

Seawater Scrubbing - reduction of SO_x emissions from ship exhausts



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exhausts

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Seawater Scrubbing - reduction of SO_x emissions from ship exhausts

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Executive Summary

It is shown that seawater scrubbing is a promising technology for reducing sulphur oxide emissions from ships. The marine chemical aspects of shipboard seawater scrubbing have been modelled and analysed, based on a 12 MW engine burning fuel with a 3% sulphur content. Calculations have been made for different efficiencies of sulphur scrubbing, different water temperatures, and for six different water types (open ocean, Kattegatt, Baltic Proper, Bothnian Sea, Bothnian Bay, and river freshwater). The results of the calculations give the volumes of water required for (i) uptake of SO_x (the scrubbing process), (ii) dilution of the scrubbing water to achieve a pH of 6.5, (iii) further dilution to achieve a pH within 0.2 units of that in the ambient water, and no more than a 1% reduction in dissolved oxygen concentration. The volumes of water required for a given efficiency of the scrubbing process increase with decreasing salinity and with increasing water temperature. The salinity dependence is non-linear, such that operation in the Bothnian Sea, Bothnian Bay and low alkalinity river freshwater would require significantly larger water volumes for scrubbing and dilution than operation in the Baltic Proper, Kattegatt or open ocean. The calculations assume access to large volumes of unaffected, ambient water. This is reasonable for a ship under way in open water, but not in enclosed or semi-enclosed waters, which would therefore require detailed case studies. It may be possible to reduce the volumes of dilution water required by, for example, aeration of the scrubbing water and addition of base to neutralise the acidic sulphur oxides. Further studies would be needed in order to assess these options.

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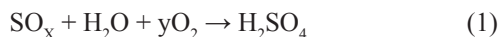
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1. Introduction

background of the study

Fossil fuels contain sulphur, which during combustion forms gaseous sulphur oxides, SO_x. The amounts of SO_x in fuel exhausts vary according to natural differences in the sulphur content of fossil fuels. These differences in sulphur content are due to the environmental conditions that prevailed at the time for deposition of a particular fossil fuel. Oil from the North Sea contains only a few tenths of one percent sulphur, while some types of coal from Spain contain 5-10% sulphur. Fossil gas is practically sulphur free [1]. The global average sulphur content for heavy fuel oil is presently 2.7% wt on a rolling three year average (2003-2005) [2].

The dominant constituent, making up approximately 95% of the SO_x emissions from combustion of fossil fuel, is sulphur dioxide, SO₂. Sulphur dioxide is a toxic gas, directly harmful for both human health and plants [3]. A secondary effect of SO_x emission to the atmosphere is formation of sulphate aerosols, very fine airborne particles, which according to WHO [4, 5] can be held responsible for increased annual mortality in Europe. A third, well recognised, result of SO_x-emissions is the formation of acid rain, when the sulphur oxides together with water and oxygen form sulphuric acid in clouds [6].



Deposition of acid rain has potentially detrimental effects both in nature and in urban environments. Acidification of soils can lead to leaching of (toxic) metals into ground waters where the metals become more bioavailable, i.e. more easily incorporated into living organisms. In the urban environment the most obvious sign of acid rain is the accelerated weathering of limestone structures such as buildings, statues and other monuments.

In a historic perspective the emissions of sulphur dioxide started to increase during the industrial revolution and continued to do so until the 1970's when regulatory legislation of industrial emissions was introduced. In comparison to the enormous industrial emissions after the Second World War, the emissions from shipping were long considered negligible. However, during the past two decades, although the worldwide sulphur dioxide emissions have decreased, the proportion due to shipping has increased and in 2002 was considered to be 7% of the total global sulphur oxide emissions [7].

Land-based emissions of sulphur oxides are mainly due to combustion plants, and the necessity to reduce such emission was identified in the late 1970s. The regulations for land-based sulphur oxide emissions have become increasingly more restrictive. Sulphur oxide emissions at sea were long regarded as less threatening, due to distance from the coast and

the neutralizing effect of seawater. Therefore, international legislation regarding sulphur oxide emissions from shipping has lagged behind, but now the trend is towards more restrictive regulations. The first pronounced step in this direction was the adoption of the Baltic Sea as the first SO_x Emission Control Area (SECA) in May 2005.

To meet the upcoming regulations on reduced sulphur oxide emissions, the use of fuel with low sulphur content is an option. However, there is limited availability of naturally low sulphur fuel and the refinery process for desulphurization of high sulphur fuel is costly. This report, with an emphasis on the marine chemical aspects of seawater scrubbing, provides a platform for the evaluation of seawater scrubbing as a potential sustainable alternative to the use of low sulphur fuel.



2. Sulphur chemistry in seawater

S O_x in fuel exhausts is present mainly as SO_2 , which in water is hydrated to form sulphurous acid H_2SO_3 , and which can in turn ionize to form bisulphite (HSO_3^-) and sulphite (SO_3^{2-}) ions (equations 2 to 4).



Where $[SO_2^*] = [SO_2(aq)] + [H_2SO_3]$

At the sea surface the natural partial pressure of sulphur dioxide in the atmosphere, ~ 1 ppb, is close to equilibrium with the seawater sulphite system according to equations (2-4). If the partial pressure of sulphur dioxide is increased, the three equilibria will be shifted to the right, resulting in increased dissolved concentration of sulphur dioxide and its ionization products, and decreased pH in the seawater. The concentration increase and the corresponding pH decrease are in turn dependent on the physical-chemical properties of the water: temperature, salinity and alkalinity (Fig 1 and Boxes 1 and 2).

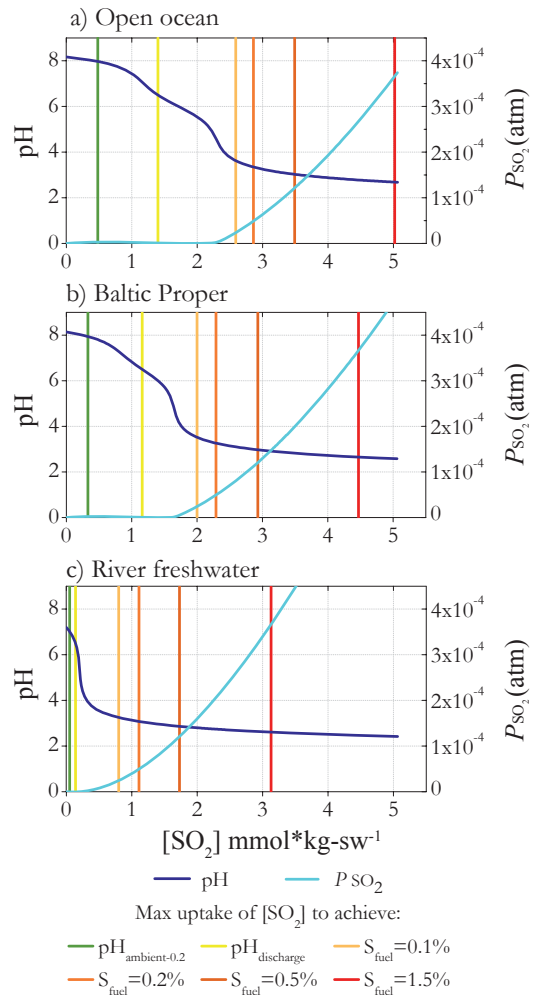


Fig 1. Relation between pH and P_{SO_2} as a function of $[SO_2]$ at 25°C.

Box 1. Alkalinity

Seawater has a slightly alkaline pH (close to 8), which means that seawater contains an excess of base over acid. This excess of base is described quantitatively by the alkalinity, which can be determined by titration of seawater with strong acid. The major contributor (ca. 95%) to the alkalinity of seawater is the carbon dioxide system in the form of bicarbonate and carbonate ions. The total alkalinity A_T of a seawater sample can be defined chemically as:

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

Where square brackets $[\]$ indicate concentrations, and “[x]” indicates additional minor contributions from trace bases such as phosphate anions.

Bases formed from weak acids (those with dissociation constant $\text{pK} > 4.5$) contribute to the alkalinity, while strong acids (those with dissociation constant $\text{pK} < 4.5$) reduce the alkalinity. Thus, the weak acid carbonic acid (formed by dissolved carbon dioxide) does not contribute to the alkalinity, while the strong acid sulphurous acid (formed by dissolved sulphur dioxide in seawater) reduces the alkalinity. The alkalinity of seawater that has taken up sulphur dioxide is thus described by the modified equation:

$$A_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+] - [\text{SO}_2^*] + [\text{SO}_3^{2-}] + [x]$$

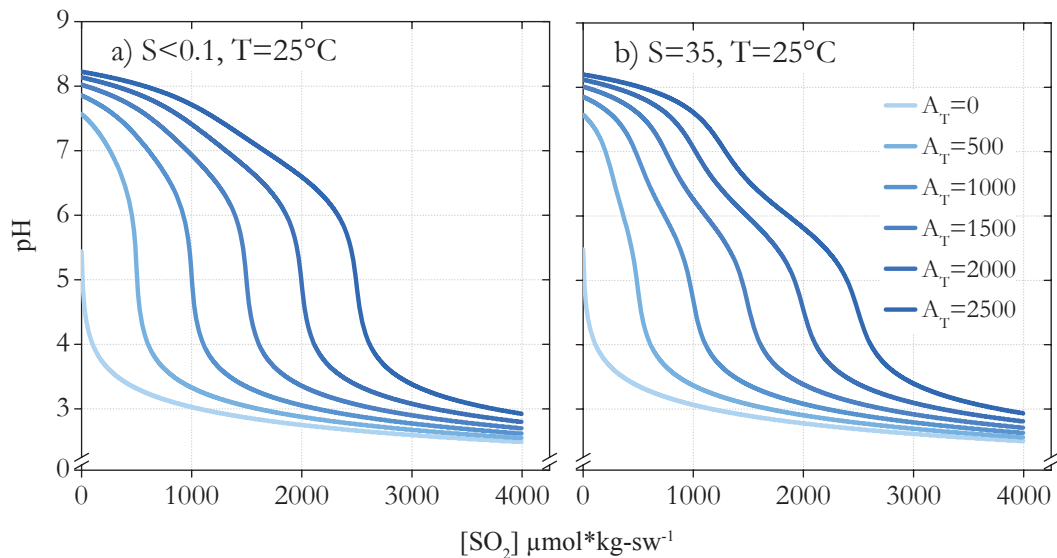
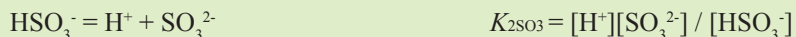
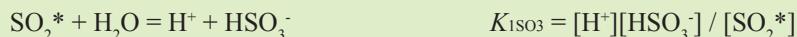
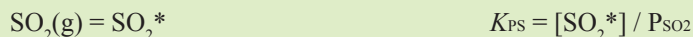


Fig 2. The relationship between $[\text{SO}_2]$ -induced pH change and alkalinity. Multiples of alkalinity in $\mu\text{mol} \cdot \text{kg} \cdot \text{sw}^{-1}$.

Box 2. Thermodynamics of sulphur dioxide in seawater

The equilibria shown in equations (2-4) are characterised by equilibrium constants K :



Where P_{SO_2} is the partial pressure of SO_2 . Since these constants are, for practical reasons, expressed in terms of concentrations rather than activities, their values are dependent on both the temperature and the salinity of the water in question.

The temperature dependence of the three constants at zero ionic strength (i.e. in pure water) has been well characterized, the most complete study being that of Goldberg and Parker (1985) [8], who reviewed the available literature, and derived equations for each constant as a function of temperature at zero ionic strength. Later experimental measurements are in good agreement with these equations, which have therefore been used to define the temperature dependence of the three equilibrium constants.

However, no direct studies have been made of the individual equilibrium constants in seawater medium, although several authors have derived values for these constants in sodium chloride and sodium chloride/magnesium chloride mixtures [9, 10]. These studies show that the values of K_{PS} and $K_{1\text{SO}_3}$ depend on the ionic strength of the solution, but are not dependent on the sodium/magnesium ratio. In contrast, the value of $K_{2\text{SO}_3}$ depends both on the ionic strength, and to a small extent on the sodium/magnesium ratio. Since sodium and magnesium are the two dominant metal ions in seawater that can affect these constants, the available literature data have been combined to derive equations for the dependence of the three constants on salinity (ionic strength).

Table 1. Ranges of temperature, salinity and alkalinity in natural surface waters

	Seawater	Baltic Sea	Estuarine waters	Freshwater
T (°C)	5-15 ^a	0-20 ^c	1-20	0-20
S	32-37 ^a	3-9 ^d	0.5-17 ^a	0-0.5 ^a
A _T (μmol·kg ⁻¹)	2300-2600 ^b	700-2000 ^d	0.1-5000 ^b	0.1-5000 ^b

^a Office of naval research [11]

^b W. Stumm and Morgan, J. Aquatic Chemistry [12]

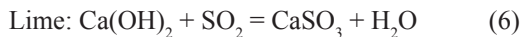
^c HELCOM [13]

^d FIMR [14]

3. Scrubbing process

3.1 Flue Gas Desulphurization

Flue gas desulphurization (FGD) has been used since the 1930's in shore-based facilities, e.g. power plants, to reduce sulphur emissions [15]. As emissions from ships were long considered to be negligible on a global scale, it was not until the early 1990's that the first trials were made to adapt FGD-technology to reduce sulphur emissions from ship exhausts. For shore-based purposes there are a variety of FGD-technologies available [16], which generally can be classified as once-through technologies or regenerable technologies. The once-through technologies all use the concept of exposing the flue gas to a neutralizing agent such as limestone, equation (5), or lime, equation (6). The neutralizing agent could either be dry (dry-FGD) or in liquid form (wet-FGD) and both types generate large amounts of solid by-products; either calcium sulphite, equations (5) and (6), or through further oxidation to gypsum, equation (7).



A special case of wet-FGD is seawater scrubbing (SWS), where the flue gases are washed by contact with seawater [17]. There are also regenerable FGD-technologies, where sulphur dioxide is temporarily absorbed and later when the sorbent is regenerated, the sulphur dioxide is released and may be further processed to yield sulphuric acid, elemental sulphur or liquid sulphur dioxide. In a land-based facility, the use of large volumes of neutralizing agents and/or the regeneration of sorbents in once-through technologies may be worth the extra operational costs. Generation of solid by-products or refined sulphur dioxide products may be profitable where these products have a commercial value. These arguments are not valid for on-board flue gas scrubbing, where the operational costs far exceed the benefits from the small volumes of generated by-products. Therefore, for maritime use, attention has been focused on regenerable technologies (seawater scrubbing). [15, 18-22].

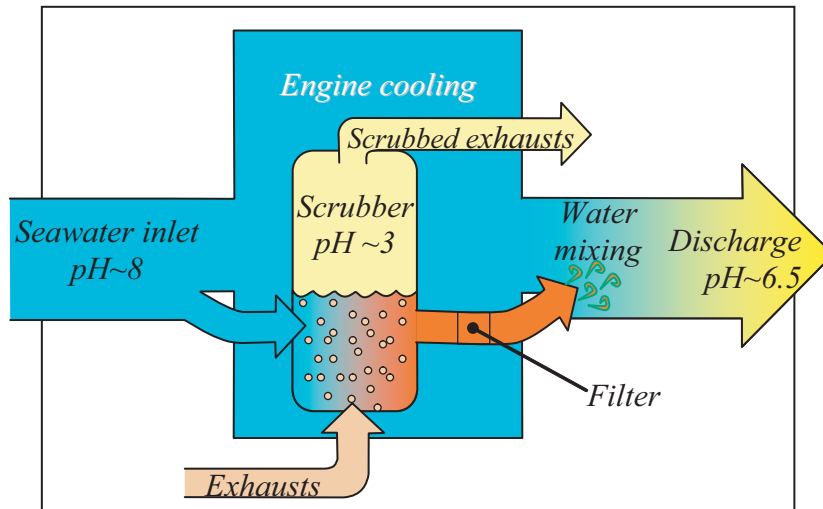


Fig 3 Scrubbing process flow chart

3.2 Seawater Scrubbing

In on-board application of SWS, a portion of the seawater used for engine cooling is utilized for the scrubbing process (Fig 3).

The basic principle of SWS is that the flue gases are exposed to seawater, which dissolves the sulphur oxides, equation (2). The sulphur oxides of shipping exhausts typically consist of ~95% sulphur dioxide and the remaining ~5% of sulphur trioxide, SO_3 . Once dissolved, the sulphur dioxide can subsequently be ionized to bisulphite, equation (3), and sulphite, equation (4). Sulphite is a strong reducing agent, which for instance is used for deoxygenation of solutes. Hence, in oxic seawater sulphite will to a large extent be further oxidized to sulphate, equation (8).



The ionization to bisulphite and sulphite (equations 3 and 4) produces excess hydrogen

ions, which initially will be neutralized through the natural buffering capacity of seawater. The main buffering capacity of seawater is determined by its alkalinity (Box 1). Below $\text{pH} \sim 8.3$ the dominant alkaline species is bicarbonate, HCO_3^- . For open ocean water the alkalinity is about $2300 \mu\text{mol kg-sw}^{-1}$ and the corresponding value for the Baltic Proper is about $1650 \mu\text{mol kg-sw}^{-1}$. Alkalinities for different types of natural waters are summarized in Table 1. In this report we will compare how natural waters with different characteristics will work for scrubbing purposes, following a gradient in the Swedish seas (Fig 4), from the Kattegat, the Baltic Proper, and the Bothnian Sea to the Bothnian Bay. Additionally, open ocean water and a hypothetical low-alkaline river freshwater were chosen as end points of the gradient. The chemical properties of the different waters considered in this report are summarized in Table 2.

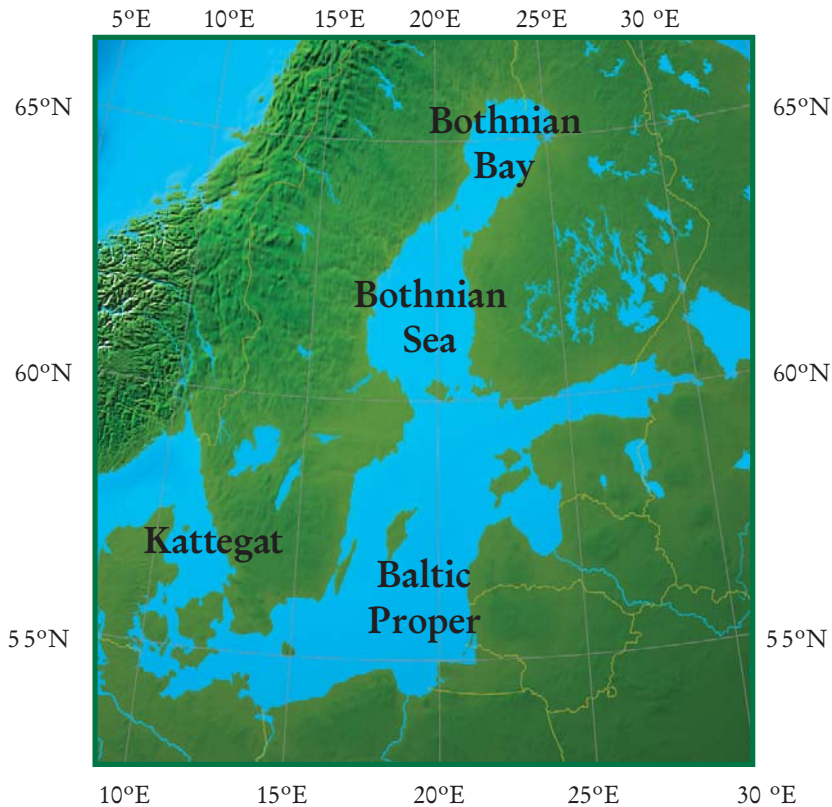


Fig 4. The seas surrounding Sweden.

3.3 Uptake of [SO₂] from exhaust gases

The theoretical performance of the scrubbing process was investigated in the temperature range 0-35°C for the six different types of natural waters. Special attention was paid to four critical levels of emission reduction, corresponding to combustion of fuel of 1.5%, 0.5%, 0.2% and 0.1% sulphur content. The 1.5% level was a natural choice as it represents the only present regulation of reduced sulphur emissions, the maximum level of sulphur emissions allowed in

the present SECA. Proposals to IMO regarding regulation of sulphur emissions from ships using alternative sulphur dioxide emission abatement also correspond to this level. However, environmental organizations in Sweden, Europe and worldwide [6, 23] are arguing that the 1.5% level is far too high. Their goal is reduction corresponding to combustion of fuel with 0.1% sulphur content, where 0.5% and 0.2% are suggested for transitional periods.

Table 2. Typical chemical properties of different types of natural waters.

	A _T (μmol*kg-sw ⁻¹)	S
Open ocean	2300	35
Kattegat	1950	18
Baltic Proper	1650	8
Bothnian Sea	1300	6
Bothnian Bay	800	4
River freshwater	210	<0.1

The global average sulphur content for heavy fuel oil is presently 2.7% wt on a rolling three-year average 2003-2005 [2]. The previous three-year rolling average for 2002-2004 was 2.67%. We have chosen to base our calculations on the combustion of fuel with 3% sulphur content. For a tanker operating at 12MW with specific fuel consumption 185g*kWh⁻¹, this generates ~2080 mol SO₂ (~133 kg) per hour. The resulting exhaust gases have a greatly increased partial pressure of sulphur dioxide (660 ppm) [24] compared to the very low partial pressure of sulphur dioxide in the atmosphere, which the surface seawater is equilibrated with. Exposure of the exhausts to seawater will therefore increase the concentration of dissolved sulphur dioxide in the seawater according to equation (2). The maximum uptake capacity of sulphur dioxide is achieved when the sulphur dioxide remaining in the exhaust gas is in equilibrium with the seawater. To achieve emissions corresponding to combustion of 1.5% sulphur content requires a scrubbing efficiency of 50%, while a reduction to emissions corresponding to 0.1% requires a scrubbing efficiency of 96.7%. The higher the degree of reduced emissions, the larger the amount of sulphur dioxide that has to be dissolved in the water.

Before the SO₂-enriched scrubbing water is re-exposed to the atmosphere, it has to be diluted to prevent re-equilibration and loss of SO₂. Following the same reasoning as above,

a higher degree of reduced emissions requires larger water volumes for dilution (Fig 5). The uptake capacity of sulphur dioxide also depends on the physical-chemical properties (alkalinity, salinity and temperature) of the water used in the process, which also affects the water volumes required. During the scrubbing process the pH drops to about pH 3 for scrubbing aimed at the 0.1-0.5% level, but lower for scrubbing with minimum water volume aimed at the 1.5% level. Ionization of sulphur dioxide to sulphite will be negligible at pH 3 i.e. during the residence of the seawater in the scrubbing chamber. Once the initial neutralizing capacity of the alkalinity is consumed, the factor determining the scope for further uptake is the solubility of sulphur dioxide. The solubility increases with increasing sulphur dioxide partial pressure and decreases with increasing temperature and ionic strength of the solution [9, 25].

The scrubbing efficiency is higher in the more saline waters than in brackish and freshwaters, but the relationship with salinity is non-linear. This is supported in trial reports, where Ives & Klokk [15] reported that their scrubbing efficiencies were valid down to S=14, whereas the FAQ of Marine Exhaust Solutions Inc. EcoSilencer® [18] claims that the scrubbing technology does not work in freshwaters. However, the Baltic Proper which has significantly lower salinity and alkalinity compared to the open ocean only requires 10%

larger water volumes than open ocean water, to achieve emissions corresponding to 1.5% at 25°C. For a further reduction of emissions corresponding to 0.5% sulphur content, the process requires 20 % larger water volumes in the Baltic Proper, compared to the open ocean. This can be compared with 50% and 100% larger water volumes for the respective emission levels (1.5% and 0.5%) in river freshwater, compared to the open ocean. The effect of temperature is also much more pronounced for river freshwater

compared to the more saline waters. An increased temperature from 5°C to 25°C, nearly doubles the required volume river freshwater to achieve emissions corresponding to 0.5% sulphur content, whereas the same temperature increase in open ocean water gives only a 20% increase in required water volume.

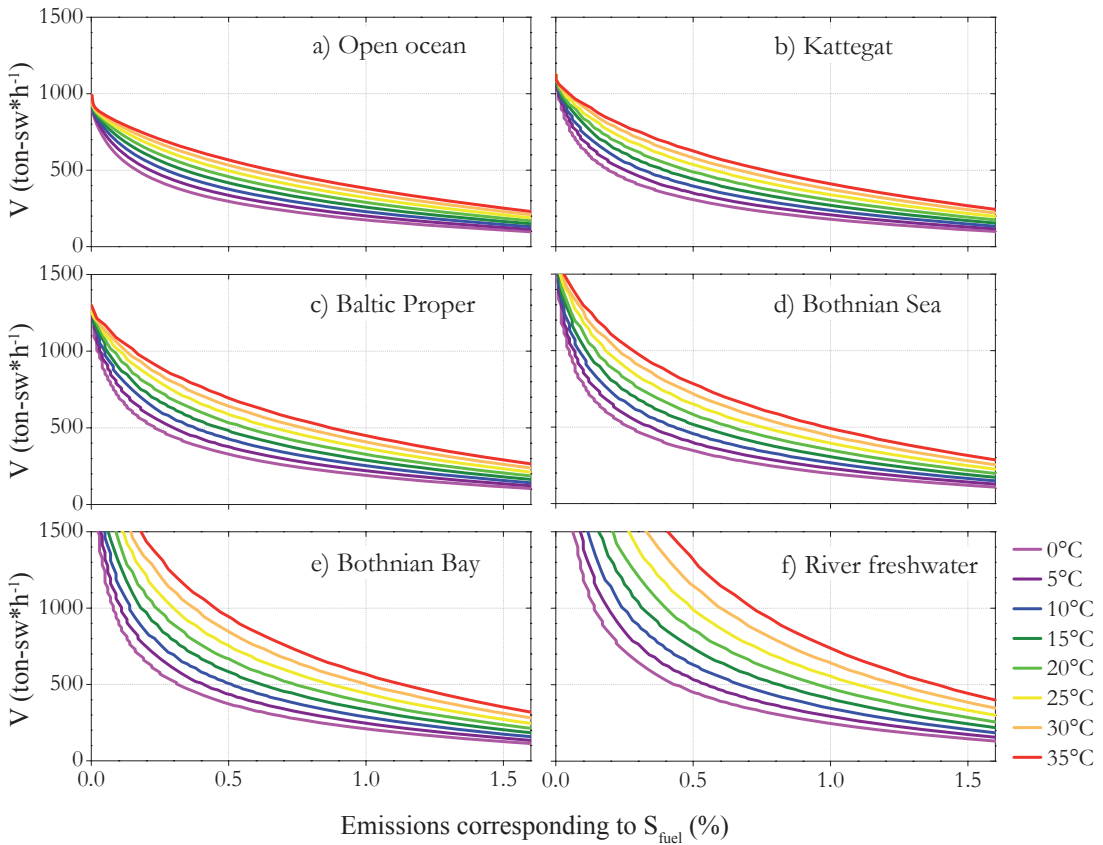


Fig 5. Required water volumes to reduce emissions from combustion of fuel with 3% sulphur content to corresponding emissions from combustion of fuels with lower sulphur content (0.1% - 1.5%). For the six different types of natural waters, the respective required water volumes at different temperatures are shown as a function of the achieved level of reduced emission. Engine power 12MW.

3.4 Dilution of discharge water to acceptable pH

Acidic scrubbing water is not only highly corrosive to any steel construction, but also poses an environmental threat to both marine plants and animals. To avoid negative environmental effects the acidic seawater, prior to discharge, is mixed with larger volumes of seawater that have been used for engine cooling. If necessary, additional water can be taken in to adjust the pH of the discharge water and thus prevent environmental effects due to acidic discharges [26]. Generally, no environmental harm is considered to arise from short-term exposure of seawater down to pH 6.5 [27]. Hence, the discharge water from the

scrubbing process is not regarded to pose any acute environmental threat due to pH-effects, if diluted to pH 6.5 before discharge (Fig 6).

Dilution to pH 6.5 requires larger water volumes than the initial uptake of sulphur dioxide. At pH 6.5 the alkalinities of the different water types will make a difference, explaining the large gap between the low-alkaline river freshwater versus the brackish and marine waters. Again, temperature effects are more pronounced for the river freshwater than for the brackish and marine waters.

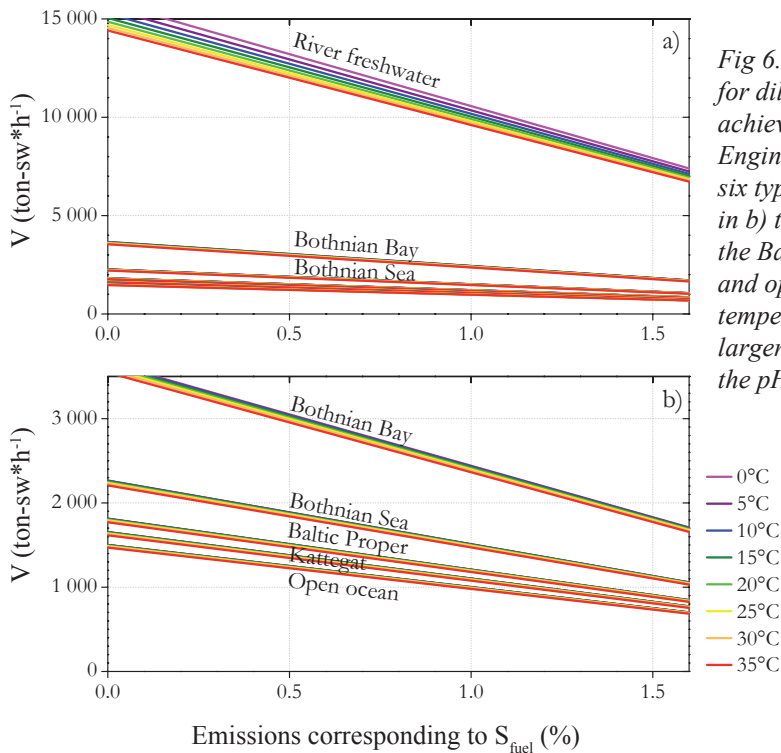


Fig 6. Water volumes required for dilution of scrubbing water to achieve pH 6.5 before discharge. Engine power 12MW. a) shows all six types of natural waters, whereas in b) the y-axis is rescaled to resolve the Baltic Proper, the Kattegat and open ocean. Note that lower temperature consistently requires larger volumes for dilution to raise the pH to pH 6.5.

4. What happens to the discharged water?

4.1 Definition of mixing zones

When discharged, the moderately acidified (pH 6.5) water will mix with the ambient water. To prevent environmental harm due to the efflux water, EPA [26] (and IMO [2]) have adopted regulations for the mixing of scrubbing effluents with ambient seawater. According to the guidelines, the mixing processes are divided into two defined zones: (i) the acute mixing zone and (ii) the chronic mixing zone (Fig 7). The critical pH limit for the acute mixing zone is 6.5, which should be reached within a maximum of 15 minutes. The residence time within the chronic mixing zone is longer, and encompasses a dilution at least 1:40,000. The conditions for

dilutions of discharge water from a ship will vary depending on travelling speed in open water, or hydrographic variations in a dock. Modelling of such mixing/dilution processes are beyond the scope of this report, which focuses on calculating the dilutions necessary to comply with the regulations, assuming a well-mixed system. However, this assumes access to large volumes of unaffected water for dilution. This might well be valid in the open ocean, but the evolution of the water chemistry in a semi-enclosed area such as a dock or river mouth would require a more detailed case study of hydrography, water chemistry and shipping activity.

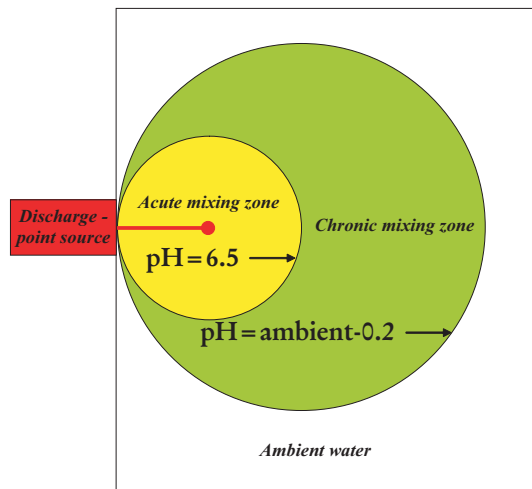


Fig 7. Mixing zones according to EPA.

4.2 Dilution from pH in the acute to the chronic mixing zone

According to EPA, the chronic mixing zone theoretically should involve a dilution of at least 1:40,000 in order to secure a pH not lower than 0.2 units below the pH of ambient water. In our example the required dilution factors to satisfy this $pH_{\text{ambient}-0.2}$ -criterion varies from 2.3 for river freshwaters at 0°C, to approximately 3.6 for water from the Bothnian Bay at 25°C. The relatively low dilution required for the river water reflects its lower natural pH than the brackish and saline waters.

4.3 Further dilution of discharged water to reduce chemical oxygen demand

The formation of sulphite, equation (4), which is a strong reductant, constitutes a potential environmental threat as it will react with dissolved oxygen, equation (8), and hence increase the chemical oxygen demand (COD). To make a realistic estimation of the COD due to scrubbing discharge water would require detailed knowledge of the oxidation rates of sulphite and bisulphite, the kinetics of equilibration with the atmosphere and diurnal variations, for example

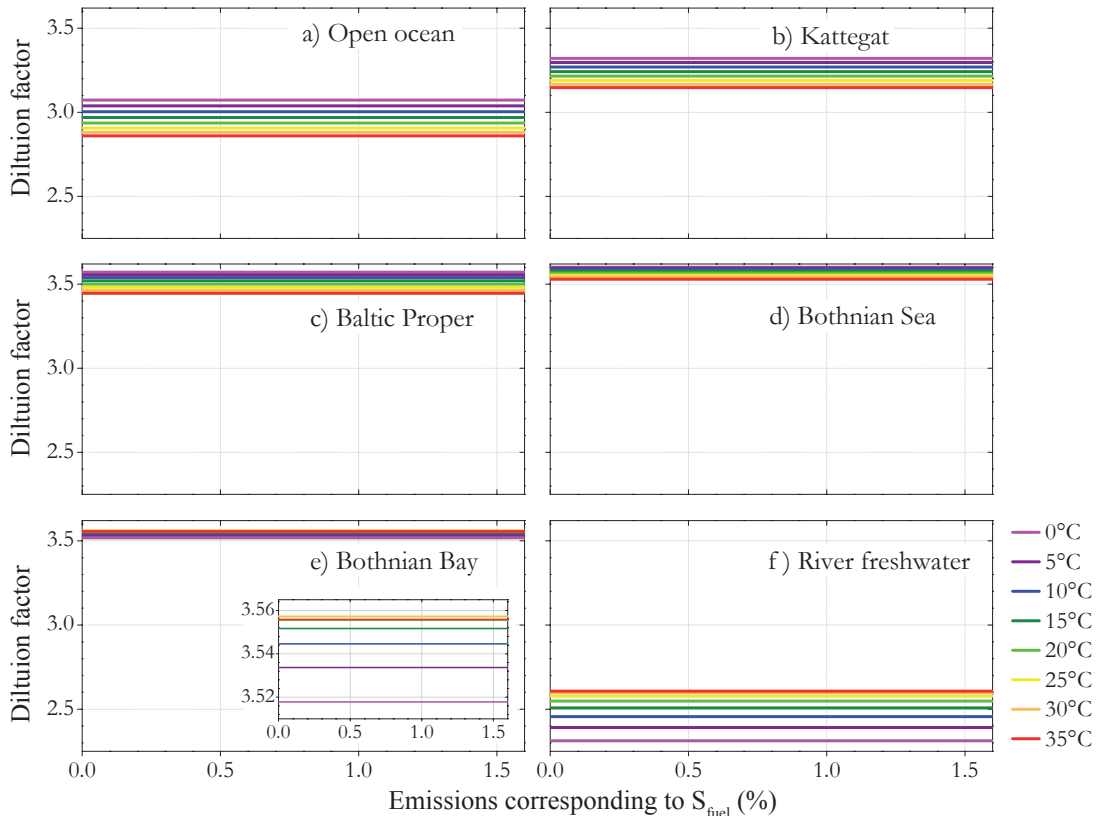


Fig 8. Dilution to satisfy $pH_{\text{ambient}-0.2}$ in the chronic mixing zone.

photosynthesis. Experimental work would also be needed. However, it is possible to make an estimate of a worst case scenario (maximum possible COD) assuming that all scrubbed sulphur dioxide is instantaneously transformed to sulphate via sulphite, and that the equilibration of oxygen with the atmosphere sufficiently slow to be negligible. In that case, the scrubbing water

that has been diluted to satisfy $pH_{\text{ambient}}-0.2$, would require further slight dilution by up to 50%, in order to not lower the ambient oxygen saturation by more than 1% (Fig 9). Compared to marine waters, fresh waters have higher oxygen concentrations at 100% saturation, which explains the larger water requirement for open ocean water than river freshwater in the example.

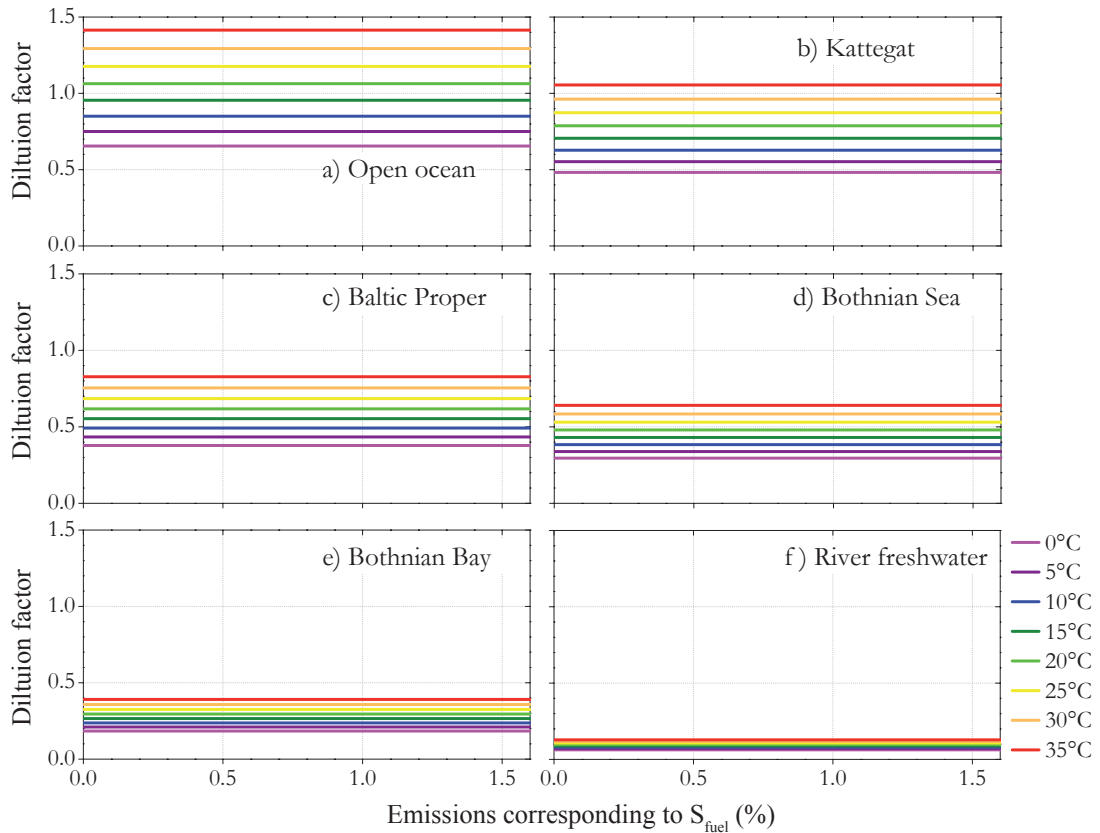


Fig 9. Required further dilution, to achieve max 1% reduction of the oxygen concentration of ambient water, of scrubbing water previously diluted to satisfy pH limits for ambient water. Dilution factors < 1 indicate that no further dilution is required, since the dilution which satisfied the pH criterion is greater than that required to satisfy the COD criterion.

Box 3. Comparison with effects of atmospheric release of the material removed through seawater scrubbing

Sulphur oxides (SO_x) released to the atmosphere are converted to sulphuric acid, and thus contribute to the acidification of wet precipitation both on land and on the oceans. The fundamental idea of SO_x scrubbing is to prevent the sulphur oxides present in exhaust gases from entering the atmosphere and contributing to acid rain, instead transferring the sulphur directly to the oceans as dissolved sulphite and sulphate. The total acidification of the global environment is the same whether or not scrubbing is applied, and depends on the total sulphur content of the fuel oil used, but scrubbing avoids acidification of terrestrial rain, and enhanced production of cloud condensation nuclei from sulphate aerosols [28].

The newly proposed guidelines (IMO [2]) for scrubbing installation, allow for emissions of sulphur to the atmosphere corresponding to 6.0 g (~ 94 mmol) of sulphur dioxide per kWh. For a vessel using a heavy fuel oil with 3% wt sulphur content this implies a minimum average scrubbing efficiency of 54%.

If the scrubbing efficiency of an onboard installation is assumed to be on average 60%, the reduction in emission to the atmosphere will be approximately 1250 moles (or 40 kg) sulphur per hour, for a tanker using 12MW power during operation. According to the standardized critical loads for acidification of forest soils [1, 29], this amount of sulphur corresponds to the annual critical load of 1.3 ha of carbonate-rich soils or 13 ha of quartz-rich soils.

Box 4. How does seawater scrubbing relate to ocean acidification?

Global climate change researchers have recently highlighted the issue of ocean acidification arising from increased carbon dioxide concentrations in the atmosphere [30]. The increase in atmospheric carbon dioxide concentrations from pre-industrial carbon dioxide levels of 280 ppm to the present 380 ppm, is calculated to have decreased the average pH of ocean surface waters from 8.18 to 8.07. If the increase continues at the same rate, average pH of ocean surface waters will approach 7.70 over the next 100 years.

The use of seawater scrubbing will also lower the average pH of ocean surface waters over time. However, it is important to remember that almost all sulphur dioxide transferred to the ocean through seawater scrubbing would eventually end up in the oceans, even if initially released to the atmosphere. The idea behind seawater scrubbing is to prevent the sulphur dioxide passing through the atmosphere, where it poses a major environmental threat. Hence, seawater scrubbing will speed up the pH decrease in ocean surface waters; however the effect is minor compared to ocean acidification due to increased carbon dioxide concentrations in the atmosphere. Corbett & Fishbeck (1997) [31] estimated the global annual sulphur dioxide emissions from ships to be 8.48 Tg. If 80% of this sulphur dioxide is removed by onboard scrubbing systems that would discharge 6.78 Tg sulphur dioxide into the oceans each year. Distributed evenly over the uppermost 100m of the ocean, this discharge would lower the pH in oceanic surface water by 0.02 units in 100 years. This global estimate assumes the upper 100m to be a homogeneous water body, which is reasonable on the timescale of 100 years. However, the Baltic Sea has limited water exchange, and thus a potential for acidification on shorter time scales (10-15 years), and may merit a closer hydrographic investigation together with detailed knowledge of the shipping activity in the area.

Box 5. How does the added sulphur affect seawater composition?

Sulphate is a natural constituent of seawater and is conservative with respect to salinity. In open ocean water, $S=35$, the sulphate concentration is about $28 \text{ mmol} \cdot \text{kg-sw}^{-1}$, and in the south Baltic Proper, $S=8$, the sulphate concentration is correspondingly five times lower; about $5.6 \text{ mmol} \cdot \text{kg-sw}^{-1}$. Following the COD-calculations above, which suggested dilution of the scrubbing water, the increased sulphate concentrations will be insignificant as long as the COD is kept within satisfactory limits.



5. Discussion

The use of seawater scrubbing as a sulphur oxide emission abatement technique is shown theoretically, in this report, and practically, in previous trial reports, to work well in marine and brackish waters. The limitation identified for use in freshwater is not primarily the decreased efficiency of the sulphur dioxide uptake process, but rather the much larger water volumes required, compared to marine and brackish waters, to dilute the scrubbing water to achieve acceptable pH. Further, the water used for dilution is assumed to be unaffected by other pH-lowering processes. This highlights the importance of case studies of water chemistry, hydrography and the extent of shipping activity, if seawater scrubbing is to be used in semi-enclosed areas.

The degree of sulphur oxide emission reduction is also of importance for the scrubbing process. Using a high fuel oil of 3% sulphur content, reduction corresponding to 0.5% sulphur content

requires volumes of water not much larger than reduction corresponding to 1.5% sulphur content. Furthermore, the non-linear relationship between sulphur removal and water volume means that further reductions corresponding to 0.2% and 0.1% fuel sulphur content result in substantial increases in the water volumes required.

It may be possible to minimise the water volumes required through additional treatment to address the COD and pH changes summarised in this report. COD could in principle be addressed by oxygenating or aerating the water, while pH changes could be minimised by addition of base to neutralize the sulphurous and sulphuric acids formed. Further investigations would be needed to assess the appropriateness and practicality of these alternative strategies.

6. Conclusions and future outlook

Seawater scrubbing is a promising technology for reducing sulphur oxide emissions from ships. The volume of scrubbing seawater required increases with increasing temperature, and also with decreasing salinity. The salinity effect is strongly non-linear. The scrubbing seawater used to take up sulphur oxides requires extensive dilution to minimise changes in the ambient chemistry of the surrounding seawater. The maximum chemical effects assessed here (reduction of pH by 0.2, 1% reduction in dissolved oxygen concentration) require similar dilutions. The calculations presented here assume access to large volumes of unaffected, ambient water. This is reasonable

for a ship under way in open water, but not in enclosed or semi-enclosed waters, which would therefore require detailed case studies. It may be possible to reduce the volumes of dilution water required by, for example, aeration of the scrubbing water and addition of base to neutralise the acidic sulphur oxides. Further studies would be needed in order to assess these options.



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