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A novel method to assess the dilution of complex mixtures in the marine environment: Application to marine scrubber water effluents☆

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ABSTRACT

A new method is introduced that, using water-quality modelling results focused on single substances, estimates the degree of the progressive dilution and degradation of a complex mixture after discharge in the marine environment, until its consistency is modified due to different biogeochemical processes acting on its constituents. The method is based on the variance between the dilution ratios of scrubber water constituents and is applied to scrubber water effluents in two case studies in the Mediterranean Sea, using both Eulerian and Lagrangian frameworks. Results reveal that, prior to the onset of biogeochemical transformations, scrubber water behaves as a homogeneous mixture through turbulent mixing with surrounding water, gradually diluting to 10^{-5}–10^{-10} ratios, in spatiotemporal scales ranging from 2 to 25 km and 2 to 60 h. The proposed method generates scrubber-water dilution maps, directly comparable to the results of "whole effluent" ecotoxicological experiments, making them suitable for risk and impact assessment studies.

1. Introduction

The use of Exhaust Gas Cleaning Systems (EGCSs; colloquially known as marine scrubbers) is gradually being introduced to a growing number of vessels globally, as one of the answers of the maritime shipping community to the International Maritime Organization's (IMO) requirements for reduced air emissions (IMO, 2015). The Global Sulphur Cap, which came into force in 2020, imposed a limit of 0.5 % in sulphur content of shipping fuel at the global level (MARPOL, 2017), while within Emission Control Areas (ECAs), such as the North Sea and the Baltic Sea, the limit was set to 0.1 % from 2015. The use of EGCSs, which treat exhaust gases to capture SO_x emissions, permits the use of regular Heavy Fuel Oil (HFO) as a viable alternative to the use of the cleaner but more expensive low-sulphur fuel oils (Zis et al., 2022). However, concerns have been raised about the environmental consequences of EGCS' use, especially when they are operated in "open loop" mode, as the scrubber wash water can be discharged into the marine surface waters without any treatment process (Endres et al., 2018; Turner et al., 2017).

Open-loop scrubber water is a very acidic mixture of various chemical substances, including metals and organic pollutants such as Polycyclic Aromatic Hydrocarbons (PAHs) (Lunde Hermansson et al., 2021). While most of the contaminants measured in scrubber water originate from the fossil fuel, others, such as Chromium (not present in fuels), are likely released by some of the scrubber systems as a consequence of corrosion processes (Teuchies et al., 2020). Recently, the development and application of suspect screening strategies to investigate the composition of open-loop scrubber water have allowed the identification of several alkyl-PAHs and other contaminants, such as biphenyls, dibenzofurans, dibenzothiophenes, and oxygenated PAHs derivatives (García-Gómez et al., 2023), confirming the very complex composition

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of this shipping waste stream.

Thus, even if the target of EGCSs' action is the removal of SO_x from shipping emissions to the atmosphere, their use results in the transfer of many pollutants from the exhaust to the wash water that is eventually released into the marine environment, a development that asks for an assessment of the risk to potentially exposed marine organisms (Teuchies et al., 2020; Turner et al., 2017).

Performing an ecological risk assessment based on the individual pollutants in the effluent would require knowing the exact chemical composition of the scrubber water as well as to have/determine a threshold limit for each scrubber water constituent, that is challenging. Moreover, the concomitant exposure to a mixture of chemicals is expected to have different effects than those determined by the sum of the effects of individual compounds (Backhaus and Faust, 2012), because synergistic or antagonistic effects are likely to occur but are difficult to predict. Whole-effluent toxicity (WET) testing (Chapman, 1999) of scrubber water instead provides a direct measure of the ecotoxicity of mixtures on target organisms accounting for effects from both known and unknown substances and for interactions between them.

WET tests have been used to investigate possible detrimental effects of scrubber water on diverse marine organisms, addressing several endpoints (Koski et al., 2017; Thor et al., 2021; Ytreberg et al., 2021). Recently, within the Horizon2020 EMERGE project (https://emerge-h2020.eu), ecotoxicological experiments have been carried out on endemic species at five European research laboratories, testing a range of scrubber water dilution rates and showing effects at lower concentrations (0.0001 % to 0.001 %) than previously reported (Jalkanen et al., 2024; Monteiro et al., 2024; Picone et al., 2023). The most sensitive endpoint was found for *Strongylocentrotus droebachiensis* eggs' fertilization, where the No Observed Effect Concentration (NOEC) could not be determined, since effects were detected even at the lowest tested scrubber water concentration (0.0001 %, dilution ratio of 10^{-6}; Jalkanen et al., 2024).

The traditional quantitative environmental risk assessment approach for ecotoxicological effects of single substances on different organisms requires the derivation of a Predicted No Effect Concentration (PNEC) (EC, 2017). This PNEC should be compared with the Predicted Exposure Concentration (PEC), and in case the PEC/PNEC ratio is >1, the environmental risk should be considered as unacceptable. The approach for risk characterization is also applicable for complex mixtures, if the WET methodology is used, as stated in the IMO Guidelines for risk and impact assessments of the discharge of water from EGCSs (IMO, 2022). In this case, the predicted exposure (PEC) should be expressed as a dilution ratio of the whole effluent (whereas in a single-substance approach, a PEC/PNEC ratio for each mixture constituent must be estimated).

However, since no consensus on a PNEC for scrubber water has been reached yet, a preliminary evaluation could be carried out using the lowest LOEC available in the dataset (although it could be significantly higher than a PNEC, which incorporates uncertainty factors). It should be noted that this value takes into account only ecotoxicological tests carried out within the EMERGE project, and it is used herein only to provide proof-of-concept results for the proposed approach. It should not be viewed as a definitive ecological risk assessment threshold regarding scrubber water exposure in the marine environment.

Note that hereafter, the term "whole effluent" refers to an effluent of the same original consistency as the original effluent released into the marine environment, in an approach similar to that of the WET approach (Chapman, 2009).

The use of numerical simulation can be a powerful tool for studying the fate of pollutants introduced into the marine environment. This approach can have several levels of complexity. The simplest approach is to treat each pollutant as a passive tracer. This requires only the use of a hydrodynamic model simulating ocean currents, ignoring the biogeochemical properties of individual compounds. In this simplified case, the mixture is subject only to dilution via mechanical mixing and dispersion, while its consistency remains constant since all constituents exhibit the same behaviour (Hong et al., 2020; Paturi et al., 2015; Romero et al., 2016; Rosenhaim et al., 2019; Xu and Chua, 2016).

A more precise approach requires a higher level of complexity, i.e., to account for the different biogeochemical behaviours of the various compounds comprising the initial mixture. This requires the use of water-quality models, which take into consideration environmental conditions such as temperature, salinity, light intensity, dissolved and particulate matter concentration, that affect the behaviour of each compound. Indeed, the coupling of circulation and water-quality models is a widely used approach for reliably simulating the spatiotemporal distribution of individual compounds (Aghito et al., 2025; Mazioti et al., 2024; Monteiro et al., 2024).

However, water quality modelling typically focuses on a single-substance approach, where each target compound is modelled separately, considering the different biochemical processes involved. Since each substance behaves differently, output concentration maps of individual compounds cannot be directly used to estimate exposure to the whole effluent (i.e., WET approach by Chapman (2009)).

To address this issue, a new approach suitable for simulating the environmental fate of complex mixtures in water bodies is presented herein. The method does not constitute a new water-quality model directly simulating the fate of complex mixtures in the marine environment. Instead, it uses the results of any existing water-quality models to record the spatiotemporal patterns of a "whole" complex mixture dispersion and mechanical dilution, prior to the onset of biogeochemical processes that break up the homogeneity of the mixture. This is achieved by considering the individual element concentrations and identifying a criterion to determine the point at which the mixture's consistency changes due to distinct biochemical processes influencing each constituent. Although developed for scrubber water risk assessment, the method is applicable to any type of effluent discharged in an aquatic environment, making it a promising tool for future risk and impact assessments. The method is implemented in two coastal areas in the Eastern Mediterranean Sea, with large ports and busy shipping lanes - Saronikos Gulf, Greece, and the Northern Adriatic Sea. Modelling results from these case studies are utilized, as they overall follow the same methodological approach but also present differences, such as the use of distinct models and frames of reference (Eulerian and Lagrangian, respectively).

The structure of the paper is as follows: first, a description of the overall modelling setup in the two case studies is provided, covering domains, models, variables, contaminants, forcing data, typical output examples, along with the explanation of how scrubber water contaminant mass fluxes were calculated. This is followed by a detailed presentation of the introduced method and its implementation in each domain. Then, the results are presented, followed by a discussion on the insights gained from the application of the method, including its usability, applicability, limitations, and potential future implementations.

2. Materials and methods

The estimation of the fate of scrubber water discharges in the marine environment requires the interaction of several simulation modules:

a) a model that provides the scrubber water volume inflow to the surface layer along the vessels' wakes, supplemented with estimates of contaminant concentrations in scrubber water to calculate the constituent mass fluxes;
b) a hydrodynamic model to simulate the circulation and transport of water masses in the region; and
c) a water-quality model that reproduces the major physical and biogeochemical processes governing the dynamics of the main components of the ecosystem, as well as their interaction with the introduced chemicals.

These simulation tasks have been coupled into a modelling framework that has been applied to the two coastal regions to provide the concentration of selected scrubber water constituents as a function of location (i.e., x, y, z) and time (i.e., t). First, the approach to simulate scrubber water releases is presented in Section 2.1 An overview of the modelling framework implemented in the two coastal regions is described in Section 2.2. Note that the scrubber-water contaminants selected for simulation (presented below) were chosen based on water quality model capabilities and data availability for model parameterization and validation. Then, Section 2.3 introduces the novel methodology that converts simulated contaminant fields to scrubber water dilution ratio fields. Section 2.4 provides further details and specifics on the implementation of the dilution methodology in each case study.

2.1. Simulation of scrubber water discharges with the STEAM model

Scrubber water volume discharges have been provided at high spatio-temporal resolution (hourly, 0.0025°) for the year 2018 in the case study areas by implementation of the Ship Traffic Emission Assessment Model (STEAM) (Jalkanen et al., 2021). These volume fluxes were combined with the best estimates of pollutants' concentration in scrubber water reported by Lunde Hermansson et al. (2021) to obtain gridded time-series of the mass flux for each compound to the sea-surface layer to be used in the water-quality models.

Both open loop and closed loop effluent discharges were considered in this study, using separate datasets for each type of release. This approach provides the emission inventory necessary for studying the dispersion of chemicals related to scrubber water discharge that is hereby examined. The accumulated scrubber water volume input in 2018 in the two regions of interest in this study (48 ships equipped with open-loop scrubbers for Saronikos Gulf and the Northern Adriatic each) is presented in Fig. 1.

2.2. Set up of water quality model experiments

The environmental behaviour of selected chemicals has been simulated through the application of a modelling framework considering

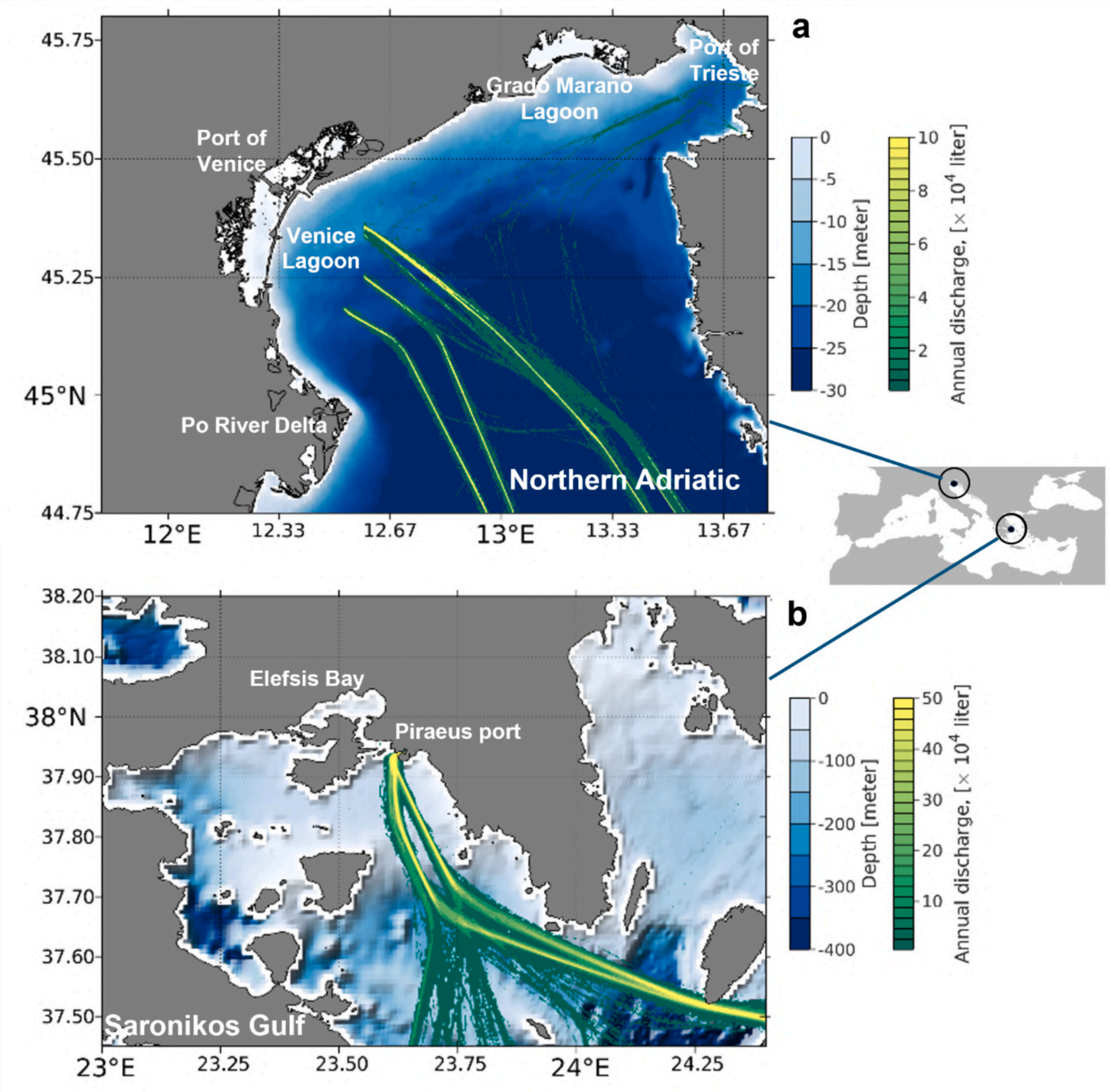

Fig. 1. Maps of the case study areas showing bathymetry and annual scrubber water discharge for (a) the Northern Adriatic and (b) Saronikos Gulf, Greece.

both hydrodynamic and biogeochemical processes in the two case study regions. Simulations were carried out for the year 2018, and details on the used modelling systems are presented in the following sections.

2.2.1. Saronikos Gulf case study

An overview of the Eulerian modelling framework implemented in Saronikos Gulf, Aegean Sea, is presented in Fig. 2 (bottom panel), showing the numerical domain of the simulations. Initially, the hydrodynamics of the study area was simulated with a high-resolution coastal ocean circulation model, Delft3D-FLOW (Deltares, 2023a). The model solves numerically a system of non-linear equations consisting of the horizontal equations of motion, the continuity equation, and the transport equations for conservative constituents, derived from the three-dimensional Navier-Stokes equations for incompressible, free surface flow. A variable horizontal resolution numerical grid, ranging from about 300 m near Piraeus Port to about 1400 m near the open boundary, with 20 sigma layers in the vertical, was used to discretize the domain. Atmospheric forcing was provided by the ECMWF ERA5 database as hourly fields of air temperature, air pressure, relative humidity, precipitation, cloudiness, net shortwave radiation and wind velocity on a 0.25° x 0.25° grid (Hersbach et al., 2023). Lateral boundary conditions (temperature, salinity, sea surface elevation) were provided by a North-Central Aegean reanalysis based on the Regional Ocean Modelling System (ROMS) (Mamoutos et al., 2021). The major water sources were considered in the simulation: i) Kifisos river, ii) Mandra and Sarantapotamos intermittent water streams (in Elefsis Gulf), iii) wastewater treatment plant (WWTP) discharges (Psittaleia and Thriassion), based on real time measurements (Bourma et al., 2022), prediction tools (SHMI HYPE hydrological model, (Lindström et al., 2010) and open data (Greek Special Secretariat for Water WWTP online monitoring database). Details on Delft3D-FLOW implementation, validation and results have been presented in Kolovoyiannis et al. (2023a, 2023b).

The hydrodynamic information produced by Delft3D-FLOW was coupled to the Eulerian water quality model Delft3D-WAQ to simulate the fate of the various compounds present in scrubber water after its release in the marine environment. The compounds simulated for this case study were five metals (Cadmium-Cd, Lead-Pb, Nickel-Ni, Copper-Cu and Zinc-Zn) and two Polycyclic Aromatic Hydrocarbons (PAHs)

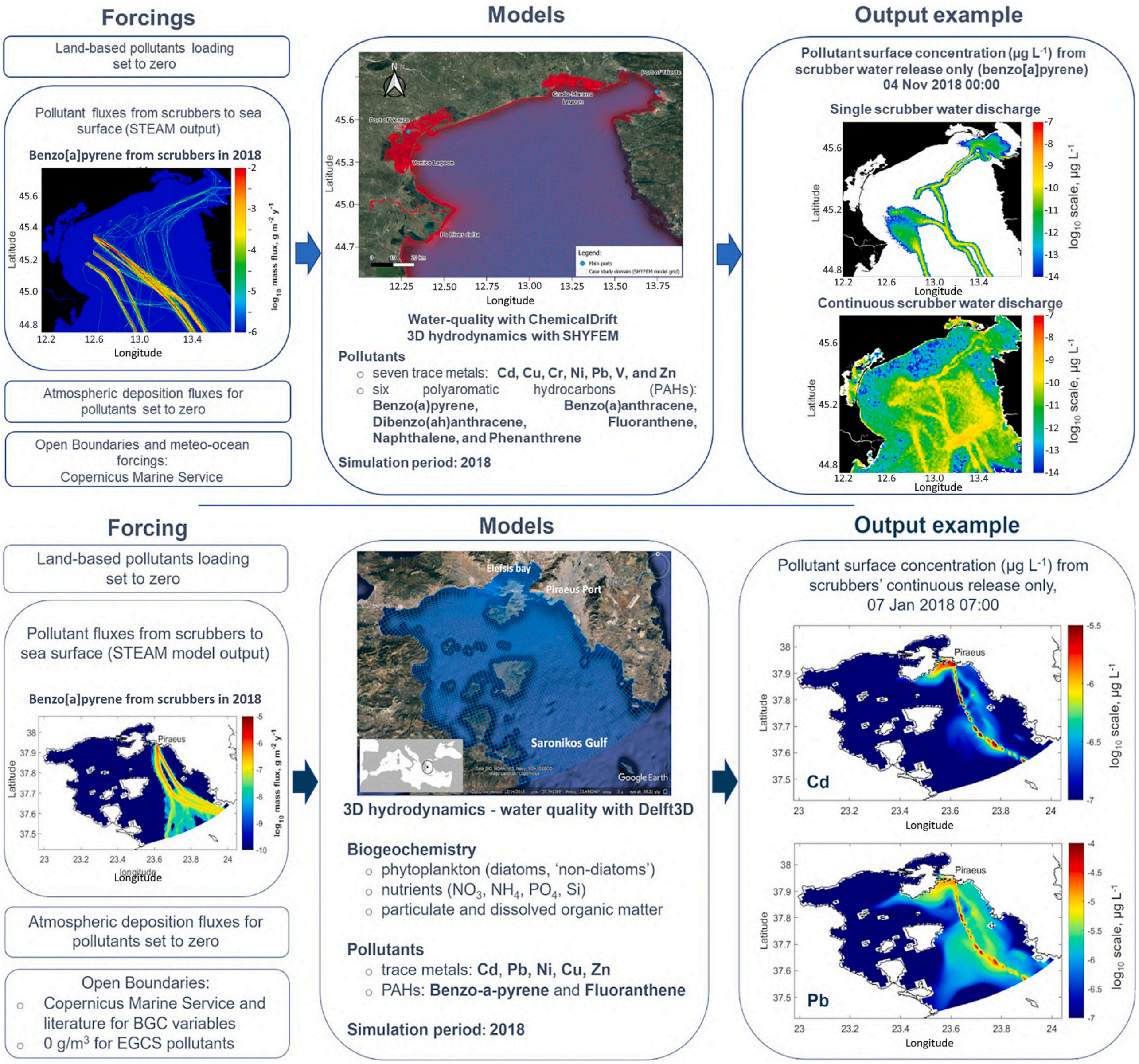

Fig. 2. Set up of modelling experiments for the case study areas, Northern Adriatic (top) and Saronikos Gulf, Greece (bottom), showing forcing data, models used, initial conditions, modelling domains, and output examples.

(Benzo(*a*)pyrene-BaP and Fluoranthene-Flu). Additionally, components of the marine ecosystem such as nutrients (NO_3^{-1}, NH_4^{+1}, PO_4^{-3}, and Si), dissolved and particulate organic matter (DOC, DON, DOP, POC), inorganic matter and phytoplankton (diatoms, non-diatoms) have been simulated, to account for the biogeochemical processes involved in the fate of the various pollutants. Parameterization (both for biogeochemical and pollution components) followed the recommendations by Deltares (2023b). The model was initially set-up for the period of 2009–2010 for which there was a wealth of in-situ marine environmental data (HCMR, 2011) valuable for tuning and evaluation of model performance. After model setup, the period of 2018 was simulated, using both (a) all maritime and land effluents (as a comprehensive collation of coastal pollution sources enabled the inclusion of these pollutant fluxes in the simulations) and atmospheric deposition and (b) only marine scrubber effluents as pollutant forcing. The latter is the simulation used in the present study. Details on the Delft3D-WAQ parameterization, validation and results are discussed in Mazioti et al. (2023, 2024).

2.2.2. *Northern Adriatic case study*

The Adriatic Sea can be subdivided in three basins characterized by different bathymetry, physico-chemical, biological properties. In this work we considered the Northern Adriatic (NA) Sea, a semi-enclosed basin whose southern boundary is conventionally defined at the 100 m isobath (Fig. 1 and Fig. 2 top panel) (Calgaro et al., 2025). To investigate the fate of scrubber water in the Northern Adriatic marine environment, the ChemicalDrift module of the Lagrangian OpenDrift suite (Aghito et al., 2023; Calgaro et al., 2025; Dagestad et al., 2018) was applied to simulate the environmental behaviour of seven metals (Cadmium-Cd, Copper-Cu, Chromium-Cr, Nickel-Ni, Lead-Pb, Vanadium-V and Zinc-Zn) and six PAHs (Benzo(*a*)pyrene-BaP, Benzo(*a*) anthracene-BaA, Dibenzo(*ah*)anthracene-DahA, Fluoranthene-Flu, Naphthalene-Naph, and Phenanthrene-Phe). The model considers physical (advection, diffusion, and sinking) and chemical processes (partitioning among water/suspended particle matter (SPM)/dissolved organic carbon (DOC)/sediments, degradation, and volatilization of chemicals) in a Lagrangian framework using forcing data from several sources. Lagrangian elements considered as dissolved or bound to dissolved organic carbon are only advected along water currents, while elements associated to SPM are also subjected to sinking processes. Resuspension and diffusion back into the water column of Lagrangian elements associated with the sediment layer are modelled based on shear stress at seabed and sorption/desorption equilibria, respectively. Oceanography forcings was taken from application of the finite element model SHYFEM (hourly 3D fields of currents, temperature, and salinity) (Ferrarin et al., 2019). SHYFEM simulations were carried out over a domain that covers the whole Adriatic Sea and the Northern Adriatic Lagoons (Venice and Marano-Grado) with a horizontal mesh resolution ranging from a few tens of meters in the coastal areas to about 5 km in the open sea. Vertically the SHYFEM model applies 34 layers with varying thickness, ranging from 1 m (in the topmost 10 m) to 100 m (for the deepest layer of the Adriatic Sea) (Ferrarin et al., 2019). Ancillary data of wind speed, SPM concentration and mixed layer depth were retrieved from the Copernicus Marine Service (Table S1).

Two sets of modelling experiments were carried out starting from daily discharges of scrubber water estimated by the STEAM model to investigate i) the fate and behaviour of a single discharge of scrubber water to the marine environment and ii) the concentration of scrubber water reached in the surface layer of the water column during 2018 considering all daily discharges from shipping. An overview of the modelling framework implemented in the Northern Adriatic Case Study is presented in Fig. 2 top panel.

The first set of simulations was carried out using daily STEAM output on the day with the highest discharge for each month of 2018 to cover the different circulation, temperature, and salinity conditions occurring during the year. All Lagrangian elements were seeded at the first timestep, and each simulation was run at 1-h timestep for ten days. The second set of simulations was carried out from January 1st to December 31st, 2018 at 3-h timestep considering daily STEAM output and seeding Lagrangian elements each day at midnight. The initial partitioning of each target chemical between dissolved and bound to SPM phases was calculated for all modelling experiments based on solid/liquid partition coefficient (Kd) and scrubber water particles concentration and composition (Karjalainen et al., 2022; Lunde Hermansson et al., 2021; Winnes et al., 2020). Concentration of each chemical was calculated for each timestep considering a grid resolution of 0.0025° (10-days runs) and 0.01° (yearly runs) and a fixed surface layer thickness of 5 m. Model parameterization was taken from Aghito et al. (2023), while further details on model set-up are reported in the Supplementary Material (Table S2).

2.3. *The dilution method*

The method hereby introduced aims to exploit spatiotemporal fields of the various scrubber water constituents' concentrations after their release into the marine environment, to produce maps of dilution levels of the scrubber water.

Based on water-quality modelling results, the method estimates the degree of the gradual dilution of scrubber water in the marine environment after discharge. The initial stage of the presence of scrubber water after discharge into the top layer of the water column is characterized by turbulent mixing, which is the dominant process in reducing the concentrations of the various pollutants in the sea. During this stage, the ratios of the various pollutant concentrations to each other remain constant, although scrubber water is being rapidly diluted. As the influence of turbulence is gradually reduced to background levels, biogeochemical processes take over, and the relative concentrations of the various scrubber water constituents start to diverge. A homogeneity criterion based on the variance of the dilution ratios of scrubber water constituent concentrations is developed to isolate the initial, turbulent stage, during which scrubber water can be considered a homogeneous mixture undergoing dilution. This approach enables the estimation of the spatiotemporal evolution of scrubber water presence in the marine environment, based on the ratios of the simulated concentrations of EGCS constituents to their initial concentrations in the scrubber wash water prior to its release in the marine environment.

In more detail, the analysis is based on the following hypotheses:

a) The dominant processes in determining the concentration of scrubber water as soon as it is released in the marine environment are turbulent mixing and diffusion. As the intensity of these processes is gradually reduced after discharge, other biogeochemical processes (e.g., degradation, partitioning among water/SPM/sediments, and volatilization) take over in determining different rates of concentration decrease for each pollutant.

b) During the initial stage, when turbulent mixing and diffusion are the dominant processes, the concentration ratios of the various pollutants relative to each other remain constant, and the concentration of each pollutant decreases at the same rate as the others, despite the concentrations being different. As other processes gradually become dominant, the scrubber water changes its consistency, as each pollutant's concentration changes at a different rate.

c) Based on the traditional single-substance approach applied in water quality modelling, it is not possible to directly express the dilution ratio of scrubber water as a function of time from release. However, we can employ the concentration of the least reactive scrubber water constituent available for modelling (i.e., the metal with the highest ratio of dissolved to total mass) as an index of dilution (I_d, calculated by normalizing its concentration in the water column with respect to its concentration in the scrubber water before release).

d) The scrubber water dilution approach hereby proposed can only be employed during the time for which mechanical mixing and dilution are the main processes responsible for the decay of each pollutant's concentration.

Based on the above hypotheses, we hereby introduce the following methodology:

1. Select the least biochemically active of the simulated pollutants (we hereby choose *Cd*, see Supplementary Material) to serve as basis for the basic dilution index (in this case $I_d^{Cd}(x,y,z,t)$) and apply Eq. (1):

$$I_d^{Cd}(x,y,z,t) = \frac{Cd(x,y,z,t)}{Cd^{scrubber}} \tag{1}$$

where $Cd(x,y,z,t)$) is the simulated *Cd* concentration field as function of location (i.e., x, y, z) and time (i.e., t), and $Cd^{scrubber}$ is the concentration of Cd in the original scrubber water prior to release, as provided by Lunde Hermansson et al. (2021) and employed in the calculation of the scrubber water pollutant fluxes.

2. Estimate the same ratio for each of the simulated pollutants, for example Nickel Ni (Eq. (2)):

$$I_d^{\mathrm{Ni}}(x,y,z,t) = \frac{\mathrm{Ni}(x,y,z,t)}{\mathrm{Ni}^{scrubber}} \tag{2}$$

3. Estimate the variance of the normalized dilution ratio from all the pollutants at each point in space and time ($\sigma^2(I_d)(x,y,z,t)$), with respect to the Cd-based dilution ratio to obtain an estimation of the scrubber water similarity to its original composition ratio (Eq. (3)):

$$\sigma^2(I_d)(x,y,z,t) = \frac{1}{N-1}\sum_i^N \left(\frac{I_d^i(x,y,z,t)}{I_d^{Cd}(x,y,z,t)} - 1\right)^2 \tag{3}$$

for $i = 1, 2, \ldots, N$, where i refers to each pollutant for a total of N pollutants.

4. Produce a scattergram of the variance of dilution rates from each pollutant $\sigma^2(I_d)(x,y,z,t)$ versus the inverse of the basic Cadmium-based dilution index $\frac{1}{I_d^{Cd}}(x,y,z,t)$, denoted also as 1/Cd_DI.
5. We expect the scattergram to have very small variance values immediately after the discharge of scrubber water. Then, as each chemical's behaviour will be influenced to a different degree by the emergence of diverse biogeochemical processes, there will be a marked increase of the variance value among all scrubber water components, indicating the transition from the turbulent to the biogeochemical concentration decrease regime. A maximum variance threshold for considering scrubber water "as a whole effluent" can be selected, and only 1/Cd_DI values with lower variance will be used to generate scrubber water dilution maps. This information can be used to evaluate 'whole effluent' presence in the marine environment considering levels of dilution, presence duration, and other factors. These findings can be linked to the results of the WET experiments, thus enabling ecological risk assessment.
6. Furthermore, the scattergram can be divided into two regions: i) a zone where scrubber water dilution increases while maintaining low variance values, and ii) a zone where the variance grows when higher dilutions are reached due to the emergence of diverse biogeochemical processes. The transition from the turbulent to the biochemical concentration decrease regimes is marked by the increase of variance of concentrations (or concentration ratios) among different elements of the scrubber water.

2.4. *Implementation of the dilution method in case studies*

2.4.1. *Saronikos Gulf*

A series of numerical simulation experiments was performed, based on the modelling setup described in Kolovoyiannis et al. (2023a) and Mazioti et al. (2023, 2024), with the necessary modifications needed to highlight scrubber water dilution characteristics. Initially, two 10-days-long experiments were conducted, for the 1–10 January 2018 and the 1–10 July 2018 periods respectively, with hourly simulation time steps. The idea was to simulate a winter-well mixed water column period of lower shipping activity and a summer-stratified water column period with higher shipping activity. Hourly scrubber water discharges, at spatial resolution of approximately 300 m, from the STEAM model (Jalkanen et al., 2021) were used to continuously force the model with pollutant release at the sea surface. To isolate the scrubber water from other sources of pollution, the initial and boundary conditions contaminants were set to 0 g/m^3 ('pristine' domain, without any boundary pollutant fluxes), while no other pollutant source (land-based human activity or atmospheric deposition) was considered. The release of scrubber water takes place in surface model cells.

2.4.2. *Northern Adriatic*

Based on Section 2.3, the variance between the dilution ratio of all selected chemicals was used to identify the "whole" and "degraded" scrubber water present in the simulation domain during both modelling exercises carried out for the Northern Adriatic Sea. The ratio of "whole" to "degraded" scrubber water amount was calculated for each timestep of the first set of simulations (Section 2.2.2), and a first order degradation kinetic equation was fitted to the results (U.S. EPA, 2015) to estimate scrubber water kinetic rate constant and half-life.

The scrubber water dilution map obtained from the second set of simulations was filtered based on the estimated variance value, and for each grid cell of the model domain we calculated the percentage of time in 2018 when scrubber water was present at dilutions lower than 10^{-4} %, (corresponding to the Lowest Observed Effect Concentration reported for *Strongylocentrotus droebachiensis* eggs' fertilization by Jalkanen et al., 2024).

As described in the "dilution method", it is worth noting the importance of the "variance threshold" used to evaluate if the state of scrubber water is unchanged, and how this threshold can greatly influence the results. Since scrubber water discharges in the Northern Adriatic Sea varied across about 12 orders of magnitude (Fig. 3a), it was not possible to clearly distinguish within the variance vs 1/Cd_DI scattergrams the two different regions representing the turbulent mixing and biogeochemical concentration decrease. In the absence of an objective criterion, we chose a variance value of 0.1, and report how the results change by varying this value within a factor of 5.

3. Results

3.1. *Saronikos Gulf case study*

3.1.1. *Scattergrams: information that can be retrieved*

Results from the implementation of the method in the Saronikos Gulf case study are shown in Fig. 4, where scattergrams of variance vs 1/Cd_DI (in $\log_{10}$ scale) are presented. Indicative snapshots from the 10-day experiment for January 2018 are shown. To detect any differences in the results due to forcing frequency (time step) and pollutant quantity introduced, the January 10-days experiment was initially performed with an hourly time step (Fig. 4a) and then, it was repeated with 6-hourly time step, where the sum of pollutant mass fluxes was introduced in the domain every 6 h (Fig. 4b). In both cases, the cloud of points followed the same pattern, in a form very close to the theoretically expected distribution described in point 5 of the method description (Section 2.3). Therefore, to reduce computational burden and output volume, a decision was made to proceed with a 6-hourly time step in the

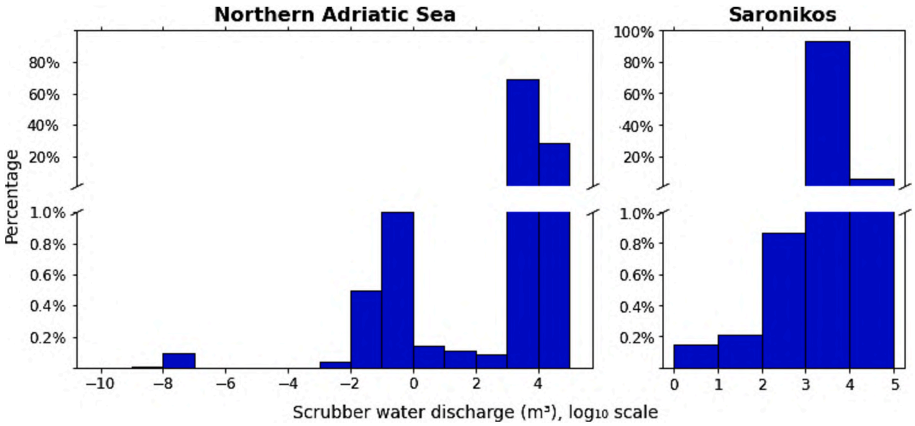

Fig. 3. Histograms of scrubber water discharges estimated for the Northern Adriatic (a) and Saronikos (b) case study for 2018 based on STEAM model output. Note that 10 must be raised to the values on the x-axis to convert volumes in linear scale.

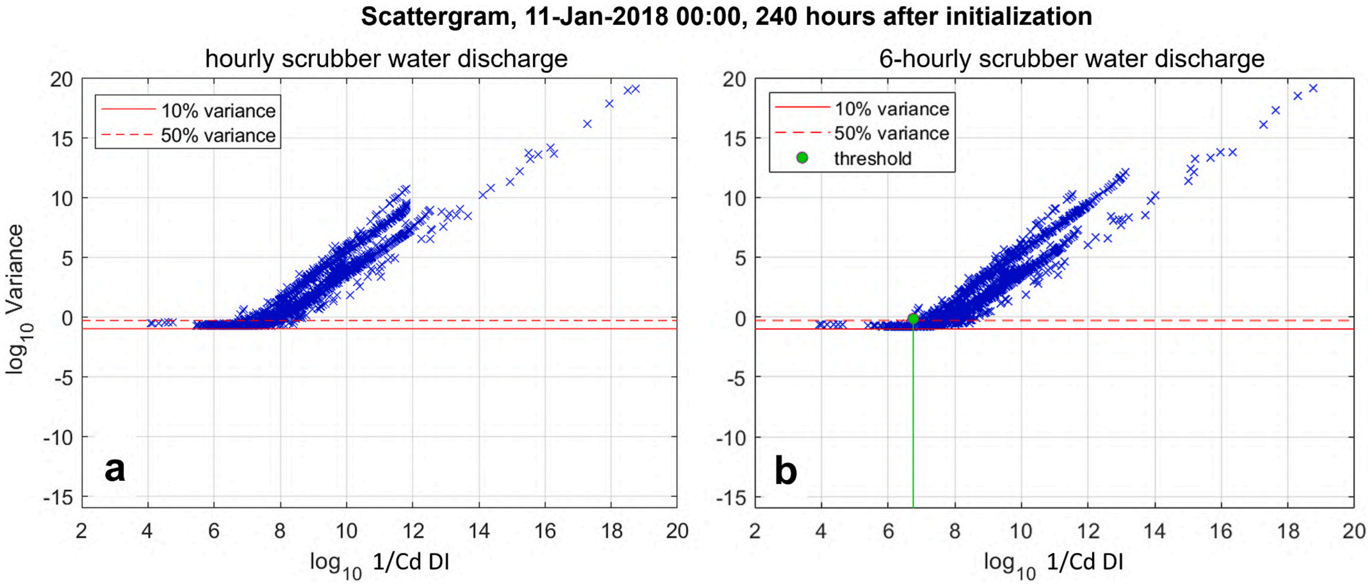

Fig. 4. Scattergrams of the variance of the inverse dilution ratios as a function of the Cd inverse dilution ratio, in log10 scale: snapshots from (a) hourly and (b) 6-hourly time step simulations for January 2018. In (b), the threshold value determined for the reported snapshot is highlighted (with green). Note that 10 must be raised to the values on the x-axis and y-axis to convert inverse dilution ratios and variances respectively to linear scale values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

annual experiments.

In Fig. 4, low variance values in the range of approximately 0.1–0.5 are observed at low 1/Cd_DI values (in subfigures a and b, up to around $10^{6.5}$). The constancy of the variance at these low 1/Cd_DI values indicates that the dominant mechanism of concentration decrease is indeed turbulent mixing, as explained in Section 2.3. As 1/Cd_DI gradually reaches higher values (i.e., higher scrubber water dilution in sea water), there seems to be a threshold value in the x-axis (or rather a zone of 1/Cd_DI values) after which the variance grows due to the rise of the diverse biogeochemical processes considered, and the concentration ratios of the selected chemicals among each other cease to be constant, thus not constituting anymore scrubber water of the same consistency as when it was discharged. The determination of this zone of threshold 1/Cd_DI values and variance values when longer simulations are performed (e.g. annual duration) is discussed next.

3.1.2. *Determination of threshold values for inverse dilution ratio and variance, and implications*

As detailed in Section 2.3, the variance value associated with each value of 1/Cd_DI can be used to assess if scrubber water is still present is the water column "as a whole effluent". In detail, since most scrubber water discharges for the Saronikos case study area were within 2–4 orders of magnitude, a quantitative technique has been applied to determine the variance and 1/Cd_DI threshold values showing the transition between the turbulent mixing and biogeochemical regimes. This technique involves the following steps:

(a) Identifying the datapoint that signifies an abrupt change in the shape of the cloud of points for each scattergram, i.e., simulation output for each time-step (e.g., green point in Fig. 4b). The implemented algorithm detects large changes in the sequence of y-axis values (in our case, the variance). This is repeated for all timesteps, i.e. all 1461 scattergrams of the annual simulation of 2018 with 6-hourly timestep (see also Supplementary Material).

(b) Determining basic statistics of the series of threshold values calculated in step (a). This information is presented in Fig. 5 as histograms.

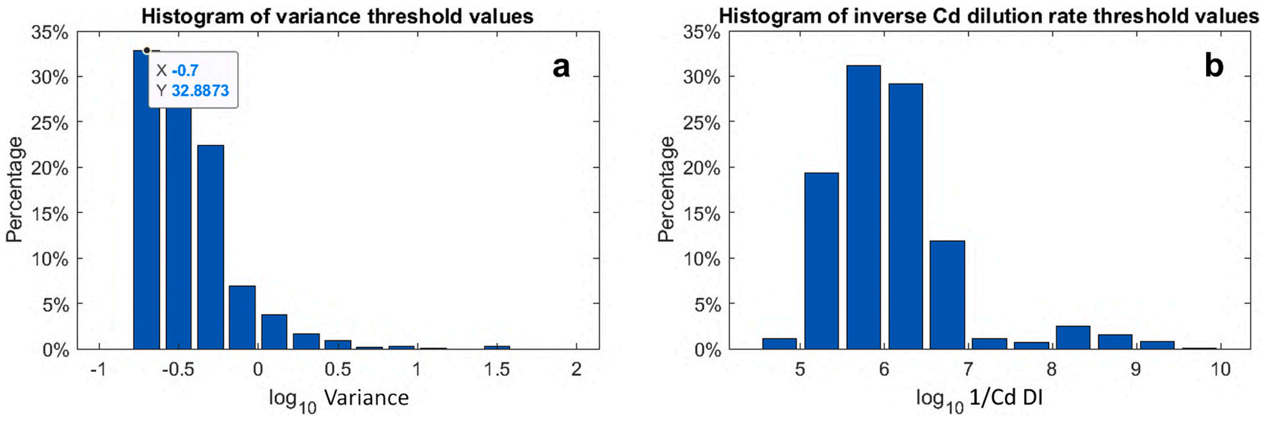

Fig. 5. Histograms of threshold values for (a) variance and (b) the corresponding inverse Cd dilution ratio. Note that 10 must be raised to the values on the x-axis to get the actual variances and inverse Cd dilution ratios.

According to the findings of this procedure, for the Saronikos Gulf area and the modelling approach implemented:

- threshold values for the variance range mainly from 0.2 to 0.7 (i.e., from $10^{-0.7}$ to $10^{-0.15}$ respectively, see Fig. 5),
- threshold values for 1/Cd_DI range from just below 10^5 to approximately 10^9, with most values between 10^5 and 10^7.

These threshold values of 1/Cd_DI correspond to respective scrubber water effluent dilution ratio values if the dilution of Cd is considered a proxy of scrubber water dilution. These values can therefore be compared directly with levels of diluted scrubber water that are found to have significant effects on marine organisms, as determined from a wide range of ecotoxicity experiments conducted within the framework of the EMERGE project (Jalkanen et al., 2024). Monteiro et al. (2024) report a level of scrubber water dilution of 0.001 % (10^{-5} dilution ratio) as the lowest observed effect concentration (LOEC) impacting larval development of the sea urchin *P. lividus* and the polychaeta *S. alveolate* and causing post-exposure feeding inhibition to the mussel *M. galloprovincialis* (their Fig. 9).

3.1.3. Scrubber-water persistence: mapping presence

Having determined in Section 3.1.2 the thresholds below which scrubber water is considered present with the same composition as when it was discharged, the next step was to locate grid points in the modelling domain where, at each time step, specific threshold values for 1/Cd_DI and variance are not exceeded (both criteria are met simultaneously) and then calculate how many times within 2018 this non-exceedance occurred. In this way, scrubber water presence maps can be constructed, as shown in Fig. 6a-b; these maps present the percentage of time that the above-mentioned 1/Cd_DI and variance thresholds were not exceeded, hence scrubber water was present at the near-surface layer within the year 2018 (here, time - or rather time instances – is measured in model time steps: dt = 6 h, so the annual period is discretized in 1461 instances). Alternatively, these maps present the frequency of occurrence of scrubber water diluted less than the determined threshold. A variance threshold of 0.2 (approx. $10^{-0.7}$, a low and most common value, as shown in the histogram of Fig. 5a) was used and two inverse dilution threshold values were tested, in line with the discussion so far: 10^5 and 10^6. This exercise enabled the designation of marine areas – 'hotspots' where scrubber water was present and the time duration of its presence at dilution ratios lower than the above thresholds, leading to presence duration maps (Fig. 6a-b).

In Fig. 6a, where the lower dilution value of 10^5 is used, lower percentages of time (or duration) when scrubber water is present (diluted up to this ratio) are calculated. The area around the port of Piraeus is indicated as the one mostly affected, with time percentages up to, or just over 10 % of 2018, followed by the marine traffic shipping lanes with a distinct percentage of time around 2 %.

When the analysis is repeated with a higher 1/Cd_DI value of 10^6 (Fig. 6b), higher percentages of time (or duration) that scrubber water is present are calculated (around 50 % of the time) along the shipping lanes and up to Piraeus port, gradually dropping to <10 % at a 10–12 km distance either side of the shipping routes. A large portion of inner Saronikos Gulf surface waters appears to be affected by scrubber water mixture diluted at the ppm level (10^6 times) for these time durations.

Fig. 6c presents the annual average level of scrubber water dilution (determined using a variance threshold of 0.2) in the surface waters of Saronikos Gulf for 2018, expressed as % percentage. The map highlights the vicinity around the port of Piraeus and at both sides of the shipping lanes as the marine areas under the influence of EGCS effluents, which are, on average, diluted approximately between 1 and 5 × 10^6 times (diluted at a level of 1 to 5 ppm).

3.2. Northern Adriatic case study

3.2.1. Single scrubber water discharge modelling experiments

By implementing Section 2.3, the variance between the dilution ratios of the chemicals was calculated for each scrubber water discharge and plotted against 1/Cd_DI values. The results obtained for the daily discharge of scrubber water on November 3rd, 2018 are reported here, as an example of the proposed approach, while additional results obtained from the other selected discharges per month is reported in the Supplementary Material (Table S3).

The scattergram of variance vs 1/Cd_DI shown in Fig. 7a highlights that after the first timestep (red circles) the entire volume of scrubber water can be considered as a whole (i.e., with the original characteristics of the effluent) with a dilution ratio ranging from 10^{-3} to 10^{-10}, depending on the volume of scrubber water discharged within each grid cell. After two hours (blue circles) a group of points corresponding to the centre of the shipping lanes is characterized by very similar variance values (about 10^{-7}), while a second group of points representing the surrounding area shows higher variance (up to 10^{-1}). Data obtained after 6 to 25 h of simulation further indicate an increase in scrubber water dilution by about three orders of magnitude, with most of the points being over the selected variance threshold (i.e., 0.1), indicating a significant transformation of scrubber water in this timeframe.

Fig. 7b shows the percentage of "whole" scrubber water remaining in the modelling domain during the simulation based on the different variance thresholds considered, as well as the results of a least-square fit of a first order degradation kinetic equation. The results indicate that this equation describes the decrease of "whole" scrubber water amount after 3–9 h. In the initial stage (time_mix), scrubber water degradation can be mainly attributed to mechanical mixing and diffusion; then first-

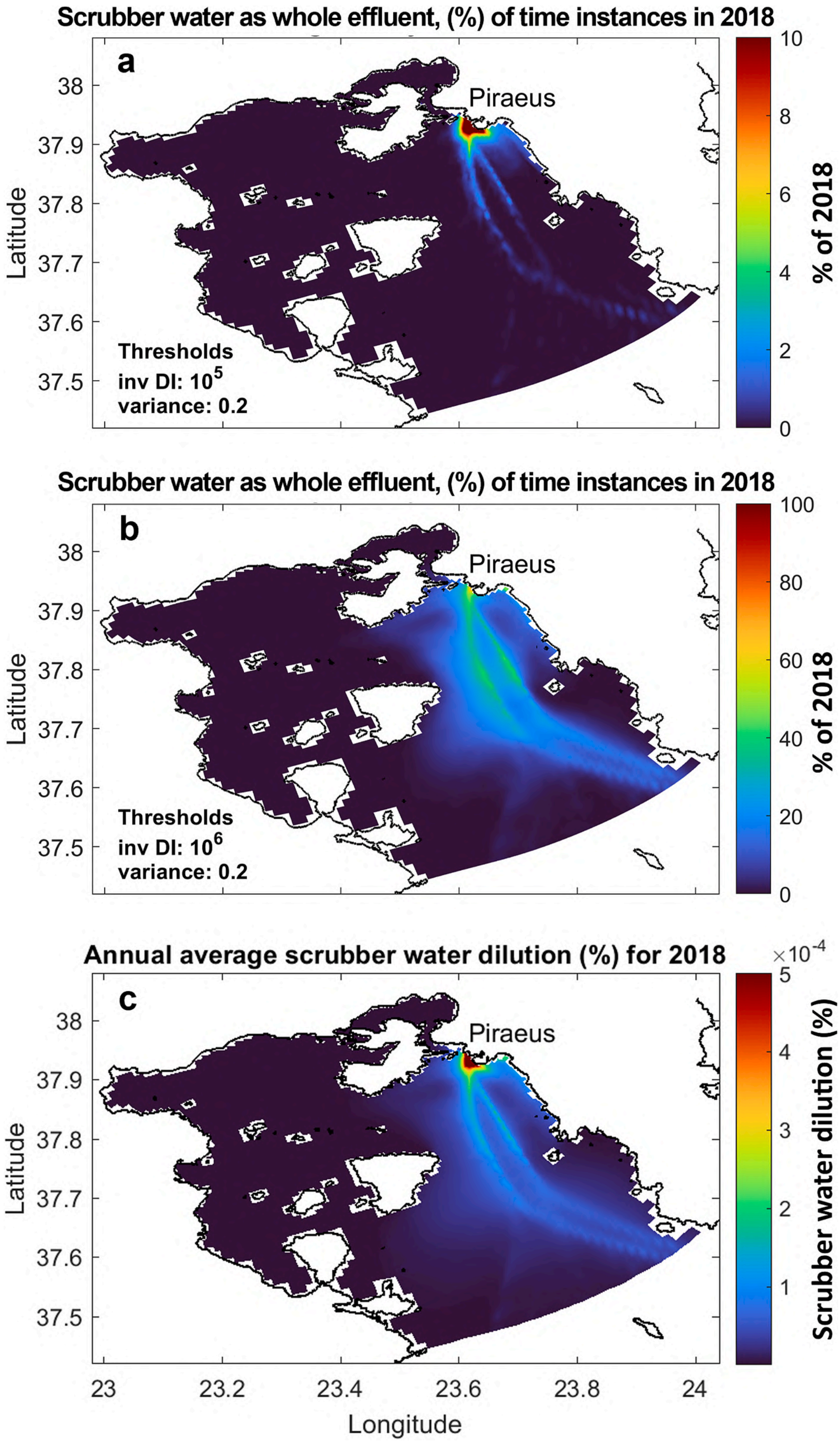

Fig. 6. Percentage of time instances (presence duration) in 2018 that scrubber water was present as 'whole effluent' at the surface waters of Saronikos Gulf based on 6-hourly model output, variance limit of 0.2 and 1/Cd_DI threshold values of (a) 10^5 and (b) 10^6 (i.e., dilution of scrubber water 10^5 and 10^6 times, respectively). Note the different percentage values of the colour scale of subfigures (a) and (b). (c) Annual average dilution of scrubber water with variance limit of 0.2.

degree degradation processes (e.g., degradation and partitioning among the dissolved, bound to DOC, bound to SPM, and settled in sediments phases) become prevalent, imposing half-lives of ca. 3–33 h. The advection of Lagrangian elements outside of the Northern Adriatic modelling domain is another process that can contribute to the elimination of scrubber water, which does not follow first order degradation kinetics. However, due to the location of the scrubber water discharges and the duration of the simulations its effects were limited. Similar results were obtained from the other single scrubber water discharge experiments per month (Table 1, Fig. S1, and Table S3).

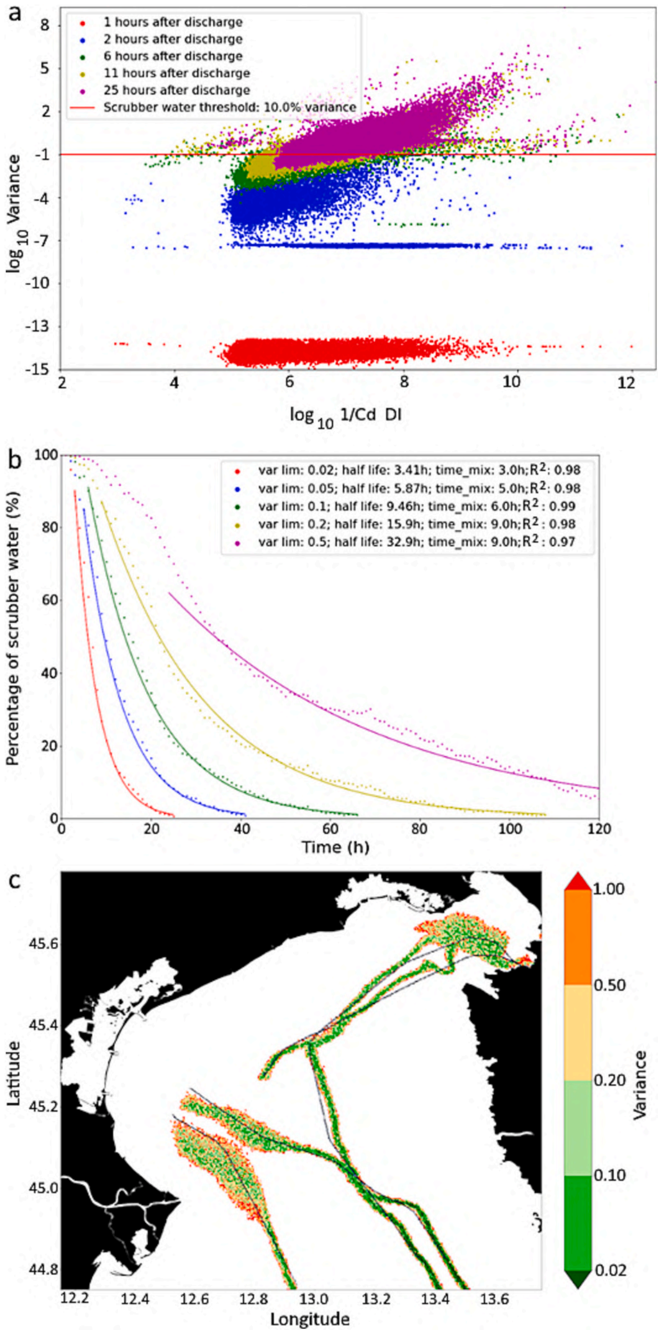

Fig. 7. (a) Scattergram of variance vs 1/Cd_DI in log10 scale for the discharge of scrubber water, showing variance change after 1, 2, 6, 11, and 25 h after discharge; (b) Decay of "whole" scrubber water (as percentage) with time using variance thresholds ranging from 0.02 to 0.5, along with corresponding fit of first order degradation kinetic equation; (c) Variance of 1/Cd_DI calculated 12 h after discharge (green to red points) together with location of the initial discharge (black points) estimated by the STEAM model. The figure refers to the modelling experiments carried out on the cumulative scrubber water discharge of November 3rd, 2018. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Furthermore, the influence of environmental conditions (water currents, temperature, salinity, wind speed, SPM concentration, and mixed layer depth) on mixing timescale (time_mix) and scrubber water half-life was investigated by the Spearman rank-order correlation (Bae et al., 2011; Flacke et al., 2016). The results (Table S4) showed the highest negative correlation for environmental parameters directly related to the partitioning of Lagrangian elements between "dissolved" and "bound to SPM" phases (i.e., SPM concentration, temperature, mixed layer depth, and salinity), since the latter are both subjected to sinking and advected significantly slower by water currents.

Table 1
Ranges obtained for scrubber water half-life (h), and turbulent mixing stage duration (time_mix, h) when concentration decrease is mainly controlled by mechanical mixing. R^2 value is used to express goodness of fit estimated by applying the proposed dilution approach in the Northern Adriatic Case Study.

	Variance value				
	0.02	0.05	0.1	0.2	0.5
half-life (h)	2.0–6.2	4.8–9.5	8.1–16.2	13.3–30.5	33.0–94.4
R^2	0.93–0.99	0.92–0.98	0.95–0.99	0.87–0.99	0.87–0.99
time_mix (h)	3–10	2–17	5–24	6–50	10–58

The information on the variance between the concentration of each scrubber water constituent was also used to map where this mixture can be considered equivalent to the original effluent, as shown in Fig. 7c. The simulations indicated the presence of scrubber water within approximately 2–3 km from the shipping lanes one hour after discharge. Afterwards, scrubber water dispersion and persistence varied significantly based on water and wind speed. The highest dispersion after 24 h was observed near the Po River delta and the Gulf of Trieste (ca. 12–20 km from the initial discharge), while in the open sea scrubber water remained at 4–8 km around the shipping lanes. Conversely, scrubber water presence lasted significantly longer in the open sea, with a persistence of about 20–24 h in contrast to the 12–14 h estimated near the coast. As shown by the estimation of mixing timescale and degradation rate, the choice of variance threshold also has a significant impact on the results, affecting scrubber water persistence and mobility by up to a factor of 3.

3.2.2. *Continuous scrubber water discharge modelling experiment*

After evaluating the environmental fate and behaviour of scrubber water after a single discharge, the dilution ratio in the Northern Adriatic Sea due to all discharges occurring in 2018 was investigated. The results showed a scattergram of variance vs 1/Cd_DI (Fig. 8a) similar to those obtained for the single-discharge experiments (not shown here), with a group of points (dilution between 10^{-5} and 10^{-10}) showing very low variance values, followed by datapoints showing the transition from the turbulent to the biogeochemical concentration decrease regimes. Furthermore, Fig. 8a shows the presence of high variance values (ca. 10^{20}) at very low dilution ratios (about 10^{-17}–10^{-20}), which could be attributed to the presence of grid cells containing a very limited number of Lagrangian elements during the simulation. Several authors have reported on the issue of modelling uncertainties occurring when switching from a Lagrangian framework to a Eulerian grid due to limited particle density within each grid cell (Diggs and Balachandar, 2016; Price and Federrath, 2010; Sun et al., 2011). Several tests were carried out and the seeding of 40 Lagrangian elements for each scrubber water discharge was chosen as a reasonable compromise between accuracy of the approximation and computational load (Graham and Moyeed, 2002; Xue et al., 2018).

Fig. 8b highlights that the average lowest scrubber water dilution ratios (about 5 × 10^{-5} %) were expected along the busiest route connecting the Port of Venice to the central Adriatic Sea. Furthermore, while scrubber water presence within the shipping lanes leading to the Port of Trieste was estimated about 5 times lower, the simulation also showed limited amounts of scrubber water within 8–10 km from the coast due to shipping lane location, water circulation patterns, and the shipping effluents discharge ban within the Venice Vessel Traffic Service area (Contini et al., 2015). Results also indicated significant seasonal variations of scrubber water dilution ratio in the Northern Adriatic (Fig. S2). In detail, the average dilution ratio reached during summer (ca. 10–4 %) is about one order of magnitude lower than the value estimated over the rest of the year. In this period the results also showed

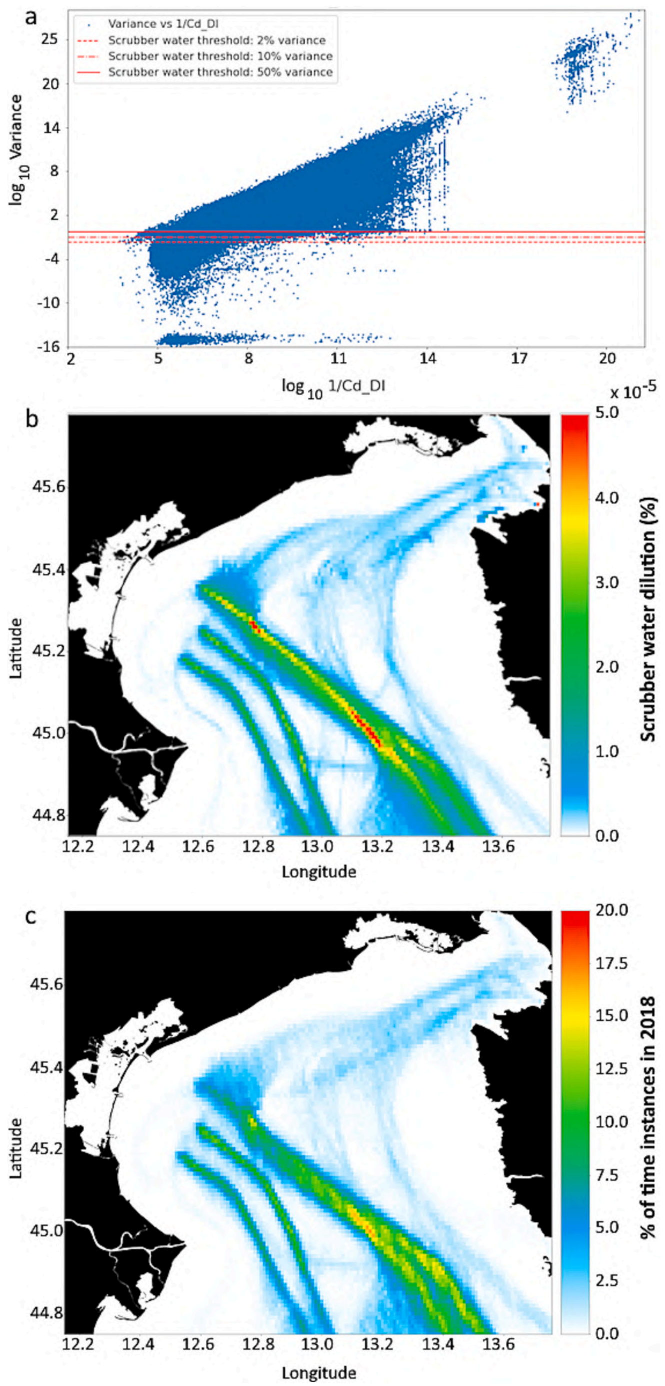

Fig. 8. (a) Scattergram of variance vs 1/Cd_DI in log10 scale for the cumulative daily discharges of scrubber water in the Northern Adriatic for 2018. This distribution of data points is consistent in corresponding experiments conducted for every month of 2018; (b) Annual average dilution of scrubber water with variance limit of 0.1; (c) Percentage of time in 2018 when scrubber water dilution is above 10^{-4} %.

the highest dispersion distance of scrubber water from the points of discharge, especially in upper-central and lower regions of the modelling domain.

Information on the scrubber water dilution ratio reached in the Northern Adriatic was also used to investigate the duration in 2018 for which the effluent concentration exceeded a threshold value of 10^{-4} % (Fig. 8c). Results highlighted that the exceedance of the threshold was limited, occurring about 20 % of the time during the simulation (mainly in summer) along the main shipping lane to the Port of Venice, while the rest of the case study area showed an exceedance between 5 and 10 % of the time. Note that due to computational limitations, scrubber discharges were modelled using daily cumulative values. Therefore, the concentrations reached in the marine environment due to the passage of each ship may be lower. As a consequence, simulations where Lagrangian elements are seeded with higher frequency (e.g., hourly) may be needed to obtain more accurate results.

The effect of using different variance limit values was investigated with regard to the annual average scrubber water dilution ratio (Fig. S3) and the consequent percentage of time during 2018 when its value was above 10^{-4} % (Fig. S4). The use of a lower variance threshold caused a decrease in the annual average concentration of "whole" scrubber water, and these effects were more evident ca. 6–10 km outside of the shipping lanes, where a decrease of about 50 and 90 % was observed when using 0.05 and 0.02, respectively. The same spatial trend was observed also when higher thresholds were applied (i.e., 0.2 and 0.5), but the effects were markedly higher with an estimated increase of about 70 and 200 %, respectively. Fig. S4 highlights that the use of different variance limits strongly influences also the percentage of time in 2018 for which scrubber dilution ratio is above the specified dilution ratio of 10^{-4} %. This change is particularly evident when a variance limit of 0.5 is used, leading to a frequency increase of about 8 times within areas about 10–30 km from the main shipping lanes. Conversely, when lower variance values are considered (i.e., 0.05 and 0.02) a decrease of 25–50 % is registered along shipping lanes, while the exceedance frequency estimated for other areas can reach a decrease of 85–100 %.

4. Discussion

Anthropogenic activity, both in the coastal zone and the open sea, often leads to releases of liquid mixtures consisting of a range of chemical compounds that may either be toxic or intervene in the biochemical functioning of the marine environment. While the fate of each compound may be investigated through advanced water-circulation and water-quality numerical simulations, the impact on the marine environment is not expected to correspond to a simple superposition of the impacts of the individual constituents. To assess the impact of the release of liquid mixtures on aquatic environments, "Whole Effluent Toxicity" tests were gradually developed since the 1940s and standardization efforts began in the 1950s and culminated in the 1990s, with the production of corresponding Technical Reports by the U.S. Environmental Protection Agency (1991, 1996) (Chapman, 1999, and references therein). WET tests have become a standard method in environmental impact assessment studies implemented on effluents of urban waste-water treatment plants (Xia and Wang, 2024), offshore oil-drilling platforms (Nielsen et al., 2023), coastal industries (Meena R et al., 2023) and, more recently, Exhaust Gas Cleaning Systems (EGCS) (Picone et al., 2023).

Numerical simulations provide a powerful tool for studying pollutant dispersion in marine environments, with varying levels of complexity. The simplest approach treats pollutants as passive tracers, using hydrodynamic models that account only for mechanical mixing and dilution. A more advanced approach incorporates water-quality models to simulate how environmental factors and biogeochemical processes further determine the fate of individual compounds. However, traditional chemical fate modelling typically focuses on single substances, thus, its ability to assess the impact of whole effluents is limited. To address this, a new approach is introduced, that leverages output from coupled 3D hydrodynamic - water quality models to track scrubber water mixture dispersion before biochemical processes alter its composition. Tested in two case study areas in Eastern Mediterranean, this method can support risk and impact assessments for various other complex effluents. Thus, the method hereby developed and applied on marine scrubber effluent can be applied on a wide spectrum of polluting activities potentially contributing to pollution of the coastal environment, since for most of them, water-quality modelling is the method of choice to assess their impact on the planning stage.

As the use of marine scrubbers is expected to significantly increase in the near future (Abadie et al., 2017), further studies are urgent and fundamental, focusing on:

i) refining the definition of thresholds to estimate scrubber water integrity after discharge taking into consideration also the variability of this mixture's composition,
ii) better understanding the effects of these complex mixtures on marine biota,
iii) incorporating new information on degradation rates of PAHs by bacterial processes (e.g., Genitsaris et al., 2023) in water quality model parameterization,
iv) including the effects of wave action in scrubber water dispersion and dilution,
v) expanding analysis from the sea surface layer further down the water column.

Although results depend upon water-quality modelling approach (domain discretization and horizontal/vertical resolution, description and parameterization of biogeochemical processes, Eulerian and Lagrangian approach, etc.) that may differ between site-specific implementations, the fact that findings from the two case studies converge to common conclusions on scrubber water spatiotemporal dilution and degradation behaviour is strong evidence of the soundness and reproducibility of the method presented in this work.

At the current stage, the implementations of the proposed methodology have produced the necessary results to prove its applicability. Further testing and collaboration with modelling and ecotoxicology groups, involving other marine areas and spatiotemporal scales (e.g., Aghito et al. (2025), regarding regional European seas) are needed to ensure its robustness and expand its applications.

5. Conclusions

This work constitutes a major step in bridging the gap between the results of (a) ecotoxicological experiments employing the "Whole Effluent Toxicity (WET)" approach to determine environmentally harmful concentrations of wastewater mixtures in the aquatic environment (Chapman, 1999, and references therein), and (b) coupled hydrodynamic – water quality numerical models providing spatiotemporal distribution maps of individual chemical compounds constituting the complex mixture that is released into the aquatic ecosystem.

A novel approach has been introduced to study the evolution of complex mixtures in the aquatic environment at the early stage upon their release, during which their composition remains constant. The development of the method is based on the initial phase of liquid waste effluents' presence in the aquatic environment, during which turbulent mixing causes a rapid dilution but the composition of the complex mixture remains constant. This distinguishes it from the biochemical phase that follows, during which this composition becomes variable. A mixture-homogeneity criterion based on the variance among the dilution ratios of each constituent's concentration has been developed and applied to quantify the homogeneity of the mixture. Individual-element dilution ratios are defined as the ratios of local elemental concentrations to the corresponding concentrations in the original mixture prior to release into the environment.

The method has been applied to spatiotemporal pollutant concentration fields produced by simulation of scrubber-water released to the coastal environments of two Eastern Mediterranean case studies, the Northern Adriatic Sea and Saronikos Gulf in the Aegean Sea. This application allowed the identification of marine areas affected by scrubber water presence, along with maps of spatiotemporal presence.

Results showed that, in both case studies, a continuous release of scrubber water over several days could lead to concentrations comparable to those detected in related ecotoxicological studies (e.g., Jalkanen et al., 2024; Monteiro et al., 2024) as causing adverse effects on the tested species. Scrubber water can be treated as diluted, uniform discharge within 2–60 h of its release in a 2–25 km zone along main shipping lanes, depending on the variance limit value used as threshold.

In Saronikos Gulf, findings indicate that, in 2018, the areas around the port of Piraeus and along the shipping lanes were the ones mostly affected, with scrubber water at a dilution ratio of 10^{-5} and 10^{-6} present up to 10 and 30 % of the time, respectively. Similarly, based on 2018 shipping traffic in the Northern Adriatic Sea, scrubber water presence occurred mostly along the main shipping lanes leading to the ports of Venice and Trieste, reaching concentrations capable of causing adverse effects to the marine environment approximately 10 % of the time.

CRediT authorship contribution statement

Vassilis Zervakis: Writing – original draft, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Vassilis Kolovoyiannis:** Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Loris Calgaro:** Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Elisa Giubilato:** Writing – original draft, Investigation, Funding acquisition. **Antonio Marcomini:** Software, Formal analysis, Data curation. **Aikaterini-Anna Mazioti:** Software, Formal analysis, Data curation. **Christian Ferrarin:** Software, Formal analysis, Data curation. **Elisa Majamäki:** Software, Formal analysis, Data curation. **Manos Potiris:** Software, Formal analysis, Data curation. **Evangelia Krasakopoulou:** Project administration, Methodology, Funding acquisition. **Elina Tragou:** Writing – review & editing, Project administration, Funding acquisition. **Jaakko Kukkonen:** Project administration, Funding acquisition. **Jukka-Pekka Jalkanen:** Supervision, Project administration, Investigation, Funding acquisition.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.

org/10.1016/j.marpolbul.2025.117956.

Data availability

Data will be made available on request.

References

Abadie, L.M., Goicoechea, N., Galarraga, I., 2017. Adapting the shipping sector to stricter emissions regulations: fuel switching or installing a scrubber? Transp. Res. Part D Transp. Environ. 57, 237–250. https://doi.org/10.1016/j.trd.2017.09.017.

Aghito, M., Breivik, Ø., Majamäki, E., Jalkanen, J.-P., Hänninen, R., Hassellöv, I.-M., Hermansson, A.L., Ytreberg, E., Kolovoyiannis, V., Zervakis, V., Granberg, M., Moldanová, J., Dagestad, K.-F., Hole, L.R., 2025. Projected changes of the emission and transport of organic pollutants and metals from shipping in European seas 2018-2050. Mar. Pollut. Bull. https://doi.org/10.2139/ssrn.4881716.

Aghito, M., Calgaro, L., Dagestad, K.-F.F., Ferrarin, C., Marcomini, A., Breivik, Ø., Hole, L.R., 2023. ChemicalDrift 1.0: an open-source Lagrangian chemical-fate and transport model for organic aquatic pollutants. Geosci. Model Dev. 16, 2477–2494. https://doi.org/10.5194/gmd-16-2477-2023.

Backhaus, T., Faust, M., 2012. Predictive environmental risk assessment of chemical mixtures: a conceptual framework. Environ. Sci. Technol. 46, 2564–2573. https://doi.org/10.1021/es2034125.

Bae, M.-J., Kwon, Y., Hwang, S.-J., Chon, T.-S., Yang, H.-J., Kwak, I.-S., Park, J.-H., Ham, S.-A., Park, Y.-S., 2011. Relationships between three major stream assemblages and their environmental factors in multiple spatial scales. Ann. Limnol. - Int. J. Limnol. 47, S91–S105. https://doi.org/10.1051/limn/2011022.

Bourma, E., Perivoliotis, L., Petihakis, G., Korres, G., Frangoulis, C., Ballas, D., Zervakis, V., Tragou, E., Katsafados, P., Spyrou, C., Dassenakis, M., Poulos, S., Megalofonou, P., Sofianos, S., Paramana, T., Katsaounis, G., Karditsa, A., Petrakis, S., Mavropoulou, A.-M., Paraskevopoulou, V., Milatou, N., Pagonis, P., Velanas, S., Ntoumas, M., Mamoutos, I., Pettas, M., Christodoulaki, S., Kassis, D., Sotiropoulou, M., Mavroudi, A., Moira, A., Denaxa, D., Anastasopoulou, G., Potiris, E., Kolovogiannis, V., Dimitrakopoulos, A.-A., Petalas, S., Zissis, N., 2022. The Hellenic marine observing, forecasting and technology system—an integrated infrastructure for marine research. J. Mar. Sci. Eng. 10, 329. https://doi.org/10.3390/jmse10030329.

Calgaro, L., Cecchetto, M., Giubilato, E., Jalkanen, J.-P., Majamäki, E., Ytreberg, E., Hassellöv, I.-M., Fridell, E., Semenzin, E., Marcomini, A., 2025. The contribution of shipping to the emission of water and air pollutants in the northern Adriatic Sea - current and future scenarios. Mar. Pollut. Bull. 212, 117573. https://doi.org/10.1016/j.marpolbul.2025.117573.

Calgaro, L., Giubilato, E., Aghito, M., Jalkanen, J.-P., Majamaki, E., Ferrarin, C., Hänninen, R., Palamarchuk, Y., Sofiev, M., Semenzin, E., Marcomini, A., 2025. Influence of shipping activities on air and water quality in the Northern Adriatic Sea: a high-resolution modelling study (This issue). Mar. Pollut. Bull.

Chapman, P.M., 1999. WHOLE Effluent toxicity testing—usefulness, level of protection and risk management. Environmental toxicology and chemistry. Environ. Toxicol. Chem. 19, 3–13.

Chapman, P.M., 2009. Whole effluent toxicity testing—usefulness, level of protection, and risk assessment. Environ. Toxicol. Chem. 19, 3–13. https://doi.org/10.1002/etc.5620190102.

Contini, D., Gambaro, A., Donateo, A., Cescon, P., Cesari, D., Merico, E., Belosi, F., Citron, M., 2015. Inter-annual trend of the primary contribution of ship emissions to PM 2.5 concentrations in Venice (Italy): efficiency of emissions mitigation strategies. Atmos. Environ. 102, 183–190. https://doi.org/10.1016/j.atmosenv.2014.11.065.

Dagestad, K.-F., Röhrs, J., Breivik, Ø., Ådlandsvik, B., 2018. OpenDrift v1.0: a generic framework for trajectory modelling. Geosci. Model Dev. 11, 1405–1420. https://doi.org/10.5194/gmd-11-1405-2018.

Deltares, 2023a. Delft3d-FLOW. Simulation of multi-dimensional hydrodynamic flows and transport phenomena, including sediments. User Manual, v4.05.

Deltares, 2023b. D-Water Quality. Versatile water quality modelling in 1D, 2D and 3D systems including physical, (bio)chemical and biological processes. User Manual, v5.06.

Diggs, A., Balachandar, S., 2016. Evaluation of methods for calculating volume fraction in Eulerian–Lagrangian multiphase flow simulations. J. Comput. Phys. 313, 775–798. https://doi.org/10.1016/j.jcp.2016.02.066.

EC, (European Commission), 2017. Technical guidance for deriving environmental quality standards (Guidance Document No. 27), p. 210. https://data.europa.eu/doi/10.2875/018826.

Endres, S., Maes, F., Hopkins, F., Houghton, K., Mårtensson, E.M., Oeffner, J., Quack, B., Singh, P., Turner, D., 2018. A new perspective at the ship-air-sea-interface: the environmental impacts of exhaust gas scrubber discharge. Front. Mar. Sci. 5, 1–13. https://doi.org/10.3389/fmars.2018.00139.

Ferrarin, C., Davolio, S., Bellafiore, D., Ghezzo, M., Maicu, F., Mc Kiver, W., Drofa, O., Umgiesser, G., Bajo, M., De Pascalis, F., Malguzzi, P., Zaggia, L., Lorenzetti, G., Manfè, G., 2019. Cross-scale operational oceanography in the Adriatic Sea. J. Oper. Oceanogr. 12, 86–103. https://doi.org/10.1080/1755876X.2019.1576275.

Flacke, J., Schüle, S., Köckler, H., Bolte, G., 2016. Mapping environmental inequalities relevant for health for informing urban planning interventions—a case study in the City of Dortmund, Germany. Int. J. Environ. Res. Public Health 13, 711. https://doi.org/10.3390/ijerph13070711.

García-Gómez, E., Gkotsis, G., Nika, M.C., Hassellöv, I.M., Salo, K., Hermansson, A.L., Ytreberg, E., Thomaidis, N.S., Gros, M., Petrović, M., 2023. Characterization of scrubber water discharges from ships using comprehensive suspect screening strategies based on GC-APCI-HRMS. Chemosphere 343, 140296. https://doi.org/10.1016/j.chemosphere.2023.140296.

Genitsaris, S., Kourkoutmani, P., Stefanidou, N., Michaloudi, E., Gros, M., García-Gómez, E., Petrović, M., Ntziachristos, L., Moustaka-Gouni, M., 2023. Effects from maritime scrubber effluent on phytoplankton and bacterioplankton communities of a coastal area, Eastern Mediterranean Sea. Ecol. Inform. 77, 102154. https://doi.org/10.1016/j.ecoinf.2023.102154.

Graham, D.I., Moyeed, R.A., 2002. How many particles for my Lagrangian simulations? Powder Technol. 125, 179–186. https://doi.org/10.1016/S0032-5910(01)00504-6.

HCMR, (Hellenic Centre for Marine Research), 2011. Monitoring of the Inner Saronikos Gulf Ecosystem under the Influence of the Psittalia Wastewater Treatment Plant - Final Report. Athens.

Hersbach, H., Bell, B., Berrisford, P., Biavati, G., Horányi, A., Muñoz Sabater, J., Nicolas, J., Peubey, C., Radu, R., Rozum, I., Schepers, D., Simmons, A., Soci, C., Dee, D., Thépaut, J.-N., 2023. ERA5 hourly data on single levels from 1940 to present. Copernicus Climate Change Service (C3S) Climate Data Store (CDS) [WWW Document]. https://doi.org/10.24381/cds.adbb2d47.

Hong, B., Wang, G., Xu, H., Wang, D., 2020. Study on the transport of terrestrial dissolved substances in the pearl river estuary using passive tracers. Water (Switzerland) 12. https://doi.org/10.3390/W12051235.

IMO, (International Maritime Organisation), 2015. Resolution MEPC.259(68) 2015 GUIDELINES FOR EXHAUST GAS CLEANING SYSTEMS. MEPC. 269(68).

IMO, (International Maritime Organisation), 2022. IMO: Guidelines for risk and impact assessments of the discharge water from exhaust gas cleaning systems, MEPC.1/Cir (0), 0–26.

Jalkanen, J.-P.P., Johansson, L., Wilewska-Bien, M., Granhag, L., Ytreberg, E., Eriksson, K.M., Yngsell, D., Hassellöv, I.-M.M., Magnusson, K., Raudsepp, U., Maljutenko, I., Winnes, H., Moldanova, J., 2021. Modelling of discharges from Baltic Sea shipping. Ocean Sci. 17, 699–728. https://doi.org/10.5194/os-17-699-2021.

Jalkanen, J.-P., Fridell, E., Kukkonen, J., Moldanova, J., Ntziachristos, L., Grigoriadis, A., Moustaka, M., Fragkou, E., Tsegas, G., Maragkidou, A., Sofiev, M., Hänninen, R., Grönholm, T., Palamarchuk, J., Majamäki, E.E., Winiwarter, W., Gueret, S., Sokhi, R. S., Kumar, S., Ozdemir, U.A., Kolovoyiannis, V., Zervakis, V., Mazioti, A.-A., Krasakopoulou, E., Hassellöv, I.-M., Hermansson, A.L., Ytreberg, E., Williams, I., Hudson, M., Restrepo, L., Hole, L.R., Aghito, M., Breivik, O., Petrovic, M., Gross, M., Rodriguez-Mozaz, S., Neophytou, M., Monteiro, A., Russo, M.A., Oikonomou, F., Gondikas, A., Marcomini, A., Giubilato, E., Calgaro, L., Jaakkola, J.J.K., Shiue, I., Kiihamäki, S.-P., Broström, G., Hassellöv, M., Kaitaranta, J., Granberg, M., Magnusson, K., 2024. Environmental Impacts of Exhaust Gas Cleaning Systems in the Baltic Sea, North Sea, and the Mediterranean Sea Area. Finnish Metereological Institute, Helsinki, Finland. https://doi.org/10.35614/isbn.9789523361898.

Karjalainen, P., Teinilä, K., Kuittinen, N., Aakko-Saksa, P., Bloss, M., Vesala, H., Pettinen, R., Saarikoski, S., Jalkanen, J.-P., Timonen, H., 2022. Real-world particle emissions and secondary aerosol formation from a diesel oxidation catalyst and scrubber equipped ship operating with two fuels in a SECA area. Environ. Pollut. 292, 118278. https://doi.org/10.1016/j.envpol.2021.118278.

Kolovoyiannis, V., Mazioti, A.A., Krasakopoulou, E., Zervakis, V., Tragou, E.A., Mamoutos, I., Potiris, E., Petalas, S., Chatzilaou, C., Mosiou, K., Kontoyiannis, H., Paraskevopoulou, V., Athiniotis, A., 2023a. Implementation of a modelling system for the investigation of the Saronikos Gulf marine ecosystem (Eastern Mediterranean). In: EGU General Assembly 2023, Vienna, Austria, 24–28 Apr 2023. https://doi.org/10.5194/egusphere-egu23-12514.

Kolovoyiannis, V., Petalas, S., Mamoutos, I., Krasakopoulou, E., Zervakis, V., Tragou, E., Kontoyiannis, H., 2023b. Optimizing the Parameterization of a High Resolution Numerical Simulation of the Saronikos Gulf Hydrodynamics, in: 2nd International Conference on Design and Management of Port, Coastal and Offshore Work - May 24–27 2023. Aristotle University of Thessaloniki, Greece.

Koski, M., Stedmon, C., Trapp, S., 2017. Ecological effects of scrubber water discharge on coastal plankton: potential synergistic effects of contaminants reduce survival and feeding of the copepod Acartia tonsa. Mar. Environ. Res. 129, 374–385. https://doi.org/10.1016/j.marenvres.2017.06.006.

Lindström, G., Pers, C., Rosberg, J., Strömqvist, J., Arheimer, B., 2010. Development and testing of the HYPE (hydrological predictions for the environment) water quality model for different spatial scales. Hydrol. Res. 41, 295–319. https://doi.org/10.2166/nh.2010.007.

Lunde Hermansson, A., Hassellöv, I.-M.M., Moldanová, J., Ytreberg, E., 2021. Comparing emissions of polyaromatic hydrocarbons and metals from marine fuels and scrubbers. Transp. Res. Part D Transp. Environ. 97, 102912. https://doi.org/10.1016/j.trd.2021.102912.

Mamoutos, I.G., Potiris, E., Tragou, E., Zervakis, V., Petalas, S., 2021. A high-resolution numerical model of the North Aegean Sea aimed at climatological studies. J. Mar. Sci. Eng. 9, 1463. https://doi.org/10.3390/jmse9121463.

MARPOL, (International Convention for the Prevention of Pollution from Ships), 2017. IMO Annex VI of MARPOL 73/78, Regulations for the Prevention of Air Pollution from Ships Reg. 14.

Mazioti, A.A., Kolovoyiannis, V., Petalas, S., Mamoutos, I., Potiris, E., Krasakopoulou, E., Tragou, E.A., Zervakis, V., Maziotı, A.A., Kolovoyıannıs, V., Petalas, S., Mamoutos, I., Potırıs, E., Krasakopoulou, E., Tragou, E.A., Zervakıs, V., 2023. Simulating the fate of selected PAHs in Saronikos gulf, eastern Mediterranean, using a far-field water-quality model, in: CEST2023 -18th International Conference on Environmental Science and Technology, 30 August to 2 September 2023, Athens, Greece. Doi:10.30955/gnc2023.00221.

Mazioti, A.A., Kolovoyiannis, V., Krasakopoulou, E., Tragou, E., Zervakis, V., Assimakopoulou, G., Athiniotis, A., Paraskevopoulou, V., Pavlidou, A., Zeri, C., 2024. Implementation of a far-field water quality model for the simulation of trace elements in an eastern Mediterranean coastal embayment receiving high anthropogenic pressure. J. Mar. Sci. Eng. 12, 797. https://doi.org/10.3390/jmse12050797.

Meena, R., A.A., J, M, Banu, J.R., Bhatia, S.K., Kumar, V., Piechota, G., Kumar, G., 2023. A review on the pollution assessment of hazardous materials and the resultant biorefinery products in palm oil mill effluent. Environ. Pollut. 328, 121525. https://doi.org/10.1016/j.envpol.2023.121525.

Monteiro, A., Rodrigues, V., Picado, A., Dias, J.M., Abrantes, N., Ré, A., Rosa, M., Russo, M., Barreirinha, A., Potiris, M., Aghito, M., Hänninen, R., Majamäki, E., Grönholm, T., Alyuz, U., Sokhi, R., Kukkonen, J., Jalkanen, J.P., 2024. Holistic evaluation of the environmental impacts of shipping in the sensitive region of Ria de Aveiro. Sci. Total Environ. 946. https://doi.org/10.1016/j.scitotenv.2024.174314.

Nielsen, A.F., Baun, A., Andersen, S.I., Skjolding, L.M., 2023. Critical review of the OSPAR risk-based approach for offshore-produced water discharges. Integr. Environ. Assess. Manag. 19, 1172–1187. https://doi.org/10.1002/ieam.4715.

Paturi, S., Boegman, L., Watt, S., Rao, Y.R., 2015. Transport of municipal wastewater, industrial and tributary discharges in eastern Lake Ontario and upper St. Lawrence River during the ice-free period of 2006. J. Great Lakes Res. 41, 549–559. https://doi.org/10.1016/j.jglr.2015.03.010.

Picone, M., Russo, M., Giuseppe, G., Baccichet, M., Marchetto, D., Volpi, A., Lunde, A., Petrovic, M., Gros, M., Garcia, E., Giubilato, E., Calgaro, L., Magnusson, K., Granberg, M., Marcomini, A., 2023. Impacts of exhaust gas cleaning systems (EGCS) discharge waters on planktonic biological indicators. Mar. Pollut. Bull. 190, 114846. https://doi.org/10.1016/j.marpolbul.2023.114846.

Price, D.J., Federrath, C., 2010. A comparison between grid and particle methods on the statistics of driven, supersonic, isothermal turbulence. Mon. Not. R. Astron. Soc. no-no. https://doi.org/10.1111/j.1365-2966.2010.16810.x.

Romero, L., Siegel, D.A., McWilliams, J.C., Uchiyama, Y., Jones, C., 2016. Characterizing storm water dispersion and dilution from small coastal streams. J. Geophys. Res. Ocean. 121, 3926–3943. https://doi.org/10.1002/2015JC011323.

Rosenhaim, I.L., Riemann-Campe, K., Sumata, H., Koeberle, C., Brauner, R., Herber, A., Gerdes, R., 2019. Simulated ballast water accumulation along Arctic shipping routes. Mar. Policy 103, 9–18. https://doi.org/10.1016/j.marpol.2019.02.013.

Sun, Z.-X., Tang, Z., He, Y.-L., Tao, W.-Q., 2011. Proper cell dimension and number of particles per cell for DSMC. Comput. Fluids 50, 1–9. https://doi.org/10.1016/j.compfluid.2011.04.013.

Teuchies, J., Cox, T.J.S.S., Van Itterbeeck, K., Meysman, F.J.R.R., Blust, R., 2020. The impact of scrubber discharge on the water quality in estuaries and ports. Environ. Sci. Eur. 32, 103. https://doi.org/10.1186/s12302-020-00380-z.

Thor, P., Granberg, M.E., Winnes, H., Magnusson, K., 2021. Severe toxic effects on pelagic copepods from maritime exhaust gas scrubber effluents. Environ. Sci. Technol. 55, 5826–5835. https://doi.org/10.1021/acs.est.0c07805.

Turner, D.R., Hassellöv, I.-M.M., Ytreberg, E., Rutgersson, A., 2017. Shipping and the environment: smokestack emissions, scrubbers and unregulated oceanic consequences. Elem. Sci. Anthr. 5. https://doi.org/10.1525/elementa.167.

U.S. EPA, (United States Environmental Protection Agency), 2015. Standard Operating Procedure for Using the NAFTA Guidance to Calculate Representative Half-life Values and for Characterizing Pesticide Degradation, Version 2. - Degradation Kinetics Equations.

Winnes, H., Fridell, E., Moldanová, J., 2020. Effects of marine exhaust gas scrubbers on gas and particle emissions. J. Mar. Sci. Eng. 8, 299. https://doi.org/10.3390/jmse8040299.

Xia, Y., Wang, W.-X., 2024. Subcellular responses of fish cells to sewage effluents: cell line-based and whole-animal based approaches. Sci. Total Environ. 906, 167528. https://doi.org/10.1016/j.scitotenv.2023.167528.

Xu, M., Chua, V.P., 2016. A numerical study on flow and pollutant transport in Singapore coastal waters. Mar. Pollut. Bull. 111, 160–177. https://doi.org/10.1016/j.marpolbul.2016.07.014.

Xue, P., Schwab, D.J., Zhou, X., Huang, C., Kibler, R., Ye, X., 2018. A hybrid Lagrangian–Eulerian particle model for ecosystem simulation. J. Mar. Sci. Eng. 6, 109. https://doi.org/10.3390/JMSE6040109.

Ytreberg, E., Åström, S., Fridell, E., 2021. Valuating environmental impacts from ship emissions – the marine perspective. J. Environ. Manage. 282, 111958. https://doi.org/10.1016/J.JENVMAN.2021.111958.

Zis, T.P.V., Cullinane, K., Ricci, S., 2022. Economic and environmental impacts of scrubbers investments in shipping: a multi-sectoral analysis. Marit. Policy Manag. 49, 1097–1115. https://doi.org/10.1080/03088839.2021.1937742.