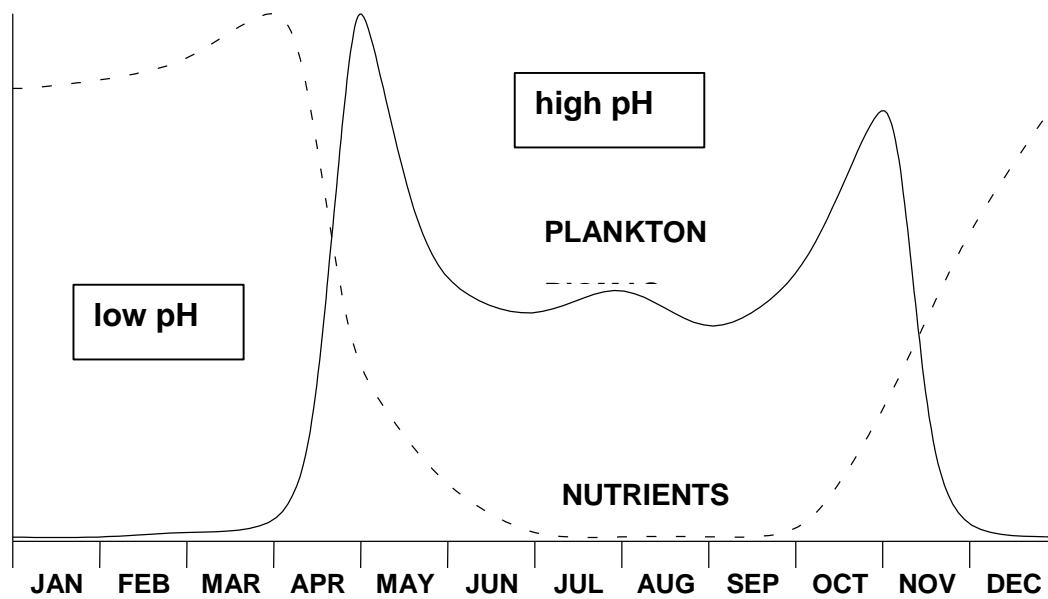
3. Chemoautotrophy under oxic conditions:



This reaction is performed by species of Thiobacilli in environments with free elemental sulphur or with  $\text{H}_2\text{S}$ , for example near deep-sea hydrothermal vents.

### 3.2 Marine nitrogen cycle

In contrast to sulphate, nitrate is strongly linked to primary production in the sea. The general seasonal development of nutrient concentrations in seawater is characterised by a decrease during springtime (Fig. 3). During phytoplankton blooms, inorganic nitrate is transformed into organic nitrogen compounds such as proteins or nucleic acids. In summer, the nutrients reach a minimum leading sometimes to limitation of certain nutrients. Remineralisation processes in the sediment may support a second phytoplankton bloom in late summer. In autumn, nutrients increase because of low primary production to maximum concentrations in winter.



*Fig. 3: Schematic seasonal variation of nutrients and phytoplankton biomass in temperate areas.*

Deposition of organic material (plankton and detritus) into surface sediments supports benthic mineralisation. Mineralisation of organic nitrogen compounds occurs in several enzymatic steps (proteins - peptides - amino acids). Finally ammonia is liberated from amino acids by deamination. Degradation of organic material by heterotrophs leads to dissolved inorganic nitrogen (DIN) again (Schlegel, 1981). Ammonia production is highest under anoxic conditions (Fig. 4). The concentration of ammonia in the porewater is governed by production, adsorption to particles, diffusion and reaction processes.

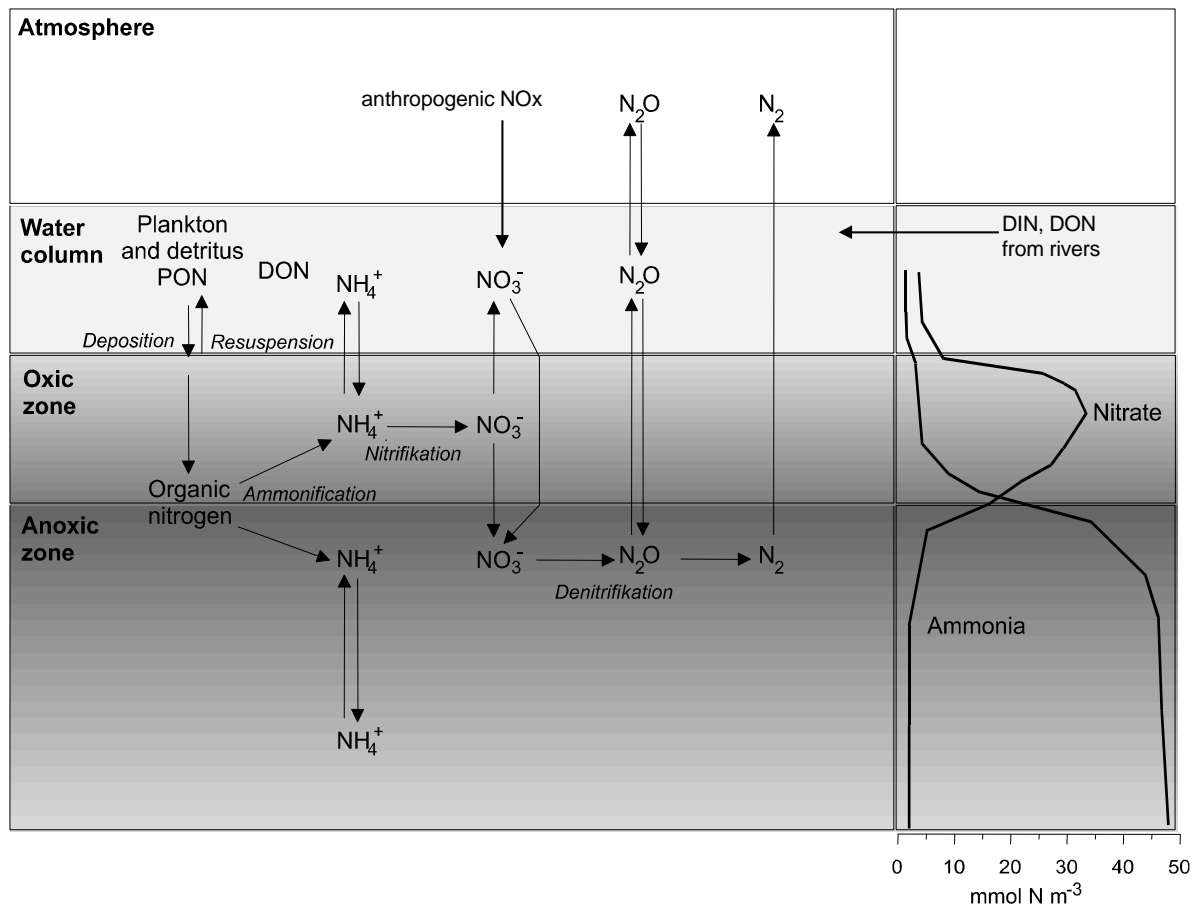


Fig. 4: Major reactions and pathways in the marine nitrogen cycle (Lohse, 1996). DIN = dissolved inorganic nitrogen (NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>), DON = dissolved organic nitrogen, PON = particulate organic nitrogen.

In the presence of oxygen, ammonia is oxidised in two steps via nitrite to nitrate. This process is called nitrification and is performed by the bacteria species *Nitrosomonas* spp. and *Nitrobacter* spp. These are restricted to the upper oxic part of the sediment column. Nitrate is the end product of nitrification and can diffuse into the overlying water column or deeper into the sediment where it undergoes further reactions. During denitrification nitrogen and dinitrogen oxide are released to the atmosphere, the latter contributing to the greenhouse gases. During summer months when input of organic material is high and hence high remineralisation rates prevail oxygen deficiency can impede nitrification. Under these conditions ammonification becomes the dominant process.

All these processes are seasonal dependent and are in exchange with the atmosphere. Quantification is difficult. The marine system also receives anthropogenic nitrogen via the rivers and the atmosphere.

### 3.3 The pH of seawater: the carbonate system

The pH of surface seawater usually ranges from 8.1 to 8.9 and is thus slightly alkaline. This is largely due to the presence of carbonate (and other weak acid) species in natural waters. These are needed to balance the excess positive charge of the major cations. There is a balance between carbonate and dissolved and atmospheric carbon dioxide. When carbon dioxide dissolves in water, carbonic acid is formed and thus the pH becomes lower due to increased acidity. Dissolved inorganic carbon (CO<sub>2</sub><sup>\*</sup>, HCO<sub>3</sub><sup>-</sup> +

$\text{CO}_3^{2-}$ ) varies by ~20 % due to vertical transport in the water column and remineralisation of both  $\text{CaCO}_3$  and organic matter.

Natural changes of seawater pH are related to primary production, which converts inorganic to organic carbon, and degradation of the produced material (Fig. 3). Photosynthetic activity increases the pH while the opposite, organic matter remineralisation, leads to a decrease in pH values.

The ability to neutralise acids and bases to a certain extent is termed the buffer capacity or alkalinity of seawater. Total alkalinity is measured by measuring the amount of acid (e.g. sulphuric acid) needed to bring a sample of seawater to a pH of 4.2. At this pH, all the alkaline compounds in the sample are "used up." The result is reported as milligrams per litre of calcium carbonate ( $\text{mg L}^{-1} \text{CaCO}_3$ ).

The amount of bicarbonate and other weak bases in seawater buffers the system, thus keeping the pH within a narrow range. Dissolved  $\text{CO}_2$  and carbonates belong to the buffer system and are all related by the following four equations:

1.  $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons (\text{CO}_2)_{\text{aq}}$
2.  $(\text{CO}_2)_{\text{aq}} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$  (carbonic acid)
3.  $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$  (bicarbonate)
4.  $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$  (carbonate)

$(\text{CO}_2)_{\text{aq}}$  and  $\text{H}_2\text{CO}_3$  are difficult to measure and are usually given as  $\text{CO}_2^*$ . The solubility of  $\text{CO}_2$  in water is  $1,7 \text{ g L}^{-1}$  ( $0,04 \text{ mol L}^{-1}$ ) and is governed by Henry's Law, assuming ideal gas behaviour:

$$S_{\text{CO}_2} = [\text{CO}_2] = K_H^* p_{\text{CO}_2}$$

I.e. the solubility (S) of a gas is proportional to its partial pressure ( $p_A$ ).

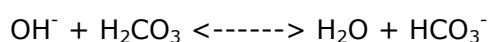
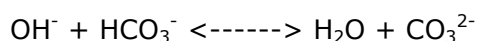
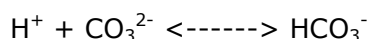
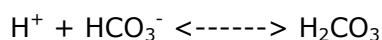
Henry's law is derived from

$$K_D = [\text{CO}_2(\text{aq})]/[\text{CO}_2(\text{gas})]$$

$$[\text{CO}_2(\text{gas})] = p_{\text{CO}_2}/RT \text{ \{Dalton's law of partial pressure\}}$$

$$[\text{CO}_2(\text{gas})] = (K_D/RT) p_{\text{CO}_2} = K_H^* p_{\text{CO}_2} \text{ \{ } K_H \text{ [mol L}^{-1} \text{ atm}^{-1}\text{] \}}$$

As the carbonate system encompasses polyprotic acids, it is able to buffer against changes in pH caused by addition of either acid and base:



As calcium carbonate (solid) reacts with water in presence of free hydrogen ions, the solid calcium carbonate dissolves forming free  $\text{Ca}^{+2}$  ions and free bicarbonate ions, hence consuming free hydrogen ions, decreasing hydrogen ion activity, and by definition increasing pH (becoming more basic). i.e. calcium carbonate acts to neutralise or buffer the solution by consuming hydrogen ions.

Both, carbonic acid and bicarbonate are weak acids with pK values of  $\text{pK}_1 = 6.5$ ,  $\text{pK}_2 = 10.4$ . When pure water is equilibrated with  $\text{CO}_2$  the system is defined by two independent variables (in addition to total pressure), e.g. temperature and  $p_{\text{CO}_2}$ . From this the equilibrium concentrations, all components can be calculated using Henry's law, the acidity constants and the proton condition or charge balance, if besides temperature one other variable such as  $p_{\text{CO}_2}$ ,  $[\text{CO}_2^*]$  or  $[\text{H}^+]$  is known.

The pH of a pure aqueous CO<sub>2</sub> solution is defined by the charge balance

$$[H^+] = [HCO_3^-] + 2 [CO_3^{2-}] + [OH^-]$$

If the system is kept in equilibrium with constant  $p_{CO_2}$ , the pH can be varied only by addition of a base C<sub>B</sub> or an acid C<sub>A</sub>. Electroneutrality must be observed for such an addition.

As B is equivalent to the concentration of a monovalent cation (e.g. [Na<sup>+</sup>] from NaOH) and A is equivalent to the concentration of a monovalent anion (e.g. [Cl<sup>-</sup>] from HCl).

$$C_B + [H^+] = [HCO_3^-] + 2 [CO_3^{2-}] + [OH^-] + C_A$$

$$C_B - C_A = C_T (\beta_1 - 2\beta_2) + [OH^-] - [H^+]$$

with  $C_T$  = total CO<sub>2</sub> concentration,

$$\beta_x = \text{Bunsen coefficient } (\beta_x = K_H * 22,414 \text{ [atm}^{-1}\text{]})$$

$C_B - C_A$  is the acid neutralising capacity of the solution with respect to the pure solution of CO<sub>2</sub>. This difference is defined as the alkalinity.

$$[\text{Alk}] = C_B - C_A = \frac{K_H p_{CO_2}}{\beta_0} (\beta_1 - 2\beta_2) + [OH^-] - [H^+]$$

This model has three independent variables in addition to total pressure. It is therefore sufficient to give T,  $p_{CO_2}$ , and alkalinity to define the system. The pH is given by [Alk] and  $p_{CO_2}$ .

There are other bases than those present in the carbonate system are present in seawater, which contribute to total alkalinity. These are B(OH)<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> and, under specific environmental conditions, hydrogen sulphide HS<sup>-</sup>.

If this is included then

$$C_B + [H^+] = [HCO_3^-] + 2 [CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + C_A$$

$$C_B - C_A = C_T (\beta_1 - 2\beta_2) + B_T \beta_B^- + [OH^-] - [H^+]$$

with  $B_T = [H_3BO_3] + [B(OH)_4^-]$  and  $\beta_B = [B(OH)_4^-]/B_T$

and

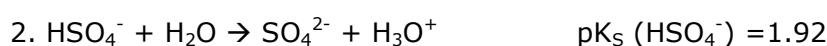
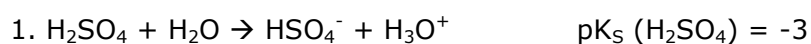
$$[\text{Alk}] = C_B - C_A = \frac{K_H p_{CO_2}}{\beta_0} (\beta_1 - 2\beta_2) + B_T \beta_B^- + [OH^-] - [H^+]$$

In the system containing only carbonate species alkalinity is commonly referred to as titration or carbonate alkalinity (CA). Incorporating other bases alkalinity is then referred as total alkalinity (TA). CA and TA differ by about 100  $\mu\text{equivalents L}^{-1}$  only.

TA of seawater averages 116 mg L<sup>-1</sup> and is greater than fresh water, which vary significantly, depending on the drainage area. TA can have a total alkalinity of 30 to 90 mg L<sup>-1</sup>. Brackish waters like in estuaries, where river water is mixed with seawater, have TA varying between these values.

The pH values after addition of acid or base can be calculated using the above equation(s) taking into account ionic strength effects on the constants. Corrected values are tabulated.

The neutralisation of sulphuric acid in seawater occurs in two steps:



Both, sulphuric acid and hydrogen sulphate have low pK<sub>S</sub> values (-3 and 1.92, respectively), and are hence strong acids dissociating completely. Therefore all protons of the sulphuric acid contribute to the pH-shift. The carbonate system will

buffer the additional protons by the release of CO<sub>2</sub> to keep the pH constant. One molecule sulphuric acid will therefore produce 2 molecules CO<sub>2</sub>. The equations 1-3 of the carbonate system (see above) will shift from the right to the left sides, finally releasing the dissolved CO<sub>2</sub> to the atmosphere.

### 3.4 Laboratory measurements

A model of Abdulsattar et al. (1977) allows the prediction of the pH of effluent from seawater scrubbers, but leads to an overestimation of acidity (Baalina, et al., 1997). The reason is that the oxidation of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> is not taken into account. Further, the temperature of the seawater has an impact on pH (Hunter, 1998). The calculations in the previous chapter are based on an ideal seawater composition and do not take other seawater constituents into account (e.g. organic acids like amino or humic acids). As the above described equations are simplified and some data are difficult to obtain or absent, laboratory measurements were carried out at Terramare to quantify the ability of seawater to buffer sulphuric acid solutions.

#### 3.4.1 Impact of diluted sulphuric acid (pH 4) on seawater

To mimic the conditions of the seawater scrubber effluent, concentrated sulphuric acid (98 %) was diluted with seawater to a pH of 4 (assumed worst case for scrubber effluent, Ref 1.4.1). The amount of sulphuric acid in 1 L was 1.25 g H<sub>2</sub>SO<sub>4</sub>. Assuming that this effluent would be discharged directly to the sea, this solution was added in small portions to natural seawater (salinity = 29 PSU), taken at the Nassau Bridge in Wilhelmshaven, Germany in October 2002. The concentration of the sulphuric was recalculated, because of the changing end-volume. The pH shift, caused by the addition of sulphuric acid was measured directly (Fig. 5).

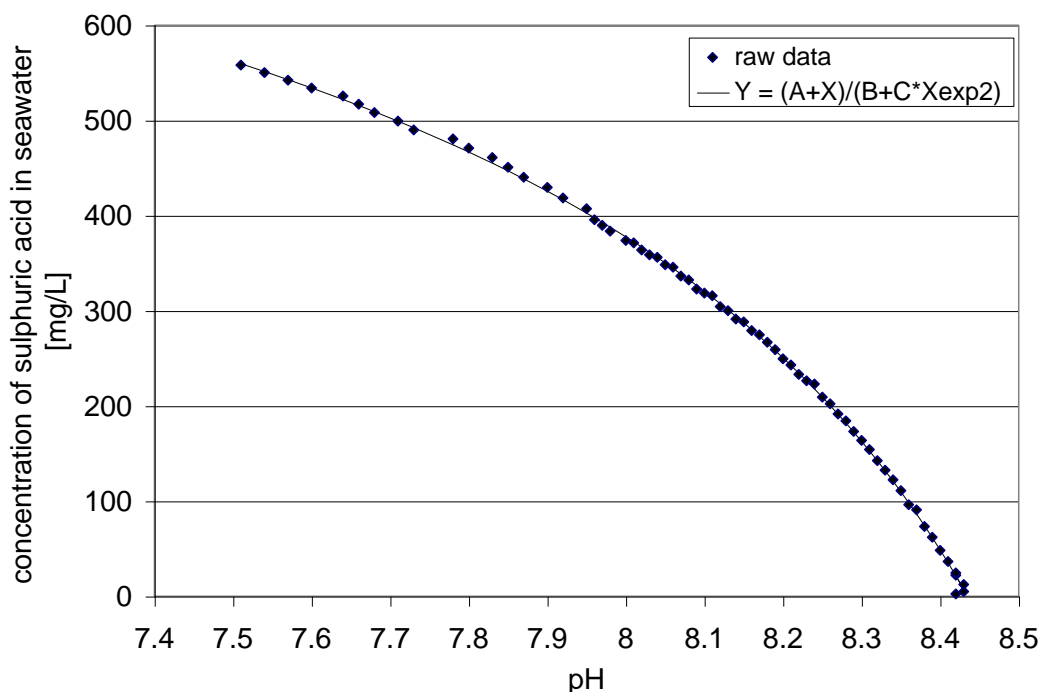


Fig. 5: Impact of sulphuric acid (pH 4) on the pH of seawater (S = 29 PSU) corresponds to regression line.

The addition of 54 ml seawater adjusted to pH 4 (68 mg sulphuric acid) to 500 mL seawater results in a total volume of 554 mL, which caused a pH-shift of pH 0.1 units



only. The end-concentration is therefore 68 mg in 554 mL, or 1.2476 mmol sulphuric acid L<sup>-1</sup> (2.49 mmol H<sup>+</sup>). This corresponds with a mixture of 1:10 (v:v, sulphuric acid in seawater pH 4 : natural seawater). Even a mixture of 1:5 (2.54 mmol sulphuric acid L<sup>-1</sup>, or 5.08 mmol H<sup>+</sup> L<sup>-1</sup>) only caused a pH-shift of 0.23.

The scrubber effluent is diluted with natural seawater ten times. Thus, the requirements of US-EPA (1976) that changes in pH shall not exceed 0.2 units for marine waters are fulfilled.

The regression line in Fig. 5 was calculated using the Lab-Fitting software.

The equation for the regression line is:

$$Y = (A+X)/(B+C*X^2); R^2 = 0.999$$

$$A = -8.43463908$$

$$B = -0.00536647$$

$$C = 0.00006588$$

### 3.4.2 Impact of diluted sulphuric acid (pH 4) on brackish waters

In a second experiment, the same test was carried out with brackish water (Ems-Jade Kanal, Wilhelmshaven, Salinity = 14 PSU). Different ratios of the original and the acidified brackish water (pH 4) were mixed. The pH was measured directly after mixing, and after stirring the solutions for 1 hour again. Within this time, the carbonate system was able to buffer the pH by release of CO<sub>2</sub> to the atmosphere, while the pH increased again (Tab. 5, Fig. 6).

Tab. 5: Percentage of sulphuric acid (pH 4) in brackish water with resulting pH (t = 0 and t = 1 h)

Percent sulphuric acid in brackish water (pH 4) [%]	Percent natural brackish water [%]	pH measured immediately	pH measured after 1 hour	Δ pH between t = 0 and t = 1 h
0	100	7.60	7.63	
10	90	6.63	7.50	0.87
20	80	6.52	7.35	0.83
30	70	6.45	7.02	0.57
40	60	6.31	7.01	0.70
50	50	6.08	6.88	0.80
60	40	5.85	6.47	0.62
70	30	5.63	6.15	0.52
80	20	5.38	5.65	0.27
90	10	4.54	4.95	0.41
100	0	4.03	4.07	

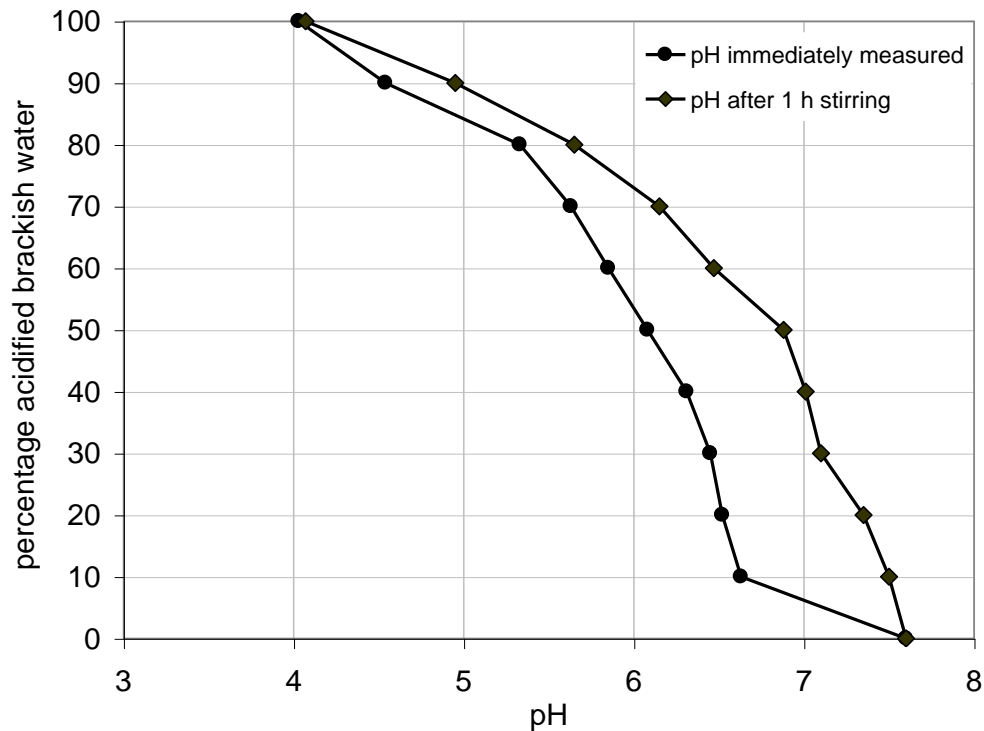


Fig. 6: Percentage of sulphuric acid (pH 4) in brackish water with resulting pH ( $t = 0$  and  $t = 1$  h).

The test with the brackish water ( $S = 14$  PSU) showed that the same dilution factor of 1:10 caused an immediate shift of about 1 pH-unit. After one hour the pH returned to almost its original value ( $\Delta\text{pH} = 0.1$ ). These preliminary experiments show that the addition of sulphuric acid in seawater to pure seawater is not only dependent on the amount of sulphuric acid, but also on time. The carbonate system reacts in two steps: first the production of dissolved ( $\text{CO}_2_{\text{aq}}$ ), second the release of gaseous carbon dioxide ( $\text{CO}_2_{\text{(g)}}$ ) from the system, to keep the pH almost constant.

### 3.5 Summary of laboratory experiments

The experiments with the hypothetical effluent of the SWS (pH 4) showed that even with a dilution factor of only 10, the discharge would not change the pH of the receiving sea water more than 0.2 standard units. Brackish water reacted with a spontaneous pH shift around 1, but returned within one hour almost to the original pH (pH shift 0.1).

These measurements were carried out in closed systems, where only gas-exchange was allowed. To transform these results to realistic conditions, like in this case the impact of a sulphuric acid discharge from a (moving) ship into the sea, more factors have to be taken into account. The mixing of the effluent with seawater is dependent on the current speed of the water. This parameter varies geographically. Additionally, tidal currents vary hourly. In estuaries, the exchange rate with the open sea and the inflow of freshwater are important factors.

### **3.6 Impact of the acidic effluent of the EcoSilencer on the pH of the receiving water**

In chapter 1.4.1 the theoretical composition of the effluent is described. The lowest pH would be 4.8. The experiments were carried out with acidified seawater pH 4, representing an assumed worst case. Next to sulphuric acid, nitric acid contributes to the acidity of the effluent, but to a lesser extent.

1. NO<sub>x</sub> reduction is around 20 %, compared to 95 % SO<sub>2</sub> reduction
2. Nitric acid delivers only one hydrogen ion per mol, whereas sulphuric acid delivers two hydrogen ions.

Based on data delivered by DME for different scenarios (ship in service and ship in harbour) and sulphur contents of the fuel, the composition of the resulting effluent was calculated (Tab. 6). Noticeable is the changing amount of cooling water, which is finally discharged. This variable has a significant impact on the concentrations.

The maximum relative contribution of nitrate to the acidity is calculated to be 9.66 %, but this is of minor importance regarding the pH of the discharged effluent and its impact on the environment. The proportion of nitric acid is relevant, as it delivers nitrate to the marine system.

The calculations are based on data obtained from DME about the EcoSilencer. The SO<sub>2</sub> adsorbing recirculation water is diluted with cooling water (seawater) and discharged at a pH level between 4.5 and 5.5. The laboratory experiments showed that a dilution of the effluent with seawater of 1:10 causes a pH-shift less than 0.2 pH units.

Tab. 6: Contribution of nitric acid to the acidity of the effluent

		at sea <sup>1</sup>			in harbour <sup>2</sup>		
		3.50	1.50	0.50	3.50	1.50	0.50
Sulphur content in fuel	%	3.50	1.50	0.50	3.50	1.50	0.50
Specific NOx emissions <sup>3</sup>	g/kWh	20	20	20	20	20	20
SO <sub>2</sub> removed	%	30	95	95	95	95	95
NOx removed	%	20	20	20	20	20	20
discharged cooling water	t/h	30	30	50	70	70	70
SO <sub>2</sub> in cooling water	mg/L	412	177	59	47	20	6.7
H <sub>2</sub> SO <sub>4</sub>	mg/L	631	270	90	72	31	10
	mmol/L	6.44	2.76	0.92	0.74	0.32	0.11
hydrogen ions delivered by H <sub>2</sub> SO <sub>4</sub>	mmol/L	12.88	5.52	1.84	1.47	0.63	0.21
NO in cooling water <sup>4</sup>	mg/L	20.4	20.4	8.14	2.3	2.3	0.9
	mmol/L	77.1	77.1	77.1	10.5	10.5	10.5
NO <sub>2</sub> in cooling water <sup>4</sup>	mg/L	33.04	33.04	33.04	4.48	4.48	4.48
	mmol/L	0.72	0.72	0.72	0.10	0.10	0.10
HNO <sub>3</sub> equivalent to hydrogen ions	mmol/L	3.29	3.29	3.29	0.45	0.45	0.45
sum of hydrogen ions	mmol/L	16.16	8.80	5.13	1.92	1.08	0.66
contribution of NO <sub>2</sub> to acidity	%	20.34	37.34	64.13	23.27	41.44	67.98

)<sup>1</sup> four main engines and two generators running 85 % MCR

)<sup>2</sup> two Generators running 95 % MCR

)<sup>3</sup> Marpol Annex VI limits emissions of NOx to between 10 – 17 g N/kWh, (worst case assumed as 20 g N/kWh)

)<sup>4</sup> based on the assumption that 70 % of N is converted to NO and 30 % is converted to NO<sub>2</sub>.

## 3.7 Estuaries

### Salinity and pH in the estuarine ecosystem

In estuaries a salinity gradient is caused by the permanent freshwater input by the rivers into marine waters. The most important estuarine characteristic is that nowhere is variation in salinity more pronounced. As seawater mixes with river water, the conservative seawater components will co-vary directly in concentration with salinity. Any component that is added during mixing will increase in concentration versus a conservative mixing line. A component that is lost during mixing (e.g. precipitation of some metals as hydroxides with decreasing pH) will decrease in concentration versus a conservative mixing line. Such non-conservative behaviour will only be evident when the addition or loss processes are relatively rapid versus water mixing in the estuary.

Other factors causing horizontal, vertical and seasonal variability of salinity in estuaries are:

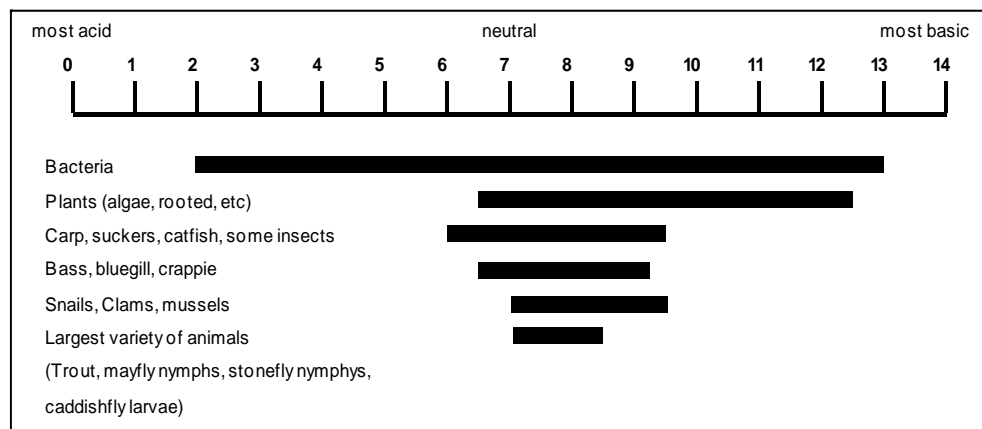
- amount of freshwater input,
- evaporation,

- water density (vertical variability),
- tides and
- the Coriolis effect

Human activities that cause significant, short-term fluctuations in pH or long-term acidification of a water body are exceedingly harmful. For instance, algal blooms that are often initiated by an overload of nutrients in the rivers can cause pH to fluctuate dramatically over a few hours' period. Changes of the pH can greatly stress local organisms.

The pH of an estuary can vary from 7.0 to 7.5 in the fresher, low salinity sections to between 8.0 and 8.6 in the more marine parts. The slightly alkaline pH of seawater is due to the natural buffering from carbonate and bicarbonate dissolved in the water (chapter 3.3). The pH of water is critical to the survival of most aquatic plants and animals. Many species have trouble surviving if pH levels drop below 5.0 or rise above 9.0 (Fig. 7).

Fig. 7: pH ranges that support aquatic life (source: see Internet-sites)



pH ranges that support aquatic life.

Changes in pH can alter other aspects of the water's chemistry, usually to the detriment of native species. Even small shifts in the water's pH can affect the solubility of some metals such as iron and copper. Such changes can influence aquatic life indirectly. If the pH levels are lowered, toxic metals in the estuary's sediment can be re-dissolved in the water column. This can have impacts on many aquatic species.

### 3.7.1 Harbour areas like the Port of Rotterdam

The port of Rotterdam is a very complex area, with vital inflow from the North Sea and several rivers and canals. The complex geometry and hydrography of the port of Rotterdam was approached in the Mam-Pec model (in CEPE report, 1999) with two different scenarios. In the first scenario the geometry of the Rotterdam port area was conceptualised as a rectangular area (2 x 20 km; 4000 ha; depth 20 m), with a 5 km wide open front to the river in order to mimic a harbour segment with an average water exchange of 32 % per tidal period. A second scenario, with a 10 km wide open front to the river was chosen to represent harbour segments with a water exchange of 65 % per tidal period. The hydrodynamic exchange in the Mam-Pec model is derived from the following parameters: density differences (between marine and freshwater), tidal period and height, river flux and the dimensions of the rectangular port area.

#### Shipping:

The Port Statistics 2001 of the Port Rotterdam show that the number of ship arrivals of seagoing vessels is around 30 000/a in the recent years and 133 000 arrivals of inland vessels per year. Movements of seagoing vessels are on average 82 000/a.

Within the EU the port of Rotterdam has the maximum NO<sub>x</sub>, SO<sub>2</sub> and CO<sub>2</sub> emissions.

Tab. 7: Ports in the EU ranked by estimated annual emissions of NO<sub>x</sub> in 2000 reported by Entec, 2002.

Rank	Port Name	Country	NO <sub>x</sub> [kT]	SO <sub>2</sub> [kT]	CO <sub>2</sub> [kT]
1	Rotterdam	NLD	3.8	3.7	219.9
2	Antwerp	BEL	2.2	2.2	134.0
3	Milford Haven	GBR	2.0	2.2	130.4
4	Hamburg	DEU	2.0	1.9	115.5
5	Augusta	ITA	1.8	2.0	121.4
6	Agioi Theodoroi	GRC	1.7	1.8	107.0
7	Piraeus	GRC	1.6	1.6	93.9
8	Eleusis	GRC	1.5	1.6	95.1
9	Gothenburg	SWE	1.5	1.5	91.1
10	Immingham	GBR	1.3	1.4	82.0

A rough calculation using data from Tab. 7 indicates that on an annual basis total SO<sub>2</sub> discharge into Rotterdam port waters will contribute about  $2 \times 10^{-4}$  mol H<sup>+</sup>/L assuming that all SO<sub>2</sub> will be transferred to the aqueous phase. Using data from Table 6 and assuming the presence of 100 vessels in the port area, the H<sup>+</sup> concentrations will increase by 5.7, 9.4 and to  $16.7 \times 10^{-6}$  mol H<sup>+</sup>/L h for 0.5 %, 1.5 % and 3.5 % sulphur fuel. This corresponds to 0.5 – 2 pH units. This calculation does not take into account the buffer capacity of seawater, the exchange of CO<sub>2</sub> with the atmosphere, nor the tidal exchange with the open sea. Preliminary experimental data presented above (chapter 3.4) suggest that the re-equilibrium is rapid although effects of continuous addition of acid need to be investigated in detail.

### 3.8 The Baltic Sea

The Baltic Sea is a relatively shallow inland sea surrounded by the countries of North-eastern Europe and Scandinavia. Its total area is about 377,400 km<sup>2</sup>, and its volume about 21,000 km<sup>3</sup>. The catchment area extends over an area about four times as large as the sea itself. The mean depth is 55 m, while the maximum depth is 459 m in the Landsort Deep. The Baltic also receives surface water drainage from five other countries: Belarus, Czech Republic, Slovak Republic, Norway, and Ukraine.

The Baltic Sea is connected to the North Sea through narrow and shallow sounds between Denmark and Sweden. The outlet consists of a series of basins separated by shallow sills, which obstruct efficient water exchange. Consequently, it takes 25 - 35 years for all the water from the Baltic Sea to be replenished by water from the North Sea and beyond.

Salinity in the Baltic varies from fully marine at the Skagerrak/Kattegatt boundary to almost fresh water conditions in the Bothnian Gulf. Due to the high riverine input of fresh water a pronounced year-round stratification of the water column, especially in the Baltic Proper, can be observed. This results in a reduced mixing of surface with bottom waters. Ice coverage occurs regularly in the northern parts.

More than 500 million tonnes of cargo are transported across the Baltic Sea each year, along many busy shipping lanes. More than 50 passenger ferries also ply routes between Baltic ports.

### **3.8.1 Vital inflow from the North Sea**

The inflow of water from the North Sea is the main source of oxygen for the deep waters of the Baltic Proper, and is very significant for nutrient cycles throughout the Baltic Sea. A stagnation period of more than sixteen years ended in January 1993 when masses of high-salinity water entered the Baltic, and for the first time since 1977, the Baltic Sea was free of hydrogen sulphide. Unfortunately, the effects of this water exchange did not last, and within a couple of years the depths of the Eastern Gotland Basin were again becoming anoxic. In 1996 hydrogen sulphide was once more recorded in the depths of the Bornholm and Eastern Gotland Basins. Contaminants and nutrients enter the Baltic Sea in rivers, in runoff from coastal areas, through exchange of water with the North Sea, through atmospheric deposition, and due to human activities at sea. A complete water renewal takes about 25-30 years, so persistent pollutants can remain in the Baltic for a long time.

## **3.9 Acidification of surface waters**

The deposition of atmospheric acids is not a recent phenomenon, but the extent of the consequences are still unclear. Acidification of soils and surface waters is to some extent a natural process but has accelerated in the last decades. The main causes of acidification are acid rain and the use of certain fertilisers in agriculture, which reach the oceans by surface water runoff and rivers. A drop of the pH to 5.5 in soil for example causes a decline in agricultural harvests as certain micronutrients become less available and microbial turnover of nitrogen and carbon are impaired.

The acidity of a water body is dependent on the amount of acid deposited, the amount of acid already present in the water body, and the ability of the water body to absorb and neutralise acid (buffer capacity). Seawater has a tremendous ability to neutralise acids, so significant acidification does not occur in coastal waters and most estuaries. Some freshwater bodies, however, may be very sensitive to atmospheric inputs of acidic compounds (US EPA, 1976).

The overall effects of seawater acidification on marine ecosystems are not clear yet. For example the potentially harmful effects of changing environmental CO<sub>2</sub> concentrations on energy metabolism and growth of marine invertebrates fishes still have to be studied in detail.

Acidification affects ecosystems in many ways. Aquatic organisms in acidified waters often suffer from calcium deficiencies which can weaken bones and exoskeletons and can cause eggs to be weak or brittle. It also affects the permeability of fish membranes and, particularly, the ability of gills to take up oxygen from the ambient water. Additionally, increasing amounts of acid in a water body change the mobility of certain trace metals like aluminium, cadmium, manganese, iron, arsenic, and mercury. Species that are sensitive to these metals, particularly fish, can suffer as a result. The effects of acidification on aluminium mobility has received the most attention because this metal is toxic to fish. The effects of increasing levels of cadmium and mercury, which are atmospheric pollutants of concern for water quality, are also becoming known.

### 3.10 Experiences with acid disposals at sea.

The waste of titanium dioxide production contains heavy metals and sulphuric acid (around 12 %; Rat von Sachverständigen, 1981; Carlson, 1986). Beginning in 1969 this waste was dumped into the sea about 12 nautical miles north of Heligoland in the central German Bight with increasing amounts. This disposal was stopped in 1989, because the heavy metal content of the acid caused dramatic changes in the ecosystem. At that time 750 000 t of sulphuric acid (12 %) were dumped into the sea per year. The pH of the water in the disposal area changed only slightly, due to the buffer capacity of the receiving seawater (Dethlefsen, 1990).

Data provided by Weichart (1975) indicate that pH changes resulting from titanium dioxide waste dumping were within the range of naturally occurring pH values. Even in the core of the screw water of the dumping vessel in 5 - 10 m water depth the pH after one hour was 7.77, increasing to 8.04 after 4.7 h and 8.15 after 4.7 h. With the exception of fresh screw waters no indications of long term pH changes were found.

### 3.11 Eutrophication effects

Any inorganic nitrogen and phosphorus compound added to natural waters will promote primary productivity. Enhanced production of biomass can lead to eutrophication effects under certain circumstances.

In marine systems phytoplankton biomass is usually produced in -within limits- fixed relations of carbon : nitrogen: phosphorus, the so-called Redfield ratio of 106 : 16 :1. Thus, any mole P added will result in the fixation of 106 moles carbon and 16 moles nitrogen.

In cases where only nitrogen is added as in scrubber effluents the extent to which additional biomass is produced will depend not only on the actual amount added but also on the phosphorus available for primary production. In open ocean situations P is generally regarded as the limiting nutrient. Here, additional N will not have any effects on planktonic biomass production.

In near-shore or harbour situations, where P is available from e.g. riverine inputs, runoff from agriculture or direct input of domestic sewage, addition of inorganic nitrogen may lead to enhanced primary production.

On the other hand, addition of nitrogen may also have beneficial effects as it counteracts the development of cyanobacteria blooms which may occur in the absence of inorganic nitrogen when there is still sufficient phosphorus in the euphotic zone. Certain cyanobacteria are able to use molecular nitrogen instead of nitrate or ammonia. This is often the case in the Baltic Sea where such blooms occur regularly. Here, phosphate is still present in measurable quantities even after the phytoplankton spring bloom has reduced nitrate levels to below the detection limit (Wasmund et al. 2001).

Based on the assumption that there will be ample phosphate then an input of 3.29 or 0.45 mmol NO<sub>3</sub><sup>-</sup>/L, respectively, (Tab. 4) will result in an additional biomass production of 43.6 or 6 mg/L assuming that carbon accounts for 50 % of the produced biomass. This figure, however, does not include further dilution of the scrubber input by turbulent mixing along the ship's path.

Primary production, at least in temperate and polar regions, is strongly connected to the seasonality of insolation. This results in high productivity in spring when there are sufficient inorganic nutrients available and lower ones in summer and early autumn when nutrients are production limiting. Thus, relative contributions of additional nitrogen-containing nutrients will be low in spring but higher in summer. Furthermore,



inter-annual variability will also have an effect on the relative contribution of any additional nitrogen added.

In coastal areas and harbours neither P and N are usually production limiting factors. Here, it is rather the availability of light which prevents usage of inorganic nutrients by primary producers (e.g. Colijn and Cadée 2003).

#### **4 Environmental impact of scrubbing waters - Synthesis**

During removal of sulphur in refineries catalysts are used in the production of low S fuels. These contain transition metals (molybdenum, cobalt, nickel, zinc, copper) which need to be replaced at more or less regular intervals. Only part of these metals can be recycled, the remainder, especially fine material released into the gas stream, has to be safely deposited. In addition the amine used to remove the hydrogen sulphide produced during Hydrotreating also can be recycled or needs to be safely deposited.

The costs and environmental impacts incurred from either recycling or deposition cannot be specified on a global scale. Van Oudenhoven et al. (1993) report that in 1993 a total of 6,368 tons of spent desulphurisation catalyst was produced by 89 refineries in Europe.

Thus, processes that are cheaper or more environmentally benign are attractive alternatives. One of these is removal of combustion gases. Of the processes listed above Flue Gas Desulphurisation with Seawater Scrubbing (FGD-SWS) appears to be attractive for operation of seagoing vessels.

Both laboratory experiments and field evidence indicate that acidic waste streams from FGD-SWS introduced in full strength seawater leads to observable effects on ambient pH only for extremely short periods of time. From the dumping of much higher concentrated sulphuric acid in the North Sea it is known that the area affected is restricted to a few hundred meters behind the dumping vessel.

Preliminary laboratory experiments with seawater indicate that at a 1:10 dilution the observable pH change did not exceed 0.1 pH units. For brackish waters a time lag of about one hour was observed. These values coincide with EPA requirements.

Considering that in this case a 12 % acid ( $=2.634 \text{ mol H}^+/\text{L}$ ) was dumped then it can be expected that the maximum of about 6 mmol  $\text{H}^+/\text{L}$  produced during waste discharge from FGD-SWS will affect neither the pH values nor the sulphate contents of the receiving waters to a noticeable degree. This is not only due to the low concentrations of sulphate in the waste stream. Ship movements and screw rotation causing turbulent mixing will provide further dilution. In addition, natural mixing processes also will contribute to this.

It should, however, be noted that the conclusion given above holds for fully marine salinities only. In waters such as the Baltic with generally lower salt contents and slightly different ionic composition, especially in the northern parts, the 1:10 dilution may not be sufficient. Also, during harbour times when there will be no ship movements and only limited water movement this dilution factor may also be too low. Under these conditions, additional sulphate precipitation with limestone or the use of low sulphur fuels might become necessary. Detailed analysis of this case remains to be done. The other factors worth considering are the total mass of sulphur emitted in harbour versus at sea. Vessels in port do not burn the amount of fuel as at sea due to the lower demand for propulsion. A typical ferry may have 27 MW of installed power available at sea, while only 3 MW of this would be available in harbour. The amount of sulphur discharge is proportional to this power use, thus even in brackish harbours, the sulphur dilution ratio may be sufficient.

In the case of nitrate open sea discharge from FGD-SWS is, again due to the high dilution rate, not likely to cause any eutrophying effects. In ports, however, the high

concentrations in the discharge stream together with restricted water exchange may lead to nitrate values high enough to cause unwanted effects such as exceptional phytoplankton blooms. Just as sulphur emission is linked to engine total output, so is the nitrogen emission rates. Vessels that are moving slowly, or anchored in harbour with only generators running will be producing much lower levels of nitrates than under full speed at sea. The effect of 2-4 MW of engine power per ship in harbour may be insignificant in terms of nitrate amounts. Even when main engines are started, it is difficult to conceive of how massive amounts of fuel can be burned for propulsive motors in a small harbour. The use of propulsion engines is to get out of harbour and manoeuvre, so these sources are not continuous.

Nevertheless, as experimental evidence is lacking, it appears necessary to conduct a series of laboratory and field experiments to elucidate the actual changes in pH and sulphate as well as nitrate concentrations under a variety of conditions. Similarly, it might be useful to adopt models developed for port sediment and water exchange to include pH and sulphate also.

Comparing these results with the harmful effects of the SO<sub>2</sub> and NO<sub>x</sub> emissions of ships, the use of the SWS seems to be a shortcut: most of the produced sulphate and nitrate will reach the oceans by surface run-off via the rivers. At land however the acidification of soils, lakes and rivers causes considerably higher damage. The change of atmospheric aerosol composition by NO<sub>x</sub> emissions, which has been observed in the German Bight for example should also be taken into account.

Other positive side-effects of the SWS are 80 % removal of the particulates and noise reduction.

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### **Internet sites**

Advances in power technology, issue 4:

<http://www.powertech.co.uk/downloads/R&D/fgdSeaWater.pdf>

US-EPA What are the Major Effects of Common Atmospheric Pollutants on Water Quality, Ecosystems, and Human Health?

<http://www.epa.gov/owow/oceans/airdep/air3.html>

pH ranges that support aquatic life.

<http://www.bpa.gov/corporate/kr/ed/kidsinthecreek/materials/waterquality/graph.htm>

Oceanography - Salt balance, residence times, element addition and removal.

<http://www.ncl.ac.uk/>