

A Theoretical Environmental Impact Assessment of the Use of a Seawater Scrubber to Reduce SO_x and NO_x Emissions from Ships

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List of used abbreviations

amu	atomic mass units
CCN	cloud condensation nuclei
DIN	dissolved inorganic nitrogen (NH_4^+ , NO_2^- , 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
MCR	Maximum continuous rating
NO_x	Oxides of Nitrogen
PAH	polycyclic aromatic hydrocarbons
PON	particulate organic nitrogen
PSU	practical salinity units
SO_x	Oxides of Sulphur
SWS	seawater scrubber
VOC	volatile organic compounds

1 Introduction

The burning of fossil fuels is one of the most significant contributors 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. Additionally, NO_x enhances eutrophication of terrestrial and aquatic ecosystems. A large number of emission reducing technologies have been developed for power stations (see chapter 1.3), but 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 main objective of this report is therefore the reduction of atmospheric emissions from ships, by use of a seawater scrubber technology (flue gas desulphurisation process).

Eutrophication is the process whereby a body of water becomes over-enriched with nutrients which results in overgrowth of algae and depleted oxygen levels in the water

1.1 Air pollution

Air pollutants are substances that are introduced into the atmosphere via anthropogenic activities. Air pollution occurs both in gaseous and particulate forms which, when present in excess, are harmful to human health, buildings and ecosystems. Five 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;
- ◆ eutrophication of ecosystems, especially by nitrogen compounds;
- ◆ 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 the burning of fossil fuels (coal, oil and natural gas). 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 by 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 that by 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 carbon, hydrocarbons, metal oxides 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 ammonium sulphates and nitrates formed from reactions involving sulphur dioxide, nitrogen oxides and ammonia. 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. Due to the ability of these particles to serve as condensation nuclei, soot contains polycyclic aromatic hydrocarbons (PAHs), a family of semi-volatile organic pollutants encompassing compounds such as extremely small amounts of anthracene, and some pyrene, or benzo[a]pyrene. Some 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 (SO_2 , NO_x , NH_3). Ships emit sulphur dioxide and nitrous oxides through the

combustion of fossil fuels. The primary air pollutants sulphur dioxide and nitrogen oxides are oxidised 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 emission of NO_x and SO_x have different consequences for the atmosphere: 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. SO_2 is oxidised to 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 SO_2 emissions are deposited locally; therefore shipping contributes mainly to coastal air pollution.

Corbett and Fischbek (1997) give annual emissions of 3.08×10^6 ton N and 4.24×10^6 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 is related to the operation of ships. This implies that ship engines although highly efficient at converting fuel into power, emit very high levels of 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 ⁽²⁾ [10 ⁶ t]	SO ₂ [10 ⁶ t]	NO _x [10 ⁶ 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 CO₂ 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 (216 nautical miles) width. Similarly, Oftedal (1996) estimates that 74 - 83 % of all vessels are within 200 nautical miles (370km) of land at any time. Consequently, the impact of shipping on NO_x and SO₂ levels is highest in the northern hemisphere, particularly along the west and east coasts of the United States, in northern Europe and the North Pacific.

1.2.1.1 Legislation:

As soon as the IMO regulation for the prevention of air pollution from ships (Marpol 73/78 Annex VI) came into force, emissions from ship exhausts had to be reduced. Annex VI contained provisions allowing for special "SO_x 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_x emissions. Currently the Baltic Sea, the North Sea and the Channel are designated as SO_x Emission Control Areas in the Protocol. [Marpol Annex VI entered into force on the 19th May 2005.](#)

1.3 Techniques to reduce atmospheric emissions in power plants

The technology for the reduction of atmospheric pollutants should be environmentally benign. Otherwise, the problem is merely being shifted to another area. There are three possibilities to reduce SO₂ 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

After World War II, production of high sulphur crude oils increased considerably. As a result of increased use of high sulphur crudes and increasing awareness of environmental considerations, product specifications became more stringent. The oil industry had to develop techniques for the removal of sulphur and the platinum reforming process was developed. However it should be noted that platinum reforming is only suitable for white oils containing relatively low ppm levels of sulphur.

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 reduced by conversion to hydrogen sulphide (H₂S) in the presence of a catalyst. As only sulphur is removed, high yields of liquid end products result. In addition, H₂S can be washed from the product gas stream by an amine wash. H₂S 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 recycled gas and reacted at temperatures of 300 - 380 °C. Pressures of 10 - 20 bar for naphtha and kerosine and 30 - 50 bar for diesel are applied. Removal of sulphur from heavier oils such as marine fuel oil often requires pressures of up to 200 bar. 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 alumina extrudates.

More recent developments include biological conversion of sulphur-containing petroleum components to elemental sulphur. Biological removal of hydrogen sulphide

and light mercaptans from refinery streams has been commercially implemented. A biological process for removal of sulphur from diesel oils was under development for several years, but the firm has subsequently ceased operation. Sonocatalytic treatment (optional) with hydrogen peroxide oxidation in the presence of iron(III) complexes at low temperatures has removed sulphur from diesel oils. Several developers are engaged in advanced pilot plant studies seeking to commercialise such a process. This approach will remove dibenzothiophenes, compounds which are of particular concern to the oil industry. The effectiveness of this method for removing sulphur from heavy fuel oils has not yet been quantified, and disposal of product sulphones must be factored into any process design.

1.3.2 Flue Gas Desulphurisation

The removal of SO₂ 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 suspension of crushed limestone in water is sprayed into the flue gases. The SO₂ 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 of or used by the building trade. Although the reduction of SO₂ is around 90 %, the process has the disadvantage that limestone has to be stored and large quantities of gypsum waste 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 SO₂ 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 SO₃ are removed. After pre-scrubbing, the gases are then cooled and fed into an absorption tower, where the SO₂ 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 SO₂ - 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_x 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 SO₂ 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 through 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 SO₂ is efficiently absorbed by the seawater. Air is supplied to oxidise the absorbed SO₂ 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. As the Norwegian Sea is deep and well mixed, further water treatment was regarded unnecessary (Glenna and Tokerud, 1991). Several other seawater scrubbing flue gas desulphurisation systems have been installed in power plants around the world.

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 SO₂, 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.

Conclusion of Marine 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 emission control technologies affect more than one pollutant and have different impacts on environmental effects. FGD simultaneously removes SO₂, NO_x and particulate matter.

1.4 Technologies to reduce atmospheric emissions by ships

- the seawater scrubber

For ships 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 Krystallon Seawater Scrubber removes 90-95 % of SO₂ and 10 - 20 % of NO_x. 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 system needs little extra space, as the majority of the system replaces existing exhaust silencers of the exhaust system. The accompanying positive side effects are the reduction of engine noise and a reduction of the diesel smell.

As the conversion of SO₂ to SO₄²⁻ and NO_x to NO₃⁻ consumes oxygen, aeration of the effluent is necessary. The system incorporates a high degree of recirculation, thus ensuring that sulphur oxides are given adequate time and oxygen contact to be converted to SO₄. In the following calculations complete oxidation will be assumed.

The Krystallon Seawater Scrubber 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

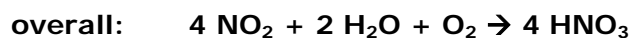
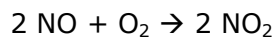
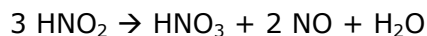
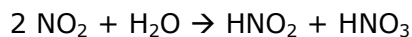
the water, there are a set of mixing baffles which break up large gas flow into smaller bubbles, forcing the gas to come in contact with water, and thereby encouraging transfer of species from gas to water. The SO_x in exhaust gas is relatively soluble in seawater, so this transfer happens to a very high degree. Larger particles (greater than 2.5 micron) are predominantly captured in the water. Fine particles (smaller than 2.5 micron) may pass through without capture.

Since the recirculated water is maintained at a pH of 2.0-4.0, this makes a very good medium for scrubbing of NO_x (eg Scheme 1). Measurements have shown up to 20 % removal of NO_x, and this is enhanced due to the acidity of scrubbing liquor.

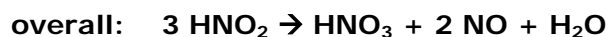
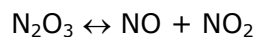
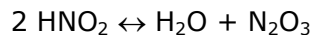
The following reactions should take place:



As this is an exothermic reaction the equilibrium is shifted to the left of the equation with increasing temperature. Accordingly, there is no reaction of NO with oxygen at temperatures >650 °C.



The following reaction also takes place at higher temperatures:



The final product in any case will be nitric acid.

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 extremely low concentrations of hydrocarbons, making it safe for discharge to sea.

1.4.1 Composition of the effluent

While NO_x production depends on the engine design and engine operating conditions, SO_2 production depends on the sulphur content of the fuel. During seawater scrubbing the SO_2 is finally converted to sulphuric acid and NO_x to nitric acid. 95 % of the SO_2 is eliminated by this technique and ca. 20 % of NO_x . The salts in the effluent are SO_4^{2-} , SO_3^{2-} , NO_3^- and 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?
- ◆ Does the addition of nitrate from nitric acid lead to higher primary production of biomass, i.e. to eutrophication?
- ◆ 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 is provided in the following section and then the effects of acid discharge are 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 (SO_4^{2-}), dissolved sulphide (HS^-), and hydrogen sulphide gas (H_2S). 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).

Uses 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

	1992	1993	1994	1995	1996	1997
	10^6 tonnes H_2SO_4					
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

(EFMA, 2000)

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, paper and petrochemical industries. By discharging these sulphate containing wastes to the rivers, all sulphate finally ends up in the sea.

2.1.2 Sulphur emissions to the 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_2S) and sulphur dioxide (SO_2) are oxidised to sulphur trioxide (SO_3), which dissolves in water droplets of the clouds to form sulphuric acid (H_2SO_4). This process is responsible for acid rain. However a significant concentration is neutralised by gaseous ammonia in the atmosphere to form the corresponding ammonium salts e.g. ammonium sulphate (this is a secondary particulate).

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 $60 * 10^6 \text{ S yr}^{-1}$ ($2 * 10^{12} \text{ mol S yr}^{-1}$). 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 of sulphur emissions. This estimate is very imprecise with 35 to $315 * 10^6 \text{ S yr}^{-1}$, 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_2SO_4 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 in the Southern Indian Ocean has been reported to be by a factor of 20 or higher in the summer compared to the winter (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 $110 * 10^6 \text{ t S yr}^{-1}$ ($2 - 3 * 10^{12} \text{ mol yr}^{-1}$) 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 (SO_x) are transformed into particles via physical and chemical processes. The main source of SO_x is stationary and mobile fuel combustion. The types of sources that emit SO_2 are generally located in urban areas. Secondary sulphate particles formed from 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

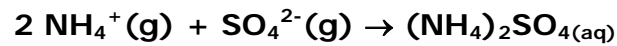
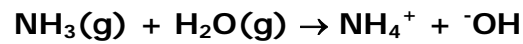
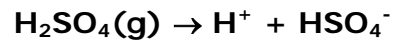
Gases in the atmosphere can reach the earth's surface by wet and dry deposition processes. For wet deposition, precipitation is the delivery mechanism to the surface. The gases can dissolve in clouds and rain drops or adsorb to frozen precipitation elements. Sulphate particles represent good condensation 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 SO_2 to particles is still poorly understood.

Secondary particles formed through chemical reactions are typically much smaller ($<2.5 \mu\text{m}$ diameter) than particles derived from physical processes ($>2.5 \mu\text{m}$ 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 via sulphuric acid to ammonium sulphate (Scheme 1) is an example of a gas to aerosol conversion process.

Scheme 1



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

2.2 Nitrogen cycle

Elemental nitrogen (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). Nitrogen compounds, especially ammonia, are of great importance for the world economy for use, among others, 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 (NO_2) is a reddish brown, highly reactive gas that is formed in the air through the oxidation of nitric oxide (NO). Nitrogen oxides (NO_x), the term used to describe the sum of NO , NO_2 and other oxides of nitrogen, play a major role in the formation of ozone. The major sources of man-made NO_x 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 (NH₃) is the most reduced form of nitrogen, and is released in small quantities from anaerobic degradation of organic matter containing nitrogen. The major contribution to natural emissions is from agriculture. 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 (N₂O) and nitrogen dioxide (NO₂).

2.2.1.2 Anthropogenic emissions of nitrogen

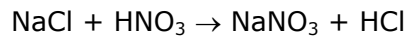
Combustion processes release mostly nitrogen oxide (NO) and nitrogen dioxide (NO₂). The exact composition of nitrogen oxides emitted from combustion processes varies with the temperature of the combustion process, therefore the nitrogen oxides from combustion are often referred to as NO_x to indicate 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

Nitrogen oxide	Oxidation state
N ₂ O	+1
NO	+2
NO ₂	+4
HNO ₃ , N ₂ O ₅	+5

Atmospheric nitrogen compounds are transported over long distances (Schulz et al. 1998). During transport they undergo specific physical-chemical changes (Fig. 1). NO_x-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 sea-salt aerosols in coastal areas has been observed by Schulz et al. (1998). This change is caused by the reaction of sodium chloride with (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. 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⁻/m³ have been determined which rapidly decrease landwards. Thus, the reaction outlined above will take place preferentially in coastal areas and hence a remarkable amount of nitrogen deposition occurs in the coastal area. Although higher NO_x emissions may occur in regions remote from the coast the chloride exchange reaction does not play a major role in NO_x removal here due to the low level of atmospheric NaCl. Schulz et al. (1998) regard this reaction as one of the most important sinks for oxidised nitrogen compounds in the coastal marine atmosphere.

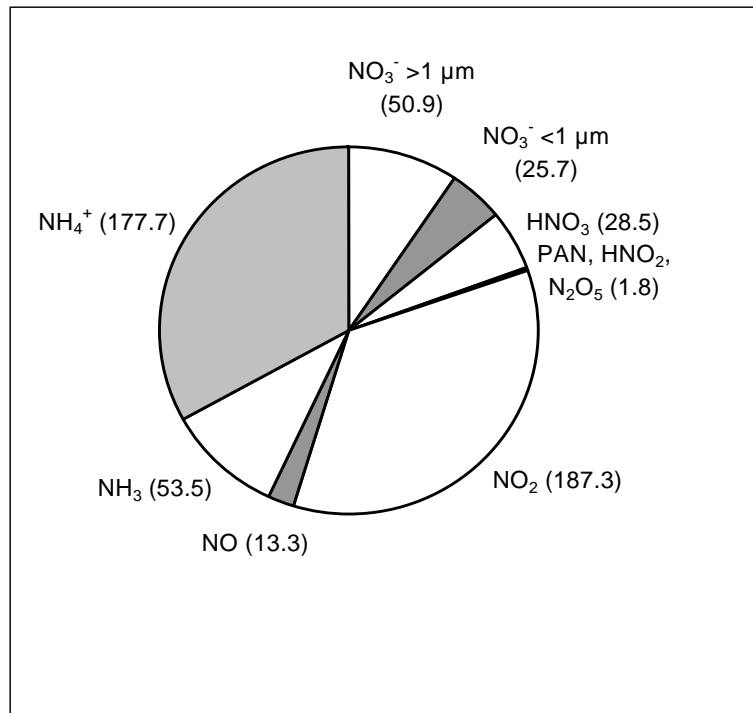


Fig. 1: Mean composition of atmospheric nitrogen compounds (nmol m⁻³) in the German Bight (Schulz et al., 1998), PAN: peroxyacetylnitrate.

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 the 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

		Freshwater (river)		Seawater	
		mg/L	weight %	mg/L	%
Sodium	Na ⁺	7	5.83	10800	30.72
Potassium	K ⁺	2	1.67	400	1.14
Magnesium	Mg ²⁺	4	3.33	1300	3.70
Calcium	Ca ²⁺	15	12.50	410	1.17
Chloride	Cl ⁻	8	6.67	19400	55.19
Bicarbonate	HCO ₃ ⁻	58	48.33	140	0.40
Sulphate	SO ₄ ²⁻	12	10.00	2700	7.68
Silica	SiO ₂	14	11.67	2	0.01

(internet site)

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 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 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 H₂S. Bacteria carry out various transformations of sulphur (Fig. 2).

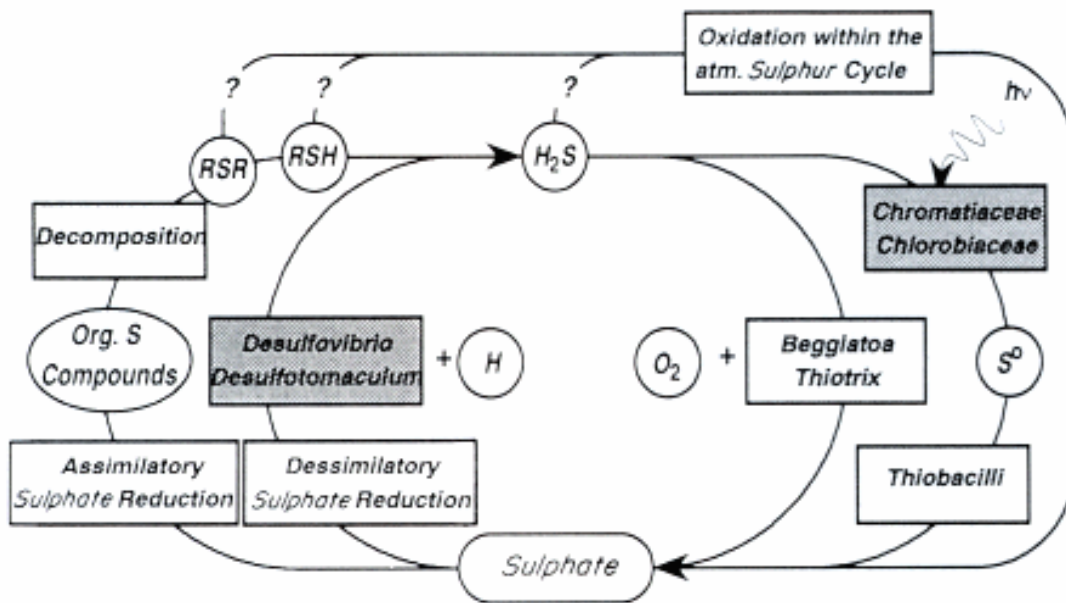
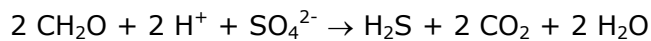


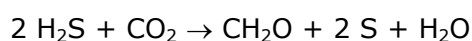
Fig. 2: Scheme of the microbiological cycle of sulphur and its possible influence on the atmosphere

1. Sulphate reduction in anaerobic environments (CH₂O represents organic matter such as carbohydrates):



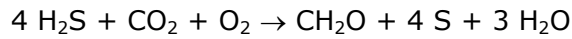
This reaction is analogous to aerobic respiration but with SO₄²⁻ rather than oxygen acting as the terminal electron acceptor in the oxidation reaction. The H₂S produced may precipitate as authigenic minerals such as greigite, mackinawite and pyrite or may be used in one of the following reactions:

2. Sulphur-based (anaerobic) photosynthesis:



This reaction is probably the earliest form of photosynthesis using H₂S rather than H₂O as the hydrogen donor in the reduction of CO₂. 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 H₂S, 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) when phytoplankton blooms, transforming inorganic nitrate into organic nitrogen compounds such as proteins or nucleic acids. In summer the nutrients reach a minimum, leading sometimes to a 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.

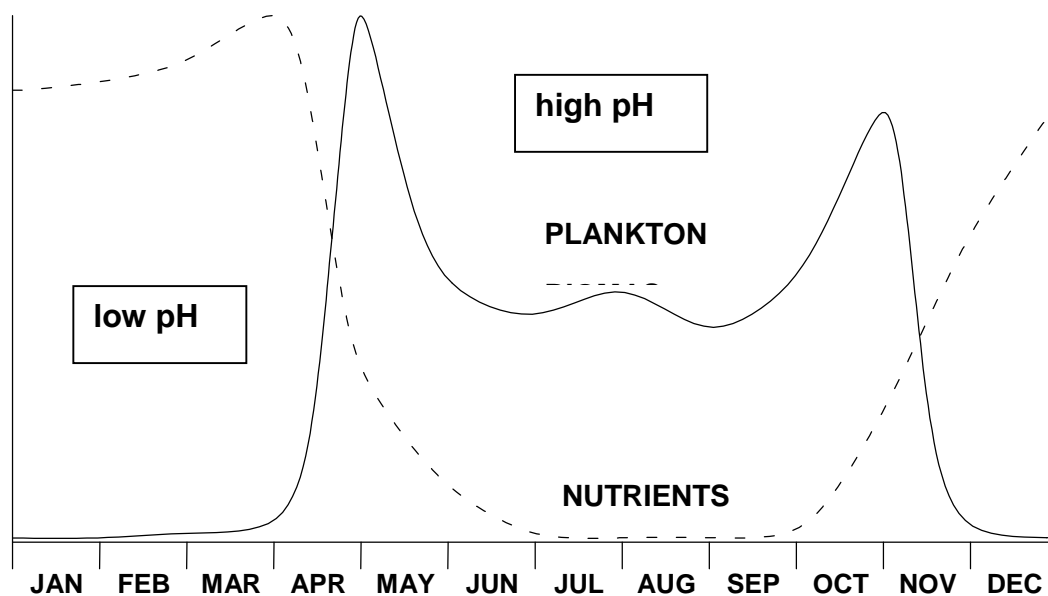


Fig. 3: Schematic seasonal variation of nutrients and phytoplankton biomass in temperate areas.

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 (NH₄⁺, NO₂⁻, NO₃⁻), 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 therefore 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 (CO₂^{*}, HCO₃⁻ + CO₃²⁻) varies by ~20 % due to vertical transport in the water column and remineralisation of both CaCO₃ and organic matter.

Natural changes of seawater pH are related to primary production, which converts inorganic (carbon?) to organic carbon, and then 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 found 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 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 H_2CO_3 are difficult to measure and are usually given as CO_2^* . The solubility of CO_2 in water is 1.7 g L^{-1} (0.04 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).

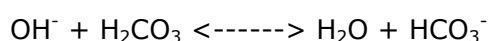
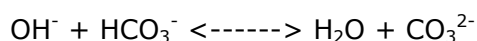
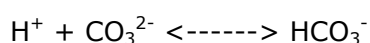
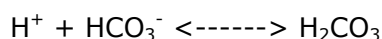
Henry's law is derived from

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

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

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

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



As calcium carbonate (solid) reacts with water in presence of free hydrogen ions, the solid calcium carbonate dissolves forming free 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 CO_2 the system is defined by two independent variables (in addition to total pressure), e.g. temperature and p_{CO_2} . If, besides temperature, one other variable such as p_{CO_2} , $[\text{CO}_2^*]$ or $[\text{H}^+]$ is known, then all components can be calculated from the equilibrium concentrations, using Henry's law, the acidity constants and the proton condition or charge balance.

The pH of a pure aqueous CO_2 solution is defined by the charge balance:

$$[\text{H}^+] = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-]$$

If the system is kept in equilibrium with constant p_{CO_2} , the pH can be varied only by the addition of a base, C_B or an acid, C_A . Electroneutrality must be observed for such an addition.

As B is equivalent to the concentration of a monovalent cation (e.g. $[\text{Na}^+]$ from NaOH) and A is equivalent to the concentration of a monovalent anion (e.g. $[\text{Cl}^-]$ from HCl).

$$C_B + [\text{H}^+] = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] + C_A$$

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

where, C_T = total CO_2 concentration; β is the Bunsen coefficient ($\beta_0 = K_H * 22.414$ $[\text{atm}^{-1}]$); and $(C_B - C_A)$ is the acid neutralising capacity of the solution with respect to the pure solution of CO_2 . This difference is defined as the alkalinity, $[\text{Alk}]$.

$$[\text{Alk}] = C_B - C_A = \frac{K_H p_{\text{CO}_2}}{\beta_0} (\beta_1 - 2\beta_2) + [\text{OH}^-] - [\text{H}^+]$$

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 $[\text{Alk}]$ and p_{CO_2} .

There are other bases apart from those present in the carbonate system which contribute to the total alkalinity of seawater. These are $\text{B}(\text{OH})_4^-$, HPO_4^{2-} and PO_4^{3-} and, under specific environmental conditions, hydrogen sulphide HS^- .

If this is included then

$$C_B + [\text{H}^+] = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + C_A$$

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

$$\text{with } B_T = [\text{H}_3\text{BO}_3] + [\text{B}(\text{OH})_4^-] \text{ and } \beta_B = [\text{B}(\text{OH})_4^-]/B_T$$

and

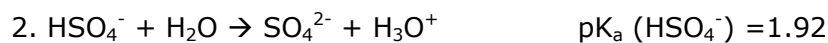
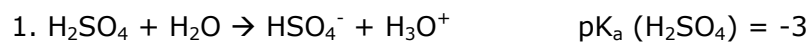
$$[\text{Alk}] = C_B - C_A = \frac{K_{\text{HPCO}_2}}{\beta_0} (\beta_1 - 2\beta_2) + B_T \beta_B^- + [\text{OH}^-] - [\text{H}^+]$$

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 to as total alkalinity (TA). CA and TA differ by about 100 $\mu\text{equivalents L}^{-1}$ only.

Total alkalinity of seawater averages 116 mg L^{-1} and is greater than fresh water, which varies significantly, depending on the drainage area. TA can have a total alkalinity of 30 to 90 mg L^{-1} . 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_a values (-3 and 1.92, respectively), and are hence strong acids which dissociate completely. Therefore all the protons of sulphuric acid contribute to the pH-shift. The carbonate system will buffer the additional protons by releasing CO_2 in order to keep the pH constant. One molecule of sulphuric acid will therefore produce 2 molecules of CO_2 . The equations 1-3 of the carbonate system (see above page 27) will shift from the right to the left sides, finally releasing the dissolved CO_2 to the atmosphere.

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_2 to SO_4^{2-} is not taken into account nor is the impact that the temperature of the seawater has on pH (Hunter, 1998). The calculations in the previous chapter are based on an ideal seawater composition and do not take into account other seawater constituents (e.g. organic acids like amino or humic acids). As the above described equations are simplified, and some data is difficult to obtain or absent, laboratory measurements were carried out at Terramare to quantify the ability of seawater to buffer sulphuric acid solutions.

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_2SO_4 . 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 acid was recalculated because of the changing end-volume. The pH shift caused by the addition of sulphuric acid was measured directly (Fig. 5).

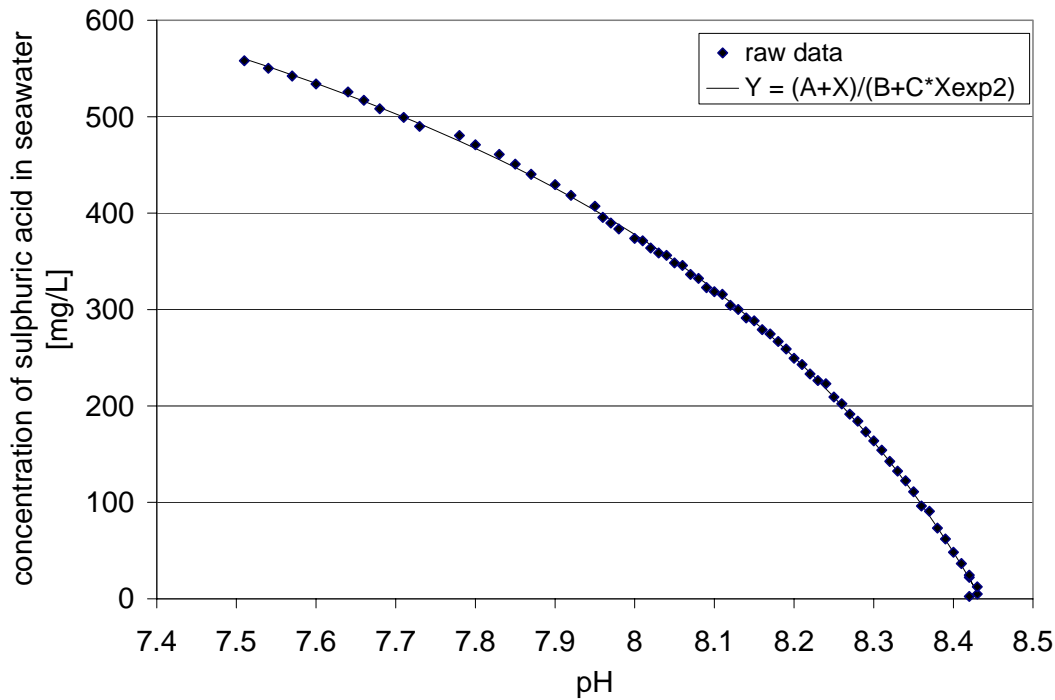


Fig. 5: Impact of sulphuric acid (pH 4) on the pH of seawater ($S = 29$ PSU) corresponds to regression line.

The addition of 2.48 mmol (68 mg) sulphuric acid to 1 L seawater caused a pH shift of pH 0.1 units only. This amount of sulphuric acid corresponds with a mixture of 1:10 (v:v, sulphuric acid in seawater pH 4 : natural seawater). Even a mixture of 1:5 (5.08 mmol L⁻¹) 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:

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

$$A = -8.43463908$$

$$B = -0.00536647$$

$$C = 0.00006588$$

4.2 Impact of diluted sulphuric acid (pH4) 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 CO₂ 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	

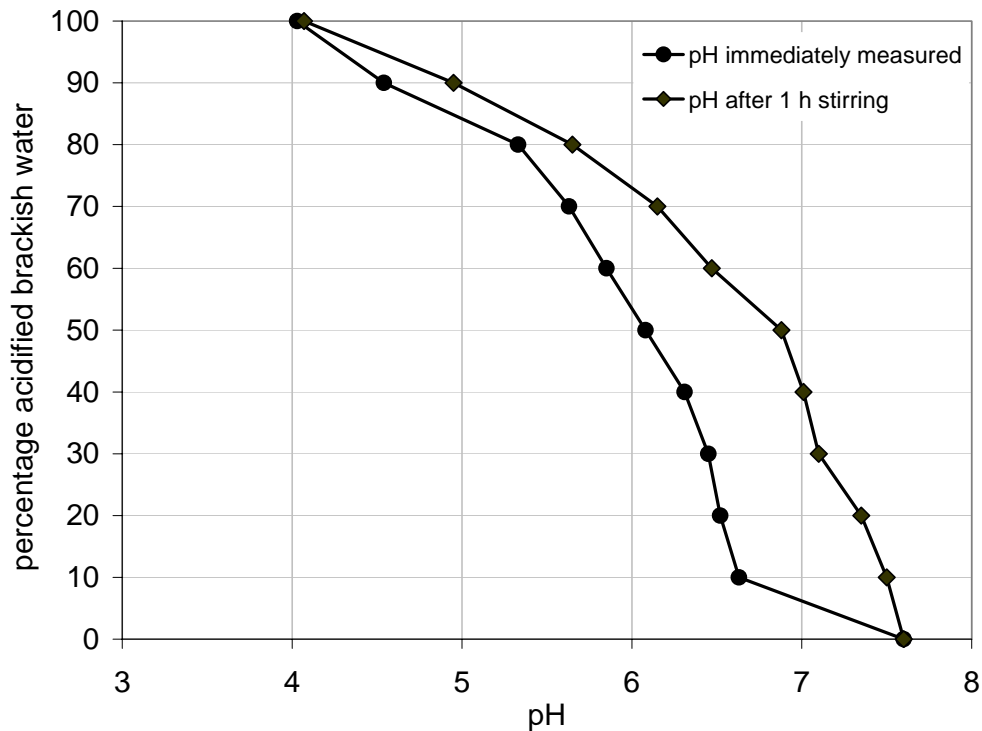


Fig. 6: Percentage of sulphuric acid (pH 4) in brackish water with resulting pH ($t = 0$ and $t = 1$ h).

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.

4.3 Summary of laboratory experiments

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

These measurements were carried out in closed systems, where only gas-exchange was allowed. However the results for any experiments conducted to demonstrate the impact of releasing a sulphuric acid discharge from a (moving) ship into the sea, must take into account realistic conditions. For example, the extent to which the effluent mixes with the seawater is dependant on the speed of the water at the time of discharge (a parameter which varies with ship speed), and the tidal currents which vary hourly. In estuaries, the exchange rate with the open sea and the inflow of freshwater are important factors.

4.4 Impact of the acidic effluent of the Krystallon Scrubber 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_x reduction is around 20 %, compared to 95 % SO₂ reduction
2. Nitric acid delivers only one hydrogen ion per mol, whereas sulphuric acid delivers two hydrogen ions.

Based on data 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 on the Krystallon Scrubber. The SO₂ 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 ¹			In Harbour ²		
		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 NO _x emissions ³	g/kWh	20	20	20	20	20	20
SO ₂ removed	%	95	95	95	95	95	95
NO _x removed	%	20	20	20	20	20	20
Discharged cooling water	t/h	30	30	50	70	70	70
SO ₂ in cooling water	mg/L	412	177	59	47	20	6.7
H ₂ SO ₄	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 ₂ SO ₄	mmol/L	12.88	5.52	1.84	1.47	0.63	0.21
NO in cooling water ⁴	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 ₂ in cooling water ⁴	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 ₃ 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 ₂ to acidity	%	20.34	37.34	64.13	23.27	41.44	67.98

¹) four main engines and two generators running 85 % MCR

²) two Generators running 95 % MCR

³) Marpol Annex VI limits emissions of NO_x to between 10 - 17 g NO_x/kWh, (worst case assumed as 20 g NO_x/kWh)

⁴) based on the assumption that 70 % of total nitrogen is converted to NO and 30 % is converted to NO₂.

4.5 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.

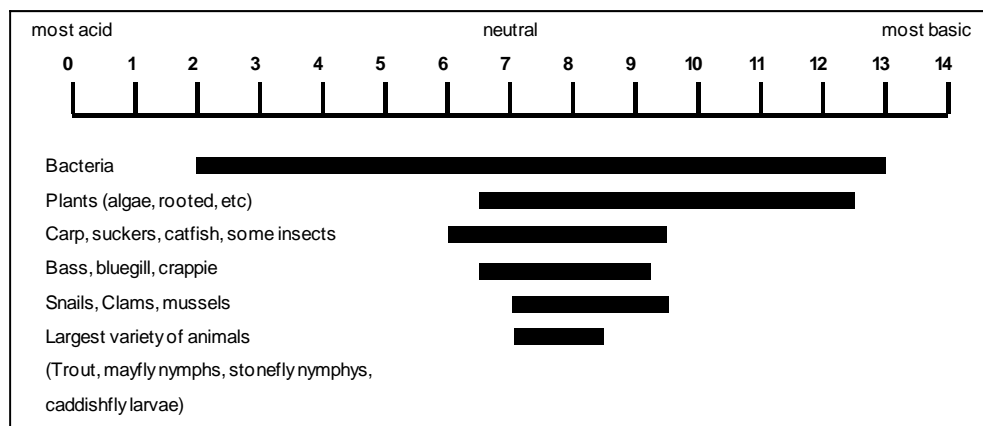
Other factors causing horizontal, vertical and seasonal variability of salinity in estuaries are:

- 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 period of a few hours. Changes in pH can put great strain on 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.

4.5.1 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 from 2001 for the Port of Rotterdam show that the number of ship arrivals of seagoing vessels is around 30 000/annum in 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_x, SO₂ and CO₂ emissions.

Tab. 7: Ports in the EU ranked by estimated annual emissions of NO_x in 2000

Rank	Port Name	Country	NO _x [kT]	SO ₂ [kT]	CO ₂ [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

reported by Entec, 2002.

A rough calculation using data from Tab. 7 indicates that on an annual basis total SO₂ discharge into Rotterdam port waters will contribute about 2×10^{-4} mol H⁺/L assuming

that all SO₂ 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⁺ concentrations will increase by 5.7, 9.4 and to 16.7 × 10⁻⁶ mol H⁺/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 CO₂ 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.

4.6 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 km², and its volume about 21,000 km³. 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.

4.6.1 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 25-35 years, so persistent pollutants can remain in the Baltic for a long time.

4.7 Acidification of surface waters

The deposition of atmospheric acids is not a recent phenomenon, but the extent of the consequences is still unclear. Acidification of soils and surface waters is to some extent a natural process but has accelerated in recent 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 in the pH of soil to 5.5 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 yet clear. For example, the potentially harmful effects of changing environmental CO₂ concentrations on energy metabolism and growth of marine invertebrates and fish 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 the amount of acid in a water body can 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.

4.8 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) indicates that pH changes resulting from titanium dioxide waste dumping were within the range of naturally occurring pH values. Even in the core of the propeller wake 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. With the exception of fresh propeller wake no indications of long term pH changes were found.

4.9 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 (e.g. from 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 an input of 3.29 or 0.45 mmoles NO_3^-/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 productivity 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 nor 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).

5 Environmental impact of scrubbing waters - Synthesis

Catalysts are used during the removal of sulphur in the production of low S fuels in refineries. 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, can also 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, 89 refineries in Europe produced a total of 6,368 tons of spent desulphurisation catalyst .

Thus, processes that are cheaper or more environmentally benign are attractive alternatives. One of these is the removal of combustion gases. Of the processes listed above Flue Gas Desulphurisation with Seawater Scrubbing (FGD-SWS) appears to be the most attractive option for the 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 H^+/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. Turbulent mixing caused by ship movements and screw rotation will provide further dilution. Natural mixing processes will also 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 be too low.

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 do not burn as much fuel in port as they do 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 total engine 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.

Tab. 8: discharge of sulphate and nitrate per hour

Sulphate					Nitrate		
Sulphur in fuel	%	3.5	1.5	0.5	NOx emission ^{3,4}	g/kwh	20
3MW ^{1,2}					3MW ^{1,2}		
SO ₂	kg/h	37.8	16.2	5.4	NOx	kg/h	57
Reduction	%	95	95	95	Reduction	%	20
Discharged SO ₄ ²⁻	kg/h	56.7	24.3	8.1	Discharged NO ₃ ⁻	kg/h	20
27MW ²					27MW ²		
SO ₂	kg/h	323	138	46	NOx	kg/h	432
Reduction	%	95	95	95	Reduction	%	20
Discharged SO ₄ ²⁻	Kg/h	485	207	69	Discharged NO ₃ ⁻	kg/h	153

- 1) In harbour situation with two generators running (3 MW)
- 2) Fuel consumption 180 kg/kWh
- 3) For 20 g NO_x/kWh
- 4) Assuming an NO_x composition of 70 % NO, 30 % NO₂

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 concentration.

Comparing these results with the harmful effects of the SO₂ and NO_x 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. On land however, the acidification of soils, lakes and rivers causes considerably higher damage. The change of atmospheric aerosol composition by NO_x 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 particulates and noise reduction.

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