Evaluation, control and Mitigation of the EnviRonmental impacts of shippinG Emissions (EMERGE)

Deliverable 2.4,

"Multivariate prediction of scrubber water toxicity"

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 874990. The content of the deliverable reflects only the author's view and CINEA is not responsible for any use that may be made of the information it contains.

Grant Agreement No.	874990
Project acronym	EMERGE
Project full title	Evaluation, control and Mitigation of the EnviRonmental impacts of shippinG Emissions
Dissemination level	Public
Due date of deliverable	M36
Actual submission date	M39
Deliverable name	D2.4 "Multivariate prediction of scrubber water toxicity" *Alternatively:* *D2.4 "Predicting potential toxicity of scrubber discharge water"*
Type	Report
Status	Final
WP contributing to the deliverable	WP2
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ABBREVIATIONS

AF	Assessment Factors
ChV	Chronic effect Values, geometric mean of NOEC and LOEC
EC10	Effect Concentration 10%, the concentration at which 10% of the test population is affected
EC50	Effect Concentration 50%, the concentration at which 50% of the test population is affected
ECOSAR	ECOlogical Structure-Activity Relationship Model
EQS	Environmental Quality Standard
HC5	Hazardous Concentration 5%, the concentration at which 5% of species in an SSD are affected (conditioned that the SSD is based on Chronic NOEC data, which for REACH, is the only allowable one from a legal standpoint, and therefor applicable in this report)
IC50	Inhibition 50%, the concentration of an inhibitor where the response is reduced by 50%
IMO	International Maritime Organization
LC50	Lethal Concentration 50%, the concentration at which 50% of the test population is dead
LOD	Limit of Detection
LOEC	Lowest Observed Effect Concentration
LOEL	Lowest Observed Effect Level
MATC	Maximum Acceptable Toxicant Concentration, geometric mean of NOEC and LOEC
MC	Measured Concentration
MEC	Measured Environmental Concentration
NOEC	No Observed Effect Concentration
NOEL	No Observed Effect Level
PAH	Polycyclic aromatic hydrocarbons
PEC	Predicted Environmental Concentration
PNEC	Predicted No Effect Concentration
QSAR	Quantitative Structure-Activity Relationship
RCR	Risk Characterization Ratio
RoPax	roll-on/roll-off passenger-vessel, i.e. vessel that transports cargo and passengers
SSD	Species Sensitivity Distribution
SO_X	Sulphur oxides
TGD	Technical Guidance Document
US EPA	United States Environmental Protection Agency

EXECUTIVE SUMMARY

The daily operations of maritime shipping give rise to several different waste streams, each contributing to the total load of chemical substances to the marine environment. Risk can be assessed by calculating the risk characterisation ratio (RCR) as the relation between the predicted (or measured) environmental concentration (P(M)EC) and the predicted no effect concentration (PNEC), which is a measure of the environment sensitivity of a specific substance derived from ecotoxicological tests. Since all liquid waste streams from shipping, e.g., scrubber water, grey water and sewage, contains more than one substance, a PEC/PNEC summation approach can be applied as a conservative first step methodology to predict the risks for adverse effects from mixture exposure. The summation approach is based on the concept of concentration addition which means that all substances present in a mixture contribute to a cumulative effect. However, if PNEC values are not available for substances identified in a liquid waste stream, these will not be included in the risk assessment. For substances where PNEC values are not available, Quantitative Structure-Activity Relationship (QSAR) models, can be applied to predict the toxicity based on the chemical structure and/or properties of a substance. In this report, QSAR model output were used as complement to the experimentally derived ecotoxicological PNEC values, to allow for more substances to be included in the risk assessment of waste streams. Cumulative risk characterization ratios (RCR_{sum}), summarising the substance specific risks, were calculated for open and closed loop scrubber water and compared to the ecotoxicological response from EMERGE D2.3, where whole effluent tests of scrubber water were conducted on different marine organisms. The results showed that the inclusion of alkylated PAHs in the risk assessment improves the prediction of scrubber water toxicity. The results suggestt that alkylated PAHs contribute to >85% of RCR_{sum} of open loop scrubber water, yet the ecotoxicological response can still not be fully explained. The variability of the ecotoxicological responses, both within species and between species, indicates there are several unknowns related to scrubber water mixture toxicity.

Scrubbers have the highest RCR_{sum} of all liquid waste streams included in the assessment (grey water, bilge water, sewage, ballast water, open and closed-loop scrubber water). Also, when comparing the volume weighted RCR_{sum} for each waste stream for a model ship operating with an open or a closed loop scrubber for one year, it is apparent that the scrubbers have the highest contribution to risk of all waste streams and that open loop scrubbers contribute to more than 99% of the total volume weighted RCR_{sum}.

The output from this deliverable can be used in the future work within EMERGE where work packages 6 and 7 will synthesise the output for the different case study regions and to further assess the environmental impact from shipping in general, with the use of scrubbers in particular.

1 INTRODUCTION

Shipping gives rise to a range of onboard-generated liquid waste streams (Figure 1-1). Of these, scrubber discharge water has been reported to be responsible for the highest contaminant loads to the marine environment (Hassellöv et al., 2020; Jalkanen et al., 2021; Ytreberg et al., 2022).

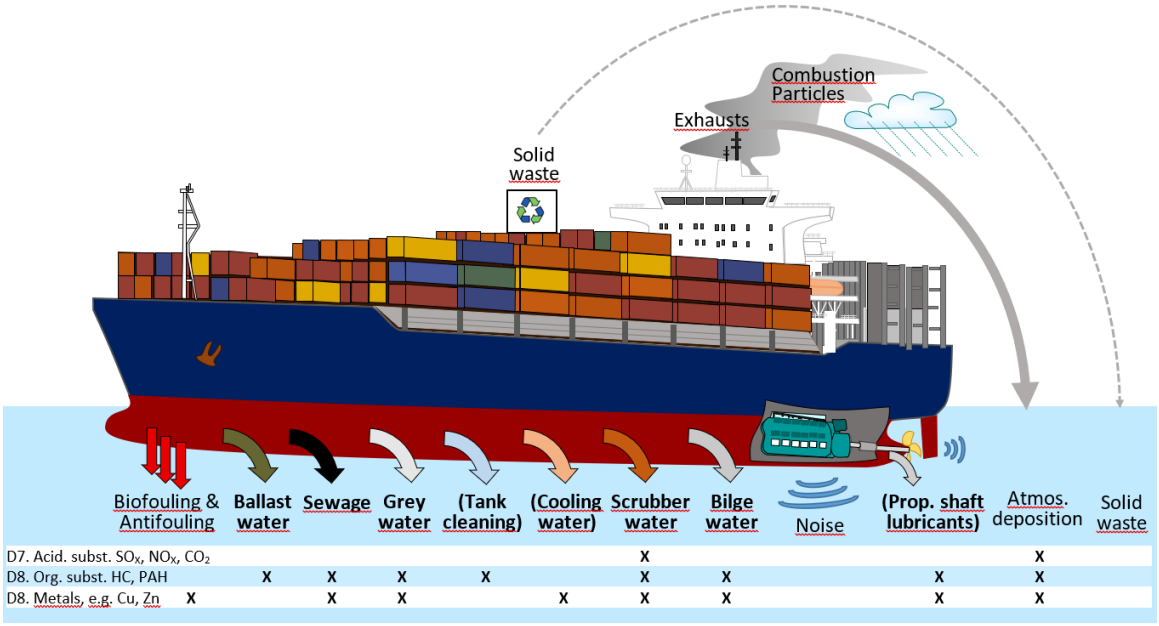

Figure 1-1. Emissions and discharges from a ship. Five out of the eight different liquid waste streams (in bold) are included in the analysis in this report. Due to limited data availability, the three in brackets are omitted from the analysis. The annotation of the rows refers to the EU Marine Strategy Framework Directive, *Descriptor 7 - Permanent alteration of hydrographical conditions does not adversely affect the ecosystem*, which includes pH, and *Descriptor 8 - Concentrations of contaminants give no effects*, here divided into organic substances and metals. Modified from Jalkanen et al. (2021).

Scrubber discharge water, from both open- and closed-loop operations, has been shown to be toxic to marine organisms. However, the response of whole effluent testing of scrubber water cannot be fully explained by the toxicity of the individual substances previously identified in scrubber water (Koski et al., 2017; Thor et al., 2021; Ytreberg et al., 2021). It has therefore been proposed that the response could also depend on mixture or synergetic effects, also due to possible modifying factors due to effluent conditions (e.g., increased metal toxicity at lower pH), or the presence of un-identified chemical substances.

The EMERGE approach of WP2 therefore included: i) extensive literature review of chemical substances in different liquid waste streams, compiled and reviewed in *EMERGE D2.1- "Database and analysis on waste stream pollutant concentrations, and emission factors"*, ii) a wide-scope chemical screening of scrubber water (*EMERGE D2.2-* "*Report on measurements of dissolved and particulate contaminants in case study regions"*) and, finally, iii) whole effluent toxicity testing (*EMERGE D2.3-* "*Report on scrubber water whole effluent toxicity testing, at different geographical regions"*) to provide more complete data sets on scrubber water chemical composition and resulting toxicity and thus advance the available literature data.

The primary aim of Task 2.4 was then to use the data provided in D2.1, D2.2 and D2.3 to develop a methodology for prediction of scrubber water toxicity, based on its chemical composition. The secondary aim was to assess the relative risk posed by open- and closed-loop scrubber water respectively, as compared to other onboard generated liquid waste streams (ballast water, bilge water, sewage (also known as black water) and grey water). Toxicity prediction was planned to be based on multivariate modelling (e.g., Principal Component Analysis) to explain the toxicity with the variations in chemical composition of different scrubber waters. However, following the pandemic adaptation of the EMERGE project execution, the planned onboard sampling of 3-5 ships per case study were reduced to one larger onboard campaign, in addition to studies of scrubber water produced in Chalmers' scrubber lab. Hence, the possibilities to use the originally proposed multivariate approach was disabled and an alternative approach was used.

Risk Characterization Ratios (RCR) were used to estimate the risk associated to scrubber discharge water and to rank different liquid waste streams in relation to their environmentally hazardous properties. The idea behind the RCR approach is to relate the concentration of a chemical substance, expressed as either the Measured Environmental Concentration (MEC) or the Predicted Environmental Concentration (PEC) to the Predicted No Effect Concentrations (PNEC). PNEC is the concentration of the substance below which adverse effects in the environmental sphere of concern are not expected to occur. The original data from the EMERGE project (D2.2-D2.3) allow for comparisons between whole effluent ecotoxicity testing and concentrations of chemical substances in the scrubber discharge water, which can also be compared to literature data (compiled in D2.1). PNEC values are available for many substances known to be found in scrubber discharge water, including metals and polycyclic aromatic hydrocarbons (PAHs) (EU EQS directive Council Directive (EC), 2008; SwAM, 2019; Verbruggen, 2012). An overlooked group of substances in scrubber discharge water is alkylated PAHs, which were identified in high

concentrations in scrubber discharge water by EMERGE (D.2.2). However, since PNEC values is lacking for individual alkylated PAHs, it is currently impossible to estimate how important they are in governing the overall toxicity of scrubber effluent. As a first step towards an improved understanding of the substances potentially driving the toxicity in different liquid waste streams, Quantitative Structure–Activity Relationship models (QSAR models) were applied to generate predictions of effect data from ecotoxicological tests for the subsequent derivation of PNEC. Finally, a comparison of RCRs between different liquid waste streams was illustrated through a case study of a RoPax vessel equipped either with an open- or a closed-loop scrubber.

2 THEORY

Environmental risk assessments (ERA) of chemical substances (hereafter referred to as substances) comprise comparisons between the exposure of the ecosystem to a substance on the one hand, and the sensitivity of the ecosystem to that particular substance on the other. The exposure is usually estimated using chemical fate models that determine PECs in different environmental compartments. The concentration of the substance below which adverse effects in the environmental sphere of concern are not expected to occur is known as PNEC (REACH Council Regulation (EC), 2006). If the PEC/PNEC ratio (also referred to as risk characterization ratios, RCR) exceeds 1, the risk of adverse effects on the environment is denominated as *unacceptable*. If the RCR ratio is below 1, the risk of adverse effects on the environment is denominated as *acceptable*. If a product, or a waste stream, contains more than one substance, a PEC/PNEC summation approach is typically applied as a conservative first-step methodology to predict the risks for adverse effects of mixtures of contaminants (Backhaus & Faust, 2012).

The summation approach is based on the concept of concentration addition which means that all substances present in a mixture contribute to a cumulative effect.

Equation 1 $$\boldsymbol{RCR_{sum}} = \sum_{i=1}^{n} \frac{\boldsymbol{PEC_i}}{\boldsymbol{PNEC_i}}$$

The summation of RCRs (Eq. 1, where n is the total number of substances in the mixture) is also supported by the recently approved IMO guidelines for environmental risk and impact assessments of scrubber discharge water (MEPC, 2022), stating that:

The cumulative effects of mixtures should be taken into account and a PEC/PNEC summation approach is recommended where PEC/PNEC ratios of all mixture components (PAHs and metals) are summed up to a final Risk Quotient.

Also, the *Technical Guidance No 27 for Deriving Environmental Quality Standards* (hereafter TGD 27) by the European Commission (2018) approves using a summation of toxic units (derived in a similar matter as RCRs) if the mixture is well defined. TGD 27, and the development and Environmental Quality Standards (EQS), is part of the implementation strategy of the Water Framework Directive (2000/60/EC) as EQS are important tools used for assessing the chemical and environmental status of waterbodies (Council Directive (EC), 2000).

Shipping is known to emit hundreds of different substances and the liquid waste streams (Figure 1-1) are often chemical mixtures and the composition of each waste stream may be highly variable (EMERGE D2.1). Although it is possible to calculate emission factors for individual substances, it would be very time-consuming to develop and apply a chemical fate model that has the capacity to accurately predict environmental concentrations of the hundreds of substances discharged in harbours and/or ship lanes. Thus, a simplified approach is to assess the potential risk for adverse environmental effects from the cumulative RCR (hereafter referred to as RCR_{sum}) of a specific waste stream, e.g., scrubber discharge water, where Measured Concentrations (MC) of substances based on available data on average concentrations in the waste stream (instead of modelled PEC values) are compared with PNEC-values to derive RCR_{sum}. With this approach the different waste streams potential risks can be compared to each other.

To assess the cumulative risk of the mixture, a PNEC value is required for each substance. PNECs are derived from ecotoxicological studies where representative species from different trophic levels (or taxonomic groups) are exposed to the specific substance. According to the TGD 27, two methods can be used to derive PNEC values, the deterministic and the probabilistic approach. For the deterministic approach, the lowest effect concentration is divided by an assessment factor (AF) whose size is dependent on the available data. The AF is used to account for the uncertainty in extrapolating between the performed tests and the field situation. The probabilistic approach requires more data, and all available ecotoxicity data (usually chronic NOEC and/or EC_{10} data) are ranked and a species sensitivity distribution (SSD) curve is fitted to the data. Finally, a certain percentile (usually the 5^{th} corresponding to the concentration estimated to affect 5% of all species) of the distribution is selected as threshold value (also called HC5 value). The probabilistic approach is also associated to uncertainties and requires that an assessment factor, but this is often lower than for the deterministic approach due to the increase data availability and inclusion of several species. If no ecotoxicological studies have been conducted for a certain substance or the number and quality of the obtained data is not satisfactory, no PNEC can be derived, and the substance cannot be included in the RCR_{sum} assessment. To fill the data gap of these substances for which no toxicity data are available, non-testing methods, such as computational approaches with Quantitative Structure-Activity Relationship (QSAR) models, can be applied to predict the toxicity (as described by a specific ecotoxicological parameter, such as EC_x or NOEC) based on the chemical structure and/or properties of the substance. However, as stated in the (European Commission, 2018) the QSAR models "should not be used to generate critical data to derive an EQS; however, predicted data can play a role in reducing uncertainty and thereby influence the size of AF chosen for

extrapolation.” For more information regarding the application of QSAR and recent technological advances where QSAR has been used, visit (Muratov et al., 2020).

3 MATERIAL AND METHODS

The structure of this deliverable can be divided into four segments where the first was to evaluate the QSAR model output of ecotoxicological effect concentrations and to compare those to experimentally measured ecotoxicological responses (section 3.1 and 4.1). In the second segment, new PNEC values were derived based on available data from 1) experimentally measured ecotoxicological data, 2) modelled data from QSAR and 3) by combining experimentally measured and modelled ecotoxicological data. Where applicable, the PNEC values from experimentally measured ecotoxicological data were then compared to those derived from the QSAR model output. In the third segment, the lowest PNEC values derived from this work, (see "segment 2") or r from previously established PNECs used by EU member states, were used when calculating RCR_{sum} of scrubber water. The RCR_{sum} of the characterised scrubber water were also compared to the ecotoxicological responses from whole effluent testing of the same water (EMERGE D2.3). As a final step, the RCR_{sum} of scrubber water was compared to RCR_{sum} of other liquid waste streams from onboard operations and weighted to annual discharge volumes by a model ship.

3.1 Collection of ecotoxicological data

The selection of substances to be included in the QSAR analysis was based on their previously reported occurrence in open and/or closed loop scrubber water, compiled from the dataset in EMERGE D2.1 (Appendix B) and the chemical analysis results from the EMERGE onboard campaign (EMERGE D2.2). The selection was amended with all substances included in the chemical analysis of closed loop scrubber sludge (D2.1 dataset) and the unpublished results from a collaboration with the BSH IMPEX project (Marin-Enriquez et al., 2020).

In total, 123 substances were used as input in the QSAR analysis. 60 substances were ranked as 'high priority', meaning they have been detected above the limit of detection (LOD) in at least one scrubber water or sludge sample. The substances were grouped as Inorganics, US-EPA 16 PAHs, Alkylated PAHs, PCBs & dioxins and Organics with sulphur, nitrogen or oxygen derivatives (section APPENDIX A Figures A-2 to A-5).

3.1.1 Experimental ecotoxicological data

Ecotoxicological results of single-substance exposure testing were downloaded from the US EPA knowledgebase ECOTOX in February 2023 (US EPA, 2023). The experimental dataset was then amended with ecotoxicological test results previously compiled by Verbruggen (2012) or included in the EU commissioned dossiers to derive environmental quality standards (EQS) (anthracene (Ant), fluoranthene (Fla), naphthalene (Nap) and 5-6 rings polyaromatic hydrocarbons (PAH)) (European Commission, 2022). Both freshwater and seawater species and tests were included and the data was pooled. The primary source of the empirical data from the ECOTOX database was peer-reviewed literature (US EPA, 2023) and were not further assessed with respect to reliability or relevance (such as CRED (Moermond et al., 2016)). The relevance and reliability of the data collected from Verbruggen (2012) and the EU commissioned dossiers (European Commission, 2022) have been assessed and data with a Klimisch code (Klimisch et al., 1997) of less than 2 were omitted from the dataset.

3.1.2 Modelled ecotoxicological data

The SMILES (Simplified Molecular Input Line Entry System) for each CAS were retrieved from the American Chemical Society's database SciFinder) in January 2023 (SciFinder, 2023) and used to generate toxicity predictions with three different QSAR tools; ECOSAR *v*2.2 (Wright et al., 2022), VEGA v1.1.5 (Benfenati et al., 2013) and T.E.S.T. v5.1.1.0 (Martin, 2020) (Benfenati et al., 2013; Martin, 2020; Wright et al., 2022). The QSAR models provide predicted effect concentrations of different trophic levels and endpoints (Table 3-1).

Table 3-1. Summary of the comparison between the three different QSAR tools

QSAR model	Trophic level/species	Endpoint	Reliability assessment within the separate model tools
ECOSAR *v*2.2	Fish (FW and SW)	ChV and LC50	N/A
	Daphnia	ChV and LC50	
	Mysids (FW and SW)	ChV and LC50	
	Green algae	ChV and LC50	
VEGA v1.1.5	Fish	NOEC and LC50	Experimental, good, moderate (low is omitted)
	Guppy	LC50	
	Fathead minnow	LC50	
	Daphnia	NOEC, EC50 and LC50	
	Green algae	NOEC and EC50	
T.E.S.T. v5.1.1.0	Fish	LC50	Experimental or prediction
	Daphnia	LC50	

Sludge and earthworm data were excluded from the QSAR dataset as the organisms cover environmental compartments not related to the present project. With ECOSAR, for each individual chemical and species group (fish, crustacean and algae), the predictions from the most sensitive modelled endpoint per species were selected, an approach suggested in the current ECOSAR user manual (Wright et al., 2022). The chronic effect values from ECOSAR (ChVs), i.e. the geometric mean of the NOEC and LOEC, were then divided by $\sqrt{2}$, in accordance with current guidance (ECHA, 2008), to 'recalculate' them into NOEC-values which are useable in a REACH regulatory setting. All predictions where the VEGA tool evaluated the reliability as 'low' was removed, as these datapoints are predicted out of bounds of the model.

3.1.3 Merging of the experimental and modelled dataset

All species names were checked using Tree of Life (R-package Taxize v0.9.99) to ensure that updated and correctly spelt names were used. Species taxonomic grouping was harmonized using the US EPA classification whenever available. Data were merged (n=23209) and further assessed using an in-house developed script in MATLAB. First, the effect endpoints were controlled and endpoints corresponding to mortality, growth, immobility, reproduction, feeding behaviour or abundance were kept for further analysis (n=16956).

Further filtration removed data where the endpoint specification (e.g., LC50, NOEC, EC10) or the effect concentration was lacking, resulting in a final dataset of 13501 rows. Effect concentrations were harmonized to the same unit (mg/L) and, if NOEC did not exist, recalculated based on the specified endpoint according to:

Equation 2

$$NOEC = \frac{LOEC\ or\ LOEL}{2} = \frac{MATC}{\sqrt{2}}$$

Where LOEC and LOEL are the Lowest observed Effect Concentration and Lowest Observed Effect Level and MATC is Maximal Acceptable Toxicant Concentration, also the geometric mean of NOEC and LOEC (TGD 27, European Commission, 2018). According to TGD 27, the LOEC can only be divided by 2 (Eq. 2) if the LOEC correspond to an effect percentage concentration between 10 and 20%. As raw data could not be checked for all endpoints and substances, the recalculation of LOEC(L) to NOEC was done for all substances and endpoints where NOEC values were not available.

3.2 Evaluating the output of the modelled dataset

For the evaluation of the models, the inorganic substances, i.e., metals, were exempted from the comparative analysis between modelled and experimental data due to low model performance for inorganic substances. The experimentally measured and modelled datasets were divided into two groups: acute (LC50, EC50, IC50) and chronic (NOEC, LOEC, NOEL, LOEL and EC10) and compared with respect to three trophic levels. Where possible (i.e., where both experimental and modelled data existed for the specific substance and trophic level), the experimental and modelled effect concentrations (median and minimum value) were compared for three trophic levels (algae, crustacean and fish) (Figures 4-1 and 4-2 in Results). As this segment aim to evaluate the model output, additional experimental data covering for example sea urchins were not considered for this part. However, when deriving PNEC values and comparing to measured whole effluent ecotoxicological test, all available data was included, both with respect to species (e.g., sea urchins) and substances (e.g., metals).

3.3 Deriving Predicted No Effect Concentration (PNEC) values

PNEC values were only derived for the 60 high priority substances as these have been detected in scrubber water or sludge. When deriving PNECs for each substance, three different methods were applied:

- Method 1: only experimentally measured values from the ECOTOX database or from literature (section 3.1.1) are included,
- Method 2: only the QSAR model outputs (section 3.1.2) are included
- Method 3: both the experimental and QSAR datasets are included

For all methods, the PNEC was derived in accordance with the TGD No 27 where the data availability for of the trophic levels, species and endpoints determined which method to use and what assessment factor to apply. The method for deriving a PNEC can be either deterministic, i.e., the assessment factor method, or probabilistic, i.e., the species sensitivity distribution (SSD) method (Figure 3-1).

With the deterministic approach, a critical value, i.e., the lowest available effect concentration, is divided by an assessment factor. The assessment factor will increase with increased uncertainty and can range from 10-10000 for the deterministic approach. With the probabilistic approach a curve is fitted to the median value of the most sensitive endpoint of each species and the concentration at which 5% of all species are affected (HC5 value) is determined. The HC5 value is then divided by an assessment factor between 1-5 to yield the PNEC. If less than two marine species are represented in the SSD dataset, an additional AF of 5-10 should be applied to the HC5 value but this was not applicable to the datasets presented here (Appendix A, Table A-1).The decision tree in Figure 3-1 illustrate how the assessment factors were determined. For the probabilistic approach, all assessment factors were given a default value of 5.

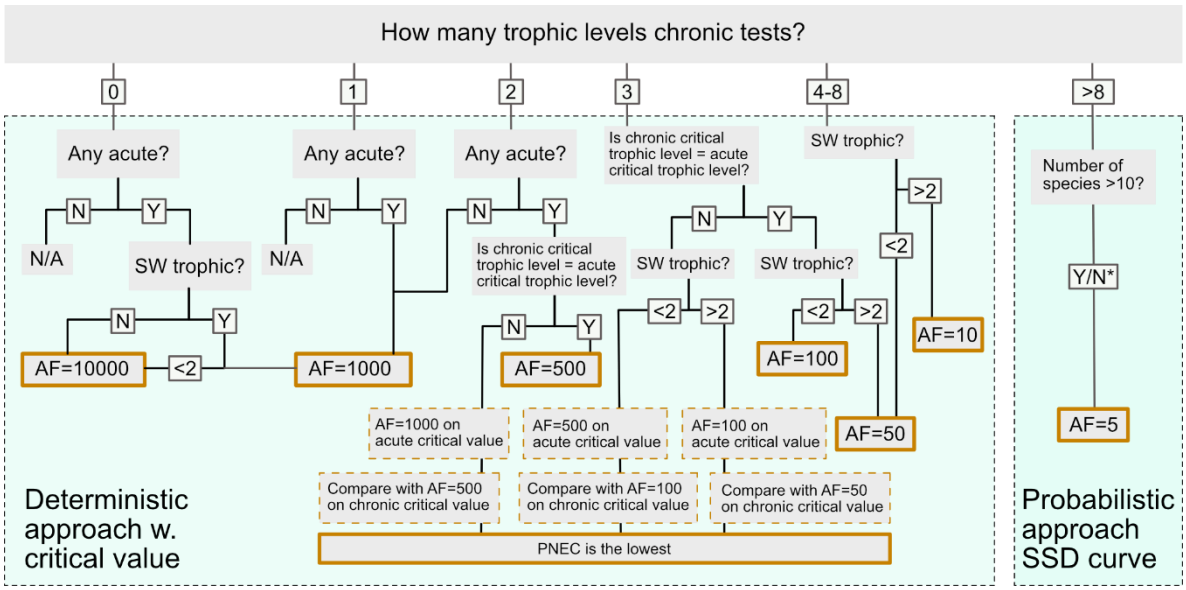

Figure 3-1. Decision tree for determining correct assessment factor (according to TGD 27) and deriving PNEC values for substances with different data availability. SW=seawater. Y=Yes. N=No. AF=Assessment Factor. If only three trophic levels are represented with chronic endpoints, the critical value trophic level should be compared to the trophic level of the acute critical value. If these are not represented by the same trophic level, a higher AF should be applied to the acute critical value and the PNEC is then the lowest value. *According to TGD 27, the required chronic values are 10 (preferably 15), covering at least 8 different trophic levels (or taxonomic groups). Here, all datasets covering >8 trophic levels have been analysed with a probabilistic approach.

3.4 Comparing predicted and actual response of scrubber water exposure

The RCR_{sum} also indicate the dilution required to reach concentrations that are considered to have acceptable risk. As an example, if a sample has RCR_{sum}=10000, this would also be the theoretical dilution required to reach RCR=1. In the same way, the theoretical dilution, required to reach $RCR_{sum} \leq 1$ for the specific scrubber water samples used in the ecotoxicological tests (Table 4-2), could be estimated. For the RCR_{sum} calculation, the final PNECs to be used for each substance were determined by selecting the lowest PNEC value from the three derivation methods (described in section 3.3) and comparing those with PNECs that have previously been derived in the REACH dossier (https://echa.europa.eu), in previous reports (EU-RAR, 2008; Verbruggen, 2012) or as part of the Water Framework Directive (Council Directive (EC), 2013). When a group of alkylated PAHs contained more than one substance (Table 3-2), the lowest PNEC of the individual substances were selected for the group.

The experimental ecotoxicological responses were based on results from EMERGE D2.3, where marine organisms were exposed to dilution series (0.0001%-50%) of open loop scrubber water from different scrubbers (Table 4-2). The dilution required to reach the no observed effect concentrations (NOECs) in the experiments could then be compared to the predicted dilution required based on the scrubber water constituents and the specific RCR_{sum} of the samples. Three different scrubber water sources were used in the ecotoxicological tests: 1) samples from Vessel 1 were collected during the EMERGE onboard campaign (EMERGE D2.2. and D3.1 *Compilation and analysis of experimental data from on-board campaigns, including emission and activity data and profiles*), 2) samples from an additional partner vessel (Vessel 2) 3) samples collected from the Chalmers pilot scrubber in Gothenburg. The scrubber water samples were analysed with respect to metals, US EPA 16 PAHs and 19 alkylated PAHs (listed in Table 3-2). The alkylated PAHs corresponded to five of the US EPA 16 PAH, and belong to 13 homologue clusters (C1, C2, C3 and C4). More information regarding the chemical analysis can be found in EMERGE D2.2.

Table 3-2. Alkylated PAHs analysed in the scrubber waters from the EMERGE onboard campaign (Vessel 1), Vessel 2, and the Chalmers pilot scrubber.

	Grouping chemical analysis	Substance name	CAS
2-rings	C1-Naphthalene-1-methyl	1-Methylnaphthalene	90-12-0
	C1-Naphthalene-2-methyl	2-Methylnaphthalene	91-57-6
	C2-Naphthalene	2,6-Dimethylnaphthalene	581-42-0
		1-Ethylnaphthalene	1127-76-0
		2-Ethylnaphthalene	939-27-5
	C3-Naphthalene	2,3,5-Trimethylnaphthalene	2245-38-7
		2-Isopropylnaphthalene	2027-17-0
	C4-Naphthalene	1,4,6,7-Tetramethylnaphthalene	13764-18-6
	C1-Fluorene	1-Methylfluorene	1730-37-6
	C2-Fluorene	1,7-Dimethylfluorene	442-66-0
3-rings	C1-Phenanthrene	1-Methylphenanthrene	832-69-9
	C2-Phenanthrene	1,3-Dimethylphenanthrene	16664-45-2
		2-Ethylanthracene	52251-71-5
	C3-Phenanthrene	1,2,6-Trimethylphenanthrene	30436-55-6
	C4-Phenanthrene	1,2,6,9-Tetramethylphenanthrene	204256-39-3
		7-Isopropyl-1-methylphenanthrene (retene)	483-65-8
4-rings	C1-Fluoranthene/Pyrene	1-Methylfluoranthene	25889-60-5
		1-Methylpyrene	2381-21-7

3.5 Ranking of potential toxicity of several waste streams

Concentrations of substances in the different waste streams were obtained from *EMERGE D2.1-* "*Database and analysis on waste stream pollutant concentrations, and emission factors",* but updated with the analytical data of scrubber discharge water produced in *EMERGE D2.2-* "*Report on measurements of dissolved and particulate contaminants in case study regions"*. The database contains concentrations of hundreds of substances identified in open- and closed loop scrubber discharge water, ballast water, grey water, sewage, bilge water, and biocides leached from antifouling paints. Cumulative risk characterization ratios (RCR_{sum}) for each waste stream *j* were calculated by dividing the average measured concentration (MC) of substance *i* by the

corresponding $PNEC_i$ or EQS_i obtained from legal documents published by the European Commission (Council Directive (EC), 2008, 2013), the Swedish Agency for Marine and Water Management (SwAM, 2019: HVMFS 2019:25), the Dutch Institute for Public Health and the Environment (Verbruggen, 2012), the GESAMP-Ballast water database (2023, see references in Appendix B), or derived using QSAR in accordance with the three different methods described in section 3.3 :

Equation 3

$$RCR_{sumj} = \sum_i \frac{MC_{ij}}{PNEC_{ij} or\ EQS_{ij}}$$

A RoPax model ship, with design and operational properties typical for RoPax ships operating in the Baltic Sea (Table 3-3), was used to compare the RCRs from different waste streams. The RoPax model ship was also used in EMERGE D2.1, where the discharge rates of open loop and closed loop scrubber water was based on 48 open loop and 8 closed loop measurements onboard ships.

Table 3-3. Data for the Baltic Sea model ship used in the analysis.

Parameter	Value	Unit
Ship Type	RoPax (ferry)	-
Gross Tonnage	40000	-
Main engine size	23	MW
Auxiliary Engine size	6.5	MW
Passengers and crew	1450	Persons
Operating time	4546	Hours/year
Scrubber	Open or closed loop	
Ballast water	6000	m^3/day
Grey water	157	L/person-day
Black water	33.1	L/person-day
Bilge water	3400	L/day
Scrubber water	90 (open loop) or 0.45 (closed loop)	m^3/MWh

Firstly, the annual discharge volumes from the different waste streams were calculated based on an operating time of 4546 hours per year. Secondly, the annual volumes were multiplied with the average RCRs of the specific waste stream to obtain a volume weighted RCR_{sum}. The number of passengers and crew was assumed to be 1450. The production rate of grey water (157 L/person-day) and sewage (33.1 L/passenger-day) are from DNV (2009) where all of the waste water streams

were expected to be discharged back to the sea. For ballast water exchange, the ship was assumed to discharge their full capacity once a day. The ballast capacity was determined by multiplying the gross tonnage with a factor collected from Hoffrén (2007 Appendix 2). RoPax vessels were not included in the ballast water survey and an average factor from passenger ferries (0.09) and RoRo vessels (0.21) resulted in 6000 m^3/day of ballast water to be discharged (factor 0.15). The ship was assumed to have either an open or a closed loop scrubber for SO_X abatement on the main engine and operated on an average load of 75%. The annual discharge volumes per waste stream is shown in Table 3-4.

Table 3-4. Total annual volumes discharged (L) from the model ship, per waste stream

Waste stream	Annual volume discharged (L)
Open loop scrubber	7.1E+09
Closed loop scrubber	3.5E+07
Bilge water	6.4E+05
Ballast water	1.1E+09
Sewage	9.1E+06
Grey water	4.3E+07

4 RESULTS AND DISCUSSION

4.1 Comparing model vs. experimental data

The experimentally measured ecotoxicological effect concentrations, both acute (LC50 and EC50) and chronic (NOEC, EC10) were compared to the predicted ecotoxicological effect concentrations from the three QSAR models (ECOSAR, VEGA, T.E.S.T.) for three trophic levels (fish, crustacean and algae) (Figure 4-1, full data set and Figure 4-2, 'high priority' data set). For each substance, the chronic and acute effect concentrations of fish, crustaceans and algae were compared with respect to the median (Figures 4-1 and 4-2, A and C) and minimum (Figures 4-1 and 4-2, A and C) values, from the modelled dataset (X-axis) and the experimentally measured dataset (Y-axis). Both freshwater and seawater species were included if they belonged to one of the selected trophic levels (fish, crustaceans and algae) covered by the QSAR models. The results show that the model output tend to indicate a lower acute toxicity response compared to experimental data (Figure 4-1, C and D) while the chronic comparison show deviations in both directions where the modelled toxicity response of algae is generally lower while the toxicity responses of fish and crustaceans are more frequently higher as compared to experimental data (Figure 4-1, A and B).

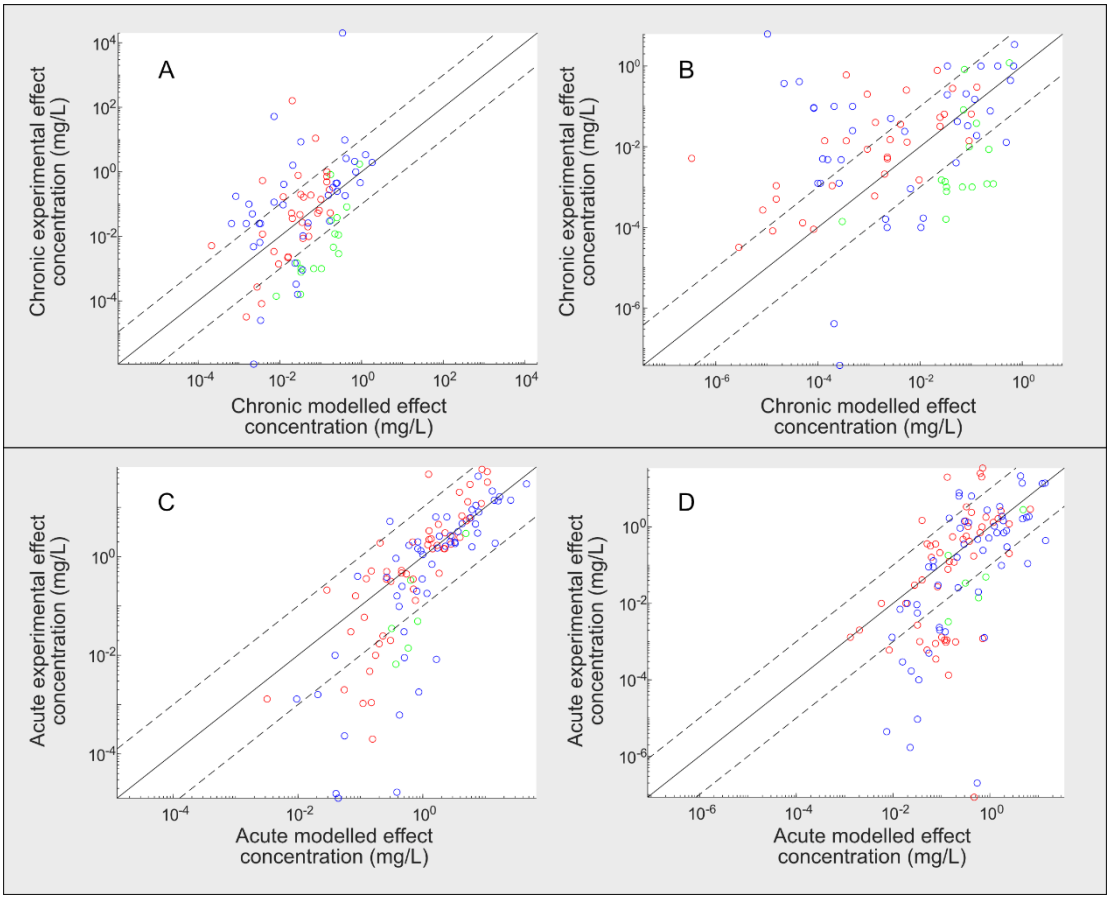

Figure 4-1. Log-log scatter plots comparing modelled effect concentrations to experimentally measured effect concentrations of three trophic levels: algae (green), crustacean (red) and fish (blue). The full dataset was used. Top panel (A and B) shows results of chronic values and lower panel (C and D) shows acute. The left-hand side (A and C) shows the calculated median effect concentrations, and the right side (B and D) shows the minimum effect concentration. The full line marks the 1:1 ratio and the dashed lines define one order of magnitude deviation. Points above the full line indicate that the models predict a higher toxicity compared to experimental data and points found below the full line represent cases where the models predict a lower toxicity as compared to experimental data. Number of substances in each figure are listed in Table A-3.

When omitting low priority substances i.e., when only the substances that have been detected >LOD in scrubber water or sludge are included, the number of chronic datapoints deviating with more than one order of magnitude (outside the dashed lines) decrease marginally from 40% to 38% for the median values and from 50% to 48% for minimum values (Figure 4-1).

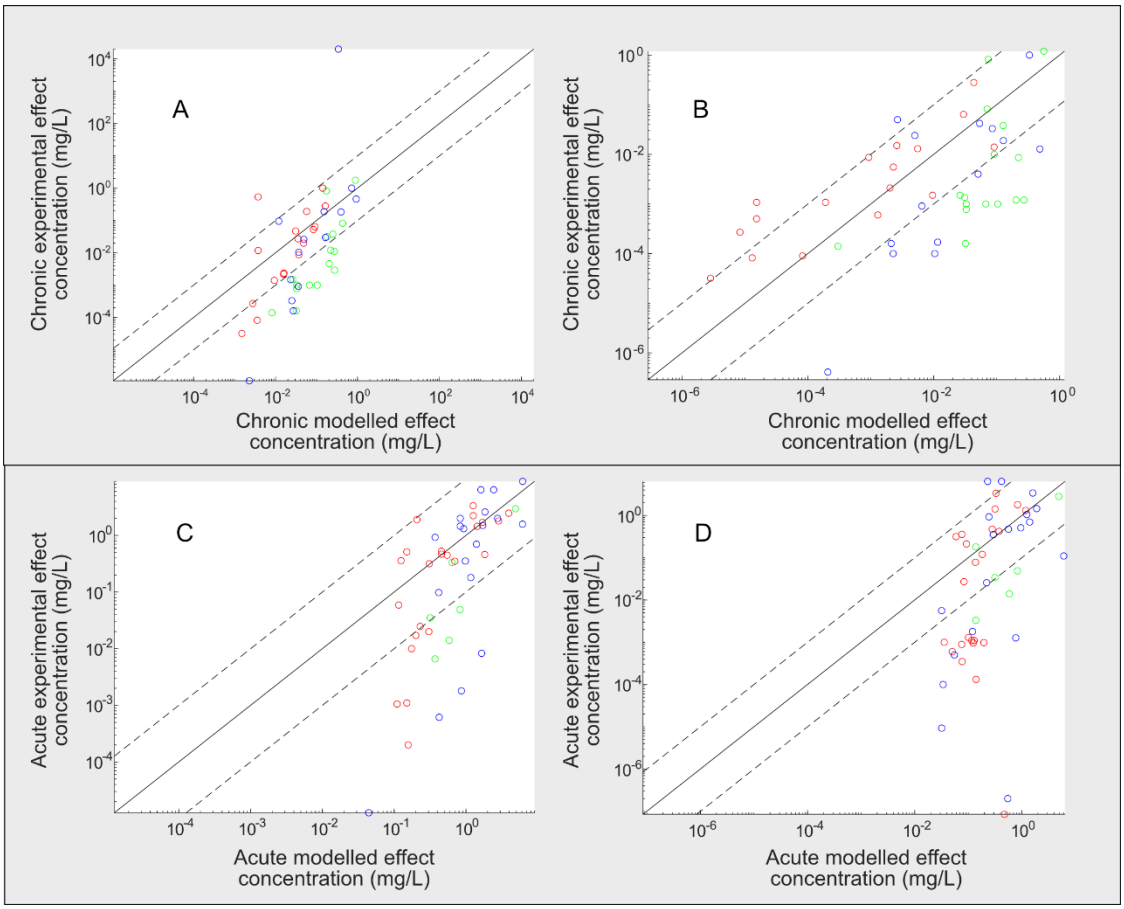

Figure 4-2. Log-log scatter plots comparing modelled effect concentrations to experimentally measured effect concentrations of three trophic levels: algae (green), crustacean (red) and fish (blue). Only high priority substances were selected. Top panel (A and B) shows results of chronic values and lower panel (C and D) shows acute. The left-hand side (A and C) shows the calculated median effect concentrations, and the right side (B and D) shows the minimum effect concentration. The full line marks the 1:1 ratio and the dashed lines define one order of magnitude deviation. Points above the full line indicate that the models predict a higher toxicity compared to experimental data and points found below the full line represents cases where the models predict a lower toxicity as compared to experimental data. Number of substances in each figure are listed in Table A-3.

For both fish and crustacean, the models indicate higher chronic toxicity of some of the chlorinated benzene/benzol substances, PCBs and phenols. The toxicity of the same substances is better predicted with the acute endpoints but then the model performs poorly, i.e. the predicted toxicity is lower as compared to experimental data of several PAHs (e.g., BaA, Ant and BghiP). In the chronic dataset, the modelled toxicity of the larger PAHs (e.g., BbF, BaP and BghiP) appears to be lower for crustaceans but, at the same time, higher for algae and fish as compared to experimental

data (Appendix, Figure A1). As shown with the full dataset, the model output of high priority substances is lower for the acute toxicity (Figure 4-2, C and D).

It should be noted here that during development the models are fitted against data from a set of different species per trophic group. Thus, within each trophic group the models will estimate the toxicity towards an average species. The accuracy of the predictions when compared against experimentally measurements from the most sensitive species will thus be lower than when compared to the average species. However, the same problem of course occurs if only one species is tested experimentally for an individual chemical as there is no way of knowing how sensitive that species is in relation to all others within the trophic group. When models do not manage to represent the most sensitive species or trophic levels, there are large deviations between modelled and experimental output. As the models will be fitted to match the average (tested) species (Figure 4-1 and Figure 4-2 A and C), there is a continued risk for underestimating toxicity.

4.2 Comparing PNEC derivation scenarios

PNEC values were derived for a total of 60 substances applying the three different methods: 1) only include experimentally measured values, 2) only base the derivation on model output or 3) combine the experimental and modelled dataset. All the derived PNEC values, including the applied assessment factor, can be found in the Appendix, Table A-1. Most PNEC values were derived using the deterministic approach. For methods 1 and 3, seven and eight substances fulfilled the requirements for a probabilistic approach, deriving HC5 values from an SSD curve (Table A-2 Appendix).

From method 1, a total of 27 PNEC values (Figure 4-3) could be derived and compared to the PNEC derived by method 2 (the model output). For most of the substances, the PNEC derivation from the model results in lower PNECs than from the ecotoxicological data. Despite the modelled effect data generally indicate a lower toxicity than experimental derived effect data set (Figure 4-2), the model derived PNECs are in many cases lower, i.e., more protective, than the PNEC derived from the experimental dataset. This can be explained by the higher assessment factor applied to the model dataset (Table A-1), due to less representation of seawater species and fewer trophic levels. The comparison suggests that, for this specific dataset, the model result may be protective in accordance with the precautionary principle. There are however some substances (e.g., dibenzothiophene, BaA and naphthalene-2-methyl, 2,3,7,8-tetraCDF) where the model output

result in higher PNEC values and for these substances there is a risk to underestimate the effects if their model-based PNEC values are used.

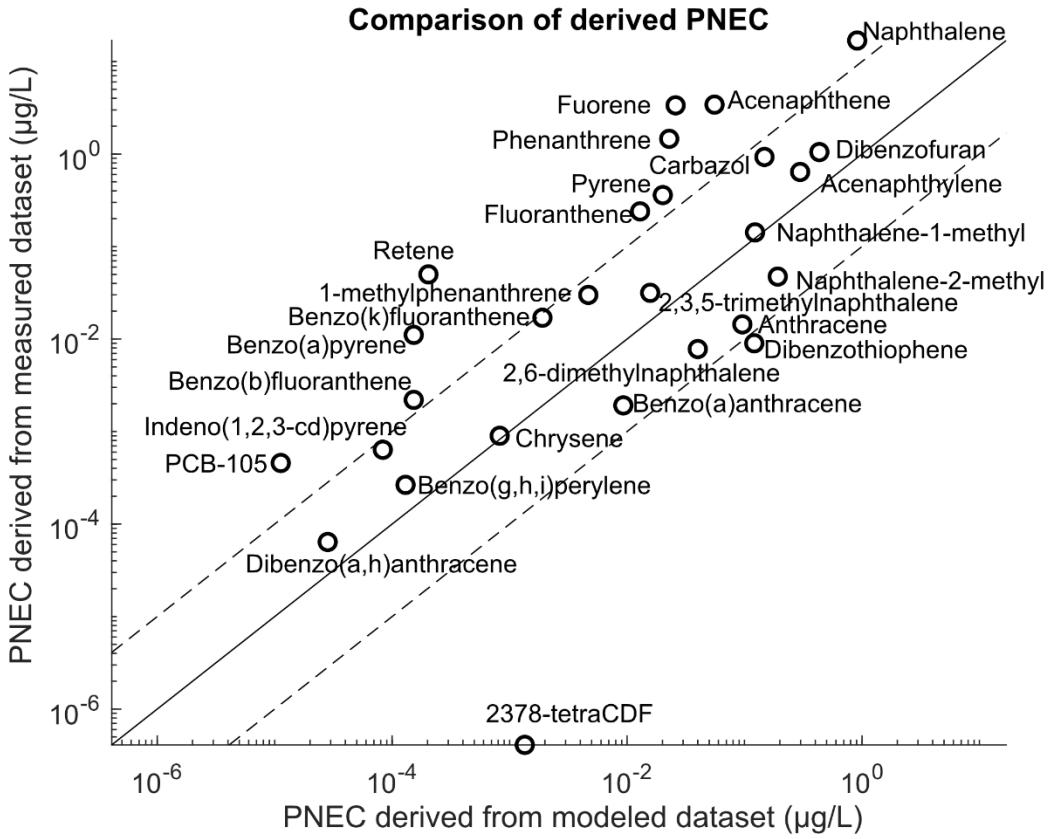

Figure 4-3. Comparison of 27 PNEC values (µg/L) derived from method 1 (only including experimentally measured ecotoxicological data) and scenario 2 (only including model output). The full line marks the 1:1 ratio and the dashed lines define one order of magnitude deviation. Substance names are indicated for each point.

4.3 Comparing predicted risk and measured responses of scrubber water exposure on marine species

The lowest derived $PNEC_{M1-3}$ from the three different methods (section 3.3) can be compared to the $PNEC_{final}$, i.e., the lowest PNEC from all derivations, in Table 4-1. The lowest PNECs, i.e., $PNEC_{final}$ for each substance, were selected when comparing predicted and measured ecotoxicological response due to scrubber water exposure. The EQS values for substances listed as priority substances (Council Directive (EC), 2013) or as river basin specific pollutants (SwAM, 2019) were often found to be the lowest. The derivation of EQS values within the Water Framework

Directive, consider all matrices, including toxicity due to human consumption, and may thus generate much lower PNEC values compared to if only the water column concentration is considered. This can explain some of the discrepancies found, e.g., Fluoranthene (Table 4-1). For all of the alkylated PAHs, the lowest $PNEC_{M1-3}$ were applied, mostly based on the modelled or combined data output (method 2 or 3).

Table 4-1. Final PNEC values (µg/L), $PNEC_{M1-3}$ refers to the lowest PNEC value derived from method 1, 2 or 3 described in section 3.3.

		$PNEC_{M1-3}$ (µg/L)	$PNEC_{final}$ (µg/L)	Source $PNEC_{final}$
Alkylated PAH	Naphthalene-2-methyl	4.74×10^{-2}	4.74×10^{-2}	Section 3.3 this report, Method 1
Alkylated PAH	Naphthalene-1-methyl	1.23×10^{-1}	1.23×10^{-1}	Section 3.3 this report, Method 3
Alkylated PAH	Naphthalene-C2	7.80×10^{-3}	7.80×10^{-3}	Section 3.3 this report, Method 1
Alkylated PAH	Naphthalene-C3	1.46×10^{-2}	1.46×10^{-2}	Section 3.3 this report, Method 3
Alkylated PAH	Naphthalene-C4	1.70×10^{-3}	1.70×10^{-3}	Section 3.3 this report, Method 2
Alkylated PAH	Phenanthrene-C1	4.68×10^{-3}	4.68×10^{-3}	Section 3.3 this report, Method 3
Alkylated PAH	Phenanthrene-C2	9.53×10^{-4}	9.53×10^{-4}	Section 3.3 this report, Method 2
Alkylated PAH	Phenanthrene-C3	1.67×10^{-3}	1.67×10^{-3}	Section 3.3 this report, Method 2
Alkylated PAH	Phenanthrene-C4	2.04×10^{-4}	2.04×10^{-4}	Section 3.3 this report, Method 2
Alkylated PAH	Fluorene-C1	9.65×10^{-3}	9.65×10^{-3}	Section 3.3 this report, Method 2
Alkylated PAH	Fluorene-C2	7.24×10^{-3}	7.24×10^{-3}	Section 3.3 this report, Method 2
Alkylated PAH	Fluoranthene-Pyrene-C1	1.45×10^{-3}	1.45×10^{-3}	Section 3.3 this report, Method 2
USEPA 16 PAH	Acenaphthene	2.26×10^{0}	3.80×10^{-1}	EU RAR CTPHT (2008); Verbruggen (2012)
USEPA 16 PAH	Acenaphthylene	5.95×10^{-1}	1.30×10^{-1}	EU RAR CTPHT (2008); Verbruggen (2012)
USEPA 16 PAH	Anthracene	1.44×10^{-2}	1.44×10^{-2}	Section 3.3 this report, Method 1 (*AA-EQS=0.1 µg/L)
USEPA 16 PAH	Benzo(a)anthracene	1.92×10^{-3}	1.20×10^{-3}	EU RAR CTPHT (2008); Verbruggen (2012)
USEPA 16 PAH	Benzo(a)pyrene	7.84×10^{-3}	1.70×10^{-4}	AA-EQS marine (EU, 2013)
USEPA 16 PAH	Benzo(b)fluoranthene	3.06×10^{-4}	3.06×10^{-4}	Section 3.3 this report, Method 3
USEPA 16 PAH	Benzo(g,h,i)perylene	2.60×10^{-4}	2.60×10^{-4}	Section 3.3 this report, Method 3
USEPA 16 PAH	Benzo(k)fluoranthene	1.69×10^{-2}	1.69×10^{-2}	Section 3.3 this report, Method 3
USEPA 16 PAH	Chrysene	9.00×10^{-4}	9.00×10^{-4}	Section 3.3 this report, Method 1

USEPA 16 PAH	Dibenzo(a, h)anthracene	5.66×10^{-5}	5.66×10^{-5}	Section 3.3 this report, Method 3
USEPA 16 PAH	Fluoranthene	2.40×10^{-1}	7.60×10^{-4}	Newly proposed AA-EQS marine (European Commission, 2022)
USEPA 16 PAH	Fluorene	1.74×10^{0}	2.50×10^{-1}	EU RAR CTPHT (2008); Verbruggen (2012)
USEPA 16 PAH	Indeno(1,2,3-cd) pyrene	1.67×10^{-4}	1.67×10^{-4}	Section 3.3 this report, Method 3
USEPA 16 PAH	Naphthalene	1.53×10^{1}	2.00×10^{0}	AA-EQS marine (Council Directive (EC), 2013)
USEPA 16 PAH	Phenanthrene	1.12×10^{0}	1.10×10^{0}	REACH (https://echa.europa.eu/regulations/reach/understanding-reach)
USEPA 16 PAH	Pyrene	3.60×10^{-1}	2.30×10^{-2}	EU RAR CTPHT (2008); Verbruggen (2012)
Metals	Arsenic		5.50×10^{-1}	HVMSF 2019:25 (SWaM 2019)
Metals	Cadmium		2.00×10^{-1}	AA-EQS marine (Council Directive (EC), 2013)
Metals	Chromium		3.40×10^{0}	HVMSF 2019:25 (SWaM 2019)
Metals	Copper		1.45×10^{0}	HVMSF 2019:25 (SWaM 2019)
Metals	Lead		1.30×10^{0}	AA-EQS marine (Council Directive (EC), 2013)
Metals	Mercury		6.70×10^{-2}	REACH (https://echa.europa.eu/regulations/reach/understanding-reach)
Metals	Nickel		8.60×10^{0}	AA-EQS marine (Council Directive (EC), 2013)
Metals	Vanadium		2.50×10^{0}	REACH (https://echa.europa.eu/regulations/reach/understanding-reach)
Metals	Zinc		1.10×10^{0}	HVMSF 2019:25 (SWaM 2019)

The sum of the RCRs of the individual open loop scrubber water, used in the different ecotoxicological tests, were calculated according to Equation 1. The substance concentrations in the specific scrubber waters (EMERGE D2.2) were compared to the substance specific $PNEC_{final}$ listed in Table 4-1. The results from the current study indicate that the alkylated PAHs, that have previously not been included when assessing the environmental risk of scrubber water, could contribute to more than 85% of the cumulative risk (Figure 4-4). However, it must be emphasized that the QSAR models holds high uncertainties and future ecotoxicological studies should focus on testing how toxic these alkylated PAHs are for marine species (and ecosystems) in order to confirm the results.

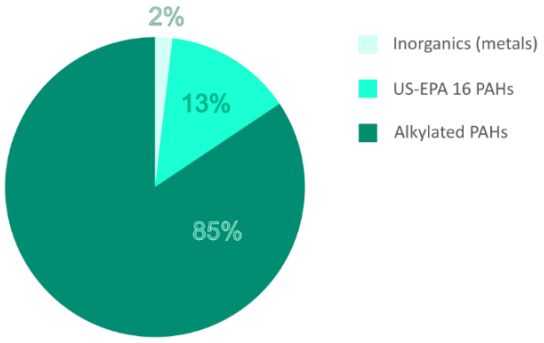

Figure 4-4. Relative contribution to the average cumulative risk quotient, calculated for open loop scrubber water from the EMERGE onboard campaign. The RCR_{sum} was 13342.

The predicted required dilution ratio was compared to the ecotoxicological responses in the whole effluent tests performed within EMERGE and described in D2.3. The exposure concentrations (in % scrubber water) from the ecotoxicological tests were recalculated to dilution ratios to enable comparison (Table 4-2). Although highly variable, the result suggests that by including alkylated PAHs, the prediction of toxicity of scrubber water can be improved (Figure 4-4). However, even when alkylated PAHs are included, the prediction does not manage to protect the most sensitive species (Table 4-2).

Table 4-2. Experimental ecotoxicological test results from EMERGE D2.2 and the predicted dilution ratios required to reach $RCR_{sum} \leq 1$ based on scrubber water constituents. The last two columns compare the predicted dilution required if alkylated PAHs are included or not. Laboratorys: University of Venice=UNIVE, University of Aveiro=UAV, University of Southampton=US

Laboratory	Scrubber water sample	Species	End-point	NOEC from ecotoxicological test (% scrubber water)	LOEC from ecotoxicological test	Dilution ratio (based on NOEC from ecotoxicological test)	Predicted dilution ratio (only metals and US-EPA 16 PAHs)	Predicted dilution ratio (metals, US-EPA 16 PAHs & alkylated PAHs)
UNIVE	Chalmers	*Acartia tonsa*	Egg production	0.001	0.01	100000	399	N/A
UNIVE	Chalmers	*Acartia tonsa*	Larval development	<0.01	0.01	>10000	399	N/A
UNIVE	Vessel 1 (nr 10)	*Acartia tonsa*	Egg production	0.001	0.01	100000	2193	15562
UNIVE	Vessel 1 (nr 10)	*Acartia tonsa*	Larval development	0.01	0.1	10000	2193	15562
UNIVE	Vessel 1 (nr 10)	*Mytilus galloprovincialis*	Larval development	0.1	1	1000	2193	15562
IVL	Vessel 1 (nr 1)	*Strongylocentrotus droebachiensis*	Egg fertilization	<0.0001	0.0001	>1000000	2297	13225
IVL	Vessel 1 (nr 1)	*Strongylocentrotus droebachiensis*	Malform. of larvae	<0.0001	0.0001	>1000000	2297	13225
IVL	Defined in Thor et al 2018	*Calanus helgolandicus*	Egg fertilization	0.01	0. 1	10000		
UAV	Chalmers	*Paracentrotus lividus*	Malform. of larvae	0.001	0.01	100000	196	599
UAV	Chalmers	*Paracentrotus lividus*	Egg fertilization	<0.01	0.01	>10000	196	599
UAV	Vessel 2	*Paracentrotus lividus*	Egg fertilization	<0.01	0.01	>10000	389	5808
UAV	Vessel 2	*Paracentrotus lividus*	Malform. of larvae	<0.001	0.001	>100000	389	5808
UAV	Vessel 1 (nr 1)	*Sabellaria alveolata*	Malform. of larvae	<0.001	0.001	>100000	2297	13225
UAV	Vessel 2	*Sabellaria alveolata*	Malform. of larvae	0.001	0.01	100000	389	5808
UAV	Chalmers	*Sabellaria alveolata*	Malform. of larvae	0.001	0.01	100000	196	599
UAV	Vessel 1 (nr 1)	*Paracentrotus lividus*	Fertilization success	0.01	0.1	10000	2297	13225
UAV	Vessel 2	*Paracentrotus lividus*	Fertilization success	1.56	3.13	64	389	5808
US	Chalmers	*Mytilus edulis*	Malform. of larvae	<0.001	0.001	>100000	?	?
US	Vessel 2	*Mytilus edulis*	Malform. of larvae	<0.001	0.001	>100000	?	?

4.4 Ranking of potential toxicity of different waste streams from ships

The RCR_{sum} of both open and closed loop scrubber discharge water is substantially higher than the RCR_{sum} from the other four waste streams (Figure 4-5).

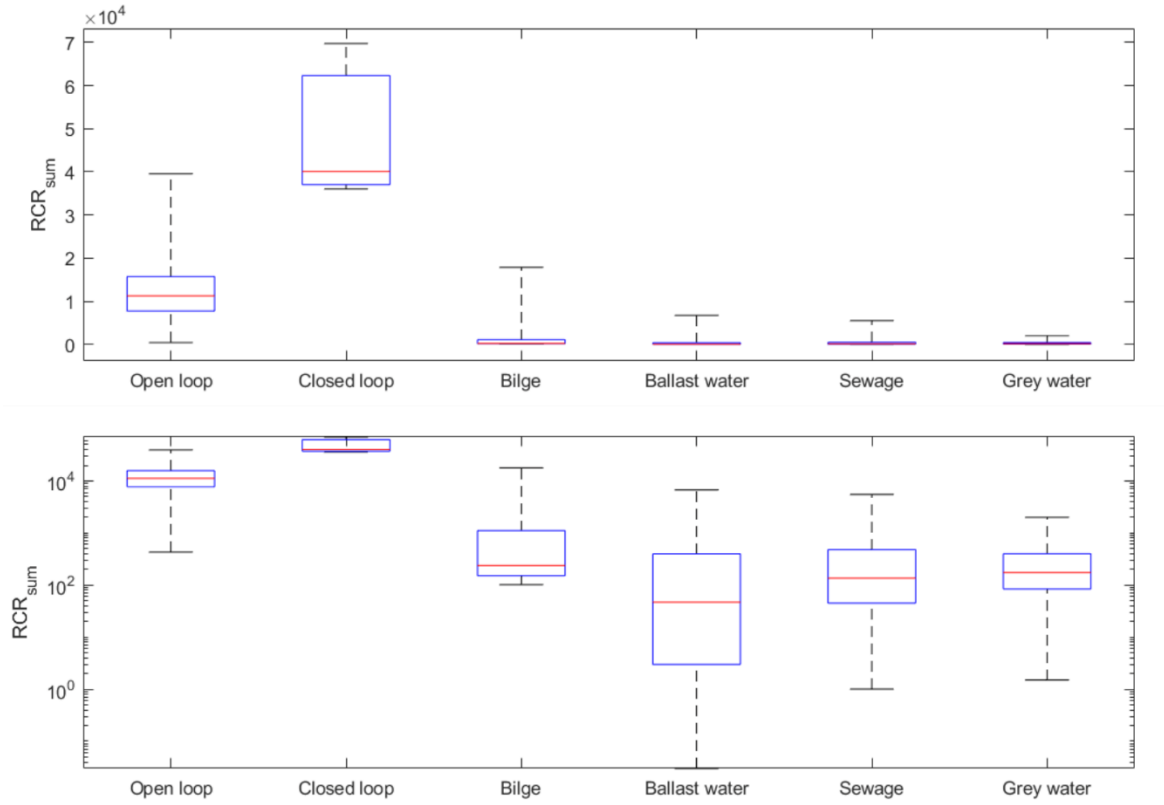

Figure 4-5. Comparing RCR_{sum} of five waste streams from ships. The y-axis on the lower panel is in log_{10}-scale for better comparison of the waste streams with lower RCR_{sum}.

To be able to compare the risk in the environment from the waste streams the volume of each stream must be considered. Therefore, the RCR_{sum} of the five liquid waste streams (Figure 4-5) were multiplied with the respective annual volumes discharged from the RoPax model ship (Table 3-4). Two scenarios were developed; i) the model ship is operating with an open loop scrubber and ii) the model ship is operating with a closed loop scrubber. In both scenarios, scrubbers were responsible for almost the entire volume weighted RCR_{sum}, 99.9% in the open loop scenario and 94.3% in the closed loop scenario. The results also showed that open loop scrubbers are responsible for a considerably higher volume weighted RCR_{sum} (7.9E+13) compared to if the ship is operating the scrubber in closed loop mode (1.4E+12) (Table 4-1).

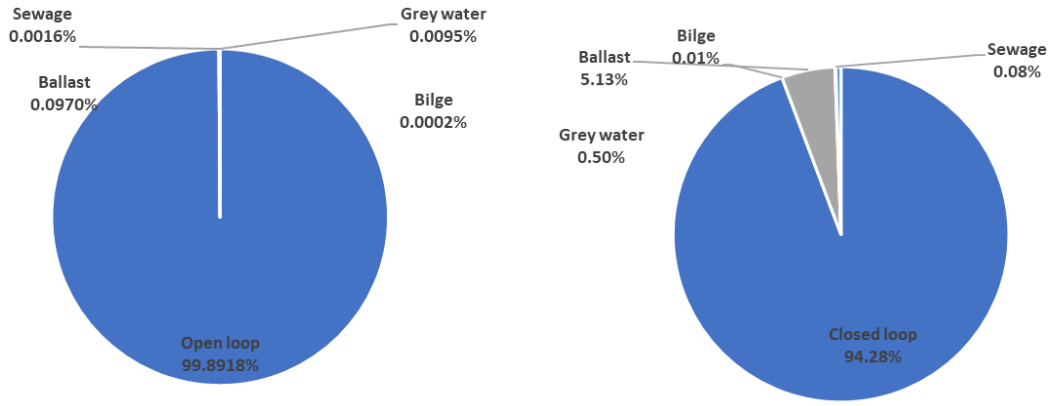

Figure 4-6. Relative (%) contribution of different liquid waste streams to the volume weighted RCR_{sum} for the RoPax model ship. The left panel shows the scenario where the ship operates with an open loop scrubber and the right panel shows the closed loop scrubber scenario.

Table 4-3. Annual volume weighted RCR_{sum} of different liquid waste streams determined for the RoPax model ship.

Waste stream	Volume weighted RCR_{sum}
Open loop scrubber	7.93E+13
Closed loop scrubber	1.42E+12
Bilge water	1.53E+08
Ballast water	7.70E+10
Sewage	1.24E+09
Grey water	7.50E+09

5 CONCLUSIONS

QSAR models can be helpful tools when identifying emerging substances of concern. The results show that when alkylated PAHs are included in this risk assessment approach, based on PNECs derived from the QSAR model output, the prediction of risks of open loop scrubber discharge water better reflects reality compared to when only including metals and US EPA 16 PAHs. The analysis also suggest that alkylated PAHs could have a significant contribution to the RCR_{sum} of scrubber water. In addition, given that ecotoxicological studies in D.2.3 have shown adverse effects at very low concentrations of scrubber water (<0.0001 %), the results from this study indicate that alkylated PAHs need to be included in future assessments. It should also be stressed that the benefit of using the RCR_{sum} approach is that different waste streams can be compared, but the accuracy of the method depends on how well characterized the waste streams are in terms of the number of substances that are chemically analysed and if PNEC values are available for the substances. Thus, given that open loop scrubber discharge water is a complex mixture of low, but variable, pH, holding numerous organic and inorganic substances, it is a great challenge to predict the magnitude of the risk based on the detected compounds' PNEC values and measured concentrations in the scrubber discharge water. In that perspective, whole effluent tests are more suitable for detecting adverse biological responses. However, the weakness with whole effluent tests is that they are time-consuming and costly and will not resolve which substances that are mainly responsible for the observed response. Hence, both methods, i.e., RCR_{sum} approach and whole effluent tests, are important complements to each other in assessing risks for adverse environmental effects from scrubber discharge water. The high concentrations of hazardous substances and the ecotoxicological response of scrubber discharge water suggest that scrubber water discharges will have adverse effects on the marine environment.

It is evident that the RCR_{sum} of open and closed loop scrubbers are substantially higher than the RCR_{sum} of other liquid waste streams. This is even more evident when the waste streams' volume weighted RCR_{sum} are compared as the open loop scrubber discharge contributes more than 99% of the overall RCR_{sum} from annual operations on a model RoPax vessel. For future outlook, the concept of comparing weighted RCR_{sum} should also be applied to non-liquid waste streams such as biocides released from antifouling paint or air emissions and their consequential depositions. These topics will be further explored in the EMERGE work packages WP6: Synthesis and integration of the results and WP7: Cost-efficient methods for mitigating and reducing the emissions and impacts.

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APPENDIX A

Table A-1. Derived $PNEC_{QSAR}$ from Method 1 (experimental), Method 2 (modelled) and Method 3 (combined) including their respective assessment factor.

	Derived PNEC value (µg/L)			Assessment factor		
Substance	**Method 1**	**Method 2**	**Method 3**	**Method 1**	**Method 2**	**Method 3**
1-ethylnaphthalene		3.04E-02	3.04E-02		100	100
Anthracene	1.44E-02	9.58E-02	3.33E-02	5	100	5
4,6-Dimethyldibenzothiophene		5.03E-03	5.03E-03		100	100
Pyrene	3.60E-01	2.01E-02	3.60E-01	5	100	5
dibenzofuran	1.05E+00	4.34E-01	4.34E-01	1000	100	500
Dibenzothiophene	9.00E-03	1.21E-01	1.21E-01	10 000	100	500
1,4,6,7-tetramethylnaphthalene		1.70E-03	1.70E-03		100	100
3,6-dimethylphenanthrene		2.83E-03	2.83E-03		500	500
3-Methyldibenzothiophene		2.47E-02	2.47E-02		100	100
1,3-dimethylphenanthrene		9.53E-04	9.53E-04		500	500
1-methylfluorene		9.65E-03	9.65E-03		100	100
2,4,6-Trimethyldibenzothiophene		1.02E-03	1.02E-03		500	500
Benzo(g,h,i)perylene	2.65E-04	1.30E-04	2.60E-04	500	500	50
Indeno(1,2,3-cd) pyrene	6.36E-04	8.33E-05	1.67E-04	1000	500	50
Benzo[c]phenanthrene		8.24E-04	8.24E-04		500	500
2-isopropylnaphthalene		1.46E-02	1.46E-02		100	100
1,2-dimethylphenanthrene		9.53E-04	9.53E-04		500	500
1,2,6,9-Tetramethylphenanthrene		3.38E-04	3.38E-04		500	500
Benzo(b)fluoranthene	2.20E-03	1.53E-04	3.06E-04	500	500	50
Fluoranthene	2.40E-01	1.29E-02	2.40E-01	5	500	5
Benzo(k)fluoranthene	1.70E-02	1.90E-03	1.69E-02	10	500	5
Acenaphthylene	6.40E-01	2.97E-01	5.95E-01	500	500	50
2-Methyldibenzothiophene		1.31E-01	3.55E-02		1000	1000
1,3,7-trimethylnaphthalene		1.71E-02	1.71E-02		100	100
1,2,5,6-tetramethylnaphthalene		1.70E-03	1.70E-03		100	100
2,4,7-Trimethyldibenzothiophene		1.02E-03	1.02E-03		500	500
Chrysene	9.00E-04	8.24E-04	1.65E-03	100	100	50
2,3,5-trimethylnaphthalene	3.16E-02	1.57E-02	1.57E-02	10 000	100	100
1-methylpyrene		4.09E-03	4.09E-03		500	500
1-methylfluoranthene		1.45E-03	1.45E-03		500	500
1,2,6-trimethylphenanthrene		1.67E-03	1.67E-03		500	500
1-Methyl-dibenzothiophene		2.68E-02	2.68E-02		100	100
PCB-118		1.13E-05	1.13E-05		100	100
3,6-Dimethyldibenzothiophene		2.19E-02	2.19E-02		1000	1000
PCB-105	4.57E-04	1.13E-05	1.13E-05	10 000	100	500
PCB-156		2.87E-06	2.87E-06		100	100

1,7-dimethylfluorene		7.24E-03	7.24E-03		500	500
1-methyl-7-isopropyl-phenanthrene (Retene)	5.00E-02	2.04E-04	2.04E-04	1000	100	100
Benzo(a)pyrene	1.11E-02	1.53E-04	7.84E-03	5	500	5
2378-tetraCDF	4.10E-07	1.35E-03	4.10E-06	1000	100	100
2-ethylanthracene		4.74E-03	4.74E-03		500	500
PCB-167		3.38E-06	3.38E-06		100	100
Dibenzo(a, h)anthracene	6.40E-05	2.83E-05	5.66E-05	500	500	50
Benzo(a)anthracene	1.92E-03	9.29E-03	1.86E-02	500	500	50
2,6-dimethylnaphthalene	7.80E-03	4.00E-02	4.00E-02	10 000	100	100
1,2,5-trimethylnaphthalene		1.71E-02	1.71E-02		100	100
2,6,9-trimethylphenanthrene		1.67E-03	1.67E-03		500	500
1234678-heptaCDF		6.24E-05	6.24E-05		500	500
123478-HexaCDF		7.71E-06	7.71E-06		500	500
4-Methyldibenzothiophene		2.47E-02	2.47E-02		100	100
1-methylphenanthrene	3.00E-02	4.68E-03	4.68E-03	10 000	500	500
Acenaphthene	3.42E+00	5.55E-02	2.26E+00	5	100	5
Phenanthrene	1.46E+00	2.28E-02	1.12E+00	5	100	5
Fuorene	3.36E+00	2.59E-02	1.74E+00	5	100	5
carbazol	9.30E-01	1.48E-01	2.96E-01	1000	500	50
2,6-Dimethyldibenzothiophene		1.15E-01	2.26E-02		1000	1000
Naphthalene-1-methyl	1.42E-01	1.23E-01	1.23E-01	10 000	100	100
Naphthalene	1.69E+01	9.10E-01	1.53E+01	5	100	5
Naphthalene-2-methyl	4.74E-02	1.92E-01	1.92E-01	10 000	100	100
2-ethylnaphthalene		4.74E-02	4.74E-02		100	100

Table A-2. Summary of ecotoxicological test result for the derivation of HC5 value with the probabilistic approach (SSD curve)

	Number of species Combined dataset Method 3	Number of species measured Measured dataset Method 1	Number of marine species Combined	Number of marine species Measured
Acenaphthene	12	8	5	3
Antracene	19	16	6	4
Benzo[a]pyrene	25	21	13	11
Benzo[k]fluoranthene	9	-	4	
Fluoranthene	40	36	21	19
Fluorene	11	8	4	2
Naphthalene	38	35	20	18
Phenanthrene	37	34	18	16
Pyrene	23	19	13	11

Table A-3. Number of substances where chronic and acute effect concentration from QSAR models could be compared to experimentally measured effect concentrations (Figures 4-1 and 4-2).

			Number of substances for comparison		
			Fish	Crustacean	Algae
Figure 4-1A	Full dataset	Chronic Median	38	32	16
Figure 4-1B	Full dataset	Chronic Minimum	38	32	16
Figure 4-1C	Full dataset	Acute Median	54	52	6
Figure 4-1D	Full dataset	Acute Minimum	54	52	6
Figure 4-2A	High priority	Chronic Median	14	17	16
Figure 4-2B	High priority	Chronic Minimum	14	17	16
Figure 4-2C	High priority	Acute Median	19	23	6
Figure 4-2D	High priority	Acute Minimum	19	23	6

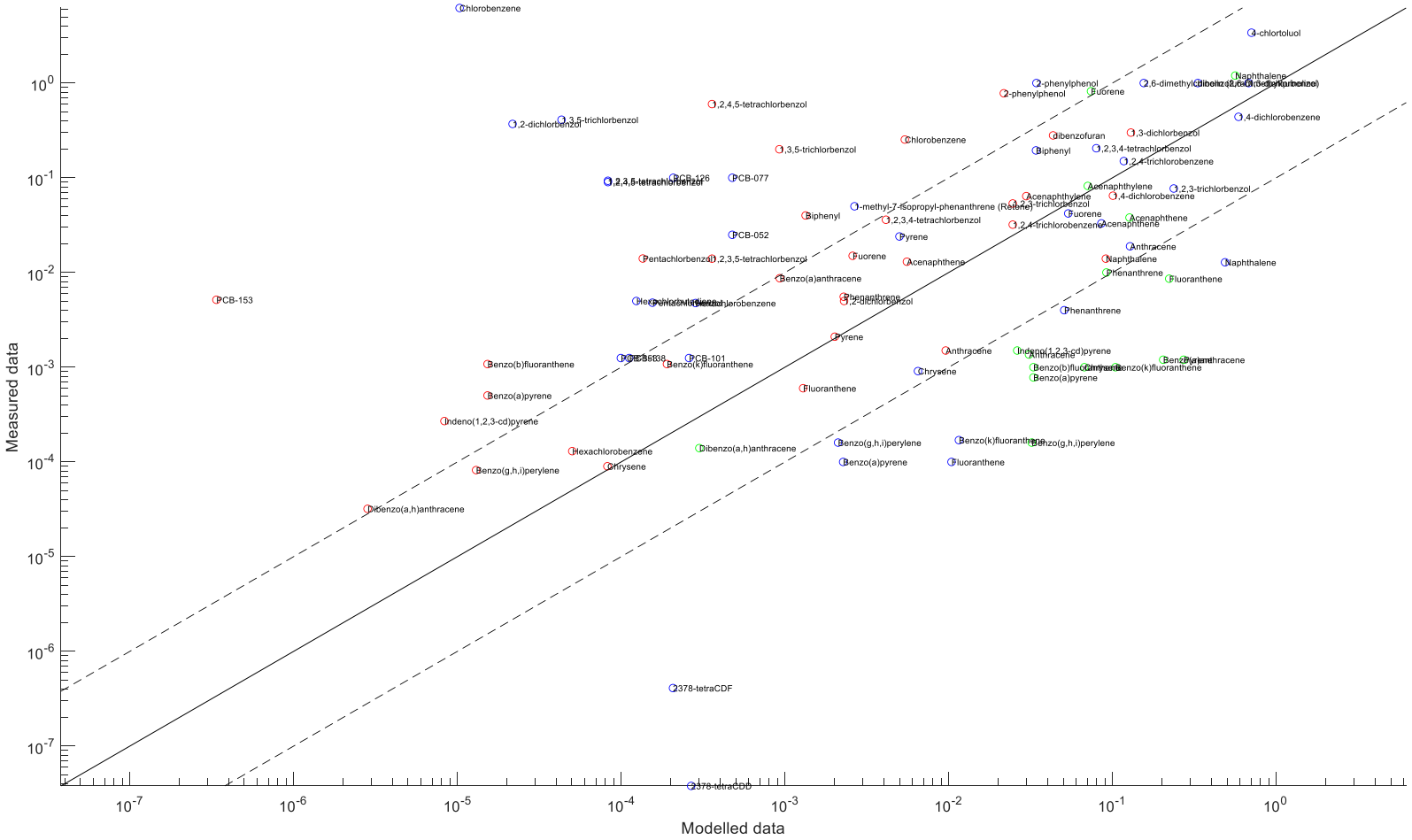

Figure A-1. Same as Figure 4-1B, but with name attached to the substances (zoom in for better overview).

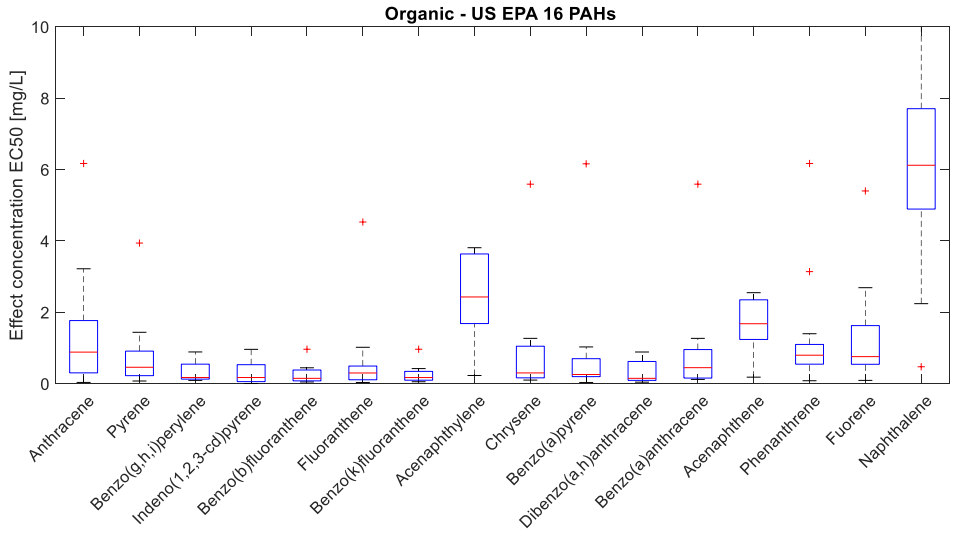

Figure A-2. Effect concentration of 50% of the population according to QSAR model output (ECOSAR, VEGA and T.E.S.T) for the US-EPA 16 PAHs. The red line shows the median value the box covers the 25-75 percentile, the whiskers the 5 and 95 percentile and red crosses mark outliers.

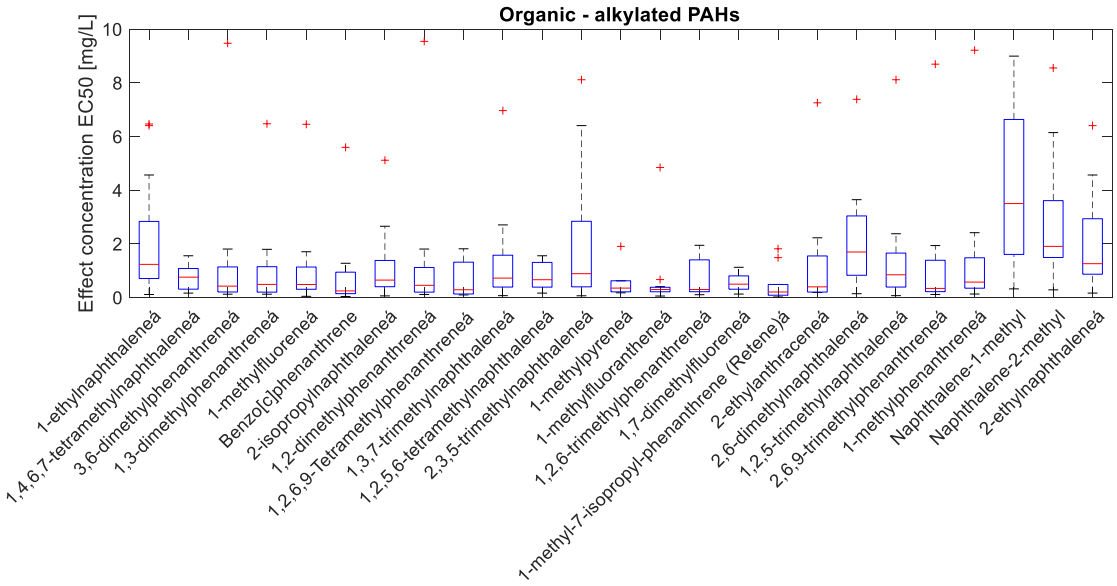

Figure A-3. Effect concentration of 50% of the population according to QSAR model output (ECOSAR, VEGA and T.E.S.T) for the alkylated PAHs. The red line shows the median value the box covers the 25-75 percentile, the whiskers the 5 and 95 percentile and red crosses mark outliers.

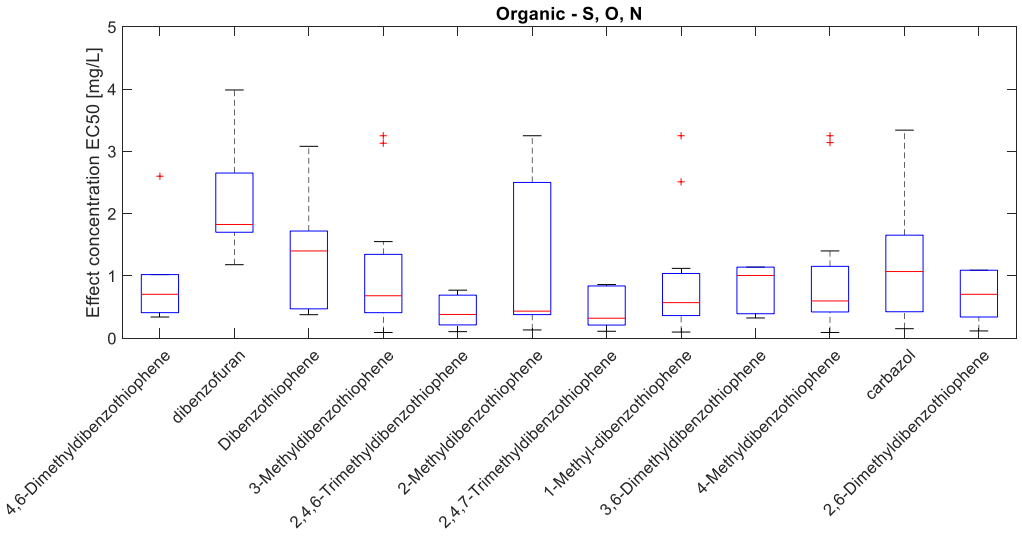

Figure A-4. Effect concentration of 50% of the population according to QSAR model output (ECOSAR, VEGA and T.E.S.T) for organic substances with S, O or N derivatives. The red line shows the median value the box covers the 25-75 percentile, the whiskers the 5 and 95 percentile and red crosses mark outliers.

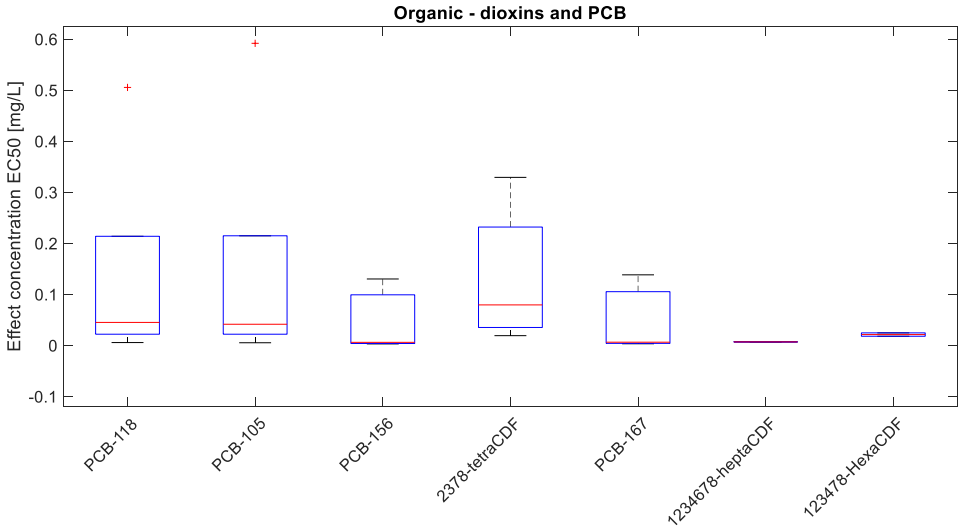

Figure A-5. Effect concentration of 50% of the population according to QSAR model output (ECOSAR, VEGA and T.E.S.T) for PCBs and dioxins. The red line shows the median value the box covers the 25-75 percentile, the whiskers the 5 and 95 percentile and red crosses mark outliers.

APPENDIX B

The complete excel file can be found in the EMERGE Google Drive by clicking on the following link: https://docs.google.com/spreadsheets/d/1EGj0mTEhC8zULP6ZfH4aoock-zmTB0zV/edit#gid=1776764410

(In case you cannot access the excel file, please contact Kari Riikonen: Kari.Riikonen@fmi.fi)