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First Measurements of the Nitrogen Stable Isotope Composition ($\delta^{15}N$) of Ship-emitted NO_x

Zeyu Sun[1,2,8], Zheng Zong[1,3], Yang Tan[1], Chongguo Tian[1,2,7,*], Zeyu Liu[4], Fan Zhang[5], Rong Sun[1,2], Yingjun Chen[4], Jun Li[6], Gan Zhang[6]

[1]CAS Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai, 264003, China
[2]Shandong Key Laboratory of Coastal Environmental Processes, Yantai, 264003, China
[3]Department of Civil and Environmental Engineering, Hong Kong Polytechnic University, Hong Kong, 999077, China
[4]Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), Department of Environmental Science and Engineering, Fudan University, Shanghai, China
[5]Key Lab of Geographic Information Science of the Ministry of Education, School of Geographic Sciences, East China Normal University, Shanghai, 210062, China
[6]State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China
[7]Center for Ocean Mega–Science, Chinese Academy of Sciences, Qingdao, 266071, China
[8]University of Chinese Academy of Sciences, Beijing, 100049, China

Correspondence to: Chongguo Tian (cgtian@yic.ac.cn)

Abstract. The nitrogen stable isotope composition ($\delta^{15}N$) of nitrogen oxides (NO_x) is a powerful indicator for source apportionment of atmospheric NO_x; however, $\delta^{15}N$–NO_x values emitted from ships have not been reported, affecting the accuracy of source partitioning of atmospheric NO_x in coastal zones with a lot of ocean vessel activity. This study systemically analyzed the $\delta^{15}N$–NO_x variability and main influencing factors of ship emissions. Results showed that $\delta^{15}N$–NO_x values from ships ranged from −35.8‰ to 2.04‰ with a mean ± standard deviation of −18.5 ± 10.9‰. The $\delta^{15}N$–NO_x values increased monotonically with the ongoing tightening of emission regulations, presenting a significantly negative logarithmic relationship with NO_x concentrations ($p < 0.01$). The selective catalytic reduction (SCR) system was the most important factor affecting changes in $\delta^{15}N$–NO_x values, compared with fuel types and operation states of ships. Based on the relationship between $\delta^{15}N$–NO_x values and emission regulations observed in this investigation, the temporal variation in $\delta^{15}N$–NO_x values from ship emissions in the international merchant fleet was evaluated by developing a mass-weighted model. These simulated $\delta^{15}N$–NO_x values can be used to select suitable $\delta^{15}N$–NO_x values for a more accurate assessment of the contribution of ship-emitted exhaust to atmospheric NO_x.

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1 Introduction

Due to its detrimental impact on the environment, ecology, and public health, the emission of nitrogen oxides (NO_x) from human-induced sources has drawn considerable attention in recent decades. Transportation exhaust (motor vehicles and ships) tends to overtake coal combustion as the most vital source of NO_x emissions in anthropogenic activities (Zhang et al., 2020; Jin et al., 2021; Shi et al., 2021), contributing 48% of total emissions at a global scale in 2014 (Huang et al., 2017). Air pollution from navigation has become a growing concern in maritime regions with increasing demand for global and regional trade activities (Johansson et al., 2017; Nunes et al., 2017). For instance, the NO_x emissions from ships in China, a major maritime trading country, have reached 130–220 kt, accounting for approximately 34% of national motor vehicle NO_x emissions (Fu et al., 2017). International organizations and national governments have developed a series of regulations on marine traffic activities, prescribing limits for NO_x emissions. For instance, the International Convention for the Prevention of Pollution from Ships (MARPOL) implemented by the International Maritime Organization (IMO) is a momentous international treaty concerning the avoidance of pollution generated by vessels during operations or from unexpected causes. To mitigate the negative effects of navigation on the environment, the IMO set stringent NO_x emission regulations with a decrease of 16–22% and 80% in 2011 (Tier II) and 2016 (Tier III), respectively, in comparison with the levels of 2000 (Tier I) through MARPOL Annex VI (Imo, 2019). While improving the quality of marine fuel, solutions for marine diesel engines that reduce emissions, mainly including exhaust after-treatment systems, precombustion control techniques and fuel optimizations are rapidly developing and applied to newly built ships for future, stricter requirements of NO_x pollution abatement (Deng et al., 2021; Selleri et al., 2021). In addition, the statistics reveal that the world merchant fleet has ships of 2.184 billion deadweight tonnage (DWT) with an average age of 11.8 years in 2021, compared with 797 million DWT with an average age of 18.8 years in 2001 (Wei et al., 2022; Yang and Zhou, 2002). The rapid development of the shipping industry indicates that emission factors of NO_x from ships are changing significantly.

Emission factors are important basic data for compiling emission inventories, on which adequate and reliable information is crucial to work effectively on controlling emissions and associated health impacts for policy makers. Thus, it is critical to estimate ship-emitted NO_x and their impact as precisely and thoroughly as feasible. Early assessment, not providing high precision spatiotemporal variability in ship

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emissions because of limited data availability, showed that about 70% of ship emissions occurred within 400 km of the coast based on emission factors and proxies highly pertinent to ship activities (e.g. fuel usage, port throughput, and seaborne trade) (Corbett and Fischbeck, 1997). A recent evaluation suggested that 60% of total emissions happened within 20 nautical miles (Nm) of the coast on the basis of emission factors and historic ship traffic activities by detailed Automatic Identification System (AIS) data, which is able to provide a ship emission inventory with high spatiotemporal resolution (Liu et al., 2016). Simulations of atmospheric air quality models further revealed that the dense emissions of NO_x from maritime areas within 12 Nm were the primary contributor, contributing more than 80% to coastal regions of the three major urban agglomerations and 30–90% to the entire Chinese mainland (Lv et al., 2018; Zhang et al., 2017). These continuous updates on ship emissions and their environmental impacts indicate that the effect of ship emissions on air quality in offshore zones is becoming increasingly significant. Therefore, in the face of the variation in NO_x emission factors from ships, some other methods independent of the emission factors are necessary to evaluate the impact of ship emissions.

NO_x released into the atmosphere principally oxidizes to nitrate (NO_3^-) and nitric acid (HNO_3) and their nitrogen stable isotope composition ($\delta^{15}N$, i.e. $^{15}N/^{14}N$) is one of the powerful methods to apportion NO_x sources due to the significant differences in $\delta^{15}N$ values of NO_x ($\delta^{15}N$–NO_x) from different sources (Walters et al., 2015a; Walters et al., 2015b; Zong et al., 2020a). In recent years, $\delta^{15}N$ values of NO_3^- ($\delta^{15}N$–NO_3^-) in the atmosphere have been proverbially adopted in tracing sources of atmospheric NO_x based on Bayesian models and $\delta^{15}N$–NO_x values emitted from various sources (Song et al., 2019; Zong et al., 2020b; Zong et al., 2017). The considered sources were mainly coal combustion, vehicle exhaust, biomass burning and biological soil emissions (Luo et al., 2019; Song et al., 2020; Song et al., 2019; Zong et al., 2020b). However, ship emissions were not considered because $\delta^{15}N$–NO_x values emitted from ships have not been reported so far. Lack of $\delta^{15}N$–NO_x values from ships affects the accuracy of atmospheric NO_x source apportionment based on $\delta^{15}N$ signals in offshore areas, especially in some ports with frequent ship activities. Aiming at the knotty problem of lacking $\delta^{15}N$–NO_x values associated with ship emissions, this study systemically collected NO_x discharged by ships to analyze the variation in $\delta^{15}N$–NO_x values and their possible influencing factors. Furthermore, based on the $\delta^{15}N$–NO_x values in our findings, the temporal variation in $\delta^{15}N$–NO_x values from ship emissions in the international merchant fleet was evaluated by developing a mass-weighted model. These insights have implications for assessing changes in $\delta^{15}N$–NO_x values of ship emissions and its potential applications in source

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apportionment.

2 Methodology

2.1 Sampling campaign

NO_x samples were collected from four types of ships between January 2020 and April 2021. These ships included 5 cargo ships, 2 fishing boats, 1 passenger ship, and 1 research ship. The number of ships per category applied for NO_x sample collection was determined based on reports in previous researches that cargo ships accounted for more than 50% of all NO_x emissions from ships in China in 2014 and the fuel consumed by fishing boats accounted for 40% of all ship fuel use in China in 2011 (Chen et al., 2017; Zhang et al., 2018; Zong et al., 2017). NO_x samples were collected under actual operating conditions of ships, and actual ship speed was monitored by the global positioning system (GPS) equipped on board. Samples were grouped based on three operating modes on the basis of the actual speed of each ship: cruising mode, maneuvering mode and hoteling mode (Chen et al., 2016). The technical parameters of ships utilized for sample collection are listed in Table S1 of the Supporting Information (SI). Considering the unpredictable weather circumstances, we attempted to pick calm weather (with zephyrs and gentle waves) and appropriate temperature to carry out ship experiments. As presented in Table S2 of SI, the temperature, wind speed and relative humidity ranged from 1 to 27°C, from 2.8 to 5.1 m s^{-1}, and from 49 to 68% during the observation period, respectively, which were obtained from the local weather station established by the China Meteorological Administration (Wang et al., 2019). These changes in meteorological conditions may affect the measured $\delta^{15}N–NO_x$ values emitted from ships, but this effect is difficult to quantify and thus ignored in this study.

A total of 146 NO_x samples were collected in the present study. These NO_x samples were collected directly from the chimney of ships to better reflect the initial condition of the emitted $\delta^{15}N–NO_x$ values. NO_x exhaust from the main engines (ME) of ships was collected. If the ship also has auxiliary engines (AE) and boilers, NO_x emitted from AE were also collected, but from the boilers were not sampled in view of the weak contribution of boiler exhaust to NO_x emissions (Chen et al., 2017). Before the ship emission test, a stainless steel bellow with a length of 1.5 or 3.0 m and an inner diameter of 40 mm was placed into the ship's chimney to direct the exhaust gas to the sampling platform. The exhaust gas was pumped at a flow rate of 1.0 L min^{-1} into a gas-washing bottle containing 100 mL of 0.25 mol L^{-1}

potassium permanganate ($KMnO_4$) and 0.50 mol L^{-1} sodium hydroxide (NaOH) absorption solution through a Teflon tube (approximately 1.5 m in length and 12.77 mm inner diameter), and NO_x were collected as NO_3^-. Particulates and HNO_3 in the exhaust were removed when passing through a microporous filter and a Nylasorb filter, respectively before entering the gas-washing bottle. The method was proved to be effective at collecting 100% (±5%, 1σ) of the NO_x and producing consistent isotope results under a wide variety of conditions (Fibiger et al., 2014; Zong et al., 2020a). Each sample was collected continuously for more than 20 min after 5 min of stable operation in each operating mode of the ship.

The whole sampling process was conducted carefully to avoid interference with isotopic measurements caused by NH_x, containing ammonia (NH_3) and ammonium (NH_4^+), and isotopic fractionation. The absorption solution prepared beforehand within 12 h before sampling was completely sealed before and after each collection, and titrated within 6 h after sampling to remove redundant $KMnO_4$ from the solution using 30% hydrogen peroxide (H_2O_2) (Zong et al., 2020a). Fibiger and Margeson et al. found that the chemical conversion of NH_3 to NO_3^- can lead to a 0.6% or 2.8% increase in NO_3^- concentration when $KMnO_4$ was not removed from the absorption solution for 36 hours or 7 days, respectively (Fibiger et al., 2014; Margeson et al., 1984). The fast removal of $KMnO_4$ from the solution in the present study indicates that the experimental error regarding NH_x was negligible. The total length of the connecting pipe (stainless steel bellows and Teflon tubes) from the ship chimneys to gas-washing bottles was about 2 m or 4 m for different ships and NO_x were accordingly present in the pipe for about 60 or 120 s, which was significantly shorter than the normal airborne NO lifespan, meaning that fractional distillation could be ignored (Zong et al., 2020a). Penetration tests for NO_x collection were performed on each vessel by connecting two gas-washing bottles in series with the same absorbent solution over a sampling period of 30 min. There was no experimental evidence of NO_x penetration into the second bottle, denoting that the approach used in this study effectively collected all of the NO_x from the sampled ship exhaust.. Additionally, background and blank samples were collected during the sampling period of each ship to quantify background NO_3^- concentrations and to correct for isotope blanks.

2.2 Chemical and isotopic analysis

The NO_3^- concentration in the samples that redundant $KMnO_4$ were removed was quantified by standard

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colorimetric absorbance techniques (AutoAnalyzer 3, SEAL Analytical Ltd.) and the detection limit was 5 ng mL^{-1}. The bacterial denitrifier method was then conducted for $\delta^{15}N$–NO_3^- analysis with the injection volume of samples calculated by the NO_3^- concentration (Sigman et al., 2001; Mcilvin and Casciotti, 2011). In short, an absorption solution containing 20 nmol N was put into the 20 mL headspace bottle and then 2 mL concentrated bacterial solution (*P. aureofaciens*; helium-purged at 30 mL min^{-1} for 4 h to alleviate the background interference) was added to convert NO_3^- to nitrous oxide (N_2O). After sealed and reacting for 12 h, 0.1 mL 10 mol L^{-1} NaOH was injected to terminate the denitrification process. Finally, the $\delta^{15}N$ of the produced N_2O was analyzed by an isotope ratio mass spectrometer (MAT253, Thermo Fisher Scientific, Waltham, MA) and the $\delta^{15}N$ values were corrected according to the repeated measurement results of the international standards (IAEA–NO–3, USGS32, USGS34, and USGS35) (Bohlke et al., 2003). The average blank NO_3^- concentration was 1.15 ± 2.02% of that for the regular samples, which was subtracted from the NO_3^- concentration of each sample to get the final value; and $\delta^{15}N$–NO_3^- for each sample was redetermined by mass balance (Fibiger et al., 2014):

$$\delta^{15}N\text{-}NO_3^- = \frac{\delta^{15}N_{total}[NO_3^-]_{total} - \delta^{15}N_{blank}[NO_3^-]_{blank}}{[NO_3^-]_{total} - [NO_3^-]_{blank}} \quad (1)$$

The analytical precision of NO_3^- concentrations and $\delta^{15}N$ values were less than 1.8% and 0.5‰, respectively, as determined by the replicates in this study.

2.3 Data analysis

Considering the high power and load, ME of ships are the main NO_x source, and emissions vary greatly between operating conditions. AE drive other power machinery on board besides ME, such as generators, oil splitters, marine pumps and air conditioning units, and the output power usually varies with the ME power during navigation. Hence the AE to ME Power Ratio (typically 0.22) was used to estimate the rated power of AE (Chen et al., 2017; Trozzi, 2010). Since a ship's ME and AE work simultaneously for most times, the emission powers of the two were used for weighted calculations, and thus the actual $\delta^{15}N$–NO_x values emitted by ships under each operating condition could be obtained as follows:

$$\delta^{15}N = \frac{0.22 \times \delta^{15}N_{AE} + LF^3 \times \delta^{15}N_{ME}}{0.22 + LF^3} \quad (2)$$

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where$\delta^{15}N_{AE}$ and $\delta^{15}N_{ME}$ are the $\delta^{15}N$–NO_x values emitted by AE and ME of the ship, respectively; LF is the load factor of ME under different operating conditions of the ship. Details on NO_x emissions of collected ship exhaust after integration of ME and AE are shown in Table S3 of SI.

Among the statistical analysis methods, the Kruskal–Wallis test and the Mann–Whitney U test were applied to support the factors influencing $\delta^{15}N$–NO_x values from ships and further compare whether there was significant discrepancy between different classifications under the influence factor, respectively. The conditional inference trees (CIT), random forest (RF), and boosted regression trees (BRT) were implemented to quantitatively evaluate the impact degree of different factors on the variation in ship-emitted $\delta^{15}N$–NO_x values. 75% of the sample data were utilized to generate the prediction model, and the remaining data were utilized to evaluate the accuracy of the simulation results of the prediction model. These methods were conducted by R 4.1.3 software and more detailed principles and algorithm were reported in previous studies (see Text S1 of SI) (Kruskal and Wallis, 1952; Elith et al., 2008; Hothorn et al., 2006; Strobl et al., 2007).

3 Results and discussion

3.1 $\delta^{15}N$–NO_x values emitted from ships

The $\delta^{15}N$–NO_x values emitted from ships sampled in this study were in the range of −35.8‰ to 2.04‰, with a mean ± standard deviation of −18.5 ± 10.9‰. NO_x produced during the combustion of fossil fuels can be divided into two groups: fuel NO_x, generated when chemically bound nitrogen in fuel oxidizes, and thermal NO_x, which is related to the thermal immobilization of atmospheric nitrogen (N_2), i.e., produced by the reaction between oxygen and nitrogen in air at high temperatures (Beyn et al., 2015; Walters et al., 2015b). Previous measurements have revealed that NO_x derived from biomass burning and coal combustion are inclined to be enriched in ^{15}N abundance, largely influenced by the nitrogen content of the biomass and coal itself (Felix et al., 2012; Fibiger and Hastings, 2016; Zong et al., 2022), and produced thermally by internal combustion engines tends to be depleted in ^{15}N abundance due to the kinetic isotope effect (Ti et al., 2021; Walters et al., 2015a; Walters et al., 2015b; Zong et al., 2020a). Moreover, it is well-known that residual oil as marine fuel remains after the removal of valuable distillates (such as gasoline) from petroleum, which contains more impurities, including nitrogen containing substrates, than gasoline and diesel (Corbett and Winebrake, 2008). If the nitrogen-containing

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substances in the residual oil are the major contributors to the vessel-emitted NO_x, it is expected that these NO_x may be enriched in ^{15}N abundance (Felix et al., 2012; Fibiger and Hastings, 2016). However, we found that there was no statistically significant difference in δ^{15}N–NO_x values emitted from vessels fueled by residual oil and diesel at the 99% confidence level ($p > 0.01$), although the former (−14.7 ± 7.72‰, n = 14) was slightly higher than the latter (−18.9 ± 11.1‰, n = 109) as indicated in Fig. S1 of SI. Therefore, it can be concluded that the δ^{15}N–NO_x values emitted from ships do not depend much on the fuel type, and this finding is in agreement with the small proportion (10%) of NO_x originating from fuel-combined nitrogen for engines burning residual oil reported in a previous study (Goldsworthy, 2003). Overall, the ship-emitted negative δ^{15}N–NO_x values with the weak influence of fuels in this research suggest that the δ^{15}N–NO_x values emitted from ships seem to be pertinent to the production of thermal NO_x rather than the conversion of nitrogen in the fuels (Walters et al., 2015a; Walters et al., 2015b; Zong et al., 2022).

It was found that the majority of the NO_x emissions from cars are derived from thermal production (Toof, 1986; Tsague et al., 2006). Figure 1 summarizes the δ^{15}N–NO_x values emitted from ships sampled in this study and from vehicles reported in previous studies to assess whether there are significant differences in δ^{15}N values of these thermally generated NO_x (Walters et al., 2015a; Walters et al., 2015b). Statistical results showed that the δ^{15}N–NO_x values were −12.3 ± 7.21‰ (n = 51), −6.13 ± 6.59‰ (n = 158) and −0.100 ± 1.76‰ (n =3) for diesel-, gasoline- and liquefied petroleum gas (LPG)-powered combustion engines, respectively. The δ^{15}N–NO_x values from ships (−18.5 ± 10.9‰, n = 123) were significantly lower than those produced by diesel-, gasoline- and LPG-powered combustion engines of vehicles at a confidence level of 99% ($p < 0.01$). The comparison suggests that it is necessary to explore the variability of the δ^{15}N–NO_x values and its main influencing factors of ship emissions for the accuracy of source apportionment of atmospheric NO_x in coastal zones, especially in some port areas with high ship activity.

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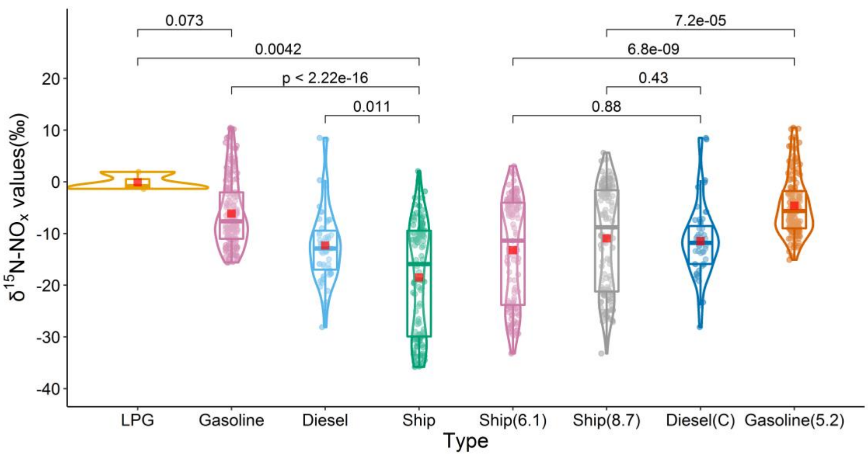

Figure 1: $\delta^{15}N–NO_x$ values emitted from ships in this study and cars fueled by diesel, gasoline and liquefied petroleum gas (LPG) reported from other references (Walters et al., 2015a; Walters et al., 2015b). The Ship(6.1) and Ship(8.7) indicate that $\delta^{15}N–NO_x$ values from ships without selective catalytic reduction (SCR) systems are corrected by 6.1‰ and 8.7‰, respectively. The Diesel(C) and Gasoline(5.2) indicates that $\delta^{15}N–NO_x$ values from diesel and gasoline cars without SCR systems are corrected using 6.1‰ or 8.7‰, and 5.2‰, respectively. (red square, mean; center line, median; box bounds, upper and lower quartiles; whiskers, 1.5 times interquartile range; points, outliers; outer line, data distribution). The p values indicating the distinction between two groups are marked on the upper of the panel (the Mann–Whitney U test).

3.2 Main factors affecting $\delta^{15}N–NO_x$ emitted by ships

The $\delta^{15}N–NO_x$ values emitted from ships had a wider range of variation than those from other sources in the source apportionment of NO_x, which is not conducive to constraining the sources of NO_x in the atmosphere (see Table S4 of SI) (Snape et al., 2003; Felix and Elliott, 2014; Li and Wang, 2008; Moore, 1977; Chai et al., 2019; Redling et al., 2013; Zong et al., 2022; Felix et al., 2012; Fibiger and Hastings, 2016; Walters et al., 2015a; Walters et al., 2015b; Yu and Elliott, 2017; Felix and Elliott, 2013; Miller et al., 2018; Miller et al., 2017; Perez et al., 2001; Ammann et al., 1999; Shi et al., 2022; Freyer, 1978; Heaton, 1990). Clarifying the main factors affecting the change of $\delta^{15}N–NO_x$ is beneficial to narrow the range of $\delta^{15}N–NO_x$ changes in source analysis. Several classification indicators including the emission regulation met by ship engines, the ship category, the ship fuel type, and the actual operational status of ships are considered for the assessment in this study. The consideration is because the IMO emission regulation is the most important measure to restrict NO_x emissions from ships and the other indicators are often used to assess the variation in $\delta^{15}N–NO_x$ values from vehicles (Walters et al., 2015a; Walters et al., 2015b). The statistics of $\delta^{15}N–NO_x$ values classified according to the four indicators are illustrated in

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Fig. S1–S3 of SI and Fig. 2. Various analytical methods were adopted to explore the impact of the four indicators on ship emission $\delta^{15}N–NO_x$ values. The outcomes of the variance analysis are shown in Table S5 of SI. The p values of $\delta^{15}N–NO_x$ values grouped by the emission regulation and the ship category from the variance analysis were both less than 0.001, indicating that the two indicators were the dominant factors influencing the variation in ship $\delta^{15}N–NO_x$ values. Similar significant differences (small p values) in $\delta^{15}N–NO_x$ values divided by the two indicators were calculated by the Mann–Whitney U test, as displayed in Fig. 2 and Fig. S2. The CIT analysis provided a more intuitive result as indicated in Fig. S4 of SI. The emission regulation was the splitting factors of the root node and the second terminal node. As the root node, the emission regulation separated $\delta^{15}N–NO_x$ values from ships before and after implementation of IMO Tier I, and then it divided $\delta^{15}N–NO_x$ values from ships between implementation of IMO Tier I & II and implementation of IMO Tier III at the second terminal node. Ship category was the splitting factor of the fourth terminal node. The splitting process suggests that the emission regulation has a greater influence on $\delta^{15}N–NO_x$ values than the ship category. A more detailed interpretation can be found in Text S1 of SI. Analogously, the results of the RF and BRT methods elucidated that the most important influencing factor on $\delta^{15}N–NO_x$ values from ships was emission regulation, followed by ship category, fuel type, and operational status, as shown in Fig. S5 and Fig. S6 of SI. The relevant parameters for the accuracy assessment of these three decision tree–based methods are listed in Table S6 of SI. The influence of ship category on ship-emitted $\delta^{15}N–NO_x$ values primarily concerns engine types of different ships and the minor influence of fuel type is due to the principle of thermally generated NO_x by internal combustion engines of ships as mentioned above (Goldsworthy, 2003). The operational condition of ships has the least effect on the variation in $\delta^{15}N–NO_x$ values. More detailed interpretations can be found in Text S2 of SI.

Figure 2 displays $\delta^{15}N$ values in NO_x emitted from ships under different emission regulations established by the IMO. The mean ± standard deviation of $\delta^{15}N–NO_x$ values and their 95% confidence intervals estimated using bootstrapping were −33.8 ± 1.83‰ (n=12, −34.8 – −32.7‰), −21.5 ± 6.67‰ (n=12, −25.2 – −17.7‰), −17.8 ± 9.88‰ (n=83, −19.9 – −15.4‰), and −8.12 ± 8.84‰ (n=16, −10.8 – −5.64‰) for the stage I, II, III and IV, respectively. In general, the $\delta^{15}N–NO_x$ values progressively increased with the tightening of ship NO_x emission standards, which is in accordance with the variation trend of $\delta^{15}N–NO_x$ values emitted from gasoline vehicles complying with the national emission standards GB I to GB VI in China (Zong et al., 2020a). The largest average growth rate of $\delta^{15}N–NO_x$ values emitted

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from ships between the three adjacent phases from I to IV occurred between the implementation of IMO Tier II and III (stage III–IV, 54.1%), followed by before and after the implementation of Tier I (stage I–II, 36.4%), and between Tier I and II (stage II–III, 17.8%). Reasons for the great discrepancy that corresponds to the initial constraint on NO_x emissions from ships established by the IMO are hard to analyze as engine and fuel information prior to the implementation of the limit was rarely reported. Fuel optimization technologies (fuel emulsification, fuel desulfurization and fuel additives) and precombustion control technologies (fuel injection strategy, water injection strategy, Miller cycle, two-stage turbocharging, and dual fuel combustion strategy) are two main control methods to meet Tier I and Tier II (Ampah et al., 2021; Deng et al., 2021; Lion et al., 2020). The insignificant discrepancy of the $\delta^{15}N$–NO_x values from ships implementing Tier I and Tier II is consistent with the fact that ship fuels have little effect on the $\delta^{15}N$–NO_x change and these optimized engines still operate in compression combustion engines, as discussed above. Previous studies have found significant differences in $\delta^{15}N$–NO_x emissions from fuel combustion sources with and without selective catalytic reduction (SCR) systems because lighter molecules of NO_x are preferentially decomposed during catalytic reduction, so the produced NO_x are inclined to be enriched in ^{15}N abundance because of balanced isotope effects (Felix et al., 2012). Comparably, distinctions were also observed in $\delta^{15}N$–NO_x values released by vehicles equipped with three-way catalytic (TWC) converters, which made the $\delta^{15}N$–NO_x values from those vehicles reliant on operating circumstances (e.g., cold start or warm start) and NO_x mitigation efficiency (Walters et al., 2015a; Walters et al., 2015b).Consequently, the progressive adoption of NO_x emission control technologies (e.g., SCR and TWC) is anticipated to bring about a rise in the $\delta^{15}N$–NO_x values of NO_x emissions associated with fuel combustion (Felix et al., 2012). Accordingly, the $\delta^{15}N$–NO_x values from ships equipped with SCR systems, which comply with the Tier III emission standard, were significantly higher than those from ships equipped without SCR systems at the 99% confidence level ($p < 0.01$) in our study; therefore, the relatively largest difference in $\delta^{15}N$–NO_x values between ships implementing Tier II and Tier III is in a great measure derived from the SCR system.

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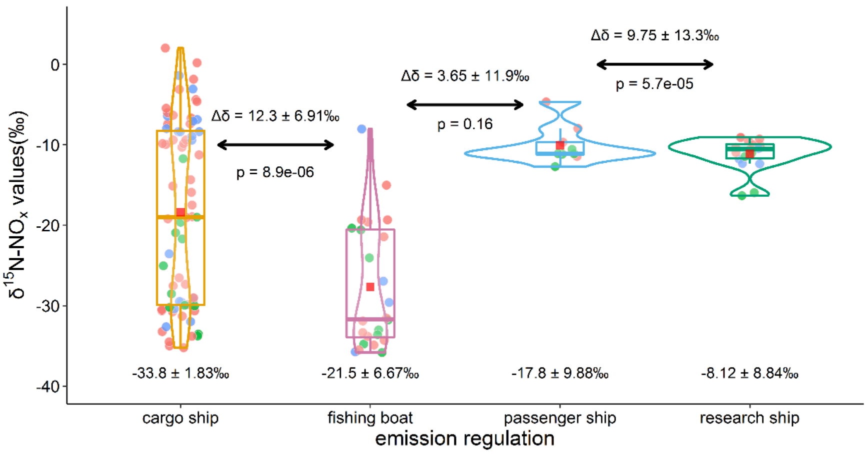

Figure 2: δ^{15}N–NO_x values emitted from ships under different emission regulations established by the IMO. (red square, mean; center line, median; box limits, upper and lower quartiles; whiskers, 1.5 times interquartile range; points, outliers (pink, cruising; green, hoteling; blue, maneuvering); outer line, distribution of data). Mean ± standard deviation of δ^{15}N–NO_x values of each group is marked on the bottom of the panel. The difference and p values indicating the distinction between two groups are marked on the upper of the panel (the Mann–Whitney U test).

Meanwhile, compared to the δ^{15}N–NO_x values which progressively increased with the tighter policing, the corresponding NO_x concentrations gradually decreased and were 239 ± 93.0 ppm, 169 ± 156 ppm, and 122 ± 91.6 ppm under Tier I, II and III, respectively. These gradually increasing δ^{15}N–NO_x values and decreasing NO_x emissions showed a negative logarithmic correlation ($r = -0.39$, $p < 0.01$), as shown in Fig. S7 of SI. Walters et al. demonstrated that there was also a negative logarithmic relationship between δ^{15}N–NO_x values and NO_x concentrations from vehicle emissions, which was stronger in vehicles with NO_x emission control technologies ($r = -0.92$) than in vehicles without NO_x emission control technologies ($r = -0.1$) (Walters et al., 2015b). The discrepancy could be attributed to the enrichment of δ^{15}N relative to the thermally produced NO_x while catalytically reducing NO_x to N_2 (Walters et al., 2015a). The strength of the correlation between δ^{15}N–NO_x values and NO_x concentrations of ship emissions is just within the range of those emitted from vehicles with or without NO_x emission control technologies because only 13% of ship-emitted samples in our research were collected from ships equipped with SCR systems, ulteriorly revealing that whether a ship is equipped with the NO_x catalytic reduction device is a major factor that affects the δ^{15}N–NO_x values.

To further determine the effect of exhaust gas treatment devices on the emission of thermodynamic

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$\delta^{15}N–NO_x$ values from different internal combustion engines, the $\delta^{15}N–NO_x$ values from ships, diesel vehicles and gasoline vehicles not equipped with NO_x catalytic reduction devices were corrected separately and compared again as shown in Fig. 1. It was found that the enrichment factors concerning catalytic NO_x reduction relative to the original thermal NO_x were 6.1‰ and 8.7‰ for light- and heavy-duty diesel-powered engines and 5.2‰ for gasoline-powered engines (Walters et al., 2015a; Walters et al., 2015b). Consequently, the $\delta^{15}N–NO_x$ values emitted from ships without catalytic reduction systems were corrected by the enrichment factors of 8.7‰ and 6.1‰, and diesel vehicles and gasoline vehicles without catalytic reduction systems were corrected by 8.7‰ or 6.1‰, and 5.2‰, respectively. After the correction, the $\delta^{15}N–NO_x$ values from ships are −11.0 ± 10.1‰ (corrected by 8.7‰) and −13.2 ± 10.3‰ (corrected by 6.1‰), and those from diesel vehicles and gasoline vehicles are −11.5 ± 6.87‰ and −4.62 ± 5.71‰, respectively. These corrected $\delta^{15}N–NO_x$ values from ships are still significantly lower than the $\delta^{15}N–NO_x$ values from gasoline vehicles but insignificantly different than those from diesel vehicles ($p > 0.1$), demonstrating that the catalytic reduction system is one of the vital reasons for the differences in $\delta^{15}N–NO_x$ values produced by various internal combustion engines. In addition, we found no significant difference in the $\delta^{15}N–NO_x$ values emitted from gasoline and LPG vehicles. Hence the $\delta^{15}N–NO_x$ values after eliminating the effect of SCR systems can be divided into two groups, one from ships and diesel vehicles and the other from gasoline and LPG vehicles. The $\delta^{15}N–NO_x$ values in the first group are emitted from compression ignition engines fueled by diesel and residual oil, and those in the second group are emitted from spark-ignition engines fueled by gasoline and LPG (Mikalsen, 2011; Mitukiewicz et al., 2015; Park et al., 2020). Engines of the same structural design using different fuels produced comparable $\delta^{15}N–NO_x$ values, which indicates that fuel type is not a major factor affecting the $\delta^{15}N–NO_x$ values once more (Mikalsen, 2011). The main reasons for the significant difference in $\delta^{15}N–NO_x$ values between the two groups may be the difference in the state variables during operation of the two different engine designs. It has been well proven that the combustion with high pressure, the extended Zeldovich mechanism and N_2O reactions are the major sources of combustion engine-emitted NO_x (Goldsworthy, 2003). The combustion chamber temperature, equivalence ratio of fuel mass to oxidizer mass, oxygen concentration and retention time of oxygen and nitrogen at high temperature are different between the types of engines and are the main factors determining the NO_x generation rate (Cho et al., 2018; Goldsworthy, 2003; Mikalsen, 2011; Querel et al., 2015; Tomeczek and Gradon, 1997). These parameters are likely to be the major causes of the large variations in $\delta^{15}N–NO_x$ values, and should be further

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quantified in future studies.

3.3 Implications for $\delta^{15}N–NO_x$ values from ships

As mentioned in Text S3 of SI, the impact of ship emissions on atmospheric NO_x pollution cannot be ignored (Fig. S8 of SI), and reliable $\delta^{15}N–NO_x$ values of ship emissions are essential for the accuracy of source apportionment when assessing atmospheric NO_x sources in coastal areas based on $\delta^{15}N$ methods. Although the $\delta^{15}N–NO_x$ values obtained in the present study are constrained and do not accurately reflect the data emitted from all types of ships, they are practical for assessing $\delta^{15}N–NO_x$ source characterization of traffic exhaust. In general, we found that ships and diesel vehicles emit lower $\delta^{15}N–NO_x$ values than gasoline and LPG vehicles because these NO_x are produced by compression ignition engines, and $\delta^{15}N–NO_x$ values emitted from ships increase with the decrease in the emission factor of NO_x to meet the requirements of tightened regulations established by the IMO, especially when ships are equipped with SCR systems. A previous study concluded that the volume of global maritime trade increased by almost 3-fold from 1980 to 2019, and approximately 90% of these goods were carried by merchant fleets (Kong et al., 2022). Thus, this study collected the age distribution of ships larger than 300 gross tonnage (GT) in the international merchant fleet during 2001 and 2021 to assess the temporal variation in $\delta^{15}N–NO_x$ emitted from ships by developing a mass-weighted model (Yang and Zhou, 2002; Zhou et al., 2004; Meng et al., 2005; Meng and Huang, 2006; Meng et al., 2007; Qi et al., 2008; Qin et al., 2009; Qi et al., 2010; Li et al., 2011; Qin et al., 2012; Qi et al., 2013; Li et al., 2014; Qin et al., 2015; Li et al., 2016; Qin et al., 2017, 2018; Shen and Qi, 2019; Qi et al., 2020; Liu et al., 2021; Wei et al., 2022). In the model, the mass-weighted $\delta^{15}N–NO_x$ value in a specified year can be expressed as:

$$\delta^{15}N=\frac{\sum_{i=1}^{4}\left(\delta^{15}N_i\times EF_i\times TS_i\right)}{\sum_{i=1}^{4}(EF_i\times TS_i)} \tag{3}$$

where $\delta^{15}N_i$, EF_i, and TS_i are the $\delta^{15}N–NO_x$ value, emission factor of NO_x, and number of ships complying with the i^{th} emission regulation, respectively. The subscript of i from 1 to 4 means before Tier I, Tier I, Tier II, and Tier III, respectively. The $\delta^{15}N–NO_x$ values in the four stages are shown in Fig. 2. The EF values in the four stages are 9.8 g $(KWh)^{-1}$, 9.8 g $(KWh)^{-1}$, 7.7 g $(KWh)^{-1}$, and 1.96 g $(KWh)^{-1}$, as suggested by the IMO (Imo, 2019; Deng et al., 2021). The TS was calculated based on the age distribution of ships during 2001 and 2021, as shown in Fig. S9 of SI. On this basis, 100000 $\delta^{15}N–NO_x$ values were stochastically generated to be the typical values of ships meeting each emission regulation

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to calculate the mass-weighted $\delta^{15}N–NO_x$ value in a specified year.

The temporal variation in the mass-weighted $\delta^{15}N–NO_x$ emitted from ships between 2001 and 2021 is displayed in Fig. 3, and the specific calculation results of the mass-weighted $\delta^{15}N–NO_x$ values used in this figure can be found in Table S7 of SI. As expected, the $\delta^{15}N–NO_x$ values from ships larger than 300 GT in the international merchant fleet continued to increase as ships implemented tightener emission standards. The growth rate of the $\delta^{15}N–NO_x$ values was relatively gentle during approximately ten years from 2001 to 2012 (0.25‰/yr), and then became faster between 2013 and 2021 (0.40‰/yr) attributed to the further tightening of emission regulations. Assuming the same age distribution of vessels after 2022 as in 2021, it can be estimated that the increase rate of $\delta^{15}N–NO_x$ values will continue to increase before 2040 (0.40‰/yr) as shown in Fig. 3. After a few years of gentle growth, the $\delta^{15}N–NO_x$ values will remain basically flat after 2046 when all ships will meet the Tier III emission standard. In conclusion, the $\delta^{15}N–NO_x$ values obtained after mass weighting based on the ship age distribution have a smaller range of variation and more valuable and practical significance. In addition, given that the calculated results only involved the age distribution and emission reduction level of the international merchant fleet, the subsequent process of using $\delta^{15}N$ to evaluate the contribution of ship emissions to atmospheric NO_x can be combined with the actual situation of ships in the study area to select more appropriate $\delta^{15}N–NO_x$ values to acquire a more accurate ship emission contribution and reduce the uncertainty in NO_x source apportionment.

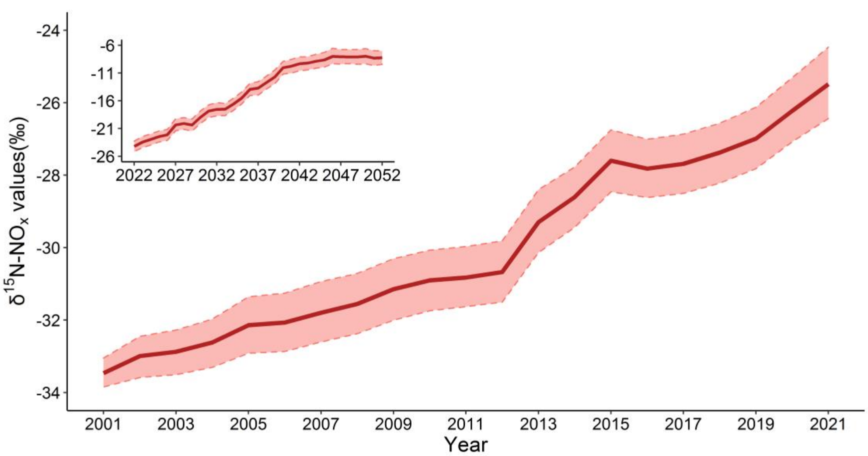

Figure 3: Temporal variation in the mass-weighted $\delta^{15}N$ values in NO_x emitted from ships larger than 300 GT in the international merchant fleet during 2001 and 2021. Predicted temporal changes in $\delta^{15}N–NO_x$ values

from these ships between 2022 and 2052 assuming that the distribution of the ship ages is the same as that in 2021 are given in the inset. (red solid line, mean; red dashed line, upper and lower quartiles)

Data availability. The $\delta^{15}N–NO_x$ values emitted from cars fueled by diesel, gasoline and LPG used in this paper can be found in researches by Walters et al (Walters et al., 2015a; Walters et al., 2015b). The age distribution of ships larger than 300 GT in the international merchant fleet during 2001 and 2021 used to develop the mass-weighted model of $\delta^{15}N–NO_x$ values emitted from ships are obtained from a series of reviews and prospects of world shipping market from 2001 to 2021 published in *Ship & Boat* (Yang and Zhou, 2002; Zhou et al., 2004; Meng et al., 2005; Meng and Huang, 2006; Meng et al., 2007; Qi et al., 2008; Qin et al., 2009; Qi et al., 2010; Li et al., 2011; Qin et al., 2012; Qi et al., 2013; Li et al., 2014; Qin et al., 2015; Li et al., 2016; Qin et al., 2017, 2018; Shen and Qi, 2019; Qi et al., 2020; Liu et al., 2021; Wei et al., 2022). Corresponding data for the collected ship-emitted NO_x samples can be accessed on request to the corresponding author (Chongguo Tian, cgtian@yic.ac.cn).

Author contributions. The manuscript was written through contributions of all authors. ZS, ZZ, CT and FZ designed the research; ZS, ZZ and ZL conducted the sample collection; ZS and YT performed the chemical analyses; ZS and CT analyzed the data, carried out the simulations and wrote the original article; RS, YC, JL and GZ helped with article submissions. All authors have given approval to the final version of the manuscript.

Competing interests. The contact author has declared that none of the authors has any competing interests.

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