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The contribution of shipping to the emission of water and air pollutants in the northern Adriatic Sea - current and future scenarios

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ABSTRACT

Marine pollution management requires identifying all sources of contaminants, yet shipping's role in marine contamination remains unexplored. To address this gap, we investigated shipping contribution to water and air pollutant loads in the Northern Adriatic Sea in 2018 and under two future scenarios. The approach integrated (i) modelled data of shipping-related emissions, (ii) load from tributaries, and (iii) land-based emissions to the atmosphere. The results showed that shipping significantly contributes to copper, zinc (from antifouling paints), nitrogen (from sewage and food waste), phenanthrene, and naphthalene (from scrubbers and bilge water) loads. Under an increased shipping traffic scenario by 2050, scrubber use reduces atmospheric emissions but increases water pollutants, while alternative fuels reduce air contaminants emission with no significant increase in water pollution. This study sets the foundation to apply water and air quality models to identify areas of concern and assess the environmental impacts of future shipping emission control strategies.

1. Introduction

Toxic chemicals and nutrients reaching the sea represent significant threats for coastal and marine ecosystems and for the relevant ecosystem services they provide (e.g., (Doney, 2010; Johnston et al., 2015; Malone and Newton, 2020). The release of these substances and their circulation in the marine environment is one of the factors hampering the achievement and maintenance of a Good Environmental Status (GES) of marine ecosystems, which is the main objective addressed by the Marine Strategy Framework Directive (MSFD, DIR 2008/56/CE) (EC, 2008) across European sea regions. The concept and regulatory implementation of GES are built around 11 Descriptors, in line with the Drivers-Activities-Pressures-State-Impact-Response (DAPSIR) framework relating anthropogenic activities and pressures to the state of the marine environment (Elliott et al., 2017). Specifically, descriptors tackling the monitoring and assessment of toxic chemicals (hereafter referred as contaminants) and nutrients are Descriptor 5 (eutrophication), and Descriptor 8 (contaminants), and Descriptor 9 (contaminants in seafood), respectively.

To support an effective and coherent implementation of monitoring activities and efficient programmes of measures, a comprehensive understanding of loads of nutrients and contaminants (i.e., pressures according to DAPSIR terminology) to the marine environment, is of pivotal importance. This assessment should consider both land-based and sea-

Abbreviation: Ace, acenaphthene; Acy, acenaphthylene; An, anthracene; BaA, benzo-a-anthracene; BaP, benzo-a-pyrene; BbF, benzo-b-fluoranthene; BghiP, benzo-ghi-perylene; BkF, benzo-k-fluoranthene; Crhy, chrysene; DbahA, dibenzo-ah-anthracene; DL, detection limit; EGCS, Exhaust Gas Cleaning Systems; F, fluorene; Fl, fluoranthene; GES, Good Environmental Status; HFO, Heavy Fuel Oil; IP, indeno-123-cd-pyrene; LNG, Liquified Natural Gas; MSFD, Marine Strategy Framework Directive; Napht, naphthalene; NECA, Nitrogen Emission Control Areas; N_{TOT}, total nitrogen; PAH, poly-aromatic hydrocarbon; Phe, phenanthrene; P_{TOT}, total phosphorus; Pyr, pyrene; SCR, Selective Catalytic Reduction; SECA, Sulphur Emission Control Areas.

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based sources (Tornero and Hanke, 2016) to result in a robust multi-source inventory of loads, providing a solid ground for an efficient integrated management of marine ecosystems.

Among sea-based sources, ship operations give rise to a range of different waste streams related both to the engine and technical systems onboard and to human activities, i.e. both crew and passengers, that eventually lead to the discharge of contaminants and nutrients to the marine environment (Jalkanen et al., 2021). Shipping discharges include waste from several sources, such as wastewater form toilets and medical facilities (i.e., sewage), from not-sanitary facilities (grey water), from ballast tanks (i.e. ballast water), from open- and closed-loop Exhaust Gas Cleaning Systems (EGCS, also known as "scrubbers"), as well as bilge water. Shipping also causes leakage of antifouling products that contain different types of biocides (Thomas and Brooks, 2010), copper being one of the most widely used (Lagerström et al., 2020).

Another significant contribution of shipping is the emission of chemicals and particulate matter to the atmosphere, which will eventually deposit on sea surface – totally or partially, depending on atmospheric transport and transformation processes, as well as influence air quality in ports and coastal regions (Shi et al., 2023; Turner et al., 2017).

To address several issues raised on the negative influence of shipping on air quality, the International Maritime Organization (IMO) mandated from January 1st, 2020 all ships to either use fuel with a sulphur content lower than 0.5 %, such as very low sulphur fuel oil (VLSFO), marine gas oil (MGO) or liquefied natural gas (LNG), or to install EGCS systems (MARPOL, 2017). However, the increased use of EGCS raised several concerns on the effects on the marine environment caused by the discharge of scrubber effluents (i.e. scrubber water) considering both their direct ecotoxicological effects upon discharge (Genitsaris et al., 2024; Jalkanen et al., 2024; Monteiro et al., 2024; Picone et al., 2023; Ytreberg et al., 2021, 2019) and how they may contribute to long-term pollution (Lunde Hermansson et al., 2023; Ytreberg et al., 2022).

A comprehensive inventory of loads to the marine environment and air emissions in the Northern Adriatic Sea area, covering contaminants, nutrients, and air pollutants and evaluating the role of shipping discharges to the overall balance, is currently missing. Such an inventory can be of relevance considering the semi-enclosed shallow nature of the basin that receives input of chemicals from a variety of anthropogenic sources. The input of chemicals and its changes over time can impact both air quality and this vulnerable coastal and marine ecosystem. Some previous works explored the entity of nutrient loads from riverine input (e.g., Volf et al., 2013), which have been also investigated by local environmental agencies in the framework of the Water Framework Directive requirements (e.g., CVN, 2020). However, these efforts are only partial, in the sense that they missed to address contaminants' release from anthropogenic sources and the contribution of commercial and cruise shipping emissions.

Furthermore, the assessment with respect to MSFD Descriptor 8 (Chemical pollution) – Indicator D8C1 (*Concentration of contaminants in environmental matrices water, sediment, biota*) - shows that, based on the "One Out-All Out" principle for the aggregation of indicators under D8, GES is not achieved in the Northern Adriatic Sea unit due to the failure in reaching the threshold for at least one indicator by the three interested Member States. In detail, for Italy and Croatia both the assessment of "ubiquitous, persistent, bioaccumulative and toxic" (UBPT) substances and not-UBPT substances is not satisfactory, while for Slovenia the GES results as achieved looking at UPBT substances (not for the others) (EEA, 2019). As for MSFD Descriptor 9 (*Contaminants in seafood*), GES was considered as not *Not Achieved* by 2018, as the geographic coverage percentage of available data was not enough to prove the achievement of GES, although chemical concentrations in seafood did not exceed threshold limits (EEA, 2019). Finally, data on dissolved oxygen and dissolved inorganic nitrogen concentration was deemed insufficient to properly evaluate the environmental status also with regards to Descriptor 5 (*Eutrophication*). Looking at the overall MSFD implementation in the Mediterranean Sea, it is worth noting that the current differences in, for examples, indicators, threshold limits, aggregation rules adopted by Mediterranean Member States are hampering a comprehensive assessment of the GES achievement in the Mediterranean Sea region and the level of harmonisation across MS has to be considered still low (Araújo et al., 2019).

Given this context, and since other works (e.g., Ytreberg et al., 2022) have already shown shipping contributions of PAHs and metals to be significant in relation to other sources in other sea regions, the main objective of this work is to estimate annual emissions of contaminants (i.e., selected metals and Polycyclic Aromatic Hydrocarbons (PAHs)), nutrients (i.e., nitrogen and phosphorous), and air pollutants (i.e., CO, SO_2, $PM_{2.5}$, and NO_x) in the Northern Adriatic Sea area, by combining available experimental data with up-to-date modelling approaches to account for shipping emissions that cannot be routinely monitored.

To conclude, it is important to estimate the current contribution of shipping activities to the loads of contaminants and nutrients to the marine environment, as well as the emission of air pollutants in the Northern Adriatic Sea. Moreover, it is fundamental to investigate also how these activities may influence the area in the future, considering that an increase of shipping traffic expected in the next decades (Sardain et al., 2019), and several legislative measures will soon be in place to tackle air pollution due to shipping (e.g., establishment of a Sulphur Emission Control Area (SECA) in the Mediterranean Sea (IMO, 2022).

For the first time, in this work the contribution of shipping to the overall emission of contaminants, nutrients, and air pollutants in the Northern Adriatic area was estimated, considering current conditions together with two future scenarios accounting for possible evolutions in the maritime shipping traffic and in the adoption of emission control options.

2. Materials and methods

2.1. Study area

The Adriatic Sea is typically divided into three regional basins characterized by different hydrography, physiographic properties, physical, chemical, and biological features. This works focuses on the Northern Adriatic Sea (Figure SI1), a semi-enclosed basin whose boundary is conventionally defined at the 100 m isobath. This basin is characterized by a quite short residence time (<3.3 months on average), as well as by a shallow bathymetry (average depth of 29 m) (Artioli et al., 2008). The hydrodynamic circulation is mainly originating from a cyclonic flow influenced by the Dalmatian current, rising along the Eastern coast of the basin, and by the descending current along the Western coast. Circulation dynamics and physical properties of the Northern Adriatic basin are primarily influenced by its low bathymetry, by freshwater discharges from the main rivers of the Italian coast, and by atmospheric forcings (e.g., wind stress and heat fluxes). Tidal currents usually range between 2 and 10 cm/s, but they can be amplified up to 10–20 cm/s by wind action (Bellafiore and Umgiesser, 2010; Scroccaro et al., 2010).

The main riverine inputs to the Northern Adriatic basin come from the Italian western coast (due to relevant rivers such as Po, Adige, Brenta, Piave, Isonzo, and Tagliamento), where slopes are gentler and muddy–sandy, while the Balkan coasts are steeper, rocky and reach greater depths, with the coastline characterized by deep fjords and bays. Temperature and salinity patterns are also different between the Eastern and Western coasts (Russo and Artegiani, 1996), leading to the presence of different habitats for marine species on the two sides of the basin.

The presence of densely inhabited and highly urbanized areas within the drainage basin, especially in the Italian Po River valley, causes a significant pollution of nutrients and toxic chemicals (Calgaro et al., 2019; Lofrano et al., 2015; Marini and Grilli, 2023; Riminucci et al., 2022). The main sources o f contaminants entering the case study coastal waters are related to urban/domestic and industrial effluents (treated and untreated), agricultural activities, and many other anthropogenic activities (e.g., transport of goods and people, tourism, mining, and aquaculture). The Northern Adriatic Sea represents an important maritime transport route used by merchant ships (in national and international trade), fishing boats, cruise ships, leisure boats, and military ships (Ghezzo et al., 2024). The main ports in the area are those of Venice and Trieste (on the Italian coast), and Koper (Slovenia).

As for the air quality, the Northern Adriatic drainage basin has two different quality trends. The western part feels the effect of the Po Valley, a ca. 45,000 km^2 wide plain/hilly territory with a population of about 16 million people and a multitude of anthropogenic emission sources, leading to major hotspots for air pollution (Pivato et al., 2023). The orography of the Alpine and Apennine Mountain chains and the topographic characteristics of the plain lead to air stagnation events and frequent wintertime thermal inversions, thus causing a build-up of air pollutants (e.g., PM, NO_x and O_3). On the eastern part, air quality is less of a problem, with significantly lower pollution concentrations (e.g., average PM_{10}: 10–15 μg/m^3 vs 25–30 μg/m^3), thanks to a limited number of emission sources present in the Alpine area and to a higher windiness. Nevertheless, concentrations of pollutants (e.g., PM_{10} and BaP) in the urban area of Trieste show strong variability in time (due to meteorological conditions) and in space (due to the local emission sources) (Bonafé et al., 2018).

Given this context, it is fundamental to investigate also the contribution of shipping emission to air quality and to the deposition of the investigated chemicals, especially considering the high freight (Trieste) and passengers (Venice) traffic in the case study area ports (Merico et al., 2021).

2.2. Shipping emissions to water and air

2.2.1. STEAM model

The Ship Traffic Emission Assessment Model (STEAM), as described in more detail in previous studies (Jalkanen et al., 2018, 2021, 2012, 2009; Johansson et al., 2017, 2013), was used to estimate the emissions of metals (i.e., arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), vanadium (V), and zinc (Zn)), PAHs; (i.e., naphthalene (Napth), fluoranthene (Fl), benzo-b-fluoranthene (BbF), benzo-k-fluoranthene (BkF), benzo-a-pyrene (BaP), benzo-ghi-perylene (BghiP), indeno-pyrene(IP), fluorene (F), anthracene (An), benzo-a-anthracene (BaA), chrysene (Crhy), dibenzo-ah-anthracene (DbahA), pyrene (Pyr), phenanthrene (Phe), acenaphthylene (Acy), and acenaphthene (Ace)), and nutrients (i.e., N and P) from the discharge of liquid wastes (i.e., open and closed loop scrubber water, bilge water, grey water, and sewage), the release of Cu and Zn from antifouling paints, and the emission to the atmosphere of CO_2, CO, SO_2, $PM_{2.5}$, ash, organic carbon, nitrogen, and volatile organic compounds.

STEAM model uses instantaneous locations, speeds, and headings of ships obtained from Automatic Identification System (AIS) data, and technical description of the global fleet, to estimate the power need, fuel consumption, and further emissions and discharges of each ship.

In this study, the STEAM model was applied using global AIS data for 2018 retrieved from Orbcomm, data on ship technical characteristics from S&P Global database, and meteo-ocean forcings retrieved from Copernicus Marine Services (CMEMS) database and Copernicus Climate Data Store (CDS) (CDS, 2018; CMEMS, 2018). Discharge rates of each waste stream and metals are described in Jalkanen et al. (2021). However, in this study more realistic discharge rates of 90 m^3 MW/h and 0.45 m^3 MW/h were applied for open and closed loop scrubbers, respectively, following the findings in Lunde Hermansson et al. (2021). Consequently, unnormalized concentrations of water contaminants and nutrients in scrubber discharge were used to maintain the mass balance of the effluent. Emission factors for atmospheric pollutants used in STEAM described in detail in Grigoriadis et al. (2021).

STEAM model was selected to be used in this study as modelling of both atmospheric pollutants and water discharges was needed, and these should be based on the observed ship traffic activity. There are several other bottom-up ship emission models (e.g., Kramel et al., 2021; Schwarzkopf et al., 2023), but these models have been developed to only focus on atmospheric emissions. ICCT's Systematic Assessment of Vehicle Emissions (SAVE) (Osipova et al., 2021) model predicts both atmospheric emissions and scrubber water discharges from shipping, however other waste streams from shipping are not included. Furthermore, as reported by Moreno-Gutiérrez et al. (2015) (Moreno-Gutiérrez et al., 2015) after a comparison of available methodologies to quantify shipping emissions, the STEAM model was recommended to obtain the most realistic estimations since it uses for each vessel a fuel oil consumption coefficient adapted for engine load instead of a constant value across the entire engine power range.

The flux of pollutants in the scrubber water depends on the unit discharge rate, instantaneous power of the engines connected to the scrubber and the concentration of various components in the scrubber effluent. Of these quantities, the instantaneous engine power prediction probably is the one which can be predicted the best. The unit discharge rate (m^3 MW/h) has been shown to vary significantly, but it is higher than the normalized 45 (open loop) and 0.3 (closed loop) m^3 MW/h (Teuchies et al., 2020). However, if the normalized rate is not used, then also the non-normalized values for pollutant concentrations in the effluent samples need to be used to keep the pollutant fluxes consistent. Regardless, the fluxes of pollutants in the scrubber effluent can be considered an order of magnitude estimate, because sea water and fuel properties have an impact on the volume of water needed to reduce the sulphur exhaust emissions to required levels.

2.2.2. Baseline and future scenarios

The year 2018 was selected as "baseline" to estimate the actual contribution of shipping activities to the overall pollution loads to the case study area since it was the most recent year when i) inventories for land-based emission sources to air (e.g. CAMS-REG-v4.2 inventory), ii) river flow and water quality information, iii) environmental monitoring data, and iv) information on shipping traffic, were available.

Two scenarios for 2050 were considered to account for several ship types, different developments regarding transport work (e.g., payload, and number of ships), fuel mix, and use of abatement equipment, as developed within the H2020 "EMERGE" project, with a special attention to the impacts of the use of scrubbers (Jalkanen et al., 2024). The use of scrubbers is modelled through an economic model, i.e. ship owners use scrubbers when it is profitable, in combination with potential restrictions on their use. The reason that scrubbers in many cases are profitable is that a ship with an installed scrubber can use a low-cost high-sulphur fuel rather than a more expensive low-sulphur fuel (Lunde Hermansson et al., 2024). In particular, large annual fuel consumption with significant price premium between high- and low sulphur fuels will favour the use of scrubbers in the global fleet and vice versa. The use of open-loop scrubbers is the least expensive and most popular option. In particular, the adoption of scrubbers was modelled for individual ships and depended on the fuel consumption of the ship and the assumed fuel prices. To develop the various scenarios, the DNV Maritime Forecast to 2050 (Longva et al., 2020) was used to define the traffic development and the introduction of renewable fuels was assumed to fulfil policy targets for the reduction of emissions of green-house gases (GHG).

Scenario 1 (S1) assumes that there is a high increase in maritime transport work and there are no further measures to reduce the use of fossil fuels in shipping other than those already in place. On top of that, there is significant use of open-loop scrubbers and high use of Selective Catalytic Reduction (SCR) in Nitrogen Emission Control Areas (NECA). In detail, a fuel price difference between HFO and VLSFO of 200 US$ was assumed, thus the adoption per ship type varied between 4 % for general cargo ships up to 74 % for container ships. It is also assumed that sulphur and nitrogen oxide emission control zones are introduced in all European seas.

Scenario 2 (S2) assumes a high increase in ship traffic too, as well as the implementation of measures aligned with the 2018 IMO initial strategy to reduce GHG emissions by 50 % by 2050 compared to 2018 (i.e., a substantial use of Liquified Natural Gas (LNG) and methanol as alternative fuels to Heavy Fuel Oil (HFO) in 2050). S2 also excludes the use of open-loop scrubbers and involves low use of SCRs.

S1 and S2 were selected to compare two contrasting situations, suitable to better investigate the impact of scrubbers' use as one of the main goals of EMERGE project. These two extreme scenarios (out of eight developed in the EMERGE project) were selected to represent the magnitude of the potential future developments of shipping as an environmental pressure in the study area. Further details on the investigated scenarios are reported in the SI and EMERGE Project Deliverable D4.1 (EMERGE Project, 2022).

2.3. Land-based emissions to water and air

The riverine loads of metals, PAHs, and nutrients to the marine water bodies in the case-study area were estimated by integrating data from national river monitoring programmes on water concentrations of target substances (e.g., according to Directive 2000/60/EU and national regulations) with daily discharge measurements of each river at the monitoring station closest to the sea. Specifically, the water concentration of each target chemical in all monitored tributaries was assumed to remain constant until the next measurement. This concentration was then multiplied by the corresponding daily water flow to estimate the chemical load (Montuori and Triassi, 2012; Steen et al., 2001; Svendsen et al., 2015; UNEP/MAP, 2004).

Data on daily flow measurements for the main rivers across Veneto, Friuli Venezia Giulia and Emilia Romagna Regions were obtained from hydrological annals, as reported by each regional Environmental Protection Agency. Daily flow measurement data for 2018 was directly used, if available, whereas data from 2010 to 2022 was used for filling gaps in the 2018 daily series, if needed. For gaps of a single day, the missing information was filled by the average of the data of the preceding and the succeeding day, while for longer gaps an artificial neural network methodology (Vega-Garcia et al., 2019) was used. Data about the few Croatian (Dragonja and Mirna) and Slovenian (Levante) rivers flowing into the Northern Adriatic basin were not retrievable. However, their very small discharges can be considered negligible in comparison to the contribution from the numerous and larger Italian rivers (Volf et al., 2013).

The load of chemicals from un-monitored areas (Figure SI1) was estimated by multiplying the average annual load (i.e., kg/km^2) of the whole Northern Adriatic drainage basin by the surface (i.e., km^2) of each area considering urbanized (for PAHs) and overall surface (for metals and nutrients) (Collavini et al., 2005; Delile et al., 2022). Data on the area and land use of each drainage basin was retrieved from the relevant river basin district authorities (Pellegrini et al., 2019) and the CORINE Land Cover Map (CLMS, 2023).

According to the approach reported by several authors (Collavini et al., 2005; Delile et al., 2022; Slymen et al., 1994), if the monitored concentration was below the detection limit (DL) the value was assumed as DL/2, and if >60 % of all available measurements for a river were below the DL, the estimated load was considered as an approximate estimation.

The emissions of pollutants to the atmosphere from land based sources were taken from the CAMS-REG-v4.2 emissions inventory for 2018 (CO, SO_2, $PM_{2.5}$, and NO_x) and provided from the INEMAR database (CO_2) by the competent Environmental Protection Agencies for 2015 (Friuli Venezia Giulia Region) and 2017 (Veneto Region and Emilia Romagna Region) (INEMAR, 2020; Kuenen et al., 2022), due to data availability at the time of this study.

An area extending for about 100 km inland from the coastline was considered for the selection of emissions to air from land-based activities (Figure SI2) and these emissions were compared with the emissions from shipping activities estimated using the STEAM model for the selected marine area (National Research Council, 1992; Northcott et al., 2019).

The contribution of shipping activities in 2018 and 2050 (i.e., shipping $_{contr.}$) to each pollutant's load to water was calculated by applying Eq. (1), while the contribution of shipping to the overall emission of each pollutant to air was calculated by using Eq. (2):

$$Shipping_{contr\ (water)} = Load_{SHIP} \Big/ (Load_{SHIP} + Load_{RIVERS}) \bullet 100 \quad (1)$$

$$Shipping_{contr\ (air)} = Emission_{SHIP} \Big/ (Emission_{SHIP} + Emission_{LAND}) \bullet 100 \quad (2)$$

Moreover, emissions of metals, PAHs, and nutrients from land-based sources estimated for 2018 were assumed to remain constant also for 2050.

3. Results and discussion

The emissions of the selected chemicals from land-based sources and shipping activities to both water and air compartments were estimated for the Northern Adriatic Sea, considering both present and future scenarios. Annual estimates are presented in this section, along with a focus regarding the contribution of land-based sources and shipping activities.

3.1. Metals, PAHs, and nutrients to the Northern Adriatic basin

3.1.1. Riverine inputs

The annual riverine load of metals, PAHs, and nutrients to the case study area is reported in Table 1. It is worth reporting that about 94 % of the Northern Adriatic drainage basin area are covered by water quality monitoring activities and river flow measurements (Figure SI1), with most unmonitored areas situated near the Lagoon of Venice, the Lagoon of Grado Marano, the Gulf of Trieste, and the Po River delta.

The overall load of N and P was about 2.2E+05 t/year and 7.5E+03 t/year, respectively, similarly to what was reported by other authors (Marini and Grilli, 2023; Sani et al., 2024; Volf et al., 2013). The Po River accounted for 40 to 85 % of these loads during the investigated period, with the highest contributions during spring and autumn seasons due a combination of higher use of fertilizers (Cao et al., 2018) and increased river flow. The remaining load of nutrients can be mostly attributed to the Adige, Livenza, Sile, and Brenta rivers.

The load of metals varied between several order of magnitude, with the highest values for As, Cu, Ni, and Zn (ca. 1.5–7.7E+02 t/year), followed by Cr and Pb (ca. 6 – 8E+01 t/year), while the load estimated for Cd and Hg was about one order of magnitude lower (ca. < 3E+00 t/year). As for nutrients, most of the overall load of metals could be ascribed to the Po River and the Adige River. However, significantly higher contributions to the load of specific metals by several rivers from a combination of anthropogenic and geogenic factors could be observed. This is the case of Cr from Fratta-Gorzone River, Pb from Adige River, and Hg from Isonzo River. For a correct interpretation of these results, it is important to stress that the Fratta-Gorzone River receives the wastewater produced from one of the biggest tanning districts in Europe (Giusti and Taylor, 2007; Ostoich and Carcereri, 2013), several industries related to chemical and metal manufacturing (Chiogna et al., 2016) are present in the drainage basin of the Adige River, and the Isonzo River basin has an high geological background of Hg, which has been extensively exploited by mining activities (Acquavita et al., 2022; Cerovac et al., 2018; Faganeli et al., 2017; Pavoni et al., 2020). Most of the concentrations of PAHs measured were below the DL (Table SI1–3), hence, the estimated load of these substances can only be considered as a approximate estimation, especially in the case of Naph whose DL was one order of magnitude higher than the rest of the studied organic chemicals. The low frequency (i.e. monthly or quarterly) of the sampling activity required by national and international monitoring programmes may result in the missing of flood events, that have been shown to be

Table 1
Load of metals, PAHs, and nutrients to water for the Northern Adriatic due to land-based sources and shipping activities, for the baseline year 2018 and under two future 2050 scenarios (S1 and S2)[c].

	Drainage Basin	Ships 2018	*Shipping contribution 2018 [%]*[a]	Ships 2050 S1	*Shipping contribution 2050 S1 [%]*[a]	*Shipping 2050 S1 vs 2018 [%]*[b]	Ships 2050 S2	*Shipping contribution 2050 S2 [%]*[a]	*Shipping 2050 S2 vs 2018 [%]*[b]
Metals [kg]									
As	1.30E+05	1.62E+01	*1.25E-02*	8.83E+02	*6.75E-01*	*5.35E+03*	2.10E+01	*1.62E-02*	*2.98E+01*
Cd	< 3.39E+03	1.32E+00	*3.90E-02*	1.02E+02	*2.91E+00*	*7.60E+03*	3.11E-01	*9.19E-03*	*−7.64E+01*
Cr	8.15E+04	3.14E+01	*3.85E-02*	1.92E+03	*2.30E+00*	*6.01E+03*	1.68E+01	*2.07E-02*	*−4.64E+01*
Cu	1.88E+05	5.22E+04	*2.17E+01*	1.38E+05	*4.24E+01*	*1.65E+02*	1.34E+05	*4.15E+01*	*1.56E+02*
Pb	6.03E+04	2.42E+01	*4.00E-02*	1.16E+03	*1.88E+00*	*4.69E+03*	4.04E+01	*6.70E-02*	*6.73E+01*
Hg	< 3.85E+03	2.23E-01	*5.80E-03*	1.17E+01	*3.04E-01*	*5.16E+03*	3.21E-01	*8.33E-03*	*4.37E+01*
Ni	1.65E+05	9.69E+01	*5.88E-02*	6.14E+03	*3.60E+00*	*6.24E+03*	5.59E+01	*3.40E-02*	*−4.23E+01*
V	–	2.92E+02	–	2.16E+04	–	*7.30E+03*	7.11E+00	–	*−9.76E+01*
Zn	7.72E+05	9.85E+03	*1.26E+00*	3.91E+04	*4.82E+00*	*2.97E+02*	2.51E+04	*3.15E+00*	*1.55E+02*
PAHs [kg]									
Napht	< 3.88E+03	5.74E+00	*1.48E-01*	3.61E+02	*8.51E+00*	*6.18E+03*	4.70E+00	*1.21E-01*	*−1.82E+01*
Fl	< 3.74E+02	2.66E-01	*7.10E-02*	2.03E+01	*5.15E+00*	*.55E+03*	5.57E-02	*1.49E-02*	*−7.90E+01*
BbF	< 3.72E+02	6.48E-02	*1.74E-02*	5.08E+00	*1.35E+00*	*7.74E+03*	8.36E-03	*2.25E-03*	*−8.71E+01*
BkF	< 3.69E+02	1.64E-02	*4.43E-03*	1.27E+00	*3.43E-01*	*7.67E+03*	2.79E-03	*7.55E-04*	*−8.30E+01*
BaP	< 3.69E+02	8.03E-02	*2.18E-02*	6.35E+00	*1.69E+00*	*7.81E+03*	9.29E-03	*2.52E-03*	*−8.84E+01*
BghiP	< 2.48E+02	3.47E-02	*1.40E-02*	2.55E+00	*1.02E+00*	*7.24E+03*	1.21E-02	*4.88E-03*	*−6.52E+01*
IP	< 2.48E+02	1.10E-01	*4.43E-02*	8.88E+00	*3.46E+00*	*7.99E+03*	4.64E-03	*1.88E-03*	*−9.58E+01*
F	–	8.07E-01	–	5.86E+01	–	*7.16E+03*	3.09E-01	–	*−6.17E+01*
An	–	1.34E-01	–	1.02E+01	–	*7.47E+03*	2.04E-02	–	*−8.48E+01*
BaA	–	1.89E-01	–	1.52E+01	–	*7.94E+03*	9.29E-03	–	*−9.51E+01*
Crhy	–	3.00E-01	–	2.41E+01	–	*7.93E+03*	1.58E-02	–	*−9.47E+01*
DbahA	–	4.71E-02	–	3.81E+00	–	*7.99E+03*	1.86E-03	–	*−9.61E+01*
Pyr	–	5.16E-01	–	3.94E+01	–	*7.54E+03*	1.14E-01	–	*−7.78E+01*
Phe	–	2.45E+00	–	1.92E+02	–	*7.72E+03*	3.41E-01	–	*−8.61E+01*
Acy	–	1.94E-01	–	1.52E+01	–	*7.76E+03*	2.69E-02	–	*−8.61E+01*
Ace	–	3.34E-01	–	2.42E+01	–	*7.14E+03*	1.32E-01	–	*−6.05E+01*
Nutrients [kg]									
P_{tot}	7.55E+06	8.97E+03	*1.19E-01*	3.08E+04	*4.06E-01*	*2.43E+02*	3.08E+04	*4.06E-01*	*2.43E+02*
N_{tot}	2.24E+08	7.14E+04	*3.19E-02*	4.29E+05	*1.92E-01*	*5.01E+02*	2.52E+05	*1.13E-01*	*2.53E+02*

[a] Calculated by means of Eq. (1) with respect to land-based loads to the marine environment in 2018.
[b] Percentage variation in shipping loads to the marine environment with respect to 2018.
[c] Numbers indicating percentage values are shown in *italics*.

responsible for significant percentage of the delivered load, especially for chemicals that have high affinity to mineral particles or organic matter (Collavini et al., 2005; Goswami et al., 2023; Littlewood, 1995).

3.1.2. Inputs from shipping to the water compartment

The number, type, and gross tonnage of ships in 2018, derived from AIS data and subsequently used to apply the STEAM model (Fig. 1) show high traffic of cargo and container vessels (2973), followed by ro-pax/passenger ships (334), service/fishing boats (362) and other ships (176). Use of scrubbers in 2018 was shown to be quite limited with only 85 scrubbers installed (ca 2 % of all vessels in 2018), mainly on vessels with high gross tonnage (45 - >80 ktonnes), differently from what was recently reported for the Baltic and North Sea where EGCS are much more used (Jalkanen et al., 2021).

The highest loads of metals from shipping were estimated for Cu (5.2E+01 t/year), Zn (9.85E+00 t/year), and V (2.92E-1 t/year) while the load of the other metals was between one (ca. 1.5–9.7E-02 t/year for As, Cr, Pb. And Ni) and three (ca. 2.3E-04–1.3E-01 t/year for Hg and Cd) orders of magnitude lower (Table 1, Fig. 2 and Figure SI3). Regarding the three most emitted metals, it is worth noting that they are associated with possible impacts on marine ecosystems. Cu and Zn are essential micronutrients for many organisms, with a role in enzymes relevant to many metabolic processes, but excessive amounts can impair physiological functions and cause cell damage, with subsequent potential risks at the ecosystem level (e.g., Karlsson et al., 2010; Cui et al., 2024). Vanadium has been reported to disrupt metabolic processes in fish, microalgae and crustaceans, causing oxidative stress, impaired growth and reproduction, thus its risks to marine ecosystems should not be neglected (Tambat et al., 2024; Tulcan et al., 2021).

Most of the load of Cu and Zn could be related to cargo ships and leakage from antifouling paints, while the load of V, Ni, Cd, and Cr was mainly associated with scrubber water discharged by large ships. However, grey water and sewage water contributed for a significant part to the load of Pb, Hg, and As (Figure SI4), highlighting the need to consider all waste streams when evaluating the contribution of shipping activities to the environmental exposure to the selected chemicals.

As for the load of PAHs in 2018, the highest emission was reached for low molecular weight compounds such as Naph (5.74E+00 g/year) and Phe (2.45E+00 g/year), while the load of other investigated PAHs was between one and two orders of magnitude lower (Table 1 and Fig. 2). These loads were shown to be associated mainly with the transit of large ro-pax and cargo vessels (Figure SI5) and to be mostly attributable to the discharge of open-loop scrubber water. However, in the case of Naph, Flu, BghiP, Ace, and F bilge water accounted for a significant portion (i.e., 15–25 %) of the load to water (Figure SI4). Under an ecological risk perspective, PAHs are of concern due to their persistence and potential to accumulate in aquatic organisms, particularly invertebrates, such as bivalves and crustaceans. PAHs are fairly rapidly metabolized in most vertebrates, but they and their toxic metabolites can cause deleterious effects in fish (Ben Othman et al., 2023; Honda and Suzuki, 2020). Moreover, PAHs can pose risks to human health through the consumption of contaminated seafood due to their carcinogenic, mutagenic, and

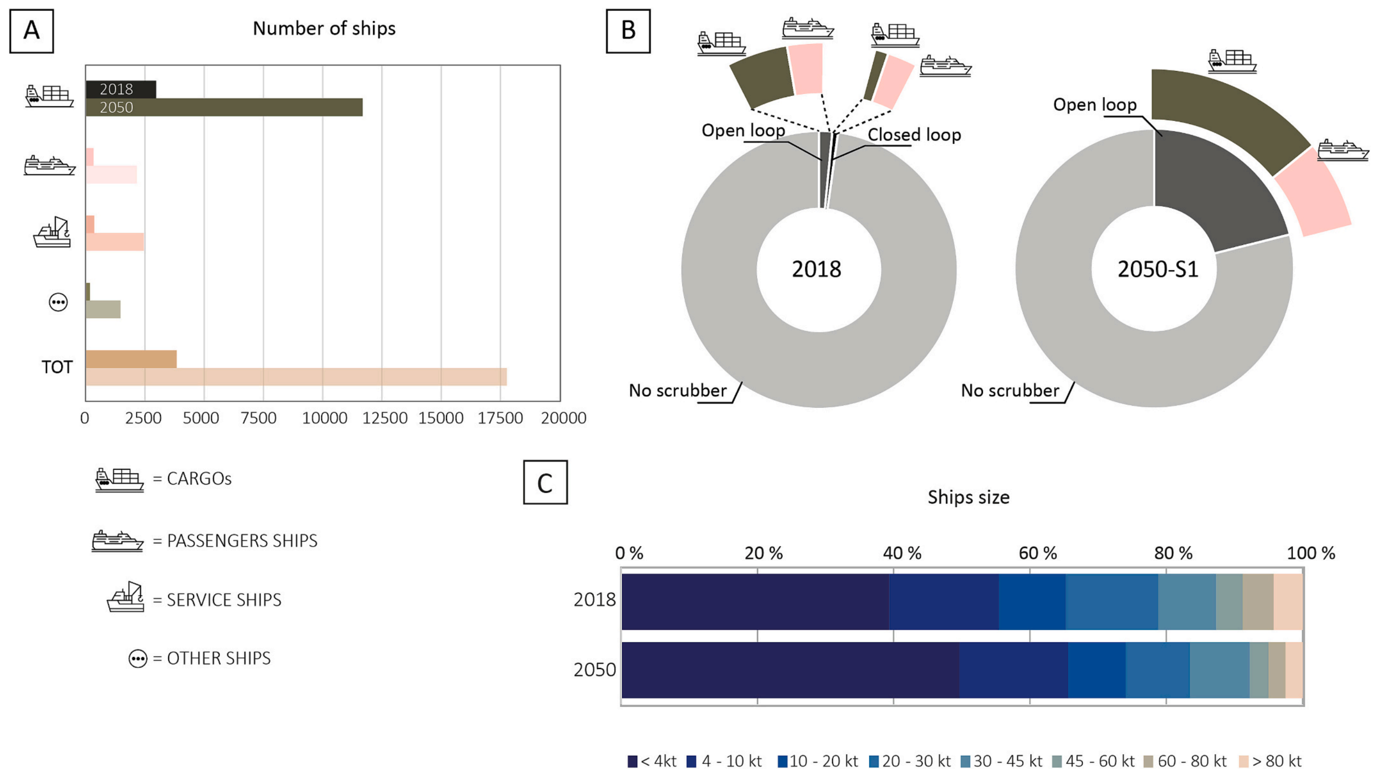

Fig. 1. Number, type, and size of ships in the case study area for 2018 and for simulated shipping traffic in 2050 (a, and c), with scrubber use for 2018 and 2050 Scenario 1 (b).

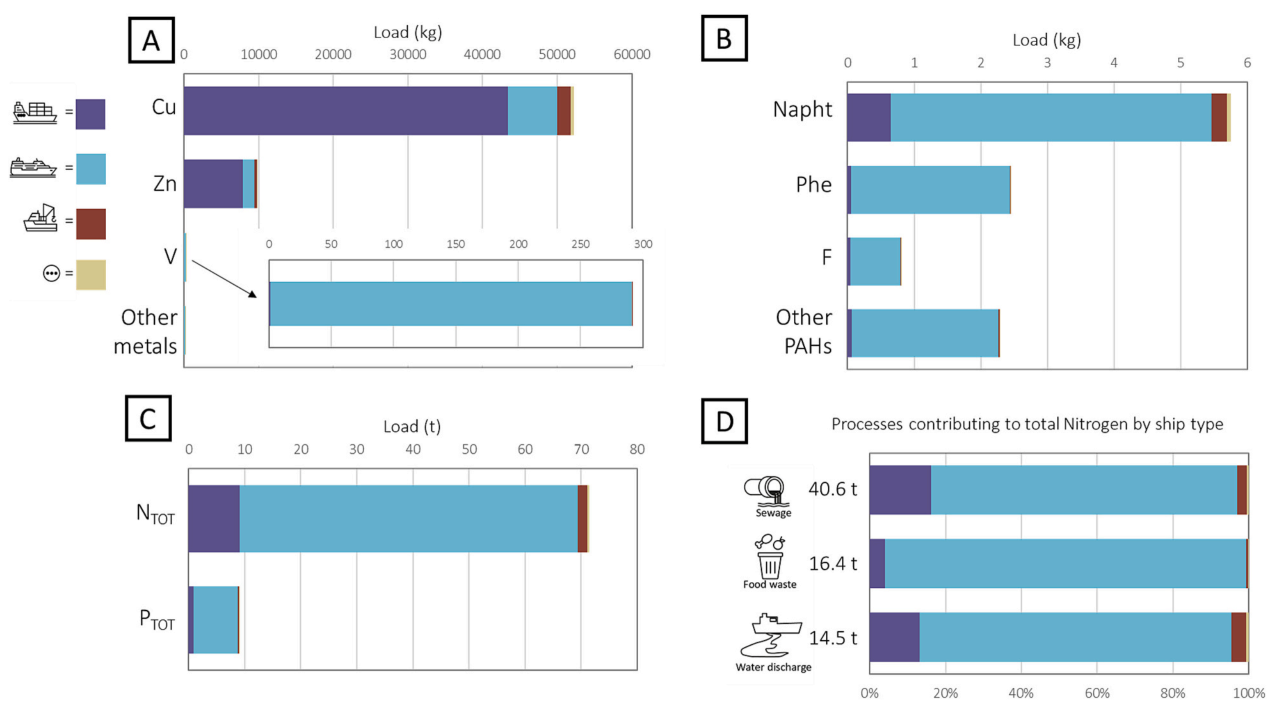

Fig. 2. Load of metals, PAHs, and nutrients for 2018 by ship type (a,b, and c), and processes contributing to N load to water by ship type (d).

endocrine disruptor properties (Barbosa et al., 2023; WHO/IARC, 2010).

Estimations of nutrients load considered the discharge of wastewaters (i.e., scrubber water, bilge water, sewage water, and grey water), sewage, and food-waste. The results (Fig. 2 and Figure SI4) showed how sewage and food-waste from ro-pax and cruise vessels contributed for the majority of the emission of N and P (Figure SI5) (their total being 7.14E+01 and 8.97E+00 t/year, respectively, as reported in Table 1).

In addition to the loads of metals, PAHs, and nutrients estimated from real AIS data for 2018, the results simulated with the STEAM model for the two scenarios described in paragraph 2.2.2 are reported in Table 1.

Scenario 1 showed how the continued use of HFO together with a widespread use of scrubbers to address SO_x air emission control is expected to cause a significant increase in the volume of discharged scrubber water (from 1.55E+06 in 2018 to 1.27E+08 m^3/year in 2050). This will lead to an increase of about 50–80 times of the loads into the water compartment of most metals (ca. 1.17 E-02-2.16E+01 t/year for As, Cd, Cr, Pb, Hg, Ni, and V) and PAHs (ca. 1.27E-03-3.61E-01 t/year). While scrubber water accounted for a significant percentage of Cu, Zn, and N loads under Scenario 1, the main contribution was still attributable respectively to anti-fouling paints and waste (i.e., foodwaste, sewage, and grey water) from passenger ships (Fig. 2 and Figure SI4). Since scrubber installations were assumed to occur for most of the fleet within the case study area, emissions of PAHs were no longer limited to high-tonnage cargo and ro-pax vessels but also to smaller vessels (Fig. 2 and Figure SI5).

Scenario 2 assumes HFO to be completely substituted with alternative fuels (i.e., methanol and LNG), and therefore scrubbers to be no longer necessary, leading to a more limited increase in the load of Cu, Zn, As, Pb, Hg, and N and to a significant decrease in the load of all PAHs. Under this scenario the main sources of contaminants from shipping are bilge water (for PAHs), anti-fouling paints (for Cu and Zn), and grey water (for the other metals). However, it is also important to consider the economic feasibility of this option, since the use of LNG and methanol, with respect to scrubber installation, would require more costly modifications of ships' engines, as well as a marked increase in fuel costs incurred by shipping companies (Winnes et al., 2021). If the use of methanol and LNG from renewable sources is considered to further reduce CO_2 emissions from shipping, fuel costs have been vaguely estimated at three times as high (Methanol Institute, 2023). Another fact to consider in the shift from HFO to LNG or methanol use is the occurrence of fuel spills through the production (well-to-gate), transport (gate-to-hull), and combustion processes (hull-to-wake) (Foretich et al., 2021).

3.1.3. Shipping contribution to the loads of metals, PAHs, and nutrients

Overall, shipping discharges for 2018 negligibly contributed to most contaminants load (ca. 6E-03 – 1E-01 %), with the exception of Cu and Zn for which shipping contributed for 2.1E+01 % and 1.3E+00 % to the overall load, respectively (Table 1). Antifouling paints are the largest source of Cu and Zn from shipping, contributing over 99 % and 95 % of the total input, respectively (Figure SI4). The STEAM model assumes that all ships are coated with a Cu-based coating that releases Cu and Zn into the marine environment (Jalkanen et al., 2021). However, increasing research indicates that biocide-free fouling release coatings can perform as well as, or even better than, Cu-based antifouling paints in preventing biofouling (Oliveira et al., 2022). Despite this, their market share remains low, at just 10 % (Lagerström et al., 2022), while most biocidal antifouling paints still contain inorganic Cu, 76 % containing cuprous oxide (Cu_2O) and 8.8 % containing cuprous thiocyanate (CuSCN) (Paz-Villarraga et al., 2022). In our 2050 scenario, we assume that Cu-based antifouling paints will continue to dominate the market. However, this assumption carries significant uncertainties due to ongoing efforts to enhance the performance of foul-release coatings (Hu et al., 2020). Figure SI6 illustrates how the contribution of shipping to pollutant emissions varies (or is expected to vary under future scenarios) over the course of the year, with peak values observed during the summer months when river flow rates are lower, and passenger traffic is higher. The load of Cu and Zn exhibit a more evenly distributed pattern over time, since it does not depend on the discharges from scrubbers (as in the case of PAHs and other metals), or from ro-pax and cruise vessels (as is the case of nutrients).

Even though the loads of nutrients from shipping activity are comparatively small at the basin scale, some areas might be significantly affected since the transit of ships is usually concentrated within specific periods and routes. In particular, the contribution of shipping to the load of nutrients and contaminants along shipping lanes may reach significantly higher values than the basin-scale average obtained in this work. Shipping emissions of nutrients may also have local effects on the biogeochemical processes, as most of them are released in spring-summer, where the photosynthetic activity is higher, as well as on areas which are not reached by the nutrients discharged by rivers (Raudsepp et al., 2019).

While this work estimated the load of nutrients from shipping directly to water due to liquid and solid waste discharge, deposition of nitrogen compounds (e.g., NOx and NH_3) emitted by ships to air should also be considered. For example, Raudsepp et al. (2019) and Neumann et al. (2020) reported a higher contribution of shipping to the water load of N for the Baltic Sea (about 3-5E+00 %). However, such estimations would require the use of air quality models, which were beyond the scope of this work.

In addition, since the loads of PAHs, Hg, and Cd were estimated by using half of the sampling DL as upper worst-case estimate of river concentrations (Table SI1–3), the effective load to the case study area from land-based sources may be markedly lower, leading shipping activities to be a relevant contribution, especially near high traffic areas.

If future scenarios are considered, the results shown in Table 1 and Figure SI6 highlight that the increase of naval traffic expected by 2050 would cause shipping to account for a more relevant fraction of the contaminants present, leading to values between 1E+00-5E+00 % for PAHs and most metals (i.e., Cd, Cr, Pb, Hg, Ni, and Zn) if scrubbers are extensively adopted (Scenario 1), while the maximum contribution is estimated for Cu (ca. 6E+01 % during summer and winter).

Similar results on the contribution of shipping traffic to the water loads of pollutants were reported by Ytreberg et al. (2022) for the Baltic Sea, where shipping was shown to account for a substantial fraction Cu and Zn load (3.7E+01 % and 3.6E+00 %, respectively) due to AFP leaching. Regarding PAHs emissions, Phe and An were reported to show the highest shipping contribution (ca. 9E+00 %), while the rest of PAHs ranged between 4E-01 % and 4E+00 %. While in our work it was not possible to assess the contribution of shipping to Phe and An loads as they are not routinely monitored in the case study area, it can be observed that shipping contribution for other PAHs in the baseline scenario is between one and two orders of magnitude lower than the values reported for the Baltic Sea. As scrubber water was shown to be the main source of these contaminants (Figure SI4), this difference can be mainly ascribed to the lower discharge in 2018 of this waste in the Northern Adriatic Sea (ca. 1.5E+06 m^3) with respect to the Baltic Sea (1.9E+08 m^3). In fact, similar shipping contributions (i.e., ca. 1E+00 – 1E+01 %) for PAHs in the case study area were estimated for S1, with an annual scrubber water discharge of about 1.3E+08 m^3. Further comparisons on the influence of other PAHs sources were not possible, as Ytreberg et al. (2022) did not account for riverine PAHs inputs and reported only on atmospheric deposition (not included in this study).

3.2. Emissions to the atmosphere

Deterioration of air quality has been shown to be directly related to increased risks towards both the environment and human health (Ghorani-Azam et al., 2016; Manisalidis et al., 2020), and atmospheric deposition has been recognized as an important source of pollution to the marine environment (Rahav et al., 2016; Xie et al., 2022; Ytreberg et al., 2022). For this reason, the investigation on the overall impact of ships on the case study area cannot leave aside the contribution of these activities to the air concentration and deposition of the investigated chemicals.

Recent studies by Raffaelli and co-workers (Raffaelli et al., 2020) showed that primary PM is produced mainly by biomass burning in non-industrial combustion plants and road transport. As far as NO_2 is concerned, the two most important emission sources are road transport and combustion in the manufactory industry. Considering ammonia, an important precursor of secondary particulate, it has been shown that most emissions are produced by agriculture, while the emission of organic compounds, contributing to the formation both of PM and ozone, is mainly related to the sector "solvent and other products". As far as SO_2 is concerned, most of the emissions can be related to the manufactory industry and to production processes.

The results reported in Table 2 and Figure SI7 show the emission of metals, PAHs, nutrients, CO_2, CO, SO_2, $PM_{2.5}$ to air from land-based sources and shipping activities. Since no atmospheric chemical transport model was applied in this work to estimate deposition fluxes to the sea, this information cannot directly be compared with the above-mentioned loads to water. It can offer a preliminary assessment of the contribution of shipping to air quality under the current and selected scenarios that can possibly be of use for future studies.

The highest emission of metals to the atmosphere from shipping in 2018 (Table 2) were estimated for V, Ni, and Zn (3.0E+00, 1.5E+00, and 1.1E+00 t/year, respectively), as they are among the most present metals in HFO (Ali and Abbas, 2006; Zhao et al., 2021, 2013). The highest emissions of PAHs were calculated for Naph and Crhy (8.2E-01 and 3.9E-02 t/year, respectively), while the other organic chemicals showed emissions about one order of magnitude lower. Due to limited data availability on metals and PAHs emissions from land-based sources, it was possible to estimate the shipping contribution only for Cd and Pb, with values of 1.89E+00 % and 1.16E-01 %, respectively (Table 2). These trends found confirmation in the emissions estimated for 2050 under Scenario 1, as the HFO remains the main emission source.

The results showed also how shipping contributes to a significant part of the emissions of SO_2, N, $PM_{2.5}$, CO_2, and CO, while there is no significant emission of phosphorus. In particular, the deposition of N from shipping may affect primary production at the local scale, especially near shipping lanes, harbours, and in the open sea where riverine input is less relevant (Claremar et al., 2017; Hongisto, 2014; Neumann et al., 2020).

The results reported in Table 2 and Figure SI7 indicates that the use of different approaches to control shipping air emissions may drastically influence air quality in the case study area, as the use of LNG and methanol instead of HFO and scrubbers is expected to cause a decrease in the emissions of metals and PAHs of about one to two orders of magnitude. STEAM results also showed that despite the increase in shipping traffic, the use of scrubbers or alternative fuels was predicted to decrease the emission of SO_2 (ca. 82–95 %), $PM_{2.5}$ (ca. 30–85 %), and NO_x (ca. 15–35 %) with respect to 2018 emissions. Conversely, the expected increase in shipping traffic in both 2050 scenarios, will lead to 2–10 fold increase of CO emissions (Table 2 and Figure SI7).

Table 2
Emissions to air from land-based sources and shipping activities[d].

	Land-based sources	Ships 2018	*Shipping contribution 2018 [%]*[a]	Ships 2050 S1	*Shipping contribution 2050 S1 [%]*[a]	*Shipping 2050 S1 vs 2018 [%]*[b]	Ships 2050 S2	*Shipping contribution 2050 S2 [%]*[a]	*Shipping 2050 S2 vs 2018 [%]*[b]
Metals [kg]									
As	–	6.15E+01	–	3.80E+01	–	*-3.83E+01*	6.02E+00	–	*−9.02E+01*
Cd	7.88E+02	1.52E+01	*1.93E+00*	9.49E+00	*1.20E+00*	*−3.76E+01*	1.53E+00	*1.94E-01*	*−8.99E+01*
Cr	–	1.14E+02	–	6.99E+01	–	*−3.87E+01*	1.09E+01	–	*−9.04E+01*
Cu	–	1.32E+02	–	8.06E+01	–	*−3.87E+01*	1.26E+01	–	*−9.04E+01*
Pb	6.34E+04	7.34E+01	*1.16E-01*	4.52E+01	*7.13E-02*	*−3.85E+01*	7.11E+00	*1.12E-02*	*−9.03E+01*
Hg	–	0.00E+00	–	0.00E+00	–	–	0.00E+00	–	–
Ni	–	1.49E+03	–	6.11E+02	–	*−5.89E+01*	1.42E+01	–	*−9.90E+01*
V	–	2.97E+03	–	1.21E+03	–	*−5.92E+01*	2.47E+01	–	*−9.92E+01*
Zn	–	1.15E+03	–	7.03E+02	–	*−3.89E+01*	1.09E+02	–	*−9.05E+01*
PAHs [kg]									
Napht	–	8.66E+02	–	1.92E+03	–	*1.22E+02*	2.75E+02	–	*−6.83E+01*
Fl	–	8.21E+00	–	2.04E+01	–	*1.49E+02*	1.45E+01	–	*7.70E+01*
BbF	–	4.16E+00	–	3.80E+00	–	*−8.77E+00*	4.65E-01	–	*−8.88E+01*
BkF	–	2.93E+00	–	2.73E+00	–	*−6.72E+00*	4.18E-01	–	*−8.57E+01*
BaP	–	3.99E+00	–	3.66E+00	–	*−8.47E+00*	4.65E-01	–	*−8.84E+01*
BghiP	–	5.00E+00	–	4.59E+00	–	*−8.18E+00*	6.04E-01	–	*−8.79E+01*
IP	–	3.40E+00	–	3.37E+00	–	*−8.57E-01*	7.89E-01	–	*−7.68E+01*
F	–	1.32E+01	–	3.06E+01	–	*1.31E+02*	1.05E+01	–	*−2.09E+01*
An	–	1.82E+00	–	4.27E+00	–	*1.34E+02*	1.78E+00	–	*−2.70E+00*
BaA	–	5.72E+00	–	5.07E+00	–	*−1.13E+01*	4.18E-01	–	*−9.27E+01*
Crhy	–	3.91E+01	–	3.37E+01	–	*−1.38E+01*	1.39E+00	–	*−9.64E+01*
DbahA	–	2.75E+00	–	2.49E+00	–	*−9.45E+00*	2.79E-01	–	*−8.98E+01*
Pyr	–	8.14E+00	–	1.97E+01	–	*1.42E+02*	1.13E+01	–	*3.88E+01*
Phe	–	6.34E+01	–	1.45E+02	–	*1.28E+02*	4.05E+01	–	*−3.62E+01*
Acy	–	5.98E+00	–	1.47E+01	–	*1.46E+02*	9.70E+00	–	*6.21E+01*
Ace	–	1.68E+01	–	3.72E+01	–	*1.21E+02*	4.76E+00	–	*−7.17E+01*
Nutrients [kg]									
Ptot	–	–	–	–	–		–	–	
Ntot	4.17E+07	3.50E+06	*7.74E+00*	2.28E+06	*5.18E+00*	*−3.49E+01*	5.26E+06	*1.12E+01*	5.05E+01
Air pollutants [kg]									
CO_2[c]	5.75E+10	6.88E+08	*1.18E+00*	1.84E+09	*3.10E+00*	*1.67E+02*	1.68E+09	*2.83E+00*	*1.44E+02*
CO	4.99E+08	1.13E+06	*2.25E-01*	2.93E+06	*5.85E-01*	*1.60E+02*	1.21E+07	*2.36E+00*	*9.73E+02*
SO_2	1.80E+07	5.55E+06	*2.35E+01*	9.46E+05	*4.98E+00*	*−8.30E+01*	2.15E+05	*1.18E+00*	*−9.61E+01*
$PM_{2.5}$	2.18E+07	6.09E+05	*2.72E+00*	4.27E+05	*1.92E+00*	*−3.00E+01*	8.29E+04	*3.78E-01*	*−8.64E+01*

[a] Calculated by means of Eq. (2) with respect to land-based emissions to air in 2018.
[b] Percentage variation in shipping air emissions with respect to 2018.
[c] Data from the CAMS-REG-v4.2 emissions inventory for 2018 was integrated with information from the INEMAR database for 2015 (Friuli Venezia Giulia Region) and 2017 (Veneto Region and Emilia Romagna Region) (INEMAR, 2020).
[d] Numbers indicating percentage values are shown in *italics*.

4. Conclusions

In this work the contribution of shipping to the loads of metals, PAHs, and nutrients to the marine environment, as well as to the emission of air pollutants, in the Northern Adriatic Sea in 2018 and under two future 2050 scenarios was investigated for the first time by integrating (i) modelled data of shipping-related emissions of contaminants, (ii) tributaries emissions from daily river flow measurements and water concentrations, and (iii) land-based emissions to the atmosphere available in local and international databases. Shipping activities were identified as significant contributors to the marine environment for Cu, Zn, N, Phe, and Napth loads due to antifouling paints, sewage, scrubber water, and bilge water. Conversely, shipping activities were shown to contribute significantly only to the air emission of SO_2, while for CO_2, CO, and $PM_{2.5}$ the contribution was between one and two orders of magnitude lower. The role of scrubber and bilge water as significant sources of contaminants was identified and quantified, however, to carry out a comprehensive evaluation of the environmental impacts of shipping, further studies should also consider other waste streams such as cooling water and ballast water, and the inherent ecotoxicological effects of all effluents.

Scenario analysis highlighted how different future emission control strategies may affects chemical pressure on water and air quality in the case study area. While both scenarios showed a significant reduction of most air pollutants' emission, Scenario 1 indicated how the high use of scrubbers would cause a significant increase of the water loads of PAHs and metals. Antifouling paints were showed to account for a significant increase of the load of Cu and Zn in both scenarios, suggesting the urgent need for alternatives to Cu and Zn-based coatings.

This work highlighted how an inventory of shipping discharges and emissions to air for the marine environment can benefit from modelling approaches, which have a great potential in complementing available experimental data, especially if we consider that ships are not obliged to report on their actual emissions/discharges of metals, PAHs and nutrients, differently from land-based industries that must follow the requirements of the Industrial Emissions Directive (Directive 2010/75/EU).

The work carried out in this study provided a robust multi-source inventory of nutrients and contaminants loads to the case study area integrating information on both land-based and shipping sources, providing policymakers and stakeholders a solid ground to quantify anthropogenic pressures and develop efficient integrated strategies for the management of the Northern Adriatic Sea marine ecosystem.

However, while the information provided and discussed in this work provides a preliminary estimation of shipping activities' contribution to the water and air quality of the Northern Adriatic Sea, a more detailed analysis to find specific areas of concern requires the investigation of the effects of chemical and transport processes affecting the environmental fate of chemicals both in the water and air compartments (e.g., dispersion, partitioning, degradation, and air/water exchange) through the application of high-resolution modelling tools.

CRediT authorship contribution statement

Loris Calgaro: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Formal analysis, Data curation. **Martina Cecchetto:** Writing – original draft, Visualization, Validation, Software, Methodology, Formal analysis, Data curation, Conceptualization. **Elisa Giubilato:** Writing – review & editing, Writing – original draft, Validation, Methodology, Conceptualization. **Jukka-Pekka Jalkanen:** Writing – review & editing, Software, Methodology, Funding acquisition. **Elisa Majamäki:** Writing – review & editing, Software, Methodology. **Erik Ytreberg:** Writing – review & editing, Methodology, Formal analysis. **Ida-Maja Hassellöv:** Writing – review & editing, Methodology, Funding acquisition. **Erik Fridell:** Writing – review & editing, Methodology, Formal analysis. **Elena Semenzin:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Antonio Marcomini:** Writing – review & editing, Methodology, Funding acquisition, Conceptualization.

Consent to participate

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Declaration of competing interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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The Scientific colour map used in Fig. 1 and Fig. 2 to prevent visual distortion of the data and exclusion of readers with colour-vision deficiencies refers to Crameri et al. (2020).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2025.117573.

Data availability

Data will be made available on request.

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