Atmospheric Pollution Research 15 (2024) 102228

Contents lists available at ScienceDirect

Atmospheric Pollution Research

journal homepage: www.elsevier.com/locate/apr

Maritime sector contributions on NO_2 surface concentrations in major ports of the Mediterranean Basin

Andreas Pseftogkas [a,*], Maria-Elissavet Koukouli [a], Astrid Manders [b], Arjo Segers [b], Trissevgeni Stavrakou [c], Janot Tokaya [b], Charikleia Meleti [a], Dimitris Balis [a]

[a] Laboratory of Atmospheric Physics, Aristotle University of Thessaloniki, Thessaloniki, Greece
[b] TNO, Air Quality & Emissions Research, Utrecht, the Netherlands
[c] Royal Belgian Institute for Space Aeronomy (BIRA-IASB), Brussels, Belgium

ARTICLE INFO

Keywords:
Nitrogen dioxide
LOTOS-EUROS
TROPOMI
Source apportionment
Maritime sector emissions

ABSTRACT

The aim of this study is to estimate the contribution of the maritime sector on the air quality of major Mediterranean ports with the Long Term Ozone Simulation-European Operational Smog (LOTOS-EUROS) chemical transport model, using two source apportionment methods: the *brute-force emission scenario* methodology and the *labelling* approach. With the brute-force method NO_2 shipping concentrations are estimated by the ratio of the difference between two model runs - with original and reduced emissions - and the equivalent emission reduction factor. In the labelling, emitted species are explicitly labelled per sector and tracked through all model processes. Simulations are performed for a one-year period, from May 2018 to May 2019 and the two methodologies are intercompared. The methods show strong agreement between NO_2 shipping contributions ($R > 0.95$) and differences of ~14%. A sensitivity analysis carried out using the brute-force method indicates that a linear regime between NO_X emissions and NO_2 concentrations holds, when adopting a low to moderate emission reduction (<50%). We applied the brute-force method with an assumed 20% emission reduction and found that the NO_2 surface concentrations attributed to maritime sector activities in selected ports were between 5% and 70% of the total NO_2 surface concentrations, with a mean value of 27%. Comparisons between measurements from the European Environment Agency (EEA) ground-based monitoring stations and LOTOS-EUROS NO_2 surface concentrations show a strong correlation (R~0.8) with an underestimation of the model (~-32%) for the whole period. The bias is reduced to −20% when air quality monitoring stations affected by traffic and industrial activities are excluded from the analysis. Moreover, observed Sentinel-5 Precursor TroPospheric MOnitoring Instrument (S5P/TROPOMI) and modelled NO_2 vertical column densities (VCDs) show a significant spatial agreement (R~0.86) for both summer and winter with biases of −25% and −1%, respectively, over the selected ports. These comparisons were carried out as an indirect way of validating the applied methodology and the performance of the model in coastal areas. The present study provides a solid background which will enable the assimilation of the satellite observations to the CTM to infer NO_X shipping emissions in the Mediterranean Basin in view of the upcoming designation of the Mediterranean Sea as an Emission Control Area in 2025.

1. Introduction

The maritime sector is a vital component of the global economy, responsible for the transportation of approximately 80% of global goods (UNCTAD, 2022; Schnurr et al., 2019). Future projections show a 40% increase of maritime trade by 2050 followed by a 90%–150% increase of greenhouse gases (GHG) compared to 2008 levels (Faber et al., 2020). In the European Union (EU), 32% of short shipping (i.e., transport of goods between ports) and 53% of seaborne passenger traffic are occurring in the Mediterranean (https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Maritime_transport_statistics_-_short_sea_shipping_of_goods, last accessed on May 24, 2024). Due to its significance as a crossroad of three continents, the Mediterranean shipping activity is expected to rise in the following years, deteriorating both air quality and

Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control.

* Corresponding author.
E-mail addresses: anpsefto@auth.gr (A. Pseftogkas), mariliza@auth.gr (M.-E. Koukouli), astrid.manders@tno.nl (A. Manders), arjo.segers@tno.nl (A. Segers), trissevgeni.stavrakou@aeronomie.be (T. Stavrakou), janot.tokaya@tno.nl (J. Tokaya), meletei@auth.gr (C. Meleti), balis@auth.gr (D. Balis).

https://doi.org/10.1016/j.apr.2024.102228
Received 8 January 2024; Received in revised form 28 May 2024; Accepted 14 June 2024
Available online 19 June 2024

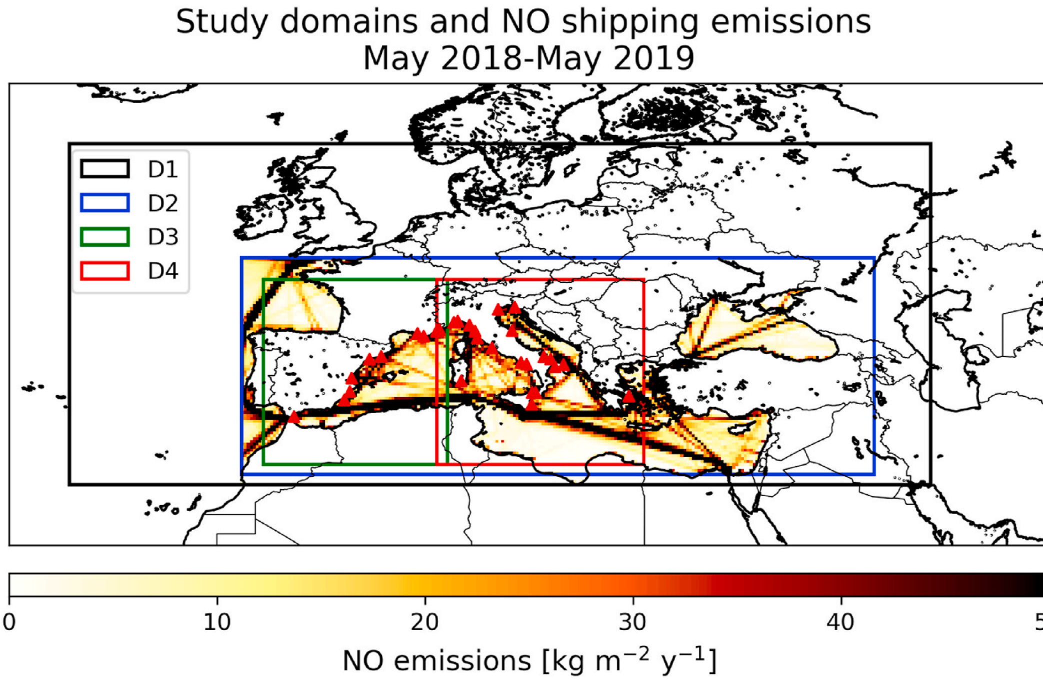


Fig. 1. Nested model runs configurations, study domains and NO shipping emissions [kg m^{-2} y^{-1}] in the Mediterranean Basin. Red triangles depict the selected EEA air quality monitoring stations used in this work. Fig. S1 shows the locations of the 29 Mediterranean ports.

human health in coastal regions (Russo et al., 2023).

The combustion of fuels in ship engines is responsible for emissions of various pollutants such as nitrogen oxides (NO_X=NO_2+NO), sulfur oxides (SO_X), particulate matter (PM), carbon monoxide (CO) and hydrocarbons (Smith et al., 2014). NO_X international shipping emissions contribute 15%–35% to total anthropogenic NO_X emissions (Crippa et al., 2018) and shipping emissions are estimated to cause 60,000 premature deaths annually, mainly affecting coastal regions (Corbett et al., 2007). Recent studies reported that particulate matter and nitrogen dioxide (NO_2) ship-related emissions increased all-cause premature deaths by 7.7% in the Iberian Peninsula in 2015 (Nunes et al., 2021) and accounted for 430 premature deaths per year in the Mediterranean (Viana et al., 2020).

To reduce the impact of shipping on air quality, the International Maritime Organization (IMO) has adopted amendments to designate the Mediterranean as an Emission Control Area (ECA) for sulfur oxides and particulate matter, entering into force in May 1st of 2024 under the International Convention for the Prevention of Pollution from Ships (REMPEC, 2019; MARPOL, (https://www.imo.org/en/OurWork/Environment/Pages/Index-of-MEPC-Resolutions-and-Guidelines-related-to-MARPOL-Annex-VI.aspx#1, last accessed on May 24, 2024). This will affect the existing limit for sulfur in fuel oil used on board ships from 0.5% m/m (mass by mass) to 0.1% m/m and reduce sulfur dioxide (SO_2) and PM shipping emissions. On the contrary, nitrogen oxides levels originating from shipping activities in the Mediterranean are not expected to decrease (Van Roy et al., 2023), negatively impacting the environment and human health in coastal regions (Brandt et al., 2013). Hence, the importance of identifying and quantifying NO_X shipping emissions and assessing their impact on air quality and human health in the Mediterranean Basin are becoming a pressing need (Khomenko et al., 2023).

The number of studies on shipping emissions has increased significantly in the last years, especially in the greater Mediterranean area. Modelling approaches have been developed to estimate the contribution of shipping emissions to concentrations of air pollutants in the Mediterranean (Aksoyoglu et al., 2016; Merico et al., 2021; Fink et al., 2023; Russo et al., 2023), and reported significant contribution (>20%) of the shipping sector to PM, NO_2 and O_3 concentrations. Furthermore, satellite observations of NO_2 vertical column densities (VCDs) have been used to identify and quantify emissions originating from various shipping activities (Georgoulias et al., 2020; Pseftogkas et al., 2021; Riess et al., 2022; Kurchaba et al., 2022; Kim et al., 2023; Rodriguez Valido et al., 2023). In combination with impact assessments of shipping emissions on human health (Merico et al., 2021; Kukkonen et al., 2022), these studies could be used in a broader context to inform policy decisions towards mitigation of ship-related air pollution.

Here, we apply two source apportionment methodologies, namely the *brute-force* and *labelling* approaches, to estimate the contributions of the maritime sector on NO_2 surface concentrations in 29 Mediterranean ports and its impact on air pollution. To this purpose, the Long Term Ozone Simulation-European Operational Smog (LOTOS-EUROS) chemical transport model (CTM) simulations are performed for a one-year period, from May 2018 to May 2019. Similarly to the work of Thürkow et al. (2023), but only for the shipping sector in the Mediterranean, we highlight the similarities and discrepancies between the two source apportionment methods and further associate the estimated impacts of shipping on NO_2 concentrations with vessel statistics obtained from the European Statistical Office (EUROSTAT). Finally, we evaluate the model skill in coastal areas through comparisons with ground-based measurements obtained from the European Environment Agency (EEA) and satellite observations from the Sentinel-5 Precursor TroPospheric MOnitoring Instrument (S5P/TROPOMI).

This work differs from previous studies (Fink et al., 2023; Vinken et al., 2011), where the impact of shipping on NO_2 and O_3 was estimated in the Mediterranean, the Pacific Ocean, and North Sea with the application of a 100% emission reduction scenario. Here, we assess the linearity of the NO_X regime to various emission reduction scenarios and estimate the range in which emission perturbations lead to proportional changes in surface concentrations, instead of directly zeroing out shipping emissions as presented by Fink et al. (2023). Our research focuses on estimating the ship contributions on heavily polluted ports with complex chemical and physical processes without accounting for a ship plume segregation, whereas Vinken et al. (2011) focus mainly on open-sea areas and chemically segregate the ship plume and the adjacent ambient atmosphere.

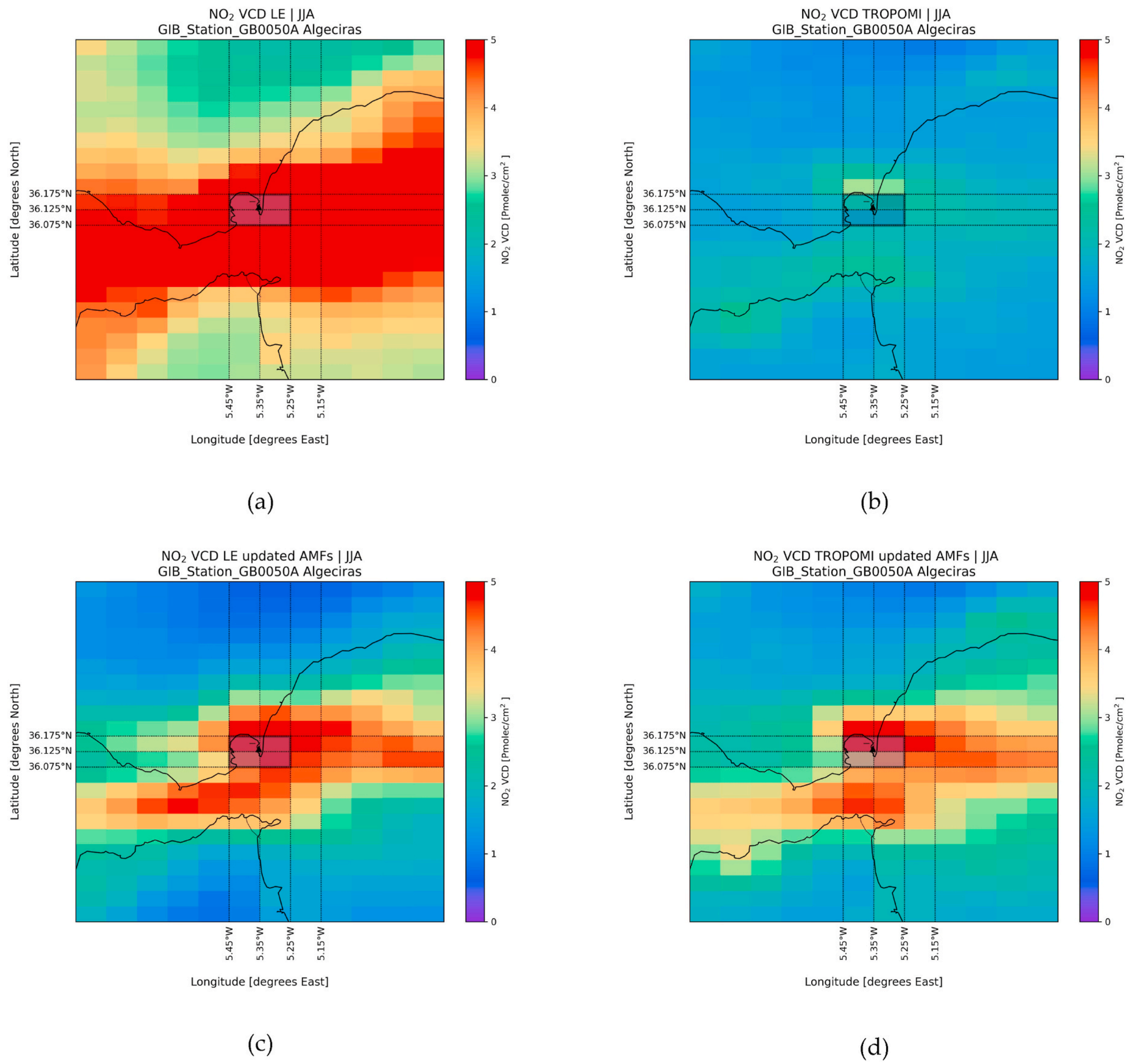


Fig. 2. Tropospheric NO_2 VCD over the port of Algeciras for the summer period (JJA) from **(a)** LOTOS-EUROS; **(b)** TROPOMI; **(c)** LOTOS-EUROS with updated AMFs; **(d)** TROPOMI with updated AMFs.

The study is structured as follows. In Section 2, all the involved datasets and the implemented methodologies are described in detail. In Sections 3.1 and 3.2, the source apportionment results, and the comparisons to observations are presented, respectively. Finally, Section 4 summarizes the main findings of this study.

2. Materials and methods

2.1. Datasets

2.1.1. LOTOS-EUROS CTM simulations

The open source v2.02.002 LOTOS-EUROS CTM (Manders et al., 2017) is used to simulate NO_2 vertical column densities and NO_2 surface concentrations over the Mediterranean. LOTOS-EUROS simulates the main tropospheric pollutants like ozone, NOx, SOx, primary and secondary particulate matter (Schaap et al., 2008). The model solves the continuity equation that describes the change in time of the concentration of a component as a result of chemistry, transport and diffusion, emissions, entrainment, dry and wet deposition (Schaap et al., 2008). Gas phase chemistry is described using the TNO Chemical Bond Mechanism-IV (CBM-IV), which is a condensed version of the original scheme (Whitten et al., 1980). Cloud chemistry is described following Banzhaf et al. (2012). Aerosol chemistry is represented using the Inorganic Species and Organic Reactivity for the Secondary Organic Model II (ISORROPIA2) module (Fountoukis and Nenes, 2007). Anthropogenic emissions are taken from the Copernicus Atmospheric Monitoring Service Regional European (CAMS-REG v5.1 2018) emission inventory available at 0.05° × 0.10° (Kuenen et al., 2022). Emissions from different sources are distributed in space and time, in a consistent manner, using relevant proxies for source categories. Emissions are gridded on a 0.05° × 0.1° grid and the temporal variation of emissions is represented by monthly, daily, and hourly time factors that distribute the annual emission totals in time for each source category (Kranenburg et al., 2013). In CAMS-REG v5.1, shipping emissions are derived utilizing an alternative novel modelling approach based on the STEAM (Ship Traffic Emission Assessment Model) model (Jalkanen et al., 2012; Johansson et al., 2017). More specifically, shipping emissions of relevant pollutants (NO_X, SO_2, PM, CO) are provided globally, on a 0.05° × 0.1° grid, based on the generation of shipping routes from the AIS (Automatic Identification System) signals and emission factors based on the characteristics of each vessel (Kuenen et al., 2022). The share of the maritime sector NO_X emissions is 97% for NO and 3% for NO_2. All model

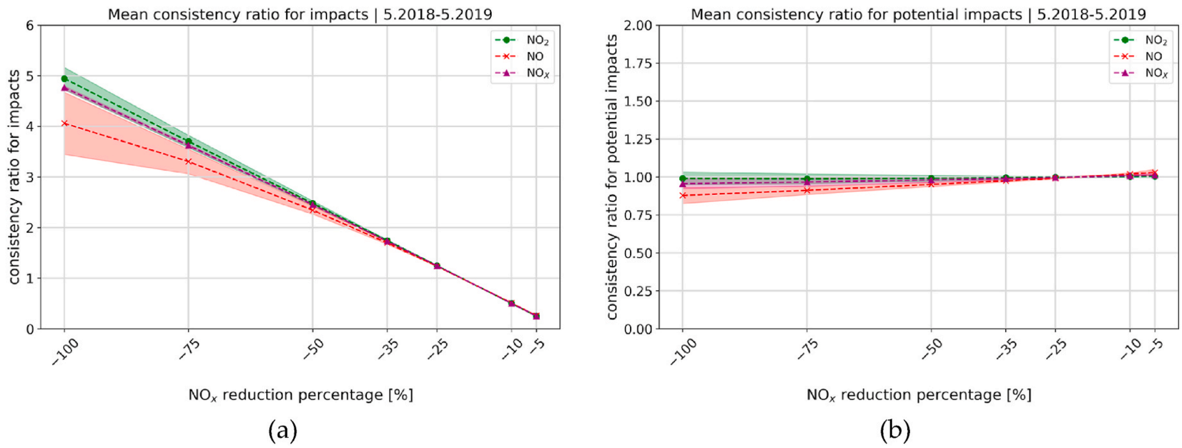


Fig. 3. (a) Consistency ratio of impacts and **(b)** consistency ratio of potential impacts for NO [red], NO_2 [green] and NO_X [purple].

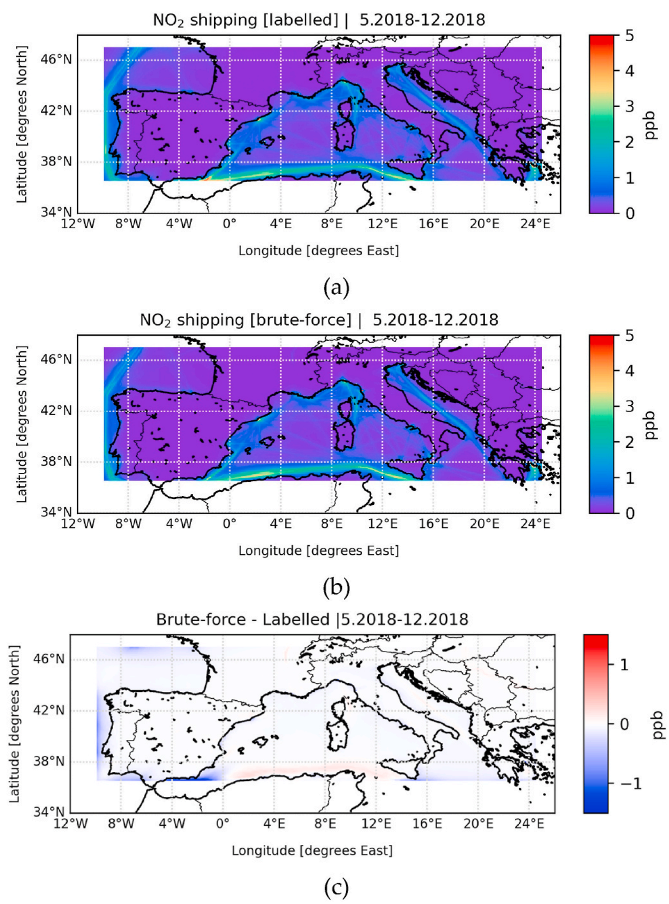


Fig. 4. (a) Labelled shipping NO_2 surface concentrations; **(b)** NO_2 potential impacts of the shipping sector with a 20% NO_X emission reduction percentage; **(c)** Differences between the labelling and brute-force approaches.

simulations are driven by the operational meteorological data from the European Centre for Medium-Range Weather Forecasts (ECMWF) provided at a horizontal resolution of 7 km × 7 km and hourly temporal resolution.

Fig. 1 demonstrates the NO shipping emissions of the inventory and the location of the European Environment Agency air quality monitoring stations later used in the assessment of the CTM simulations, while Fig. S1 shows the 29 Mediterranean ports involved in this research. Recently, the model has been used for source attribution purposes of nitrogen oxides and particulate matter (Fink et al., 2023; Thürkow et al., 2023, etc.) and for validation purposes with ground-based and satellite observations (Pseftogkas et al., 2022; Koukouli et al., 2022; Timmermans et al., 2022; Skoulidou et al., 2021, etc.).

In this work, the LOTOS-EUROS CTM was used to simulate NO_2 surface concentrations and vertical column densities for selected port locations in the Mediterranean Basin. A nested run configuration was implemented for the simulations. An outer European run (D1, Fig. 1) with coarse resolution (0.5° × 0.5°) was performed from January 2018 to December 2021. Boundary and initial conditions were obtained from the CAMS Global near-real-time (NRT) reanalysis with a spatial resolution of 35 km × 35 km. The output of the coarse run was used as boundary conditions for the Mediterranean (D2) run with a less coarse resolution (0.25° × 0.25°) in order to ensure the smooth transition of dynamics between the two runs. Both D1 and D2 runs are configured with 12 vertical coarsened layers reaching up to 10 km, 7 of which are typically within the PBL. Moreover, the Mediterranean Basin was separated into two smaller domains with a higher horizontal resolution (0.05° × 0.10°), namely the western Mediterranean (D3) and the central Mediterranean (D4), using as input the D2 domain output (Fig. 1). The separation of the Mediterranean region into two domains was done for computational efficiency due to the high vertical and horizontal resolution and the target period from May 2018 to May 2019. The two inner runs (D3 & D4) were configured with 34 vertical layers, with the same vertical structure as the ECMWF profiles. A previous study (Pseftogkas et al., 2022) has shown that NO_2 surface concentrations are higher and comparisons with in-situ measurements over central Europe result in a lower bias (by 5%–15%) when 34 vertical levels and no coarsening are used in the model, compared to 12 coarsened levels. This is in line with the research by Riess et al. (2023), who showed that LOTOS-EUROS simulates deep marine boundary layer depths when compared to aircraft measurements, over the summertime North Sea, leading to an underestimation of NO_2 concentrations close to the surface. Hence, the incorporation of more vertical layers in the boundary layer of ports leads to a more realistic mixing of pollutants and higher surface concentrations.

2.1.2. EEA ground-based monitoring stations

LOTOS-EUROS modelled NO_2 surface concentrations were evaluated against EEA [https://www.eea.europa.eu/en, last accessed on May 24, 2024] in-situ measurements for the studied period (May 2018–May 2019). 29 stations (Table S1) located in ports (Fig. S1) or in a radius of 15–20 km from ports, as shown in Fig. 1 [red triangles], were selected. The stations are categorized by the EEA as 11 traffic, 3 industrial and 15 background stations. The most prominent Mediterranean ports were selected according to EUROSTAT quarterly and annual statistics [https://ec.europa.eu/eurostat/statistics-explained/, last accessed on May

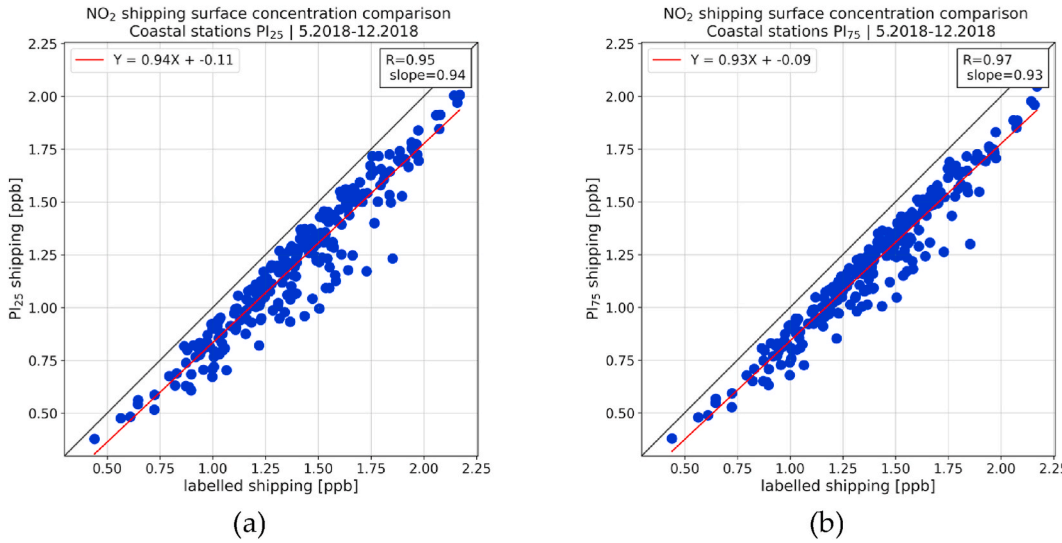


Fig. 5. Scatter plots between the mean daily labelled shipping concentrations of the selected ports and the potential impacts [in ppb] for two NO_X shipping emission reduction percentages **(a)** 25%; **(b)** 75%.

Table 1
Labelled and brute-force NO_2 mean shipping concentration estimates in all ports [first row] and the root mean square errors between the two techniques [second row].

Shipping sector	Labelled	PI_5	PI_{10}	PI_{20}	PI_{25}	PI_{35}	PI_{50}	PI_{75}	PI_{100}
Mean value[a]	1.38 ± 1.24	1.195 ± 1.07	1.194 ± 1.07	1.194 ± 1.08	1.194 ± 1.08	1.195 ± 1.09	1.195 ± 1.1	1.199 ± 1.11	1.208 ± 1.13
RMSE[b]		5.00	4.97	4.92	4.89	4.83	4.76	4.65	4.58

[a] in ppb.
[b] in 10^{-3} ppb.

2024, 2024]. Comparisons between the LOTOS-EUROS simulations and the in-situ measurements are conducted for the model grid cell containing the ground-based station (Section 3.3).

2.1.3. S5P/TROPOMI observations and the CAMS Satellite Operator

TROPOMI was launched onboard the Sentinel-5 Precursor (S5P) satellite by the European Space Agency (ESA) on October 13, 2017 (Veefkind et al., 2012). As part of the EU Copernicus Earth Observation Program, this mission aims at monitoring atmospheric composition from space. The satellite operates on a polar orbit with a spatial resolution at nadir of 3.5 × 5.5 km^2 since August 2019 (van Geffen et al., 2020; Eskes and Eichmann, 2021). The low signal-to-noise ratio combined with the high horizontal resolution have resulted in a wealth of information regarding the monitoring of nitrogen oxides (NO_X) originating from various sources in different areas globally. More specifically, these observations have been employed in monitoring NO_2 levels in urban and background areas (Lange et al., 2022; Pseftogkas et al., 2022; Koukouli et al., 2022; Goldberg et al., 2021; Stavrakou et al., 2020; etc.), in estimating NO_X emissions (Beirle et al., 2021; Lorente et al., 2019), in assessing the effect of the COVID-19 pandemic on NO_2 levels (Fioletov et al., 2022; Levelt et al., 2022; Koukouli et al., 2021; Bauwens et al., 2020), and in estimating plumes and emissions from the maritime sector (Riess et al., 2023; Rodriguez Valido et al., 2023; Kurchaba et al., 2022; Riess et al., 2022; Pseftogkas et al., 2021; Georgoulias et al., 2020).

In this study, the reprocessed, open source, v02.04.00 version of the TROPOMI NO_2 vertical column densities (van Geffen et al., 2022a, https://dataspace.copernicus.eu/, last accessed on May 24, 2024) is used for two periods, the summer of 2018 (June, July, August) and the winter of 2018–2019 (December, January, February). The operational TROPOMI NO_2 data product is thoroughly described in van Geffen et al. (2022b), Eskes et al. (2021), and Eskes and Eichmann (2021). Here, we only use satellite pixels with a quality assurance value higher than 0.75, corresponding to cloud radiance fractions below 0.5 (van Geffen et al., 2022a).

TROPOMI observations are used in this work to evaluate the performance of the LOTOS-EUROS CTM in the selected Mediterranean ports (Section 3.4). To minimize the discrepancies between the assumptions in the TROPOMI retrieval and the validation process, the application of the TM5-MP (Williams et al., 2017) averaging kernels on model simulations is important as shown in previous studies (Douros et al., 2023; Pseftogkas et al., 2022). In this work, this has been performed using the CAMS Satellite Operator (CSO, https://ci.tno.nl/gitlab/cams/cso, last accessed May 24, 2024), fully described in Pseftogkas et al. (2022). We further replace the a priori TM5-MP profile, at a resolution of 1° × 1°, used in the retrieval by the a priori profile from the LOTOS-EUROS model at a resolution of 0.05° × 0.1°. The application of the LOTOS-EUROS a priori profiles on TROPOMI satellite retrievals has resulted in a significant reduction in the mismatch between the data and model (~25%) in traffic, background and industrial locations (Pseftogkas et al., 2022).

An illustration of the importance of this process for Mediterranean ports can be seen in Fig. 2 for the port of Algeciras, Spain, in summer. The initial simulations (Fig. 2a) show high NO_2 levels in the Gibraltar Strait and the gulf of Algeciras compared to the satellite observations (Fig. 2b). After the application of the updated profiles to both the modelled and retrieved NO_2 columns, the NO_2 levels become comparable and show a very similar spatial distribution and a more pronounced depiction of the shipping lane crossing the Strait (Fig. 2c and d). Thus, this methodology provides a more detailed representation of the strong gradients near high emitting sources and shipping lanes which cannot be captured by the TM5-MP a priori profiles due to their coarse horizontal resolution.

2.1.4. Source apportionment with LOTOS-EUROS

Source apportionment methodologies are implemented in order to determine the origin of pollution, identifying and quantifying the sources that contribute to air pollution concentrations and inform on the

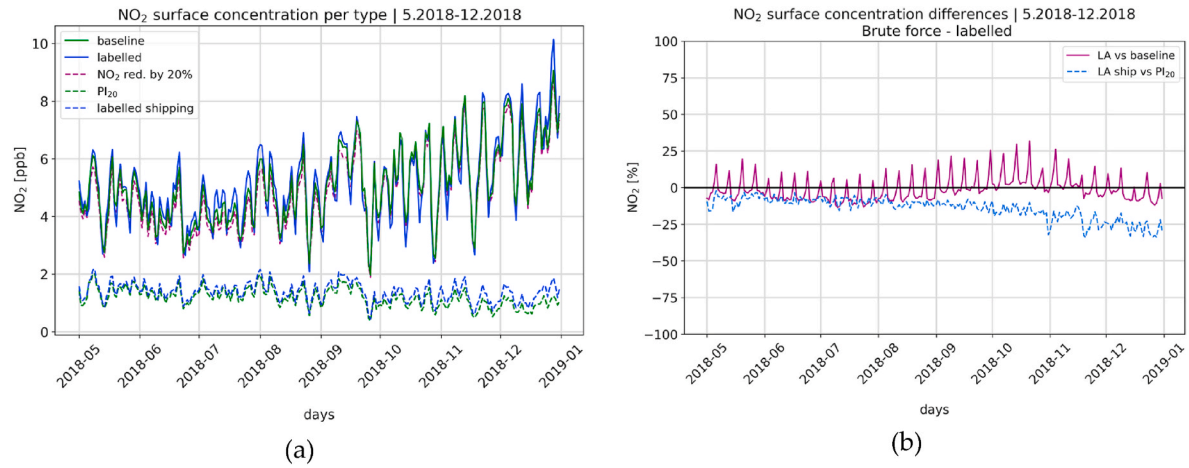


Fig. 6. **(a)** NO_2 surface concentration time series for the total labelled NO_2 levels [blue solid line], the brute-force baseline run [green solid line], the 20% NO_X reduced NO_2 levels [purple dashed line], the labelling [dashed blue] and brute-force [dashed green] shipping NO_2 estimates; **(b)** Relative differences between the labelled and the baseline run [purple] and the shipping labelled, and brute-force scenario run [blue].

effectiveness of mitigation strategies (Clappier et al., 2017). In this work, two source apportionment techniques are implemented to determine the contribution of the maritime sector on NO_2 levels, namely the Emission Reduction Impact (ERI) method, also known as brute-force methods and the Mass Transfer Method (MT), also known as labelling technique (Thunis et al., 2018). To be consistent with recent studies on source apportionment, we apply similar notations with previous studies (Thunis et al., 2020; Thürkow et al., 2023).

Brute-force method. In this work, the brute-force method is applied (Section 3.1.1) to calculate the Potential Impact (PI_s, Eq. (1)) of a specific source (s) at the receptor (r) by subtracting the concentration (C_{base}) of a model base case simulation (full emissions) and a simulation in which the source emissions (C_{red}) are reduced by a factor (a_s), divided by this factor. Hence, the potential impact corresponds to the NO_2 mass obtained by differentiating two model runs, one with the full emissions and one with sector reduced emissions, scaled by the emissions reduction factor.

$$PI_s = \frac{C_{base} - C_{red}}{a_s} \tag{1}$$

In cases of species involved in atmospheric chemistry, perturbing the emissions may cause non-linear effects and can lead to a negative impact on source apportionment (Kranenburg et al., 2013), meaning that experiments cannot be extended to other emission reduction scenarios and brute-force cannot be directly used to determine contributions. To ensure that linearity is maintained throughout the process, a proportionality analysis similar to Thürkow et al., 2023 was conducted. More specifically, this sensitivity analysis includes a base run with full emissions and eight runs with reduced NO_X emissions for the shipping sector by applying various emissions reduction scenarios (5%, 10%, 20%, 25%, 35%, 50%, 75%, 100%). To assess if the regime is linear or non-linear, the ratio between the impact (difference between the base case and an emission reduction scenario) of the shipping sector (S) of a reduction scenario (X) and the impact of the 20% NO_X shipping emission scenario was examined. The 20% reference emission reduction factor was selected to be in-line with previous approaches that used the same factor as reference criterion (Thunis et al., 2018; Thürkow et al., 2023.) This metric is called Consistency Ratio of Impacts (CRI, Eq. (2)) and the same can be implemented for the potential impacts, also known as Consistency Ratio of Potential Impacts (CRPI, Eq. (3)) presented by Thürkow et al., 2023). A linear regime can be presumed for both consistency ratios when the response to the emission reduction percentages is proportional. For example, an emission source sector reduction of 100% would yield a CRI equal to 5, a 50% emission reduction to a CRI of 2.5 and so on. Similarly, the consistency ratio of the potential impact on a linear regime should be equal to 1 for any reduction factor.

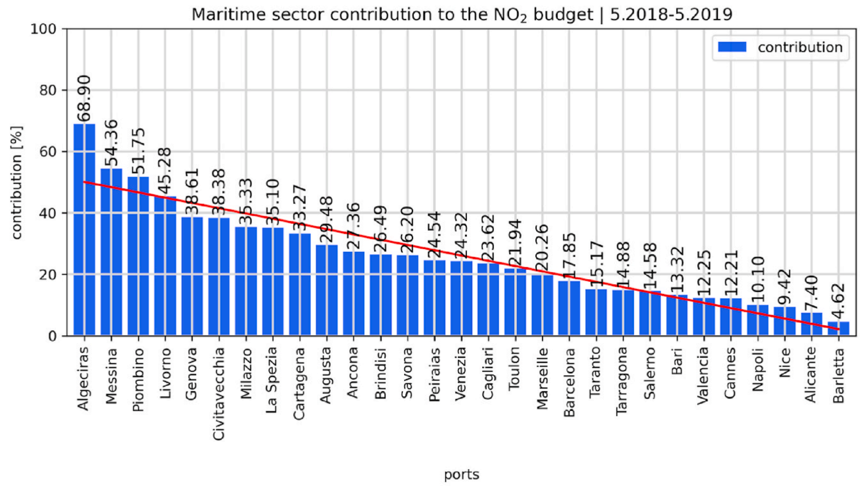
$$CRI = \frac{\Delta C_{S,X}}{\Delta C_{S,20}} \tag{2}$$

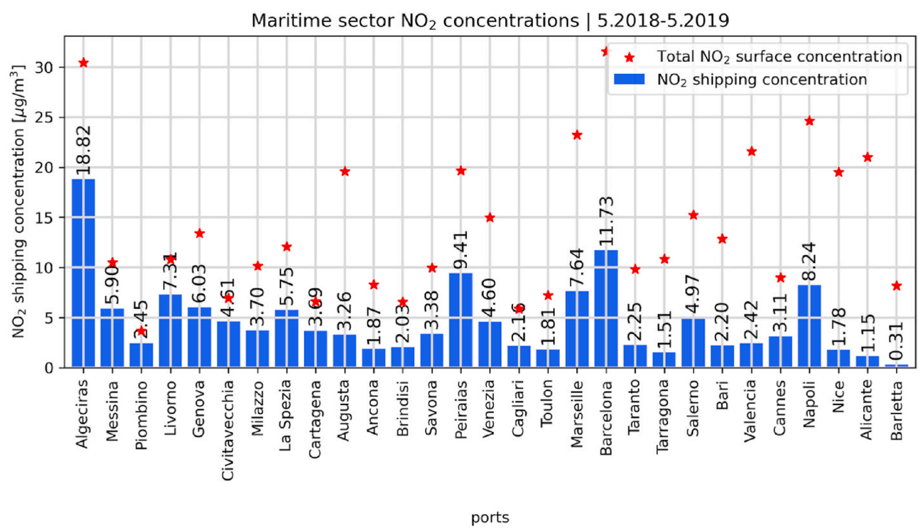
$$CRPI = \frac{PI_{S,X}}{PI_{S,20}} \tag{3}$$

Labelling technique. With the labelling technique, the contribution of specified sources for all model grid cells and time steps is estimated (Kranenburg et al., 2013) by assigning predefined labels to specific emission sectors or regions. These labelled sectors or regions are then traced during the simulation. The model tracks the contributions of separate sources for chemically active tracers using the preserved atoms, including C, S, reduced and oxidized N. The contributions per label are calculated as fractions of the total tracer concentration. Note that for each model process (e.g., emissions, transport, removal processes, gas phase chemistry, aerosol chemistry) the calculations to track the source contributions differ. As the fractions must add up to one for mass conservation, all source and sink processes must be accounted for in the source apportionment module, including initial and boundary conditions. The specification of the labels to track throughout the model simulations is done in the emission routine. In principle, the definition of the labels is very flexible (Thunis et al., 2019, 2020) and any kind of allocation is possible when the required detail is present in the input data.

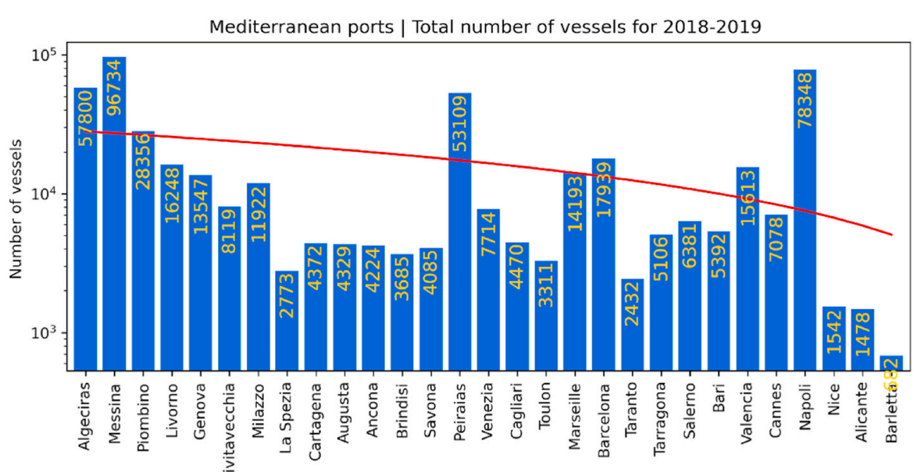
In this work, LOTOS-EUROS labelled simulations are compared with our calculated brute-force technique estimates (Section 3.1.2). Detailed information about the model labelled run can be found in the CONCAWE scientific report (Tokaya et al., 2023). This report examines the influence of shipping emissions on the air quality of 19 European port-cities, including seven Mediterranean ports. Shipping contributions on NO_2, SO_2, $PM_{2.5}$ and PM_{10} are predicted to be 18%, 11%, 5% and 3% for 2018, respectively, signifying that maritime activities are a strong contributor to air pollution in Europe.

Overall, most studies suggest that source attribution with the brute-force technique for a single sector should be avoided due to difficulties in verifying consistency and quantifying the error of the sector and the total contribution. Thus, the labelling approach is being suggested due to the consistency in the chemical and physical processes regarding nitrogen oxides, whereas explicit use of emission scenarios is preferred for evaluating the effect of emission mitigation strategies. In the following section, we demonstrate that both approaches yield similar results for the shipping sector in the Mediterranean ports for NO2.





(b)



(c)

Fig. 7. **(a)** Relative contribution of the maritime sector to the total NO_2 concentrations; **(b)** NO_2 shipping concentrations by the brute-force method; **(c)** Total number of vessels in the selected Mediterranean ports for the period 05.2018–05.2019.

3. Results

The results section is structured as follows: in Section 3.1.1, the linearity and applicability of the brute-force methodology is assessed. In Section 3.1.2 the potential impacts of the shipping sector estimated with the brute-force technique are compared with the labelling approach absolute contributions and the relative contribution of shipping to the total NO_2 surface concentrations is presented in Section 3.2. Finally, in Sections 3.3 and 3.4 the model is compared with EEA ground-based measurements and S5P/TROPOMI observations, respectively, as an

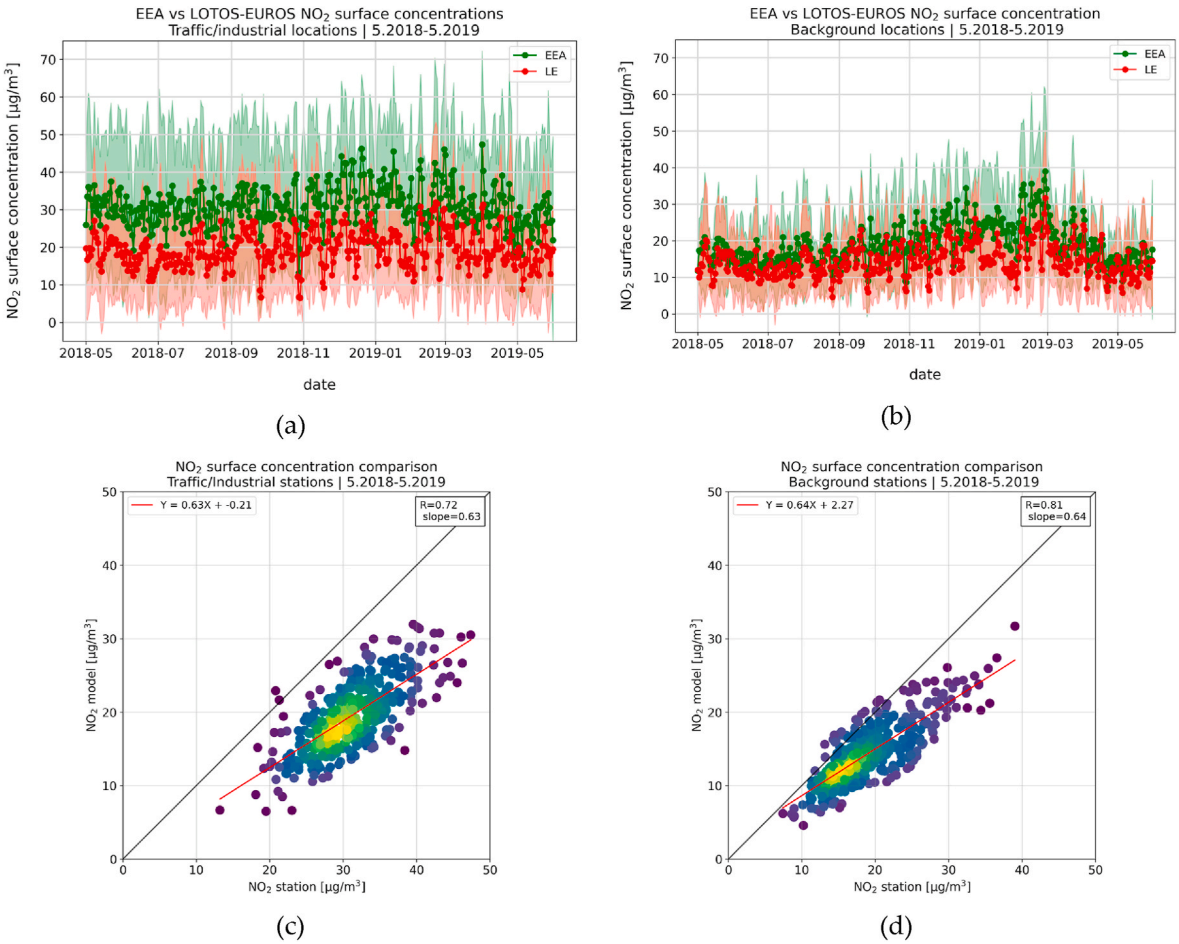


Fig. 8. Mean daily measured [green] and modelled [red] NO_2 surface concentrations from May 2018 to May 2019 and for **(a)** the traffic/industrial stations; **(b)** the background stations; Scatter density plot between the in-situ and modelled NO_2 surface concentrations for the **(c)** traffic/industrial stations; **(d)** background stations.

indirect way of validating the source attribution process and evaluating the performance of the model in coastal areas.

3.1. Maritime sector contributions on NO_2 surface concentrations

3.1.1. Brute-force technique linearity investigation

Here, we investigate the linearity of the chemical regime to ensure the validity of the brute-force methodology. To do so, the Consistency Ratio of Impacts (CRI, Eq (2)) and the Consistency Ratio of Potential Impacts (CRPI, Eq. (3)) were examined for each port separately and as the accumulated daily average of all ports over the period between May and December 2018 to coincide with the labelling approach simulations. Fig. 3 illustrates the mean CRI and the mean CRPI for NO, NO_2 and NO_X. As mentioned earlier, if the CRI shows a proportional behavior, the impacts are scalable and the potential impacts should be equal to 1 for each NO_x shipping emission reduction scenario. Hence, in this case linearity can be presumed. In the case that CRI shows a non-proportional reduction then the CRPI differs from 1 and linearity is not maintained.

The CRI for NO_2 [green dashed line] and NO_X [purple dashed line] indicates, overall, a proportional behavior to emission perturbations, hereafter defined as Xred, with higher uncertainties for high emission reduction scenarios (>75%), as shown by the amplitude of the error bar (shaded area in the plots of Fig. 3a). Moreover, low to moderate NO_X shipping emission reduction scenarios (<50%) lead to a proportional reduction of the NO [red dashed line] concentrations. As shown in Fig. 3a, any emission reduction higher than 50% leads to a slightly lower NO response (by 12%), which is verified from the offset of the Xred/20 ratio. For emission reduction factors lower than 50%, NO concentrations show a proportional behavior to emission perturbations (points equal to the Xred/20 ratio). This indicates that for smaller NO_X emission reductions the likelihood of ozone titration by NO is smaller compared to large NO_X emission reductions, minimizing deviations caused by ozone limiting conditions and leading to a linear chemical regime. The same conclusion is deduced when examining the CRPI (Fig. 3b). For NO, proportionality increases with lower NO_X shipping emission reduction factors and becomes equal to 1 in the range of 50%–5%. For both NO_2 and NO_X the CRPI is almost equal to 1 for all emission reduction scenarios. Hence, a linear regime for the shipping sector can be presumed for low to moderate NO_X emission reduction scenarios (−50% to −5%), with higher uncertainties and disproportionate responses to higher reduction scenarios.

Overall, these results are consistent with Thürkow et al. (2023), who reported that linearity could be assumed for NO_2 and various examined sectors (road transport, non-road transport, energy and industry, households, others). Here, we further conclude that linearity can be assumed for NO_2 and the shipping sector with lower possibility of error when applying moderate to low emission reduction scenarios. In the following, we compare the NO_2 potential impacts estimated with the brute-force method with the labelling approach contributions to assess the validity of the brute-force method.

3.1.2. Brute-force technique vs labelling approach

In this section, the two source apportionment methods are compared. Fig. 4 illustrates the average (May to December 2018) distribution of shipping NO_2 surface concentrations in the Mediterranean Basin either based on the labelling approach (Fig. 4a) or the brute-force (Fig. 4b)

Table 2
Statistics of the modelled and in-situ NO_2 surface concentrations for the whole study period and the summer and winter periods.

Period	Mean model concentration [μg/m^3]		Mean in-situ concentration [μg/m^3]		Relative bias [%]		Correlation coefficient [R]	
Station type	Traffic	Background	Traffic	Background	Traffic	Background	Traffic	Background
Total	19.09 ± 14.20	14.54 ± 10.95	31.00 ± 19.27	19.16 ± 12.79	−38.43	−23.57	0.72	0.81
Summer	17.44 ± 14.05	12.37 ± 9.75	29.17 ± 19.45	15.62 ± 10.53	−40.21	−20.81	0.73	0.82
Winter	20.86 ± 13.85	17.56 ± 12.02	34.00 ± 18.62	25.43 ± 15.35	−38.64	−30.97	0.63	0.76

Table 3
Statistics of the comparisons between the in-situ measurements and the modelled NO_2 surface concentrations for the whole studied period and the summer and winter periods.

Period	Mean model concentration [μg/m^3]	Mean measured concentration [μg/m^3]	Correlation coefficient [R]	Absolute bias [μg/m^3]	Relative bias [%]
Total	16.84 ± 13.02	24.81 ± 17.26	0.80	7.97	−32.12
Summer [JJA]	14.70 ± 12.15	22.13 ± 16.89	0.80	7.43	−33.57
Winter [DJF]	19.33 ± 13.33	29.47 ± 17.45	0.79	10.34	−34.40

method. A 20% NO_x emission reduction factor was applied for the brute-force method. The maps exhibit a similar spatial distribution with pronounced lanes in the coasts of Spain, France, Italy and Greece and the commercial shipping lanes moving towards the Gibraltar Strait and within the Adriatic Sea. Note that the Gibraltar Strait is not included in the LOTOS-EUROS labelled run hence comparisons cannot be performed there. Differences (Fig. 4c) between the labelled shipping NO_2 surface concentrations and the brute-force potential impacts are, overall, relatively low (0.5 ppb) attributed to the different nested approaches implemented for the two techniques. Brute-force NO_2 shipping concentrations (Fig. 4b) are slightly higher but still below 1 ppb in the Gibraltar-Suez Lane near the African coast and in the shipping lane crossing the Adriatic Sea.

The two methods were then further compared for selected port pixels (Fig. 5). Comparisons were conducted for all NO_X emission reduction factors. Here only the 25% and 75% NO_X emission reduction scenarios are shown for the sake of conciseness, but all statistics are summarized in Table 1. Overall, correlations are strong ($R \geq 0.95$) for all cases and slopes are close to unity, with a constant bias between the two methods attributable to the slightly different configurations of the two model runs. Low NO_X shipping emission reductions result in slightly lower correlation (R~0.95) and more outliers compared to higher NO_X emission reductions (R~0.98).

Mean shipping NO_2 potential impacts are identical for emissions reduction factors in the range from 5% to 50% ($PI_{S,X} = 1.194$ ppb) and are by 14% (0.18 ppb) lower compared to the labelled concentrations (Table 1). The potential impacts are higher for the 75% ($PI_{S,75} = 1.199$ ppb) and the 100% ($PI_{S,100} = 1.208$ ppb) NO_X emission reduction factors, but still ~13% (0.17 ppb) lower than the labelled concentrations. Furthermore, the root mean square errors (RMSE) between the labelled and the brute-force approach are very low and decrease with increasing NO_X emission reduction factors. Overall, the two methodologies show strong agreement with relatively small differences.

For the remaining comparisons between the two methods the 20% reduction factor was applied.

To examine possible seasonality effects, in Fig. 6a the timeseries of the mean NO_2 surface concentrations are shown for the baseline run, the labelled run and the run with 20% reduced NO_X shipping emissions. Overlain on the same plot, the shipping-only contributions by the brute-force and the labelling approaches are given.

There is a high level of agreement between the baseline and the labelled runs for all sectors throughout the whole studied period. From May until October 2018 the labelled run shows slightly higher NO_2 levels (12%), whereas from October until mid-December the brute-force baseline run accounts for higher (~20%) NO_2 concentrations (Fig. 6b). As expected, the NO_2 concentrations from the NO_X reduced regime are lower compared to both labelled and brute-force runs showing that the reduction in shipping NO_X emissions has a negative proportional impact on NO_2 concentrations and that shipping is indeed an important contributing sector in these cells. Shipping NO_2 surface concentrations, from both source attribution methods, show similar variability and overall, a strong agreement. Labelled NO_2 shipping concentrations are slightly higher compared to the potential impacts (~14%), with differences getting higher after October (~20%) but not exceeding the threshold of 0.5 ppb (Fig. 6b). In contrast to the increasing NO_2 total levels in winter, the shipping NO_2 levels remain relatively constant with a slight decreasing trend in December. These findings further corroborate the overall understanding that the applied brute-force scenario can be used for shipping emission studies and operates similarly with the more elaborate labelling approach which tracks the source contributions in all chemical and physical processes.

3.2. Maritime sector contributions on the NO_2 budget

In the following, we associate the surface NO_2 levels originating from maritime activities with vessel traffic statistics from EUROSTAT and estimate the relative contribution of the shipping sector to the total NO_2 levels. Two extra model runs were performed for the estimation of the shipping potential impacts with the 20% NO_X shipping emission reduction scenario for the D3 and D4 domains (Fig. 1) from May 2018 to May 2019. NO_2 surface levels originating from shipping activities are estimated for the model grid cell that includes the port, whereas relative contributions are estimated for four model grid cells (~200 km^2). This is done to assess the impacts of the maritime sector activities to the total NO_2 levels in the greater area of the port and the city. Although, a chemical segregation between the ship plume and the adjacent ambient atmosphere, as initially proposed by Vinken et al. (2011), would provide a more realistic description of the non-linear and temporally variable NO_X chemistry in the plumes, it seems to affect quantitively ship emissions in open seas, whereas the effect diminishes over heavily polluted areas. Over ports, the shipping signal intermingles with land-based emissions and the background signal. The estimation of the outflow signal is ambiguous due to the overlap between the different contributions near coastlines, limiting the precision of the chemical segregation of the ship plumes. Hence, the inclusion of major port cities in this study does not allow us to proceed with a further segregation of the chemical regime between ship plumes and the ambient atmosphere. Shipping contributions are estimated based on the perturbation of the model-ingested NO_X shipping emissions within the complex modelled chemical regime over ports.

Fig. 7a shows the maritime sector relative contributions to the total NO_2 levels in descending order. Three classes can be distinguished, port locations with high contributions (>40%), locations with moderate contributions (20%–40%) and locations with low contributions (<20%).

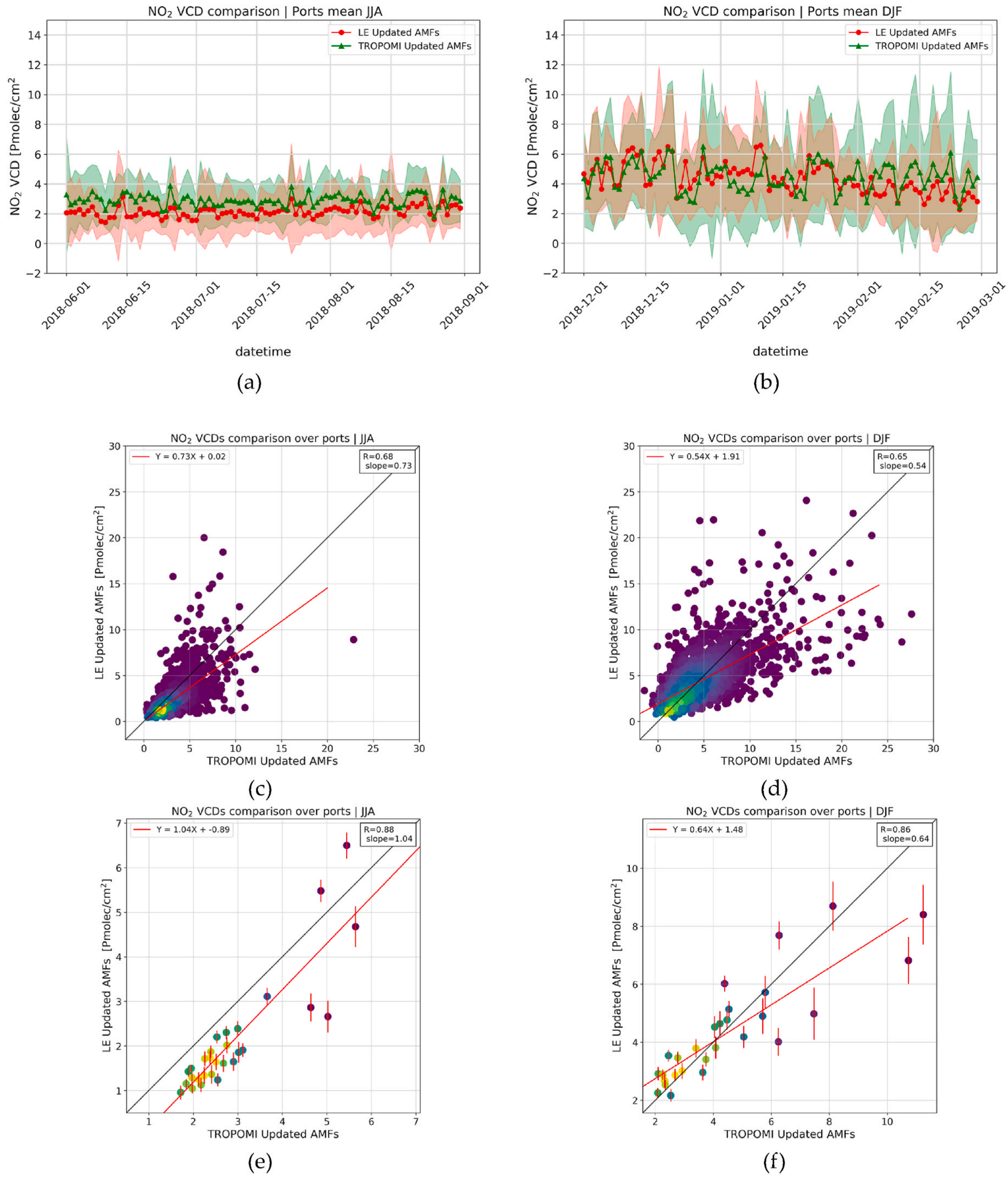


Fig. 9. Comparisons between S5P/TROPOMI and LOTOS-EUROS NO_2 VCDs of all port pixels after the implementation of the updated air mass factors for summer [left] and winter [right] periods **(a, b)** Time series of the mean model [red] and satellite [green] NO_2 VCDs; **(c, d)** Scatter density plots of the daily simulated [y-axis] and observed [x-axis] NO_2 VCDs; **(e, f)** Scatter density plots of mean NO_2 VCDs levels of each port between the model [y-axis] and the satellite [x-axis].

Algeciras, Messina, Piombino and Livorno account for the highest contributions, ranging from 45% to 70% of the total NO_2 concentrations originating from the shipping sector, whereas Nice, Alicante and Barletta show contributions lower than 10%. Maritime sector activities account for a mean of approximately 27% of the total NO_2 levels in the greater port-city areas for the selected locations.

To better explain the effect of shipping in the ports and to associate the vessel traffic with NO_2 levels, we demonstrate in Fig. 7b the NO_2 surface concentrations originating from the shipping sector for all the involved Mediterranean ports and the total NO_2 surface concentrations [red stars]. Algeciras, Barcelona, Piraeus, Napoli and Marseille account for the highest NO_2 shipping levels with concentrations ranging from 7 to 19 $\mu g/m^3$, whereas Nice, Alicante and Barletta report low NO_2 shipping levels (<1.5 $\mu g/m^3$). This is in overall agreement with the total number of vessels operated in ports between May 2018 and May 2019 as reported by EUROSTAT (Fig. 7c). There are a few cases of low NO_2 shipping levels and low total NO_2 concentrations, resulting in high relative contributions (e.g., Piombino and Milazzo), signifying, thus, that shipping is the main contributor in these areas. Cases with significant vessel traffic and high NO_2 shipping levels in port grid cells (e.g., Barcelona, Piraeus, Marseille and Napoli) can also lead to moderate contributions from the shipping sector in the greater city area.

Table 4
Modelled and observed NO_2 VCDs and standard deviations [in Pmolec/cm^2] and relative bias [in %] for the summer and winter periods.

Comparison	Mean LE NO_2 VCD [Pmolec/cm^2]		Mean TROPOMI [Pmolec/cm^2]		Relative bias [%]	
	Summer	Winter	Summer	Winter	Summer	Winter
Updated VCDs with the new AMF	2.16 ± 1.69	4.32 ± 2.89	2.88 ± 1.55	4.36 ± 3.39	−25.09	−0.90

Maps of the absolute concentrations and relative contributions (Fig. S2) of these locations were generated to better explain the NO_2 levels attributed to shipping activities. The absolute shipping NO_2 levels (Fig. S2, left column) and the relative contributions (Fig. S2, right column) are higher in the model grid cells including the ports. More specifically, in the port cells of Barcelona, Piraeus, Napoli and Marseille NO_2 average shipping levels are relatively high (12 μg/m^3, 9 μg/m^3, 8 μg/m^3 and 8 μg/m^3) compared to total average NO_2 levels (32 μg/m^3, 20 μg/m^3, 25 μg/m^{3,} 23 μg/m^3) with significant relative contributions (37%, 45%, 34% and 33%). Valencia port is an outlier accounting for low shipping NO_2 levels (3 μg/m^3) and relative contribution (11%), while EUROSTAT is reporting significant vessel traffic. This could be attributed to different meteorological conditions (prevailing winds), the topography of each studied area and the contribution of other sectors. Significant NO_2 levels and contributions can also be observed in the shipping lanes leading to the ports. Hence, the fact that LOTOS-EUROS simulates the processes within each time step per grid cell (Manders et al., 2017) combined with the available horizontal resolution (0.05° × 0.1°) allows for a first approximation on the order of magnitude of shipping contributions within the port and its surrounding grid cells, limiting the assessment of ship emissions in an area of ~50 km^2. Shipping NO_X emissions occurring in the vicinity of the port, affect mostly the model grid cell including the port and part of the city. Relative contributions are high along the shipping tracks in the open sea (Fig. S2), as shipping is the only emitting source. Near the port, absolute shipping levels are higher compared to open sea shipping lanes, indicating different emission rates due to different vessel operations (maneuvering and hoteling) in the vicinity of the ports leading to higher emissions as accounted for in the ingested model emission inventory. However, relative contributions are lower over the port, since activities within the city (road transport, industrial processes etc.) directly affect air pollution levels. Over the port-city domain, horizontal transport seems to be limited within 10 km due to physical processes (photodissociation, reaction with other species and radicals) and obstacles (i.e., small hills, buildings etc.), leading to lower NO_2 levels in the neighboring grid cells of the ports. Thus, shipping relative contribution is expected to be lower in locations dominated by road transport and industrial processes compared to smaller port cities where the maritime sector is the predominant contributor.

These findings show that policies cannot be made solely based on the number of vessels operated in ports and traditional bottom-up inventories. Cases with limited number of vessels in small ports which however result in a large impact on air quality are not uncommon and need to be assessed in non-traditional ways. Hence, source apportionment studies are very useful in providing information on the contribution of the shipping sector to total air pollution levels in ports and indicate locations where maritime emissions should be updated with inversion approaches.

3.3. Evaluation of the modelled NO_2 surface concentrations in Mediterranean ports

In this section we separate the port stations into two categories, namely 14 traffic/industrial urban stations and 15 background stations. Fig. 8 illustrates the time series for the mean in-situ and modelled NO_2 surface concentrations for the traffic/industrial stations (a) and the background (b) stations. Differences are more pronounced in the traffic/industrial stations with the mean daily in-situ NO_2 surface concentrations ranging from 20 μg/m^3 to 50 μg/m^3 (annual mean of 31 μg/m^3), whereas the modelled range from 10 μg/m^3 to 30 μg/m^3 (annual mean is 19.09 μg/m^3, see Table 2). The comparisons at background stations suggest similar NO_2 surface concentration levels, ranging between 10 μg/m^3 and 25 μg/m^3 on daily basis, with the annual mean of in-situ observations and model output equal to 19.16 μg/m^3 and 14.54 μg/m^3, respectively. With regards to daily relative differences, the traffic/industrial stations range from 10% to −70% with a mean annual relative bias of −38% whereas background differences range from 20% to −50% with a mean annual bias of −24%. Regarding the seasonal differences, the traffic/industrial stations show a similar bias for both periods (~-40%), whereas the background bias is −21% and −31% for summer and winter, respectively. We should note here that the model has a known difficulty in resolving strong gradients close to the source in traffic/industrial locations due to the temporal and spatial distribution of the corresponding emissions used as input in the model (Timmermans et al., 2022).

Fig. 8c and d shows the scatter density plots between the mean measured and simulated NO_2 surface concentrations of the traffic/industrial and the background stations. Correlations are strong for both background (R~0.81) and traffic/industrial comparisons, (R~0.72), with near identical slopes (~0.63) but smaller discrepancies are found for the background locations.

Overall, the inclusion of the traffic stations in the comparisons increases the bias by approximately 30% which is equivalent to lower modelled NO_2 surface concentrations by 3–8 μg/m^3. Ports with small differences between measured and simulated NO_2 concentrations (such as Algeciras, Cagliari, Milazzo, Alicante) exhibit also high agreement between the relative contribution of the shipping sector and the total number of vessels, already shown in Section 3.2, with a few exceptions (Piombino, Messina).

Hence, when including traffic and industrial stations located near ports the bias might be increased because of the difficulty in resolving the high near-source concentrations in traffic and industrial locations due to the limited horizontal resolution in the input dataset and the simulations, presenting a situation which is not representative for all locations. On a seasonal basis, when examining all types of in-situ reporting stations, modelled and measured NO_2 concentrations display a common variability with lows in late spring/summer and highs in winter. Differences between modelled and observed concentrations are generally constant (~-32%) throughout the whole period with higher discrepancies (~-45%) in January of 2019 and lowest in May 2019 (~-25%). The overall highest biases during wintertime may also be attributed to the fact that the resolution of the simulations is not fine enough to detect emissions on a local scale, especially in winter when NO_X emissions are enhanced. Moreover, cold and stagnant conditions in winter are difficult to represent in air quality models, as input for boundary layer height, stability and wind profiles from numerical weather prediction models is not always accurate (Bessagnet et al., 2016). The possibility that the emission inventory might not have a proper representation of the activity in the selected pixels cannot be disregarded.

The statistics for the comparisons on all stations is provided in Table 3. The main take-away message is that when comparing all collocated daily data, a high level of agreement is found (R~0.8 and a slope of ~0.71), with the ground-based measurements reporting overall higher NO_2 surface concentrations by a mean of 8 μg/m^3. On a seasonal basis, correlations are strong for both winter and summer periods (R~0.8) and slopes are closer to unity (0.79 and 0.72). The model underestimates the in-situ concentrations in both periods with mean absolute differences of 7.43 μg/m^3 in summer and 10.34 μg/m^3 in winter. Overall, the model shows a strong correlation with the in-situ measurements in coastal areas but is biased low (∼-32%). This underestimation of NO_2 concentrations close to the surface is also reported over continental areas (Pseftogkas et al., 2022), indicating that the bias is not attributed to the underestimation of shipping emissions but comes from all combined sectors. This hints difficulties in resolving specific processes in model dynamics, especially in heavily polluted urban areas. This will have an insignificant impact on the estimation of the shipping relative contributions since it depends on NO_2 surface absolute levels and perturbations in NO_X shipping emissions, which have shown to be proportional.

3.4. Evaluation of the modelled NO_2 VCDs in Mediterranean ports

In this section, a further evaluation of the model performance is conducted, as we compare the simulated and observed NO_2 VCDs for the summer of 2018 and the winter of 2018–2019 after the replacement of the coarse (1° × 1°) TM5-MP profiles with the high resolution (0.1° × 0.05°) LOTOS-EUROS profiles on the satellite retrievals. This ensures that emissions from local sources are better resolved and included in the pixel selection. Model output at 11:00 UTC is used; this roughly corresponds to the TROPOMI overpass time over the selected areas.

Fig. 9 displays the mean daily TROPOMI and LOTOS-EUROS NO_2 VCDs of all selected ports. TROPOMI reports higher NO_2 levels in summer, whereas in winter LOTOS-EUROS shows marginally higher NO_2 VCDs until mid-January and then underestimates the TROPOMI NO_2 VCDs. This also coincides with the period where the model strongly underestimates the in-situ NO_2 surface concentrations, both in background and traffic/industrial locations. Overall, the observed and modelled NO_2 VCDs show similar variability for both periods, with mean relative bias of −25.09% for the summer and 0.90% for the winter periods. More specifically, the modelled VCDs increase in summer [winter] by 43% [19%] and the observed NO_2 VCDs by 28% [16%], respectively. This is the effect of replacing the a priori coarse TM5-MP profiles with the updated profiles, leading to the detection of more emitting sources and the enhancement of NO_2 concentrations. This is in line with the latest TROPOMI Routine Operations Consolidated Validation Report (Lambert et al., 2023, https://mpc-vdaf.tropomi.eu/, last accessed May 24, 2024), suggesting that the bias between TROPOMI NO2 and ground-based instruments can be reduced when the vertical profiles of ground-based instruments are smoothed using the TROPOMI averaging kernels.

Fig. 9 c and d show the scatter density plots of the daily modelled and observed NO_2 VCDs for all the selected port cells in summer and winter. Correlations are moderate for both periods (R∼0.65) with slopes of 0.72 and 0.54 for summer and winter, respectively. Finally, Fig. 9 e and f depict the scatter density plots of the period mean of each port. Correlations are strong for both periods (R∼0.88 and R∼0.85) with slopes of 1.05 and 0.63 for summer and winter, respectively. Overall, summer simulated NO_2 VCDs are consistently lower compared to the observed NO_2 VCDs. For the winter period most port mean levels agree well between model and observation, with a few outliers. The statistics are summarized in Table 4.

4. Discussion

In this work, we used the brute-force method with the LOTOS-EUROS CTM in order to quantify the contribution of the maritime sector to the air quality NO_2 levels in 29 ports in the Mediterranean basin. The brute-force method is known to insert uncertainties and non-linear responses in the estimation of potential impacts when perturbing the sector specific emissions. Thus, a sensitivity analysis was first carried out to assess the linearity of the chemical regime to various NO_X shipping emission reduction factors. The results were compared with the labelling approach which tracks the source contributions in all processes (emissions, transport, removal processes, chemistry). Shipping sector relative contributions were further estimated with the brute-force method and associated with vessel activity in selected ports. To evaluate the results, the modelled NO_2 surface concentrations and VCDs were compared with EEA measurements and S5P/TROPOMI satellite observations. The key findings of this study can be summarized in the following:

- For NO_2, the various NO_X shipping emission reduction scenarios applied in the brute-force method led to proportional responses, ensuring a linear regime. The error is minimized when applying low to moderate (<50%) NO_X shipping emission reduction factors. Uncertainties are higher in high emission reduction scenarios- (>50%), causing non-linear responses to NO concentrations. Brute-force NO_2 shipping potential impacts show a strong agreement (R ≥ 0.95) with the labelled absolute contributions for all NO_X emission reduction scenarios. Overall, differences in estimated NO_2 shipping levels between the two methods are low (∼12%). Hence, the brute-force method can be applied to estimate shipping NO_2 levels with the same sensitivity as the labelling approach, constituting an alternative useful tool when labelling is not applicable and not included in the source codes of various CTMs.
- The contributions of the maritime sector to the air quality of 29 port-cities locations were estimated by the ratio of the potential impacts to the total NO_2 surface concentrations with the brute force method for the period between May 2018–May 2019. Three distinct contributing classes were observed; locations where the shipping contribution to the total NO_2 levels was higher than 40% (4 ports), locations where the contribution was ranging from 20% to 40% (14 ports) and locations where shipping contributed lower than 20% (11 ports). Overall, a mean contribution of 27% was found in the selected Mediterranean locations. Contributions are higher in the model grid cell including the port and horizontal transport is limited in the first 10 km from the port to the city suburbs. Furthermore, a strong agreement was observed between the EUROSTAT vessel activity and the shipping contribution to the total NO_2 levels for the selected ports. Ports with higher NO_2 loads attributed to maritime activities (>40%) also accounted for higher number of vessels compared to ports with limited number of vessels with contributions lower than 10%.
- In-situ and modelled NO_2 surface concentrations display overall a strong correlation (R∼0.72), with similar seasonal variations, but the model underestimates the ground-based measurements with a mean relative bias of −32%. The bias is −23% for 15 representative background stations when 14 traffic/industrial stations (with a bias of −38%) are studied separately.
- LOTOS-EUROS mean NO_2 VCDs in all selected port cells show, overall, a strong agreement with the TROPOMI observations for both seasons after the application of the air mass factor correction (R > 0.8). The mean simulated and observed NO_2 VCDs show similar seasonal variability with higher discrepancies in summer (relative bias ∼ −25%) compared to winter (relative bias ∼ −0.90%).

Overall, we have shown that maritime activities are a significant contributor to air pollution NO_2 levels in the Mediterranean Basin using the LOTOS-EUROS model in combination with two source apportionment methods, in-situ and satellite observations. As a next step, the satellite observations from TROPOMI will be used as top-down constraints in an inverse modelling scheme based on the Ensemble Kalman filter in order to infer NOx emissions from shipping across the major Mediterranean shipping routes.

Funding

This research has been co-financed by the European Union (European Regional Development Fund) and Greek national funds through the Operational Program "Competitiveness, Entrepreneurship and Innovation" (NSRF, 2014–2020) and co-financed by the Hellenic Foundation for Research and Innovation (HFRI) under the 3rd Call for HFRI PhD Fellowships (Fellowship Number: 5907).

Data availability statement

The S5P/TROPOMI observations are publicly available from the Copernicus Data Space Ecosystem (https://dataspace.copernicus.eu/, last accessed on May 24, 2024, ESA, 2023). The in-situ measurements are publicly available from the European Environment Agency (https://discomap.eea.europa.eu/map/fme/AirQualityExport.htm, last accessed on May 24, 2024, EEA, 2023). The LOTOS-EUROS CTM simulations shown in this work are performed with version v02.02.002 and are available upon request.

CRediT authorship contribution statement

Andreas Pseftogkas: Conceptualization, Methodology, Software, Visualization, Writing – original draft, Writing – review & editing. **Maria-Elissavet Koukouli:** Conceptualization, Methodology, Visualization, Writing – original draft, Writing – review & editing. **Astrid Manders:** Conceptualization, Writing – review & editing. **Arjo Segers:** Conceptualization, Writing – review & editing. **Trissevgeni Stavrakou:** Supervision, Writing – review & editing. **Janot Tokaya:** Methodology, Software, Writing – review & editing. **Charikleia Meleti:** Supervision, Writing – review & editing. **Dimitris Balis:** Supervision, Writing – review & editing.

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.

Acknowledgements

Results presented in this work have been produced using the Aristotle University of Thessaloniki (AUTH) High Performance Computing Infrastructure and Resources. The authors would like to acknowledge the support provided by the AUTH IT Centre throughout the progress of this research work. We further acknowledge the Atmospheric Toolbox®. T.S. would like to acknowledge support by the Belgian Science Policy Office through the PRODEX TROVA-E2 project.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apr.2024.102228.

References

Aksoyoglu, S., Baltensperger, U., Prévôt, A.S.H., 2016. Contribution of ship emissions to the concentration and deposition of air pollutants in Europe. Atmos. Chem. Phys. 16, 1895–1906. https://doi.org/10.5194/acp-16-1895-2016.

Banzhaf, S., Schaap, M., Kerschbaumer, A., Reimer, E., Stern, R., Van Der Swaluw, E., Builtjes, P., 2012. Implementation and evaluation of PH-dependent cloud chemistry and Wetdeposition in the chemical transport model REM-Calgrid. Atmos. Environ. 49, 378–390. https://doi.org/10.1016/j.atmosenv.2011.10.069.

Bauwens, M., Compernolle, S., Stavrakou, T., Müller, J.-F., van Gent, J., Eskes, H., et al., 2020. Impact of coronavirus outbreak on NO_2 pollution assessed using TROPOMI and OMI observations. Geophys. Res. Lett. 47, e2020GL087978 https://doi.org/10.1029/2020GL087978.

Beirle, S., Borger, C., Dörner, S., Eskes, H., Kumar, V., De Laat, A., Wagner, T., 2021. Catalog of NOx emissions from point sources as derived from the divergence of the NO_2 flux for TROPOMI. Earth Syst. Sci. Data 13, 2995–3012. https://doi.org/10.5194/essd-13-2995-2021.

Bessagnet, B., Pirovano, G., Mircea, M., Cuvelier, C., Aulinger, A., Calori, G., Ciarelli, G., Manders, A., Stern, R., Tsyro, S., García Vivanco, M., Thunis, P., Pay, M.-T., Colette, A., Couvidat, F., Meleux, F., Rouïl, L., Ung, A., Aksoyoglu, S., Baldasano, J. M., Bieser, J., Briganti, G., Cappelletti, A., D'Isidoro, M., Finardi, S., Kranenburg, R., Silibello, C., Carnevale, C., Aas, W., Dupont, J.-C., Fagerli, H., Gonzalez, L., Menut, L., Prévôt, A.S.H., Roberts, P., White, L., 2016. Presentation of the EURODELTA III intercomparison exercise – evaluation of the chemistry transport models' performance on criteria pollutants and joint analysis with meteorology. Atmos. Chem. Phys. 16, 12667–12701. https://doi.org/10.5194/acp-16-12667-2016.

Brandt, J., Silver, J.D., Christensen, J.H., Andersen, M.S., Bønløkke, J.H., Sigsgaard, T., Geels, C., Gross, A., Hansen, A.B., Hansen, K.M., et al., 2013. Assessment of past, present and future health-cost externalities of air pollution in Europe and the contribution from international ship traffic using the EVA model System. Atmos. Chem. Phys. 13, 7747–7764. https://doi.org/10.5194/acp-13-7747-2013.

Clappier, A., Belis, C.A., Pernigotti, D., Thunis, P., 2017. Source apportionment and sensitivity analysis: two methodologies with two different purposes. Geosci. Model Dev. (GMD) 10, 4245–4256. https://doi.org/10.5194/gmd-10-4245-2017.

Corbett, J.J., Winebrake, J.J., Green, E.H., Kasibhatla, P., Eyring, V., Lauer, A., 2007. Mortality from ship emissions: a global assessment. Environ. Sci. Technol. 41, 8512–8518. https://doi.org/10.1021/es071686z.

Crippa, M., Guizzardi, D., Muntean, M., Schaaf, E., Dentener, F., Van Aardenne, J.A., Monni, S., Doering, U., Olivier, J.G.J., Pagliari, V., et al., 2018. Gridded emissions of air pollutants for the period 1970-2012 within EDGAR v4.3.2. Earth Syst. Sci. Data 10, 1987–2013. https://doi.org/10.5194/essd-10-1987-2018.

Douros, J., Eskes, H., Van Geffen, J., Boersma, K.F., Compernolle, S., Pinardi, G., Blechschmidt, A.M., Peuch, V.H., Colette, A., Veefkind, P., 2023. Comparing sentinel-5P TROPOMI NO_2 column observations with the CAMS regional air quality Ensemble. Geosci. Model Dev. (GMD) 16, 509–534. https://doi.org/10.5194/gmd-16-509-2023.

Eskes, H.J., Eichmann, K.U., 2021. S5P mission performance Centre nitrogen dioxide [L2__NO2__] readme. Rep, 02.02.00, S5P-MPC-KNMI-PRF-NO2. https://sentinel.esa.int/documents/247904/3541451/Sentinel-5P-Nitrogen-Dioxide-Level-2-Product-Readme-File. (Accessed 29 September 2023).

Eskes, H.J., van Geffen, J.H.G.M., Boersma, K.F., Eichmann, K.-U., Apituley, A., Pedergnana, M., Sneep, M., Veefkind, J.P., Loyola, D., 2021. S5P/TROPOMI level-2 product user manual nitrogen dioxide. Report S5P-KNMI-L2-0021-MA version 4.0.2, ESA. http://www.tropomi.eu/data-products/nitrogen-dioxide/. (Accessed 29 September 2023).

EUROSTAT. Maritime Transport Statistics—Short Sea Shipping of Goods—Statistics Explained. Available online: https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Maritime_transport_statistics_-_short_sea_shipping_of_goods. (Accessed 24 May 2024).

Faber, J., Hanayama, S., Zhang, S., Pereda, P., Comer, B., Hauerhof, E., Yuan, H., 2020. Fourth IMO Greenhouse Gas Study. International Maritime Organization. Retrieved from. https://docs.imo.org. (Accessed 24 May 2024).

Fink, L., Karl, M., Matthias, V., Oppo, S., Kranenburg, R., Kuenen, J., Moldanova, J., Jutterstrom, S., Jalkanen, J.P., Majamaki, E., 2023. Potential impact of shipping on air pollution in the mediterranean region - a multimodel evaluation: comparison of photooxidants NO_2 and O_3. Atmos. Chem. Phys. 23, 1825–1862. https://doi.org/10.5194/acp-23-1825-2023.

Fioletov, V., Mclinden, C.A., Griffin, D., Krotkov, N., Liu, F., Eskes, H., 2022. Quantifying urban, industrial, and background changes in NO_2 during the COVID-19 lockdown period based on TROPOMI satellite observations. Atmos. Chem. Phys. 22, 4201–4236. https://doi.org/10.5194/acp-22-4201-2022.

Fountoukis, C., Nenes, A., 2007. A computationally efficient thermodynamic equilibrium model for K^+–Ca^{2+}–Mg^{2+}–NH^{4+}–Na^+–$SO4^{2-}$–NO^{3-}–Cl^-–H_2O aerosols. Atmos. Chem. Phys. 7, 4639–4659. https://doi.org/10.5194/acp-7-4639-2007.

Georgoulias, A.K., Boersma, K.F., Van Vliet, J., Zhang, X., van der A, R., Zanis, P., De Laat, J., 2020. Detection of NO_2 pollution plumes from individual ships with the TROPOMI/S5P satellite sensor. Environ. Res. Lett. 15, 124037 https://doi.org/10.1088/1748-9326/abc445.

Goldberg, D.L., Anenberg, S.C., Kerr, G.H., Mohegh, A., Lu, Z., Streets, D.G., 2021. TROPOMI NO_2 in the United States: a detailed look at the annual averages, weekly cycles, effects of temperature, and correlation with surface NO_2 concentrations. Earth's Future 9, 1–16. https://doi.org/10.1029/2020EF001665.

Jalkanen, J.-P., Johansson, L., Kukkonen, J., Brink, A., Kalli, J., Stipa, T., 2012. Extension of an assessment model of ship traffic exhaust emissions for particulate matter and carbon monoxide. Atmos. Chem. Phys. 12, 2641–2659. https://doi.org/10.5194/acp-12-2641-2012.

Johansson, L., Jalkanen, J.-P., Kukkonen, J., 2017. Global assessment of shipping emissions in 2015 on a high spatial and temporal resolution. Atmos. Environ. 167, 403–415. https://doi.org/10.1016/j.atmosenv.2017.08.042.

Khomenko, S., Pisoni, E., Thunis, P., Bessagnet, B., Cirach, M., Iungman, T., Barboza, E. P., Khreis, H., Mueller, N., Tonne, C., et al., 2023. Spatial and sector-specific contributions of emissions to ambient air pollution and mortality in European cities: a health impact assessment. Lancet Public Health 8, e546–e558. https://doi.org/10.1016/S2468-2667(23)00106-8.

Kim, J., Emmerich, M.T.M., Voors, R., Ording, B., Lee, J.S., 2023. A systematic approach to identify shipping emissions using spatio-temporally resolved TROPOMI data. Rem. Sens. 15, 1–26. https://doi.org/10.3390/rs15133453.

Koukouli, M.E., Skoulidou, I., Karavias, A., Parcharidis, I., Balis, D., Manders, A., Segers, A., Eskes, H., Van Geffen, J., 2021. Sudden changes in nitrogen dioxide emissions over Greece due to lockdown after the outbreak of COVID-19. Atmos. Chem. Phys. 21, 1759–1774. https://doi.org/10.5194/acp-21-1759-2021.

Koukouli, M.E., Pseftogkas, A., Karagkiozidis, D., Skoulidou, I., Drosoglou, T., Balis, D., Bais, A., Melas, D., Hatzianastassiou, N., 2022. Air quality in two northern Greek cities revealed by their tropospheric NO_2 levels. Atmosphere 13. https://doi.org/10.3390/atmos13050840.

Kranenburg, R., Segers, A.J., Hendriks, C., Schaap, M., 2013. Source apportionment using LOTOS-EUROS: module description and evaluation. Geosci. Model Dev. (GMD) 6, 721–733. https://doi.org/10.5194/gmd-6-721-2013.

Kuenen, J., Dellaert, S., Visschedijk, A., Jalkanen, J.-P., Super, I., Denier van der Gon, H., 2022. CAMS-REG-v4: a state-of-the-art high-resolution European emission inventory for air quality modelling. Earth Syst. Sci. Data 14, 491–515. https://doi.org/10.5194/essd-14-491-2022.

Kukkonen, J., Fridell, E., Jalkanen, J.P., Moldanova, J., Ntziachristos, L., Grigoriadis, A., Barmpas, F., Tsegas, G., Maragkidou, A., Sofiev, M., et al., 2022. Towards a comprehensive evaluation of the environmental and health impacts of shipping emissions. Springer Proceedings in Complexity 329–336. https://doi.org/10.1007/978-3-031-12786-1_44.

Kurchaba, S., van Vliet, J., Verbeek, F.J., Meulman, J.J., Veenman, C.J., 2022. Supervised segmentation of NO_2 plumes from individual ships using TROPOMI satellite data. Rem. Sens. 14, 1–24. https://doi.org/10.3390/rs14225809.

Lambert, J.-C., Keppens, A., Compernolle, S., Eichmann, K.-U., de Graaf, M., Hubert, D., Langerock, B., Ludewig, A., Sha, M.K., Verhoelst, T., Wagner, T., Ahn, C., Argyrouli, A., Balis, D., Chan, K.L., Coldewey-Egbers, M., De Smedt, I., Eskes, H., Fjaeraa, A.M., Garane, K., Gleason, J.F., Goutail, F., Granville, J., Hedelt, P., Heue, K.-P., Jaross, G., Kleipool, Q., Koukouli, M.L., Lorente Delgado, A., Lutz, R., Michailidis, K., Nanda, S., Niemeijer, S., Pazmino, A., Pinardi, G., Pommereau, J.-P., Richter, A., Rozemeijer, N., Sneep, M., Stein Zweers, D., Theys, N., Tilstra, G., Torres, O., Valks, P., van Geffen, J., Vigouroux, C., Wang, P., Weber, M., 2023. Quarterly validation report of the Copernicus sentinel-5 precursor operational data products #18. April 2018 - February 2023, Version 18.01.00, S5P-MPC-IASB-ROCVR-18.01.00-20230403, 196. https://mpc-vdaf.tropomi.eu/ProjectDir/reports/pdf/S5P-MPC-IASB-ROCVR-18.01.00-FINAL.pdf.

Lange, K., Richter, A., Burrows, J.P., 2022. Variability of nitrogen oxide emission fluxes and lifetimes estimated from sentinel-5P TROPOMI observations. Atmos. Chem. Phys. 22, 2745–2767. https://doi.org/10.5194/acp-22-2745-2022.

Levelt, P.F., Stein Zweers, D.C., Aben, I., Bauwens, M., Borsdorff, T., De Smedt, I., Eskes, H.J., Lerot, C., Loyola, D.G., Romahn, F., et al., 2022. Air quality impacts of COVID-19 lockdown measures detected from space using high spatial resolution observations of multiple trace gases from sentinel-5P/TROPOMI. Atmos. Chem. Phys. 22, 10319–10351. https://doi.org/10.5194/acp-22-10319-2022.

Lorente, A., Boersma, K.F., Eskes, H.J., Veefkind, J.P., van Geffen, J.H.G.M., de Zeeuw, M.B., Denier van der Gon, H.A.C., Beirle, S., Krol, M.C., 2019. Quantification of nitrogen oxides emissions from build-up of pollution over Paris with TROPOMI. Sci. Rep. 9, 1–10. https://doi.org/10.1038/s41598-019-56428-5.

Manders, A.M.M., Builtjes, P.J.H., Curier, L., Van Der Gon, H.A.C.D., Jonkers, S., Kranenburg, R., Kuenen, J., Segers, A.J., Renske, M.A., Visschedijk, A., et al., 2017. Curriculum vitae of the LOTOS-EUROS (v2.0). Chemistry Transport Model. https://doi.org/10.5194/gmd-2017-88.

Merico, E., Cesari, D., Gregoris, E., Gambaro, A., Cordella, M., Contini, D., 2021. Shipping and air quality in Italian port cities: state-of-the-art analysis of available results of estimated impacts. Atmosphere 12, 1–22. https://doi.org/10.3390/atmos12050536.

Nunes, R.A.O., Alvim-Ferraz, M.C.M., Martins, F.G., Peñuelas, A.L., Durán-Grados, V., Moreno-Gutiérrez, J., Jalkanen, J.P., Hannuniemi, H., Sousa, S.I.V., 2021. Estimating the health and economic burden of shipping related air pollution in the iberian Peninsula. Environ. Int. 156 https://doi.org/10.1016/j.envint.2021.106763.

Pseftogkas, A., Koukouli, M.E., Skoulidou, I., Balis, D., Meleti, C., Stavrakou, T., Falco, L., van Geffen, J., Eskes, H., Segers, A., et al., 2021. A new separation methodology for the maritime sector emissions over the mediterranean and black sea regions. Atmosphere 12, 1–18. https://doi.org/10.3390/atmos12111478.

Pseftogkas, A., Koukouli, M.E., Segers, A., Manders, A., Geffen, J. van, Balis, D., Meleti, C., Stavrakou, T., Eskes, H., 2022. Comparison of S5P/TROPOMI inferred NO_2 surface concentrations with in situ measurements over central Europe. Rem. Sens. 14 https://doi.org/10.3390/rs14194886.

REMPEC, 2019. Technical and feasibility study to examine the possibility of designating the Mediterranean Sea, or parts thereof, as SOx ECA(s) under MARPOL Annex VI. REMPEC/WG.45/INF 9.

Riess, T.C.V.W., Boersma, K.F., Van Vliet, J., Peters, W., Sneep, M., Eskes, H., Van Geffen, J., 2022. Improved monitoring of shipping NO_2 with TROPOMI: decreasing NOx emissions in European seas during the COVID-19 pandemic. Atmos. Meas. Tech. 15, 1415–1438. https://doi.org/10.5194/amt-15-1415-2022.

Riess, T.C.V.W., Boersma, K.F., Van Roy, W., de Laat, J., Dammers, E., van Vliet, J., 2023. To new heights by flying low: comparison of aircraft vertical NO2 profiles to model simulations and implications for TROPOMI NO2 retrievals. Atmos. Meas. Tech. 16, 5287–5304. https://doi.org/10.5194/amt-16-5287-2023.

Rodriguez Valido, M., Perez Marrero, J., Mauro González, A., Fabiani Bendicho, P., Efrem Mora, C., 2023. Evaluation of the potential of sentinel-5P TROPOMI and AIS marine traffic data for the monitoring of anthropogenic activity and maritime transport NOx-emissions in canary islands waters. Sustainability 15, 4632. https://doi.org/10.3390/su15054632.

Russo, M., Carvalho, D., Jalkanen, J.P., Monteiro, A., 2023. The future impact of shipping emissions on air quality in Europe under climate change. Atmosphere 14, 1–14. https://doi.org/10.3390/atmos14071126.

Schaap, M., Timmermans, R.M.A., Roemer, M., Boersen, G.A.C., Builtjes, P.J.H., Sauter, F.J., Velders, G.J.M., Beck, J.P., 2008. The LOTOS-EUROS model: description, validation and latest developments. Int. J. Environ. Pollut. 32, 270–290. https://doi.org/10.1504/IJEP.2008.017106.

Schnurr, R.E.J., Walker, T.R., 2019. Marine transportation and energy use. Reference Module in Earth Systems and Environmental Sciences. https://doi.org/10.1016/b978-0-12-409548-9.09270-8.

Skoulidou, I., Koukouli, M.E., Manders, A., Segers, A., Karagkiozidis, D., Gratsea, M., Balis, D., Bais, A., Gerasopoulos, E., Stavrakou, T., et al., 2021. Evaluation of the LOTOS-EUROS NO_2 simulations using ground-based measurements and S5P/TROPOMI observations over Greece. Atmos. Chem. Phys. 21, 5269–5288. https://doi.org/10.5194/acp-21-5269-2021.

IMO, Smith, T.W.P., Jalkanen, J.P., Anderson, B.A., Corbett, J.J., Faber, J., Hanayama, S., O'Keeffe, E., Parker, S., Johansson, L., et al., 2014. Third IMO Greenhouse Gas Study 2014, vol 327. International Maritime Organization (IMO). https://doi.org/10.1007/s10584-013-0912-3.

Stavrakou, T., Müller, J.F., Bauwens, M., Boersma, K.F., van Geffen, J., 2020. Satellite evidence for changes in the NO_2 weekly cycle over large cities. Sci. Rep. 10, 1–9. https://doi.org/10.1038/s41598-020-66891-0.

Thunis, P., Degraeuwe, B., Pisoni, E., Trombetti, M., Peduzzi, E., Belis, C.A., Wilson, J., Clappier, A., Vignati, E., 2018. PM2.5 source allocation in European cities: a sherpa modelling study. Atmos. Environ. 187, 93–106. https://doi.org/10.1016/j.atmosenv.2018.05.062.

Thunis, P., Clappier, A., Tarrason, L., Cuvelier, C., Monteiro, A., Pisoni, E., Wesseling, J., Belis, C.A., Pirovano, G., Janssen, S., et al., 2019. Source apportionment to support air quality planning: strengths and weaknesses of existing approaches. Environ. Int. 130, 104825 https://doi.org/10.1016/j.envint.2019.05.019.

Thunis, P., Clappier, A., With, G., 2020. Source Apportionment to Support Air Quality Management Practices, a Fitness-For-Purpose Guide (V 3.1), EUR30263, 978-92-76-19744-7.

Thürkow, M., Banzhaf, S., Butler, T., Pültz, J., Schaap, M., 2023. Source attribution of nitrogen oxides across Germany: comparing the labelling approach and brute-force technique with LOTOS-EUROS. Atmos. Environ. 292, 119412 https://doi.org/10.1016/j.atmosenv.2022.119412.

Timmermans, R., van Pinxteren, D., Kranenburg, R., Hendriks, C., Fomba, K.W., Herrmann, H., Schaap, M., 2022. Evaluation of modelled LOTOS-EUROS with observational based PM10 source attribution. Atmos. Environ. X 14, 100173. https://doi.org/10.1016/j.aeaoa.2022.100173.

Tokaya, J.P.; Hullegie, J.S.; Kranenburg, R.; Timmermans, R. M. A.; and Coenen, P.W.H. G.:2023 The impact of shipping emissions to urban air quality in Europe – Detailed port-city analysis (Report no. 2/23). CONCAWE, https://www.concawe.eu/wp-content/uploads/Rpt_23-2.pdf (last access: November 17, 2023).

UNCTAD, 2022. Review of maritime transport. UNCTAD. https://unctad.org/publication/review-maritime-transport-2022.

van Geffen, J., Boersma, K.F., Eskes, H., Sneep, M., ter Linden, M., Zara, M., Veefkind, J. P., 2020. S5P TROPOMI NO_2 slant column retrieval: method, stability, uncertainties and comparisons with OMI. Atmos. Meas. Tech. 13, 1315–1335. https://doi.org/10.5194/amt-13-1315-2020.

van Geffen, J., Eskes, H., Compernolle, S., Pinardi, G., Verhoelst, T., Lambert, J.C., Sneep, M., Linden, M. Ter, Ludewig, A., Folkert Boersma, K., et al., 2022. Sentinel-5P TROPOMI NO_2 retrieval: impact of version v2.2 improvements and comparisons with OMI and ground-based data. Atmos. Meas. Tech. 15, 2037–2060. https://doi.org/10.5194/amt-15-2037-2022.

van Geffen, J.H.G.M., Eskes, H.J., Boersma, K.F., Veefkind, J.P., 2022. TROPOMI ATBD of the Total and Tropospheric NO 2 Data Products Document Number : S5P-KNMI-L2-0005-RP.

Van Roy, W., Merveille, J.-B., Scheldeman, K., Van Nieuwenhove, A., Schallier, R., Van Roozendael, B., Maes, F., 2023. Assessment of the effect of international maritime regulations on air quality in the southern North Sea. Atmosphere 14, 969. https://doi.org/10.3390/atmos14060969.

Veefkind, J.P., Aben, I., McMullan, K., Förster, H., de Vries, J., Otter, G., Claas, J., Eskes, H.J., de Haan, J.F., Kleipool, Q., et al., 2012. TROPOMI on the ESA sentinel-5 precursor: a gmes mission for global observations of the atmospheric composition for climate, air quality and ozone layer applications. Remote Sens. Environ. 120, 70–83. https://doi.org/10.1016/j.rse.2011.09.027.

Viana, M., Rizza, V., Tobías, A., Carr, E., Corbett, J., Sofiev, M., Karanasiou, A., Buonanno, G., Fann, N., 2020. Estimated health impacts from maritime transport in the mediterranean region and benefits from the use of cleaner fuels. Environ. Int. 138 https://doi.org/10.1016/j.envint.2020.105670.

Vinken, G.C.M., Boersma, K.F., Jacob, D.J., Meijer, E.W., 2011. Accounting for non-linear chemistry of ship plumes in the GEOS-Chem global chemistry transport model. Atmos. Chem. Phys. 11, 11707–11722. https://doi.org/10.5194/acp-11-11707-2011.

Whitten, G.Z., Hogo, H., Killus, J.P., 1980. The carbon-bond mechanism: a condensed kinetic mechanism for photochemical Smog. Environ. Sci. Technol. 14, 690–700. https://doi.org/10.1021/es60166a008.

Williams, J.E., Folkert Boersma, K., Le Sager, P., Verstraeten, W.W., 2017. The high-resolution version of TM5-MP for optimized satellite retrievals: description and validation. Geosci. Model Dev. (GMD) 10, 721–750. https://doi.org/10.5194/gmd-10-721-2017.