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The impact of scrubber discharge on the water quality in estuaries and ports

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ABSTRACT

Background: The International Maritime Organization (IMO) has set limits on sulphur content in fuels for marine transport. However, vessels continue to use these residual high sulphur fuels in combination with exhaust gas cleaning systems (EGCS or scrubbers). Next to high sulphur, combustion of these fuels also results in higher emissions of contaminants including metals and PAHs. In scrubbers, exhaust gases are sprayed with water in order to remove SOx, resulting in acidic washwater with elevated contaminant concentrations discharged in the aquatic ecosystem. The number of vessels with scrubbers is increasing rapidly, but knowledge on washwater quality and impact are limited.

Results: The scrubber washwater is found to be acidic with elevated concentrations of e.g. zinc, vanadium, copper, nickel, phenanthrene, naphthalene, fluorene and fluoranthene. Model calculations on the effects of scrubber discharge under scenario HIGH (20% of vessels, 90th percentile concentrations) on the water quality in harbor docks showed a decrease in pH of 0.015 units and an increase in surface water concentrations for e.g. naphthalene (189% increase) and vanadium (46% increase).

Conclusions: The IMO established sulphur regulations to mitigate the impact of high sulphur emissions of the maritime sector. However, the use of open loop scrubbers as an abatement technology will not reduce their contribution to ocean acidification. In addition, different types of scrubbers discharge washwater that is acute toxic for aquatic organisms. However, washwater is diluted and the compounds for which a large increase in surface water concentrations was calculated in the Antwerp (Belgium) harbour docks (Naphthalene > Phenanthrene > Fluorene > Acenaphthene > Vanadium) were not the compounds that already exceed their respective Water Quality Standards (WQS). Nevertheless, the WQS of several ‘priority hazardous substances’

(Water Framework Directive) are already exceeded in the docks and the Scheldt estuary. Since these hazardous substances are also identified in the washwater, scrubber washwater discharge should be discouraged in coastal waters and estuaries with large ecological value.

Keywords: marine traffic, pollution, EGCS, SECAs, water quality, acidification

1. Background

International shipping has a significantly effect on air quality, with a contribution to global emissions of more than 20% for nitrogen oxides (NO_x), around 10% for sulphur oxides (SO_x) and almost 8% for particulate matter (PM)[1, 2]. This has a number of environmental consequences[3], such as ocean acidification[4] and disturbance of climate regulation[5], and also impacts human health in coastal regions through deteriorated air quality[6, 7]. To mitigate these effects, the IMO (International Maritime Organization) has included annex VI (Prevention of Air Pollution) to the International Convention for the Prevention of Pollution from Ships (MARPOL). This has resulted in a global cap on sulphur in fuel oil of 3.5% (mass percentage) from 2012 and a maximum sulphur content of 0.1% in dedicated SO_x Emission Control Areas (SECA's) from 2015 onwards[8]. A new stringent global limit on fuel sulphur content of 0.5% came into force on January 2020.

To comply, ships can use compliant low sulphur fuel oil or alternative fuels which are low in sulphur, such as liquefied natural gas (LNG) or methanol. The IMO sulphur limits only apply to atmospheric emissions. Consequently, it is allowed to continue to use high sulphur fuels in combination with an exhaust gas cleaning system (EGCS or scrubber). In scrubbers, the exhaust gases of vessels are sprayed with liquid in order to remove the SO_x before it will be emitted to the air. Scrubbers are capable of removing up to 95% of the SO_x in the exhaust gases and meet the IMO S exhaust limits[9]. Most scrubbers installed on vessels are wet scrubbers and use 'open loop' or 'closed loop' systems. Open loop systems, also referred to as seawater scrubbing technology, dominate the market. In these systems, the exhaust gases are sprayed with seawater at a high flow rate, and the SO_x in the exhaust gas is trapped and converted to sulphurous acid (SO_3^{2-}) and sulphuric acid (SO_4^{2-}). The washwater generated in the scrubber is discharged in the surrounding surface water at a typical flow rate of 200 – 500 L/s for a vessel operating at 15 MW. Alternatively, closed loop systems use freshwater as the scrubbing medium, which is pre-treated with sodium hydroxide (NaOH). This washwater recirculates in the scrubbing system. The scrubbing capacity is maintained by dosing extra NaOH and periodically discharging smaller volumes of washwater, typically 0.5 – 3 L/s on average for a vessel operating at 15 MW. Also 'hybrid systems' exist, whereby vessels can shift the scrubber operation between open or closed loop mode.

Given the fairly recent changes in the IMO sulphur regulations, the amount of vessels equipped with scrubbers is still limited, but changing rapidly. According to Clarksons Worldfleet Register, consulted in November 2019, nearly 3000 scrubbers have already been installed, which corresponds to 3% of the total number of vessels and 16% of the gross tonnage. This implies that mainly large vessels invest in a scrubber. Additionally, 15% in numbers or 35% in gross tonnage of all vessels ordered at this moment (November 2019) will have a scrubber installed. From an economical perspective, scrubbers are an attractive option, particularly for larger vessels[10, 11]. In order to comply, the choice between using the more expensive low sulphur fuels or the installation of a scrubber depends largely on the price difference between both, low sulphur fuels and common heavy fuels[12]. Depending on the conditions, the scrubber installation costs are found to be recouped within the span of 1 - 2 years[13, 14]. The number of scrubbers is predicted to continue to increase after the implementation of the more restrictive global sulphur cap in 2020.

The use of scrubbers result in a shift of the environmental impact of sulphur from emissions to the atmosphere towards a direct discharge into aquatic systems. Further, the high sulphur fuels used by vessels with scrubbers are generally heavy fuel oils (HFO), which are residual fuels incurred during the distillation of crude oil. Together with high sulphur emissions, these fuels are known to result in higher emissions of other hazardous species including metals and polycyclic aromatic hydrocarbons (PAHs) compared to low sulphur distillates such as marine gas oil (MGO). These contaminants originate from higher concentrations of e.g. metals and PAHs in the fuel and larger emissions during combustion of this residual fuel[15]. Several studies report that scrubbers reduce the atmospheric emissions of SO_x or PM to a level that is comparable to emissions when operating on MGO[16-20]. However, PM emissions and removal by scrubbers depend on many factors and lower removal efficiencies from scrubbers resulting in higher emissions of particles including black carbon and PAHs compared to vessels operating on MGO have been reported [21, 22]. In addition, scrubbers are an end-of-pipe solution and a substantial part of the emitted compounds will be trapped in the scrubber washwater and discharged in the surrounding surface water with potential consequences for aquatic ecosystems[18, 23-26]. Existing studies are limited, mainly focus on open marine systems and conclude that the overall impact of scrubber use on pH changes and contaminant concentrations is expected to be small under most conditions[24, 27-29]. Yet, the long term accumulation of contaminants caused by scrubber discharge can be of concern in smaller water bodies where ships are numerous, such as estuaries or harbours[30, 31].

Data on washwater contaminant concentration are scarce, often proprietary and rarely published. In present study, an extensive dataset on washwater contaminant concentrations and acidity is compiled, based on own measurements and unpublished and published datasets. This data allowed us to calculate the impact of scrubber use on water quality for two scenarios (10% and 20% scrubber use) for the Antwerp harbour docks and the Scheldt estuary. While the IMO regulatory framework primarily focuses on atmospheric emissions, also the discharge of washwater is regulated to a certain extent. Washwater discharge guidelines are set for pH (min. of 6.5, measured at 4 m from the overboard discharge point), for PAHs (max. 50 µg L^{-1} PAH Phe equivalent at a flow rate of 45 m^3 MWh^{-1}) and turbidity (max. 25 NTU (Nephlometric turbidity units) above the inlet water turbidity) (IMO, Resolution MEPC.184(59) and MEPC.259(68)). No criteria for metals are included. However, in current Belgian legislation the discharge of contaminated water from ships into their surrounding surface water is only accepted in several exceptional cases (e.g. wastewater from kitchens)[32]. Consequently, the use of open loop scrubbers or closed loop scrubbers with bleed-off discharge are not allowed in Belgian inland waters. To comply, vessels need to operate on compliant low sulphur fuel or use scrubbers in closed loop mode with the boundary condition that no washwater is discharged (zero discharge mode). While there is no current impact of scrubbers on Belgian water bodies, it is important to get insight into possible consequences for European ports, rivers, estuaries and coastal regions in order to streamline legislation. Ahead of the implementation of the SECA's, shipowners have already criticized the uncertainty and the inconsistency between the Member States on the use of scrubbers in order to comply with the requirements of the Sulphur Directive. In an open letter, the European Community Shipowners' Association (ECSA) urges that establishing legal certainty about proper compliance and enforcement together with a fair level playing field between shipping operators and between transport modes are a must[33].

The objective of present study is to identify contaminant concentrations in scrubbers washwater and get insight in effects of scrubber discharge on the water quality, with emphasis on harbour docks, rivers and estuaries.

2. Methods

2.1. Sampling

Washwater samples were collected from two separate marine vessels operating a scrubber. The first vessel was equipped with a hybrid scrubber and was sampled in Belgium on two occasions in October 2014: when at berth in the port of Antwerp, operating in closed loop mode and when sailing on the Scheldt estuary in open loop mode. The second vessel had an open loop scrubber and was sampled twice in October 2015: when sailing at the North Sea and when manoeuvring in the port of Antwerp. Discharge and sampling of washwater in these Belgian waters was permitted by the Flemish Environmental Agency for present research. Detailed information on scrubber type, fuel and operating conditions can be found in the datasheet (Table S1). Samples were taken from a tap close to the scrubber outlet. Right after sampling the temperature (°C) and pH were measured with a temperature-pH electrode connected to a portable multi meter (HQ30D, Hach, US). Water samples were collected in 1 L glass bottles for PAH analysis and in 0.25 L high density polyethylene (HDPE) bottles for metal analysis. All samples were stored cool during transport. Metal analyses were performed after acid digestion with HCl and HNO_3 by inductively coupled plasma optical emission spectrometry (ICP-OES) following standard method ISO 11885. Measured metals are Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Mercury (Hg), Lead (Pb), Nickel (Ni), Zinc (Zn) and Vanadium (V). PAHs were determined by gas chromatography/mass spectrometry (GC/MS) following standard method EPA 8270 D. Measured PAHs are Acenaphthene (Ace), Acenaphtylene (Acy), Anthracene (Ant), Benzo(a)anthracene (B(a)A), Benzo(a)pyrene (B(a)P), Benzo(b)fluoranthene (B(b)F), Benzo(g,h,i)perylene (B(ghi)P), Benzo(k)Fluorathene (B(k)F), Chrysene (Chr), Dibenzo(a,h)anthracene (D(ah)A), Fluoranthene (Fluoran), Fluorene (Flu), Indeno(1,2,3c-d)pyrene (I(123cd)P, Naphtalene (Naph), Phenantrene (Phe) and Pyrene (Pyr). These results were combined with additional datasets on pH, metal and PAH concentrations: (1) unpublished datasets from the same shipping companies as sampled in the present study, (2) dataset resulting from sampling campaigns organised by the exhaust gas cleaning system association (EGCSA) and the association representing port waste reception facility providers (EUROSHORE)[34] and (3) from literature [24, 26-28, 35]. Results are combined in a database

(Table S1). Parameters with many values below limit of quantification (BLOQ) were excluded from further analysis (Figure S1, S2, Table S2).

2.2. Scenario's and model calculation

To calculate the impact of discharged washwater on the water quality two scenarios were defined. Scenario LOW assumed that 10% of the total ship emissions were treated by scrubbers and vessels discharged at average washwater concentrations. Scenario HIGH assumed a 20% treatment by scrubbers and discharge at 90th percentile of washwater concentrations (Table 1 for scenario HIGH, Table S3 for scenario LOW). Both scenarios were calculated for closed loop mode and open loop mode separately. . From January till November 2019 about 350 unique vessels equipped with a scrubber visited the port of Antwerp, with a total of approximately 1250 calls (information Antwerp Port Authority and Clarksons Worldfleet Register). This corresponds to 8.7% of the total number of vessels and 9.5% of the total number of calls. Scrubber types of vessels in the Antwerp port are evenly distributed between open loop and hybrid scrubbers. It is difficult to estimate the future use of scrubbers. Since the installation of a scrubber is economically profitable under most scenarios[11], a further increase can be expected. However, the fuel marked is changing rapidly and low sulphur heavy fuels which are cheaper than distillates are becoming available and might influence scrubber interest[1]. The calculated scenarios included all fuel used by the vessels, from main and auxiliary engines. For manoeuvring and berthing in harbours, auxiliary engines are typically used. As these auxiliary engines are not always connected to the scrubber, the calculated changes in metal and PAH concentrations in the harbour docks surface water could be an overestimation.

The contaminant input Jc (kg y^{-1}) to the water bodies (harbour docks and estuary) was calculated as:

$$J_c = Q_w * P_t * F_s * (C_c - C_d) \qquad \text{(Eq. 1)}$$

With Q_w (L MWh^{-1}) the discharge of washwater (closed or open loop) per unit of generated power of the vessel, P_t (GWh y^{-1}) is the total power generated by the vessel in a certain water body (harbour docks or Scheldt estuary), F_s the share of total emissions treated by scrubbers (0.1 for scenario LOW or 0.2 for scenario HIGH),C_c (kg L^{-1}) is the concentration of the contaminant in the washwater and C_d is the concentration of the contaminant in the docks. The power P_t generated by the vessels in the Scheldt estuary (182 GWh y^{-1}) and Antwerp harbour docks (472 GWh y^{-1}) is well constrained (data provided by the Antwerp port Authority). An average washwater discharge was calculated for open loop (87 ± 50 m^3 MWh^{-1}, N=44) and closed loop (0.47 m^3 ± 0.25 m^3 MWh^{-1}, N=7), based on the available data (Table S1). Note however that in very few cases vessels with closed loop systems will not discharge any washwater, as they retain the washwater on board and deliver it to port reception facilities on shore (personal communication shipping companies). The concentrations of metals and PAHs measured in the inlet water were not used for the calculation because values were often below limit of quantification (BLOQ). Additionally, concentrations of e.g. zinc in inlet water samples were sometimes unrealistically high (Table S1), which can be caused by sampling inlet water from a valve on board which could have resulted in elevated metal concentrations originating from the metal tubing of the scrubber system. Instead, available data on total metal and PAH concentrations in the harbour docks (C_d) were used and average values were subtracted from the outlet concentrations prior to the calculation of fluxes and changes in surface water concentrations (see Table 1 for concentrations). All outlet washwater concentrations reported as BLOQ were replaced by the respective LOQ/2 and included in the calculations.

Changes in contaminant concentrations in the surface water resulting from the scrubber discharge are calculated as:

$$\Delta C_c = \frac{J_c}{Q_r} \qquad \text{(Eq. 2)}$$

With ΔC_c (µg L^{-1}) the mean concentration change in the receiving water body caused by scrubber discharge, J_c (kg y^{-1}) the contaminant input from scrubbers calculated with Eq. 1 and Q_r (L y^{-1}) is the water flowrate through the receiving water body. The mean flow rate of the Scheldt estuary was 100 m^3 s^{-1}, for the Antwerp harbour docks Q_r was the sum of the flow rate (16 m^3 s^{-1}) and the dispersive exchange D through the locks (100 m^3 s^{-1}, see appendix for calculation). Calculation assumptions were that all discharged contaminants were evenly distributed in the water column and stayed in suspension, i.e. during their stay in the docks (average residence time = 19 days) and in the estuary (average residence time = 2.5 months). Calculated increase in concentrations were compared with surface water concentrations measured during regular water quality monitoring programs from 2015-2016 in the receiving water body (data from the Flemish Environmental Agency and Antwerp Port Authority; in the docks n=15 (metals) and n=15 (PAHs), and in the Scheldt estuary n=115 (metals) and n=20 (PAHs).

For changes in TA, $SumCO_2$ and H_2SO_4 in the harbour docks a dynamic model was set-up. In this model, the docks are considered well mixed. The water body is affected by influx of freshwater (16 m^3 s^{-1}, fixed water composition, data provided by the Antwerp port Authority), by exchange with the adjacent estuary over the locks (data provided by the Flemish Environmental Agency, fixed water composition of the estuary, dispersive flux proportional to concentration difference, fixed bulk dispersion coefficient of 100 m^3 s^{-1}, see appendix), by the scrubber efflux, and by gaseous exchange with the atmosphere. The CO_2 (aq) in scrubber effluent was assumed to be in equilibrium with CO_2 in flue gas and assumed to have a fixed partial pressure of 0.1 atm[36]. The carbonate balance in the scrubber effluent was computed at observed effluent water temperature (T= 25 °C). Scrubber flux of H_2SO_4 and TA were determined by assuming that all sulphur in the exhaust is captured by the washing process. Further, 20% of vessels equipped with an open loop scrubber, 2.1% sulphur content in fuel, and a total of 90 x 10^6 ton fuel use per year for all vessels in the right bank of the Antwerp harbour were assumed. The model was run to steady state to assess the difference in water composition in the docks with and without scrubbers. Carbonate balances were computed with the R package AquaEnv[37]. The model was integrated with the R package deSolve[38]. The model code and scripts to run the scenario analyses are available on GitHub [link to the model will be made available upon acceptance].

3. Results and Discussion

3.1. Scrubber washwater quality

To get insight in the concentrations of contaminants present in scrubber washwater a database was compiled (Table S1). Metal and PAH concentrations in water that is discharged were found to be elevated compared to surface water concentrations or Water Quality Standards (WQS) (Table 1, Table S3). Differences between open and closed loop systems exist. The washwater in closed loop scrubbers circulates within the system, contaminants accumulate over time, resulting in higher concentrations of metals (on average 40 times higher) and PAHs (on average 1.3 times higher) in the discharged water compared to open loop mode (2-way ANOVA; metals: $F_{1,323}$= 26,7; p<0,001, PAH: $F_{1,475}$= 7.27; p=0,007) (Figure 1). However, in closed loop scrubbers the scrubbing capacity is kept high by dosing sodium hydroxide resulting in a low volume of water needed to trap SO_x efficiently. Closed loop systems discharge discontinuous and lower volumes of washwater (bleed-off) with a calculated average volume of 0.47 m³ MWh^{-1} (STDEV=0.0.25, N=7). In contrast, open loop systems need a large volume of surface water to ensure removal of SO_x from the exhaust with discharge volumes that are roughly 200 times higher (calculated average 87 m³ MWh^{-1}, STDEV=50, N=44). The circulation of water and smaller washwater volumes when operating in closed loop allows efficient treatment of the washwater using a hydrocyclone with removal of particles before discharge. Hereby, contaminants are scavenged in a sludge fraction that is stored and delivered to port reception facilities resulting in a lower total discharge of contaminants to the surrounding surface water (6 times for metals and 183 times for PAHs) for scrubbers operating in closed loop mode (differences are significant for metals: 2-way ANOVA; $F_{1,323}= 6.56$; p=0,011 and PAHs: $F_{1,475}= 30.4$; p<0,001) (Figure 2). The differences between metals and PAHs in total discharge indicate that PAHs are trapped much more efficient in the sludge fraction than metals by hydrocyclone treatment in closed loop mode. Also for scrubbers operating in open loop, the use of washwater treatment systems is reported (Table S1). However, treatment of the large washwater flow rates is less straightforward. A vessel sailing with 15 MW engine power will discharge roughly 350 L s^{-1}. The large variation in concentrations and the limited number of scrubbers that reported an open loop system with treatment in the dataset did not allow to draw conclusions on differences in concentrations between open loop with and without treatment. The acidity of the washwater in closed loop mode can be controlled by dosing the scrubbing media NaOH resulting in higher average pH values in the discharged water (6.8, STDEV=1.7, n=6) compared to the average pH values in open loop mode (4.8, STDEV=1.4, n=21).

Also within closed and open loop systems the variation in concentrations for the different parameters is large (Figure 1). This variation can be attributed to many different factors including fuel origin[39], fuel sulphur content[40], engine load[15], additives, or the presence of treatment facilities before the washwater is discharged. In general, the contaminants originate from the fuel, lubricant oil or combustion process, are transported to the smokestack, washed out by the scrubber water and end up in the washwater. Metal concentrations in fuels are known to vary substantially and are related to the crude oil origin and refinery process[39]. Since a substantial part of the metals in the fuel is expected to end up in the scrubber washwater[16, 18], the fuel origin will directly affect the washwater metal concentrations. Vessels with scrubbers usually operate on high sulphur fuel oil

(HSFO). These are residual fuels that are known to contain higher concentrations of metals compared to distillate fuel (DF), e.g. MGO[41]. The metals V and Ni and to a lesser extend Cu are typically tracers for residual fuel. For Zn the fuel and the lubricant oil have been reported to contribute equally to the emissions[41, 42]. Also in the present study V, Zn, Ni and Cu are the metals that were measured in the highest concentrations in the scrubber washwater. In open loop scrubbers average washwater concentrations with standard deviation (STDEV) were 200 µg L^{-1} (STDEV 125 µg L^{-1}) for V, 111 µg L^{-1} (STDEV 30 µg L^{-1}) for Zn, 52 µg L^{-1} (STDEV 34 µg L^{-1}) for Ni and 43 µg L^{-1} (STDEV 15 µg L^{-1}) for Cu. Concentrations in bleed-off from closed loop scrubbers were 9256 µg L^{-1} (STDEV 6050 µg L^{-1}) for V, 469 µg L^{-1} (STDEV 290 µg L^{-1}) for Zn, 2810 µg L^{-1} (STDEV 2700 µg L^{-1}) for Ni and 584 µg L^{-1} (STDEV 390 µg L^{-1}) for Cu. Besides, the concentration of Cr was found to be high in the washwater of several scrubbers operating in closed loop, while for most other washwater samples no elevated concentrations were measured. It is not clear where the high concentrations originate from, as Cr is generally not present in fuel[41]. It is possible that corrosion or abrasion of the scrubber installation, stimulated by the acidic washwater, is a source of Cr, as was previously suggested for Cu[24, 27].

The higher emissions originating from combusting HSFO compared to DF, as reported for metals, is even more pronounced for PAHs, with atmospheric emissions reported to be 200 times higher when operating on HSFO[15]. In the case of HSFO, the PAHs in the exhaust generally originate directly from the fuel[15]. The PAH concentrations in the emissions of marine engines are found to be dominated by Phe, Naph, Fluoran and Flu[43], which corresponds to the PAHs that were measured in high concentration in the washwater of present study with average values and STDEV in open loop washwater of 2889 ng L^{-1} (STDEV 2987 ng L^{-1}) for Naph, 1685 ng L^{-1} (STDEV 1367 ng L^{-1}) for Phe, 583 ng L^{-1} (STDEV 415 ng L^{-1}) for Flu and 162 ng L^{-1} (STDEV 215 ng L^{-1}) for Fluoran and closed loop bleed-off concentrations of 2175 ng L^{-1} (STDEV 2409 ng L^{-1}) for Naph, 3360 ng

L^{-1} (STDEV 2146 ng L^{-1}) for Phe, 1148 ng L^{-1} (STDEV 815 ng L^{-1}) for Flu and 280 ng L^{-1} (STDEV 210 ng L^{-1}) for Fluoran.

3.2. Impact on water quality

The concentrations of most PAHs and all metals in closed loop bleed-off largely exceeded their WQS (Tabel 1, Table S3) and are expected to be acutely toxic for most aquatic organisms. Acute toxic effects of scrubber washwater on phyto- and zooplankton are reported, even at concentrations of metals and PAHs much lower than the concentrations reported in present work[23, 25]. The synergistic effects caused by the mixture of metals and PAHs combined with low pH in scrubber washwater result in higher toxicity than estimated from the effect thresholds of the individual compounds[23, 44]. Acidification of the surface water can furthermore change the behaviour of metals in the receiving aquatic ecosystems. A decrease in pH can result in a higher bioavailability and in increase in remobilisation of metals from the sediment. However, the effects of washwater are strongly influenced by dilution with surrounding surface water. Buhaug et al. (2006) modelled that washwater at 50 m behind the vessels will be diluted 2000 times for vessels sailing in open sea and 1750 times during port operation at lower speed[28]. The extent of dilution will depend on vessel activity (at berth, manoeuvring, sailing) and physical characteristics of the receiving water body such as dimensions and flow rate, which complicates the prediction of scrubber washwater toxicity. When applying the dilution factor of 2000 on washwater metal and PAH concentrations almost no compounds will exceed their WQS whereby no acute toxicity is expected.

The increase in metal and PAH concentrations in aquatic ecosystems that originate from scrubber washwater is expected to be higher in inland waterbodies such as estuaries, rivers or harbours compared to large open marine systems. The accumulation of metals and PAHs in the surface water of the Antwerp harbour docks and the Scheldt estuary was calculated for a ‘scenario LOW’ (10%

open loop scrubbers and average washwater concentrations) and a ‘scenario HIGH’ (20% open loop scrubbers and 90th percentile washwater concentrations) (Figure 3). In particular the concentration of several PAHs (Flu, Naph and Phen) in the surface water of the Antwerp harbour docks was simulated to increase due to scrubber discharge. An increase in concentration of 39% under the ‘scenario LOW’ and 189% under the ‘scenario HIGH’ was calculated for naphthalene. The mean concentration of vanadium in the docks would increase with 9% under scenario LOW and 46% under scenario HIGH. The time vessels spend in the Scheldt estuary is shorter than in the harbour docks, which resulted in lower total amount of fuel use, a lower volume of scrubber washwater discharged and a smaller effect on metal and PAH concentrations in the surface water compared to the docks. For the Scheldt estuary mean naphthalene concentrations were calculated to increase with 5.0% (scenario LOW) to 25% (scenario HIGH). For vessels with scrubbers in closed loop mode a large part of the metals and PAHs is removed from the washwater, trapped in the sludge fraction and delivered on shore, with a smaller increase in pollutant concentrations as a consequence (Table 1). The estimated increase in surface water metal and PAH concentrations are worst case calculations as the assumption was made that contaminants stay in suspension, i.e. during their stay in the docks with an average residence time of 19 days. However, metals and PAHs might be removed from the water by adsorption to suspended solids followed by sedimentation. Furthermore, PAHs can be degraded by biological and chemical processes, with half-live values of 3 days to more than 500 days, depending on environmental conditions and the PAH being degraded [45]. Mainly the low molecular weight PAHs measured in high concentrations in the washwater (Naph, Phen, Flu) are known to degrade faster. In order to estimate the risks related to scrubber water discharge it is important to further investigate contaminant behaviour in the receiving water bodies. Yet, also in comparison with known existing emissions the total amount of contaminants discharged by scrubbers is large. The calculated flux of metals and PAHs from scrubber discharge under scenario high was lager then the sum of all known emissions to the harbour docks for Naph (57 kg y^{-1} for scrubbers compared to 19 kg y^{-1} for all other sources), for Phen (30 kg y^{-1} for scrubbers compared to 11 kg y^{-1} for all other sources), Flu (10 kg y^{-1} for scrubbers compared to 6 kg y^{-1} all other sources), and Ni (994 kg y^{-1} for scrubbers compared to 60 kg y^{-1} all other sources)[46]. Some of the pollutants that are present in scrubber washwater are already exceeding (Flu, Pyr) or close to exceedance (Ni, Zn) of their respective WQS in the surface water of the harbour docks or the Scheldt estuary (Figure 3). However, the compounds for which a large increase in concentrations was calculated (Naph>Phe>Flu>Ace>V) are not the compounds that are expected to pose the highest risk, based on the exceedances of the WQS. Nevertheless, several pollutants that were measured in elevated concentrations and discharged with the scrubber washwater are identified as 'priority substances' (Fluoran, Naph, Ni) or 'priority hazardous substances' (Ant, B(a)P, Cd) by the European Water Framework Directive (WFD) and as such are of major concern for European Waters. WQS exceedances of these compounds indicate that these aquatic systems are under pressure of high contaminant concentrations and progressive reduction of pollution from priority substances and the cessation or phasing-out of discharges, emissions and losses of priority hazardous substances is required[47]. Many European coasts and estuaries are part of Natura 2000, the largest coordinated network of protected areas in the world to safeguard valuable and threatened species and habitats. Mainly in these areas with large ecological values the discharge of scrubber washwater should be restricted. In addition, the use of scrubbers deflect attention from development of cleaner fuels[48]. However, also the emissions from vessels operating on low sulphur fuel are variable and subject to changes. With the sulphur regulations, new types of low sulphur heavy fuel oils (hybrid fuels, intermediate fuels or ECA fuels) have entered the market. How these fuels influence emission of metals and PAHs is not clear yet. It will, likely be necessary to limit the use of all low quality fuels, with high and low sulphur content and instead encourage the use of distillate fuels, mainly in coasts, estuaries and inland water bodies with large ecological value[1].

Table 1. Summarising numbers on scrubber washwater concentrations, fluxes and impact on water quality for scenario high (20% scrubbers).

	Units	Conc. Docks (1)	WQS (2)	CLOSED loop - Scenario HIGH: Discharge conc. (90th perc.)	CLOSED loop - Scenario HIGH: Flux kg y^{-1} (20% scrubbers)	CLOSED loop - Scenario HIGH: Conc. Increase docks	OPEN loop - Scenario HIGH: Discharge conc. (90th perc.)	OPEN loop - Scenario HIGH: Flux kg y^{-1} (20% scrubbers)	OPEN loop - Scenario HIGH: Conc. Increase docks
Cr		3.34	5	10120	448	0.122	45.0	342	0.093
Cu		8.38	7	1780	78	0.021	130	998	0.273
Ni	µg L^{-1}	5.86	4*	6060	268	0.073	127	994	0.272
Zn		32.9	20	1524	66	0.018	260	1863	0.509
V		3.94	4	25000	1107	0.303	500	4069	1.112
Ace		4.92	60	745	3.28E-02	8.96E-03	648	5.27	1.44
Acy		7.20	4000	185	7.87E-03	2.15E-03	536	4.34	1.19
Ant		2.67	100*	446	1.96E-02	5.37E-03	308	2.50	0.685
Fluoran		9.51	6.3*	661	2.88E-02	7.89E-03	478	3.84	1.05
Flu	ng L^{-1}	3.72	2000	2370	1.05E-01	2.86E-02	1200	9.81	2.68
Naph		8.24	2000*	6370	2.82E-01	7.70E-02	6960	57.0	15.6
Phe		7.95	100	6970	3.08E-01	8.43E-02	3700	30.3	8.28
Pyr		13.0	40	554	2.40E-02	6.55E-03	1220	9.90	2.71
Total PAH		58.1		22200	9.80E-01	2.68E-01	13620	111	30.4

(1) Average values for total concentrations in the harbour docks
(2) Water Quality Standards (WQS) from the EU WFD (*) or Flanders (dissolved concentrations for metals, total concentrations for PAHs)

3.3. Acidification

Marine transport related emissions of NO_x and SO_x cause acidification of terrestrial and marine ecosystems[49]. The contribution of anthropogenic N and S depositions to ocean acidification account only for a few percent of the acidifying impact of the global anthropogenic emissions (mainly caused by CO_2)[50]. However, in certain restricted areas such as coastal waters with important shipping lanes or large harbours, the acidifying effect caused by NO_x and SO_x can exceed the effect of overall anthropogenic CO_2 emissions[49]. In open loop scrubber systems the natural buffering capacity (alkalinity) of the sea or river water is used to neutralize the acid ions. Mean alkalinity in coastal waters varies between 2100 and 2400 µmol/l [51] and is high enough to guarantee high SO_x removal efficiencies. Due to a calcium rich bedrock, the mean alkalinity in the surface water of the Scheldt estuary (4400 µmol L^{-1}) and the docks (3400 µmol L^{-1}) is high. In closed loop systems, the acidity of the washwater is buffered by dosing NaOH to the circulating washwater in order to have a bleed-off that is neutral (pH around 6-8). Since vessels with scrubbers operate on high sulphur fuel (up to 3.5%) the acidifying sulphur compounds are discharged directly into the surface water and their acidifying capacity is much larger then vessels operating on low sulphur fuel (0.1% in SECAs). Model simulations with scenario HIGH (20% open loop scrubbers) show a decrease in pH of 0.015 units caused by washwater discharge (Figure 4). The alkalinity will comparably decrease slightly with 6 μmol L^{-1} or 0.16% and total sulphate concentrations will increase with 3 μmol L^{-1} or 0.08%. For the Baltic Sea, the water pH has previously been calculated to decrease by open loop scrubber use with roughly 0.0015 units (50% scrubbers scenario) to 0.003 units (100% scrubbers scenario)[49].

Since preindustrial times global ocean pH decreased with approximately 0.1 units with related negative consequences for marine ecosystems[52]. Among many other sources, SO_x emissions of marine transport contributes to this acidification. The IMO established sulphur regulations to mitigate the impact of high sulphur emissions of the maritime sector. However, the use of open loop scrubbers as an abatement technology will not reduce their contribution to the acidification.

4. Conclusions

The number of vessels with a scrubber is increasing rapidly. Generally, the total acidifying potential and emissions of hazardous substances of vessels with scrubbers operating on HSFO are higher than from vessels operating on low sulphur compliant fuels. A substantial part of these emissions are directly discharged with the washwater into receiving aquatic ecosystems.. This washwater is found to be acute toxic for aquatic organisms and a substantial long term increase in the concentrations of Naph, Phe, Flu, Ace and V following scrubber washwater discharge was calculated for an estuary and harbour docks. The compounds for which a large increase in concentrations was calculated (Naph>Phe>Flu>Ace>V) are not the compounds that are expected to pose the highest risk, based on the exceedances of the WQS. Nevertheless, several pollutants that are discharged with the scrubber washwater are identified as ‘priority substances’ or ‘priority hazardous substances’ by the European Water Framework Directive and as such are of major concern for European Waters. WQS exceedances of these compounds indicate that many European aquatic systems are already under pressure. As such, mainly in coast and estuaries with large ecological values the discharge of scrubber washwater should be restricted.

Figure Legends

Figure 1. Metal (A) and PAH (B) concentrations (µg L^{-1}) in washwater from scrubbers operating in closed loop (shaded boxes) and open loop (grey boxes). Boxplots with 5^{th} and 95^{th} percentile (whiskers), 25^{th}, median and 75^{th} percentile and outliers (dots). Y-axis in logarithmic scale.

Figure 2. Total discharge (g MWh^{-1}) of metals (A) and PAHs (B) in washwater from scrubbers operating in closed loop (shaded boxes) and open loop (grey boxes). Boxplots with 5^{th} and 95^{th} percentile (whiskers), 25^{th}, median and 75^{th} percentile and outliers (dots). Y-axis in logarithmic scale.

Figure 3. Increase in metal and PAH surface water concentrations (%) in the harbour docks (A) and the Scheldt estuary (B) caused by open loop scrubber discharge compared to current concentrations (grey, 100%) calculated with the scenario LOW (white) and scenario HIGH (black). The ratio between water quality standards (WQS) and current (grey) metal and PAH surface water concentrations in the docks (C) and the Scheldt estuary. The calculated concentration increase caused by open loop scrubber discharge calculated by the scenario LOW (white) and scenario HIGH (black).

Figure 4. Changes in total alkalinity (TA, µmol L^{-1}), H_2SO_4 (µmol L^{-1}) and pH in the surface water from the Antwerp harbour docks caused by open loop scrubber discharge calculated with scenario HIGH (20% open loop scrubbers).

List of abbreviations

IMO: International Maritime Organization

EGCS: exhaust gas cleaning systems

PM: particulate matter

MARPOL: International Convention for the Prevention of Pollution from Ships

S: sulphur

SOx: sulphur (x)oxide

SECA Emission Control Area

LNG: liquefied natural gas

NaOH: sodium hydroxide

HFO: heavy fuel oil

PAH: polycyclic aromatic hydrocarbons

MGO: marine gas oil

ECSA: European Community Shipowners' Association

HDPE: high density polyethylene

ICP-OES: inductively coupled plasma optical emission spectrometry

GC/MS: gas chromatography/mass spectrometry

As: Arsenic

Cd: Cadmium

Cr: Chromium

Cu: Copper

Hg: Mercury

Pb: Lead

Ni: Nickel

Zn: Zinc

V: Vanadium

Ace: Acenaphthene

Acy: Acenaphtylene

Ant: Anthracene

B(a)A: Benzo(a)anthracene

B(a)P: Benzo(a)pyrene

B(b)F: Benzo(b)fluoranthene

B(ghi)P: Benzo(g,h,i)perylene

B(k)F: Benzo(k)Fluorathene

Chr: Chrysene

D(ah)A: Dibenzo(a,h)anthracene

Fluoran: Fluoranthene

Flu: Fluorene

I’123cd)P: Indeno(1,2,3c-d)pyrene

Naph: Naphtalene

Phe: Phenantrene

Pyr: Pyrene

EGCSA: exhaust gas cleaning system association

BLOQ: below limit of quantification

TA: total alkalinity

WQS: Water Quality Standards

HSFO: high sulphur fuel oil

DF: distillate fuel

STDEV: standard deviation

WFD: Water Framework Directive

DECLARATIONS

Ethics approval and consent to participate: Not applicable.

Consent for publication: Not applicable.

Availability of data and material: All data generated or analysed during this study are included in this published article and its supplementary information files.

Competing interests: The authors declare that they have no competing interests.

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Authors' contributions: JT collected samples, performed chemical analysis, interpreted the data and drafted the manuscript. TJSC contributed to the calculations and revised the manuscript. KVI provided additional datasets and organized sampling campaigns. FJRM modelled the acidification and revised the manuscript. RB contributed to the study design and revised the manuscript. All authors have given approval to the final version of the manuscript.

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Supporting Information.

File 1: TableS1: an Excel file that contains the compiled database on scrubber use and washwater quality. A total of 127 samples, based on own sampling, received datasets and literature.

File 2: A Word document with information on calculations, 2 Tables and 2 Figures.

Table S2: all measured parameters with number of values below the limit of quantification

Table S3: Summarising numbers on scrubber washwater concentrations, fluxes and impact on water quality for scenario low (10% scrubbers). The numbers of scenario high (20% scrubbers) are included in the manuscript (Table 1).

Figure S1: All scrubber washwater metal concentrations

Figure S2: All scrubber washwater PAH concentrations

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Figures

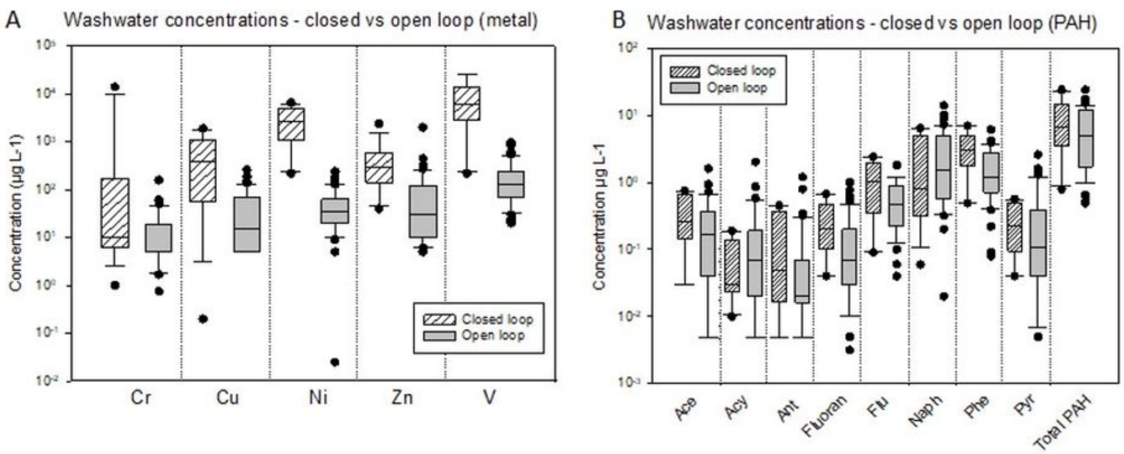

Figure 1

Metal (A) and PAH (B) concentrations (µg L-1) in washwater from scrubbers operating in closed loop (shaded boxes) and open loop (grey boxes). Boxplots with 5th and 95th percentile (whiskers), 25th, median and 75th percentile and outliers (dots). Y-axis in logarithmic scale.

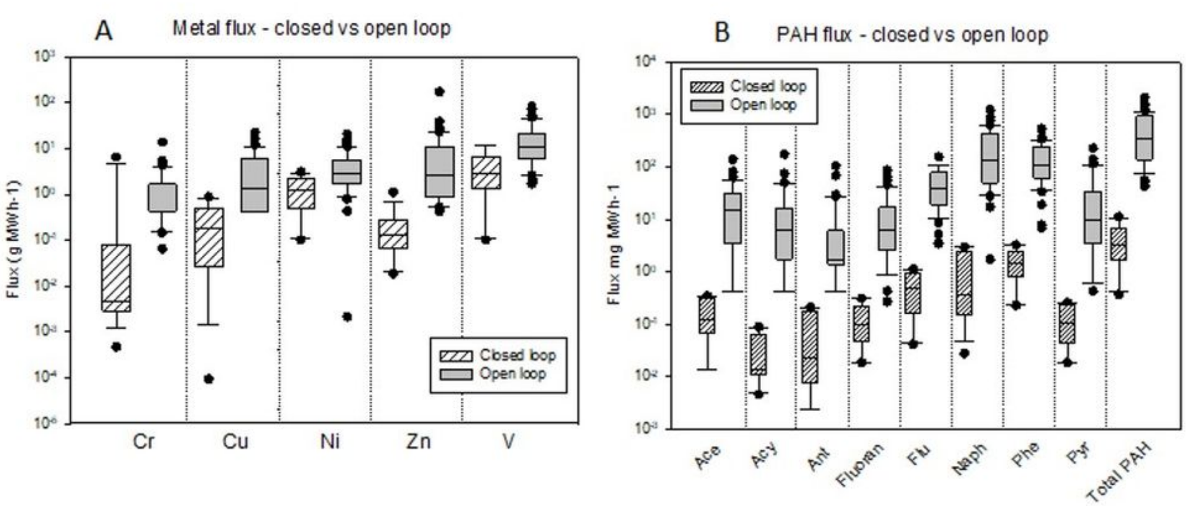

Figure 2

Total discharge (g MWh-1) of metals (A) and PAHs (B) in washwater from scrubbers operating in closed loop (shaded boxes) and open loop (grey boxes). Boxplots with 5th and 95th percentile (whiskers), 25th, median and 75th percentile and outliers (dots). Y-axis in logarithmic scale.

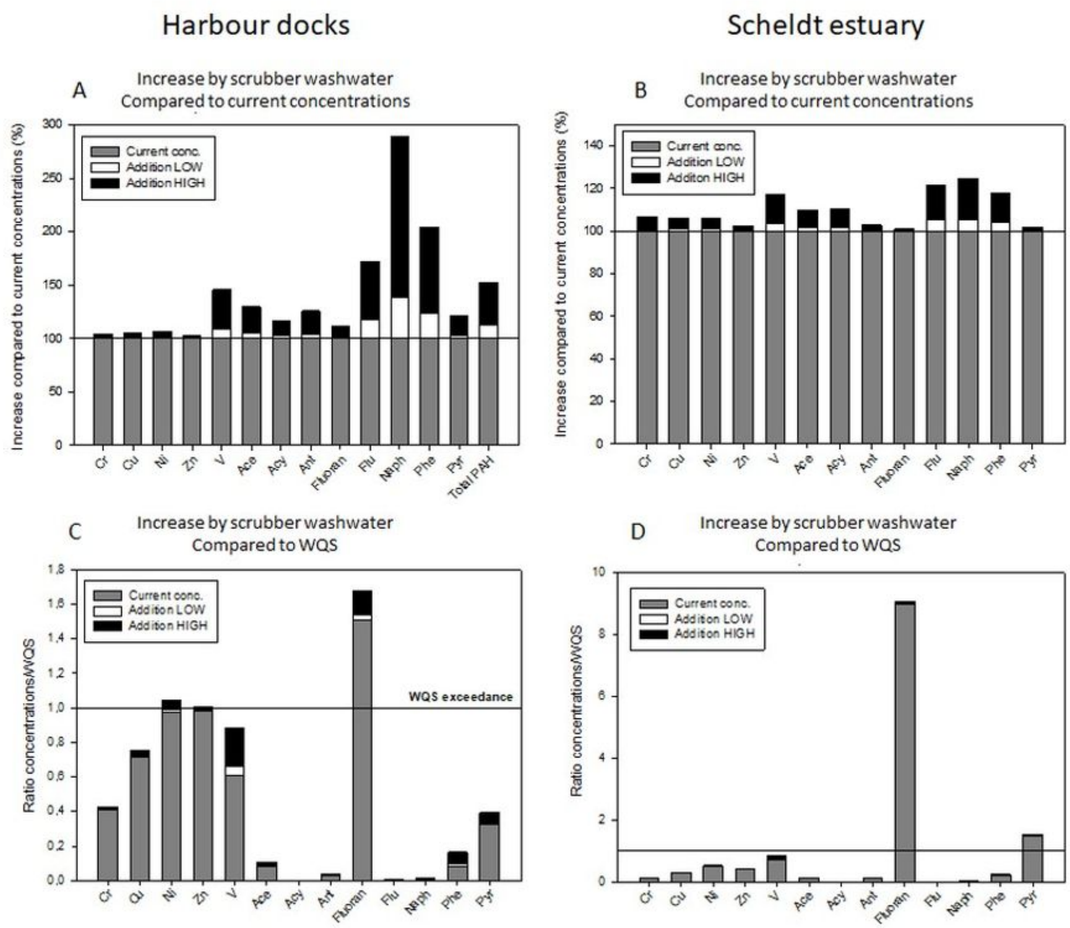

Figure 3

Increase in metal and PAH surface water concentrations (%) in the harbour docks (A) and the Scheldt estuary (B) caused by open loop scrubber discharge compared to current concentrations (grey, 100%) calculated with the scenario LOW (white) and scenario HIGH (black). The ratio between water quality standards (WQS) and current (grey) metal and PAH surface water concentrations in the docks (C) and the Scheldt estuary. The calculated concentration increase caused by open loop scrubber discharge calculated by the scenario LOW (white) and scenario HIGH (black).

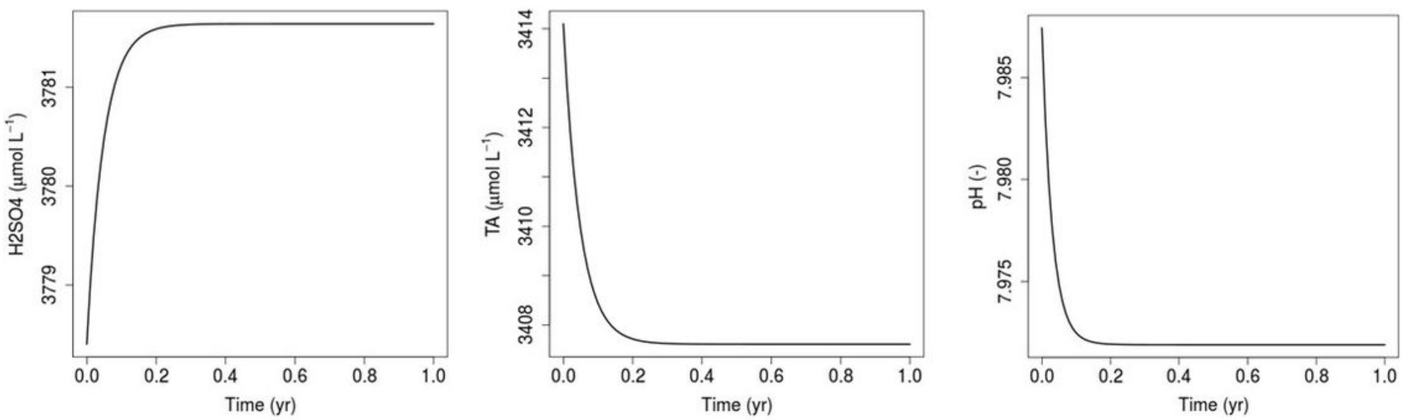

Figure 4

Changes in total alkalinity (TA, μmol L-1), H2SO4 (μmol L-1) and pH in the surface water from the Antwerp harbour docks caused by open loop scrubber discharge calculated with scenario HIGH (20% open loop scrubbers).

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- SupportingInformationrevision.docx
- SITable1revised.xlsx