



Emissions of NO, NO₂ and PM from inland shipping

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Abstract. Particulate matter (PM) and nitrogen oxides NO_x (NO_x = NO₂ + NO) are key species for urban air quality in Europe and are emitted by mobile sources. According to European recommendations, a significant fraction of road freight should be shifted to waterborne transport in the future. In order to better consider this emission change pattern in future emission inventories, in the present study inland water transport emissions of NO_x, CO₂ and PM were investigated under real world conditions on the river Rhine, Germany, in 2013. An average NO₂ / NO_x emission ratio of 0.08 ± 0.02 was obtained, which is indicative of ship diesel engines without exhaust gas aftertreatment systems. For all measured motor ship types and operation conditions, overall weighted average emission indices (EIs), as emitted mass of pollutant per kg burnt fuel of EI_{NO_x} = 54 ± 4 g kg⁻¹ and a lower limit EI_{PM₁} ≥ 2.0 ± 0.3 g kg⁻¹, were obtained. EIs for NO_x and PM₁ were found to be in the range of 20–161 and ≥ 0.2–8.1 g kg⁻¹ respectively. A comparison with threshold values of national German guidelines shows that the NO_x emissions of all investigated motor ship types are above the threshold values, while the obtained lower limit PM₁ emissions are just under. To reduce NO_x emissions to acceptable values, implementation of exhaust gas aftertreatment systems is recommended.

1 Introduction

Particulate matter (PM) and nitrogen dioxide (NO₂) are key species for urban air quality in Europe. Whereas the exceedance of PM limiting values has attracted considerable public attention during the last decade, NO₂ is a topical problem, which became prominent through the introduction of new European limiting values in January 2010.

The reduction of nitrogen oxide (NO_x = nitrogen monoxide (NO) + NO₂) emissions has historically been one of the key objectives for improving air quality in Europe. NO_x emissions have started to decrease considerably since the mid 1980s in many European areas. However, emissions from mobile sources are still important contributors to air pollution, in particular NO_x. Together with NO_x, non-methane volatile organic compounds (NMVOCs) undergo photochemical reactions that produce secondary pollutants such as ozone (O₃), peroxyacetyl nitrate (PAN) and others (Chameides et al., 1997; Atkinson, 2000).

According to the European Commission's White Paper (2011), 30 % of road freight transported over more than 300 km distance should shift to other transport modes such as waterborne or rail transport by 2030, and more than 50 % by 2050 (European Commission, 2011). Accordingly, such a shift will result in an increase of emissions from inland water transportation in the next years.

In Germany today, the contribution of inland navigation to the total freight traffic is about 12 % (BDA, 2015a). In the Rhine corridor the contribution is 16–18 % (BDA, 2015b). With respect to the goods categories “coal, crude oil and petroleum gas”; “ores, industrial rocks and minerals, and other mining products” and “coking plant and petroleum products”, inland water navigation is the most important transportation mode. In comparison to road transport, inland navigation has a contribution of 72 % for these goods categories and 52 % for container transport. Inland water navigation is a competitive alternative to road and rail transport because the energy consumption per km and ton of transported goods is only approximately 17 % of road and 50 % of rail transport (ECT, 2015). As a consequence of the lower energy consumption, inland water transportation emits significantly less CO₂ and, therefore, has a direct impact on climate change.

In the European Union the emission of NO_x, VOC, PM and CO from road and rail transport decreased from 1990 to 2000, whereas emissions from inland navigation remained more or less constant and emissions from sea transport increased slightly (Trends, 2003). However, in the Netherlands a slight reduction in inland shipping emissions was observed in the same time period when modern engines were introduced into the fleet (CTRC, 2003).

It has also been conclusively demonstrated that the fuel has an important impact on the emissions. Using liquid natural gas (LNG) as fuel for inland water vessels leads to substantial emission reductions, i.e. 75 % for NO_x, 97 % for PM and 10 % for CO₂ (Van der Werf, 2013).

The emissions from inland water transportation are regulated by several national and international guidelines. In 2005 the German national guideline “Binnenschiffabgasverordnung, BinSchAbgasV” was implemented for national waterways, which defines engine-dependent emission indices, i.e. emitted mass of pollutant per kg burnt fuel, for NO_x and PM of EI_{NO_x}: 30–42 and EI_{PM}: 1.2–2.4 g kg⁻¹ respectively (BinSchAbgasV, 2005). In 2011 an international guideline for the Rhine river, “RhineSchUO”, was implemented with engine-dependent EI_{NO_x}: 28–36 g kg⁻¹ and an EI_{PM}: 0.9–3.1 g kg⁻¹ (RheinSchUO, 2011). In addition, for river–sea ships the MARPOL guideline (International Convention for the Prevention of Pollution from Ships) (IMO, 2012) has to be applied. For example, for marine diesel engine with a medium speed of 720 min⁻¹, NO_x-emission indices of 58 g kg⁻¹ since 2000 (Tier I), 56 g kg⁻¹ since 2011 (Tier II) and 11 g kg⁻¹ since 2016 (Tier III) have been introduced.

The correct determination of emission indices (EI) is prerequisite for establishing and developing emission inventories (VBD, 2001; Klimont et al., 2002; Browning and Bailey, 2006; Rohacs and Simongati, 2007; TNO, 2008; CBS, 2009; UBA, 2013). Up to now, several studies have been published in which NO, NO₂, SO₂ and PM emissions from sea ships (Sinha et al., 2003; Chen et al., 2005; Eyring et al., 2005; Petzold et al., 2008; Moldanova et al., 2009; Murphy et al., 2009; Schrooten et al., 2009; Williams et al., 2009; Eyring et al., 2010; Beecken et al., 2014; Jonsson et al., 2011; Lack et al., 2011; Alfödy et al., 2013) and, in particular, from sea ferries (Cooper et al., 1996, 1999; Copper, 2001, 2003; Copper and Ekström, 2005; Tzannatos, 2010; Pirjola et al., 2014) were investigated. Motor test-bed studies can also be used for the determination of EIs from single ship engines (Petzold et al., 2008). However, up to now only a few studies have reported on inland water transportation emissions (Trozzi and Vaccaro, 1998; Kesgin and Vardar, 2001; Schweighofer and Blaauw, 2009; Van der Gon and Hulskotte, 2010)

In the present study, inland water transport emissions were investigated under real world conditions along the riverside of the river Rhine in Germany, during a field campaign from 20 to 22 February 2013.

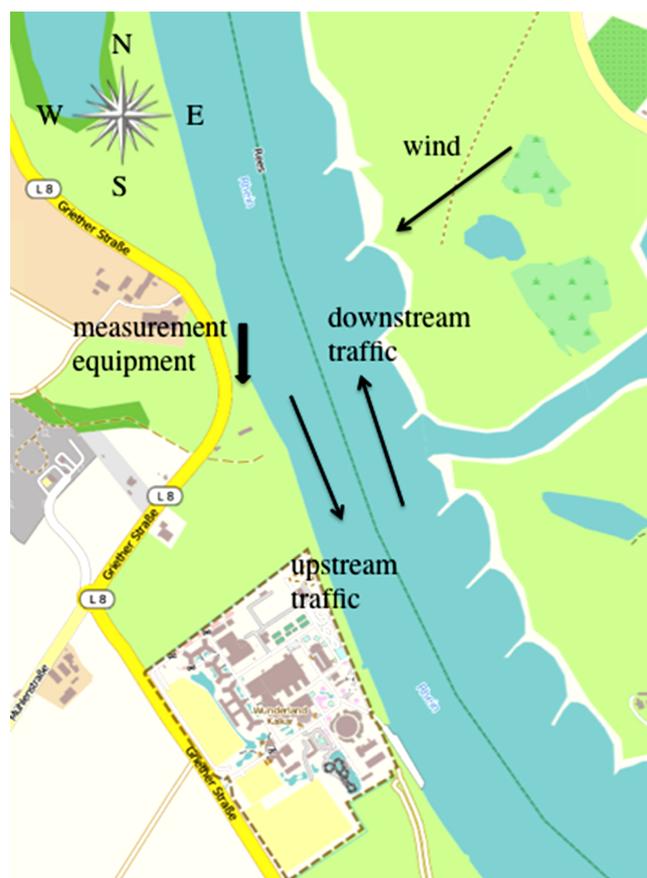


Figure 1. Location of the measurement site at Rhine kilometre 843. (This map is made available under the Open Database License: <http://opendatacommons.org/licenses/odbl/1.0/>. Any rights in individual contents of the database are licensed under the Database Contents License: <http://opendatacommons.org/licenses/dbcl/1.0/>; see more at: <http://opendatacommons.org/licenses/odbl/#sthash.hMw4LgYT.dpuf>).

2 Description of the experimental procedures

2.1 Measurement site

The measurement campaign was carried out at the river Rhine in Germany, close to the “Wunderland Kalkar” at Rhine kilometre 843. Figure 1 shows a map of the measurement site. During the campaign emissions from both upstream and downstream cruising inland ships were studied. The sampling point was located 50 m downwind from the river bank.

It is reasonable to assume that the engines of the ships passing the sampling site were under warm operation conditions.

2.2 Analytical equipment

The analytical equipment used was installed in a mobile van with an external power supply. NO and NO₂ were measured

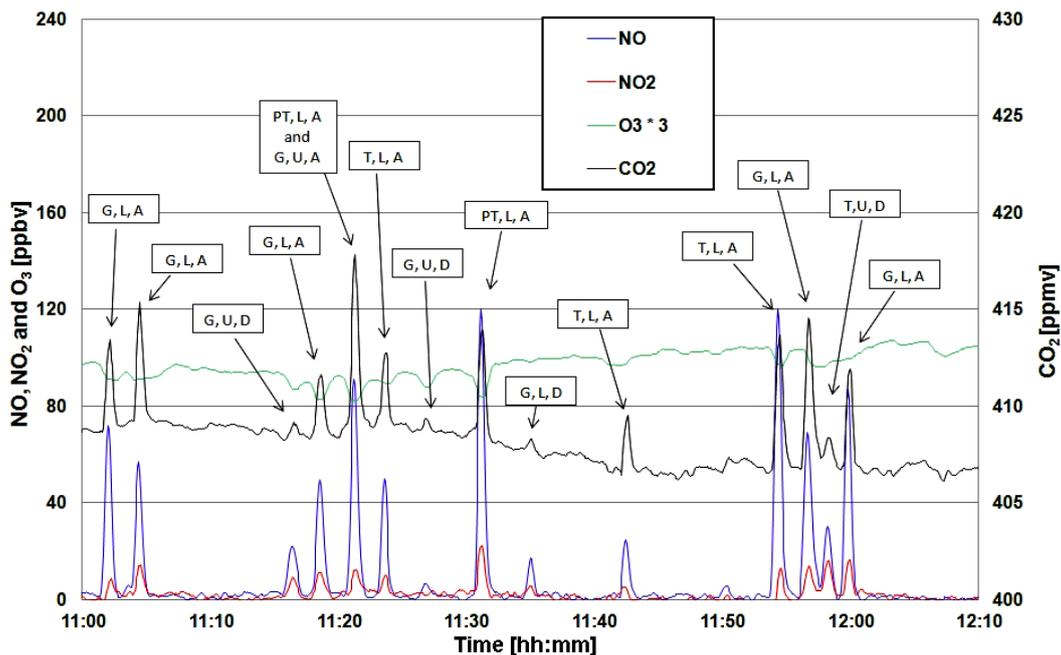


Figure 2. Temporal variation of the NO, NO₂, O₃ and CO₂ concentration at the measurement site on 20 February 2013 from 11:30 to 14:00 LT from different ship types (G = goods ship, T = petroleum tanker, PT = push-tow) and at different operation parameters (L = loaded, U = unloaded, A = upstream and D = downstream).

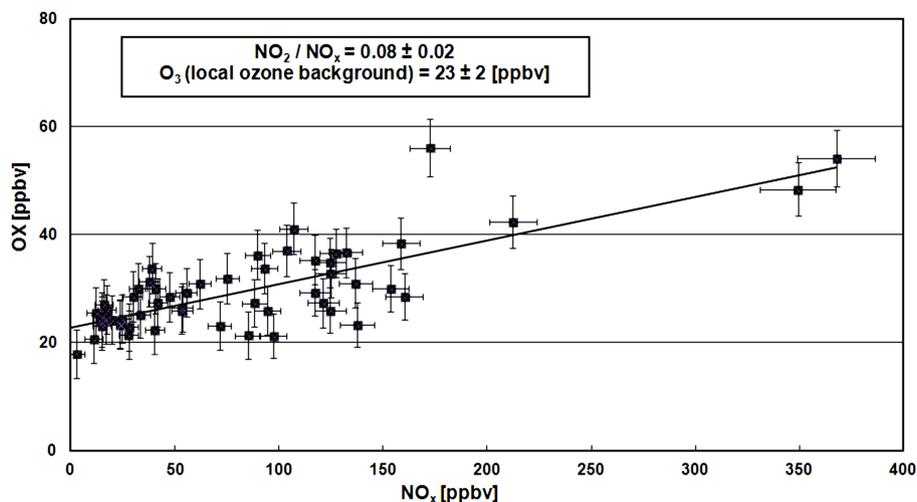


Figure 3. Plot of O_x vs. NO_x.

online with a commercial NO_x chemiluminescence analyser (Environnemental, AC 31M with molybdenum converter). The time resolution was 10 s and the detection limit, which was calculated from the variation of the zero signal, was 2 ppbv for NO and 3 ppbv for NO₂. The NO channel of instrument was directly calibrated by diluted standard NO calibration mixtures (Messer, stated accuracy 5%). The NO₂ channel was calibrated by using a NO titration unit (Environnemental, GPT). NO₂ was produced by the reaction of

NO with O₃ in a flow reactor leading to the quantitative conversion of the calibrated NO ($\Delta\text{NO} = \Delta\text{NO}_2$).

Ozone (O₃) was measured online with a commercial O₃ monitor (Environnemental, O3 41M with UV absorption). The time resolution was 10 s and the detection limit, which was calculated from the variation of zero measurements, was 1 ppbv. O₃ was calibrated by using an O₃ calibration unit (Environnemental; K-O₃, accuracy 10%). O₃ was produced by the photolysis of synthetic air in a flow reactor, leading to the quantitative formation of O₃.

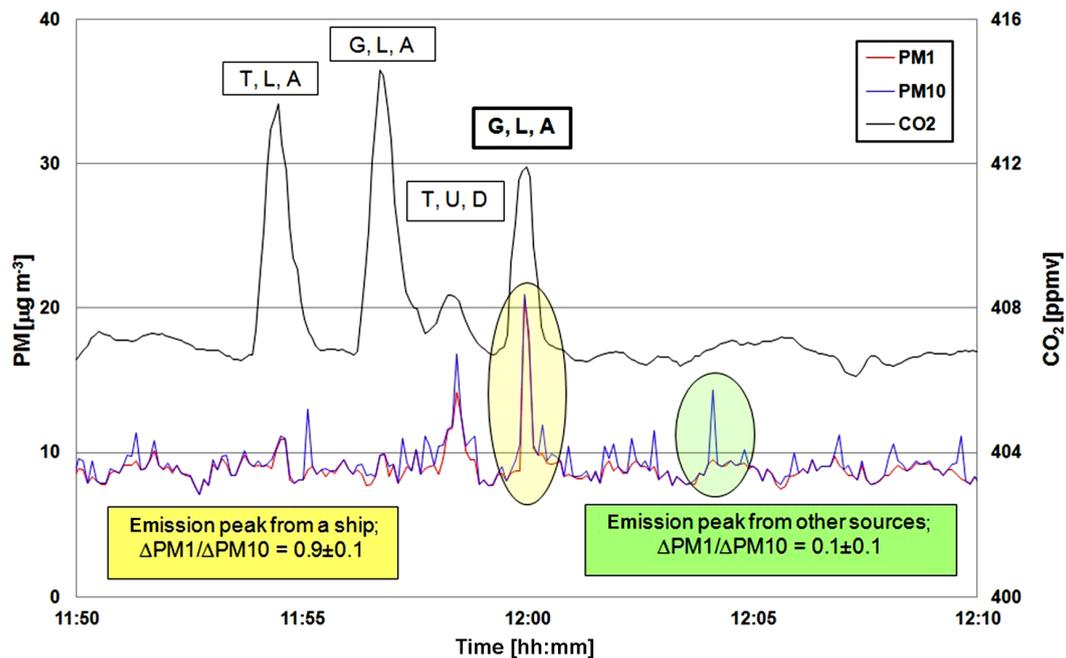


Figure 4. Temporal variation of CO₂, PM₁₀ and PM₁ at the measurement site on 20 February 2013 from 11:50 to 12:10 LT for different ship types (G = goods ship, T = petroleum tanker) and different operation parameters (L = loaded, U = unloaded, A = upstream and D = downstream).

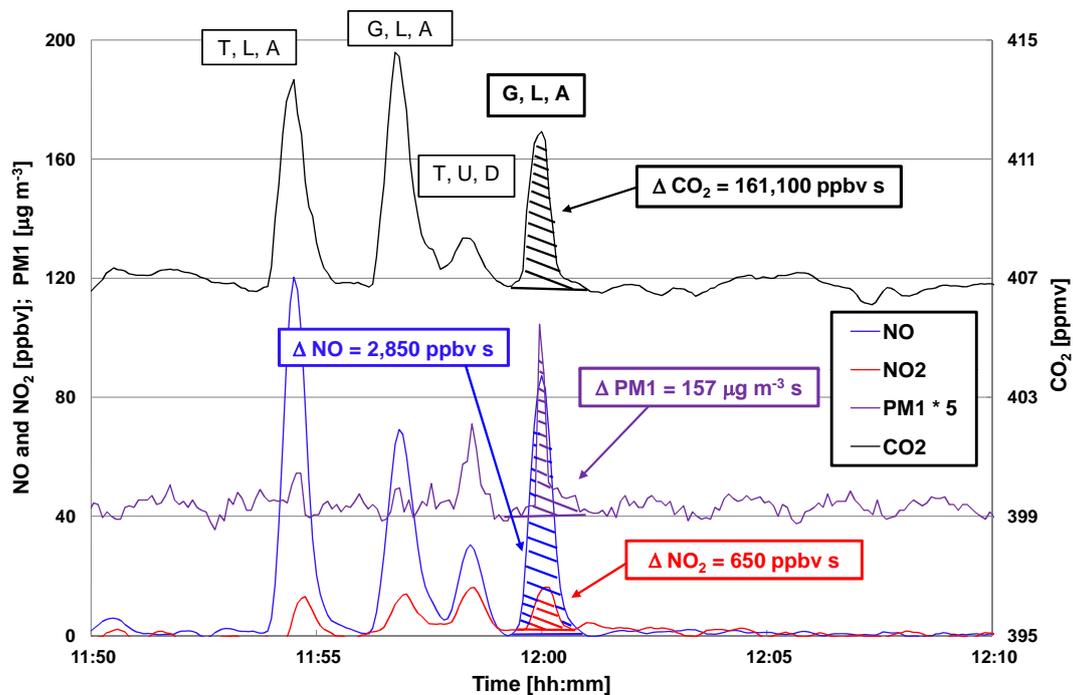


Figure 5. Temporal variation of the NO, NO₂, CO₂ and PM₁ concentration and the integrated emission peaks at Δ NO, Δ NO₂, Δ CO₂ and Δ PM₁ peak area at the measurement site on 20 February 2013 from 11:50 to 12:10 LT for goods-ship (G) under-loaded (L) and upstream (A) conditions.

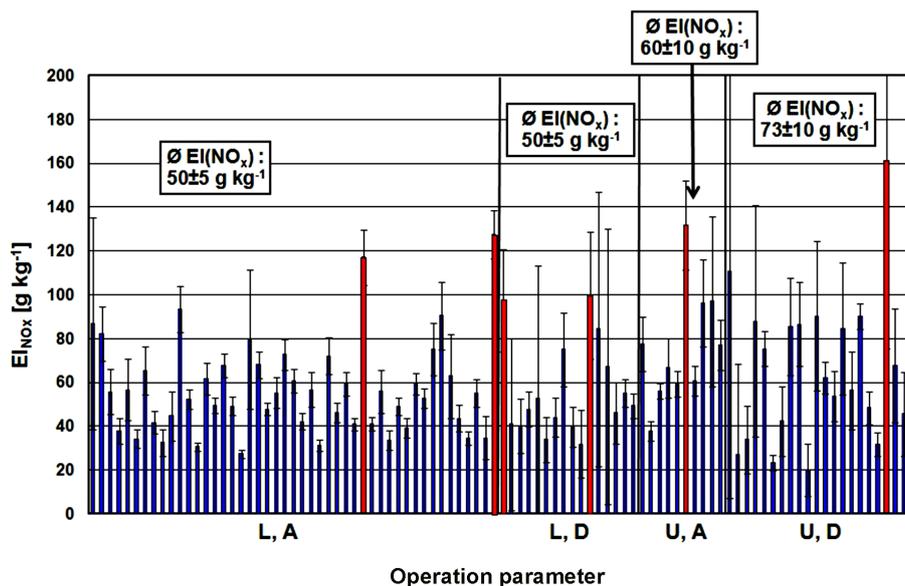


Figure 6. EI_{NO_x} (as NO_2) in $g\ kg^{-1}$ burnt fuel of single-motor ships [goods] and the weighted average value of EI_{NO_x} for different operation parameters, L = loaded, U = unloaded, A = upstream and D = downstream. Red bars show outliers (4σ limit) and were not taken into account in the calculation of the weighted average value.

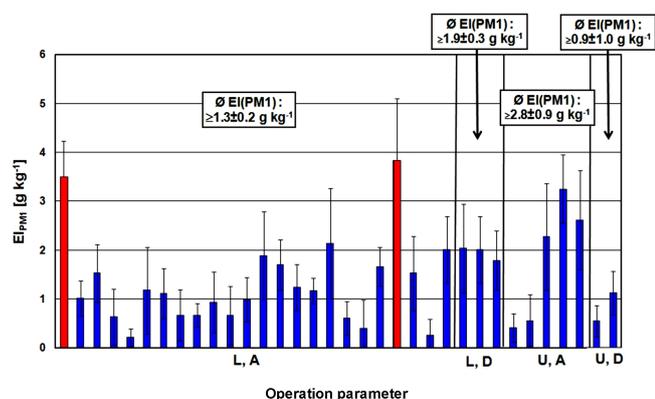


Figure 7. Lower limit EI_{PM_1} in $g\ kg^{-1}$ burnt fuel of single-motor ships [goods] and the weighted average EI_{PM_1} for different operation parameters, L = loaded, U = unloaded, A = upstream and D = downstream.

Carbon dioxide (CO_2) was measured online with a commercial CO_2 monitor (LICOR 7100 with IR absorption). The time resolution was 1 s and the detection limit, which was calculated from the variation of zero measurements, was 0.5 ppmv. CO_2 was directly calibrated by diluted standard CO_2 calibration mixtures (Messer, stated accuracy 2 %).

PM was measured by an optical particle counter (OPC) (Grimm Aerosol Technik GmbH & Co. KG, Dust Monitor EDM 107). The OPC counts particles in a size range from 0.25 to 32 μm in 31 size channels. The time resolution was 6 s and the detection limit was 0.1 $\mu g\ m^{-3}$. However, the instru-

ment only provided the concentrations of the fractions PM_1 , $PM_{2.5}$ and PM_{10} .

Meteorological parameters, such as temperature, pressure, relative humidity and wind speed were also measured. In addition to the measurement of compounds in the ambient air, the number and types of ships passing the measurement site were counted.

Samples were taken at a height of about 3 m above the stream gauge of the river Rhine.

3 Results and discussion

3.1 Inland water transportation emissions

NO , NO_2 , O_3 , CO_2 , PM_1 and PM_{10} concentrations, wind speed and wind direction at the measurement site as well as movements of the ships were measured. During the campaign more than 170 emission peaks from motor ships were observed. From these peaks almost 140 could be attributed to single ship types (G = goods ship, T = petroleum tanker, PT = push-tow) and were analysed accordingly. Figure 2 shows as an example the temporal variation of NO , NO_2 , O_3 and CO_2 mixing ratios at the measurement site on 20 February 2013 from 11:30 to 14:00 LT. The perfect correlation between NO and NO_2 with CO_2 confirms that these compounds were emitted from the same source, i.e. the engine exhaust. The anticorrelation between NO_2 and O_3 provides information about NO_x chemistry in the ship exhaust plumes, i.e. the formation of NO_2 by the titration reaction of NO with O_3 .

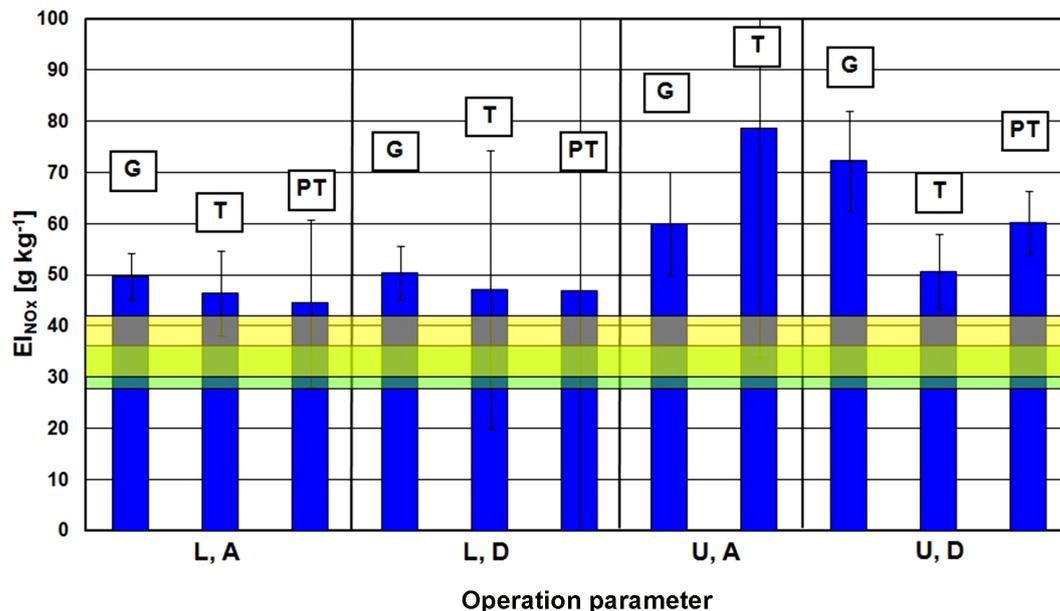


Figure 8. Weighted average emission index for NO_x (EI_{NO_x}) in g kg⁻¹ burnt fuel for different motor ship types (G = goods, T = tanker and PT = push-tow) at different operation parameters (L = loaded, U = unloaded, A = upstream and D = downstream), in comparison with German guidelines (BinSchAbgasV, 2005 (yellow) and RheinSchUO, 2011 (green)).

3.2 NO₂/NO_x emission ratio

The NO₂/NO_x ratio in the exhaust plume is an important parameter in obtaining information about the ship engine types and estimating the impact of ship emissions on ozone formation. It is well known that diesel engines without aftertreatment systems show NO₂/NO_x ratios of 0.10–0.12 for road traffic (Kurtenbach et al., 2001; Kousoulidou et al., 2008; Carslaw and Rhys-Tyler, 2013) and 0.14 ± 0.04 for navigation (Cooper, 2001; Grice et al., 2009). In contrast, the NO₂/NO_x ratio from road traffic diesel engines with aftertreatment systems, such as oxidation catalyst or PM filter systems, are in the range of 0.25–0.30. The NO₂/NO_x emission ratio from navigation diesel engines with selective catalytic NO_x reduction systems (SCR) is 0.009 ± 0.003 (Cooper, 2001).

To obtain the correct NO₂/NO_x emission ratio from the measurements it is important to distinguish between primarily emitted NO₂ and NO₂, which is formed by the reaction of NO with ozone in the exhaust plume. The correct NO₂/NO_x ratio is obtained by plotting O_x, which is the sum of NO₂ and O₃ vs. the measured NO_x concentration as shown in Fig. 3 (Clapp and Jenkin, 2001). The NO₂/NO_x emission ratio and the local O₃ background mixing ratio are obtained from the slope and intercept of the regression line respectively. From the data shown in Fig. 3 a NO₂/NO_x emission ratio of 0.08 ± 0.02 and a local ozone background volume mixing ratio of 23 ± 2 ppbv were obtained. The obtained NO₂/NO_x ratio indicates that the ships passing the measurement site

were equipped with conventional diesel engines without exhaust gas aftertreatment.

3.3 PM₁ and PM₁₀ emissions

Figure 4 shows the temporal variation of CO₂, PM₁₀ and PM₁ concentrations at the measurement site on 20 February 2013 from 11:50 to 12:10 LT. Some PM₁ peaks are well correlated with those of CO₂ mixing ratios and therefore with ship plumes. In contrast, some PM₁₀ peaks showed no correlation with ship emissions. This indicates that the main PM emissions from ships with diesel engines are in the PM₁ range. This result is in good agreement with other studies e.g. from the United States EPA (1996), Petzold et al. (2008), Beecken et al. (2014), Pirjola et al. (2014) and Westerlund et al. (2015). Therefore, in the present study particle ship emissions are defined as PM₁. According to Westerlund et al. (2015) the maximum in the particle number size distribution was observed at about 10 nm and the maximum particle mass distribution at 250 nm. Therefore, the optical particle counter (OPC) used detects only a lower limit of the emitted particle mass.

3.4 Emission indices

From the measurement data, emission indices (EIs) for NO_x (NO calculated as NO₂) and PM₁ (unit: mass per kg burnt fuel) were calculated. In Fig. 5 the integrated emission peak (peak area) for NO, NO₂, CO₂ and PM₁ as ΔNO, ΔNO₂, ΔCO₂ and ΔPM₁ are shown as an example for a single-motor ship. If one assumes that the increase of NO, NO₂,

PM₁ and CO₂ in the plume is proportional to the emission strength of the ship engine, an emission ratio to CO₂, e.g. $\Delta\text{NO}_x / \Delta\text{CO}_2$, can be easily calculated (Petzold et al., 2008). In addition, the ΔNO , ΔNO_2 , ΔCO_2 and ΔPM_1 were also calculated using the difference between background and plume mixing ratios (Schlager et al., 2008) and considering the precision errors of the background data, which are typically ± 2 , ± 4 , ± 2 ppbv, ± 1 ppmv and $\pm 2 \mu\text{g m}^{-3}$ for NO, NO₂, O₃, CO₂ and PM₁ respectively.

Both approaches were used to calculate the emission indices and were in good agreement, in general better than $\pm 6\%$. Caused by the slightly different time responses of the instruments, the integrated peaks results were finally specified. Elementary analysis of a typical ship diesel fuel yielded: 86 wt % carbon and 14 wt % hydrogen (Cooper, 2001). From the wt % carbon and under the assumption that all fuel is burnt to the final end product, CO₂, an emission index EI (CO₂) of 3150 g CO₂ per kg burnt fuel was calculated and further used to calculate the corresponding emission index (EI) for the ship engines. The emission index (EI) is calculated by the following equation (1) (Petzold et al., 2008):

$$\text{EI}(X) = \text{EI}(\text{CO}_2) \times \frac{M(X)}{M(\text{CO}_2)} \times \frac{\Delta(X)}{\Delta(\text{CO}_2)}, \quad (1)$$

where M denotes the molecular weight and Δ the peak area, mixing ratios, column densities, etc. of the species. The subsequent calculations used $M(\text{CO}_2)$ with 44 g mol^{-1} , $M(\text{NO}_x)$ with 46 g mol^{-1} and NO_x as NO₂. Table S1 of the Supplement summarizes the calculated EIs of the different ship types and operation conditions. Errors were calculated using error propagation for the different measured compounds.

As an example, Fig. 6 shows the emission index for NO_x (as NO₂) (EI_{NO_x}) of single-motor ships [goods] and the weighted average EI_{NO_x} for different operation parameters, i.e. L = loaded, U = unloaded, A = upstream and D = downstream.

As an example, Fig. 7 shows the obtained lower limit PM₁ emission index (EI_{PM₁}) for single-motor ships [goods] and the weighted average EI_{PM₁} for different operation parameters, i.e. L = loaded, U = unloaded, A = upstream and D = downstream. Red bars show outliers (4σ limit) and were not taken into account in the calculation of the weighted average value. Values are lower limits because of the detection range of the OPC system.

Although Figs. 6 and 7 show a large variation in the EIs for NO_x and PM₁, the average data exhibit that the EI_{NO_x} are almost independent of engine operation parameters within the given error limits. The same was found for tankers and push-tows; see weighted average emission index in Figs. 8 and 9.

Figure 8 exhibits that the NO_x emission indices of all motor ship types investigated are above the engine rotation speed-dependent limit values of the German guidelines, which are 29–37 g kg⁻¹ for the RheinSchUO and 36–46 g kg⁻¹ for the BinSchAbgasV guidelines.

Figure 9 exhibits that the obtained lower limit PM₁ emission values for almost all motor ship types are just within the limit values of the German guide lines, which are 0.9–3.1 g kg⁻¹ for the RheinSchUO and 1.2–2.4 g kg⁻¹ for the BinSchAbgasV guidelines, depending on the engine rotation speed.

For comparison with literature data, uncertainty(2σ)-weighted averaged EI_{NO_x} and EI_{PM₁} were calculated for all motor ship types and operation condition investigated. An EI_{NO_x} of $52 \pm 3 \text{ g kg}^{-1}$ and a lower limit EI_{PM₁} of $\geq 1.9 \pm 0.3 \text{ g kg}^{-1}$ were obtained. Minimum and maximum EIs for NO_x and PM₁ were found to be in the range of 20–161 and ≥ 0.2 –8.1 g kg⁻¹ respectively. Table 1 shows the emission indices for NO_x and PM₁ in g kg⁻¹ fuel calculated from the measured values in comparison with different literature data. Errors were calculated using error propagation for the different measured compounds.

Between 1998 and 2013 only a few studies reported EI_{NO_x} and EI_{PM₁} from inland water navigation (Trozzi and Vaccaro, 1998; Kesgin and Vardar, 2001; Schweighofer and Blaauw, 2009; Van der Gon and Hulskotte, 2010) in the range 39–57 and 0.7–1.9 g kg⁻¹ respectively; see Table 1. The uncertainty(2σ)-weighted averaged EI_{NO_x} and EI_{PM₁} were 48 ± 4 and $1.3 \pm 0.2 \text{ g kg}^{-1}$ respectively, which are in good agreement with the present study.

Emission indices for NO_x and PM₁ from inland water navigation were used in emission inventories by Klimont et al. (2002), Rohacs and Simongati (2007), Van der Gon and Hulskotte (2010), CBS (2009) and UBA (2013). The authors reported EI_{NO_x} and EI_{PM₁} in the range 46–51 and 1.5–4.0 g kg⁻¹ respectively (see Table 1). From these data uncertainty(2σ)-weighted average values for EI_{NO_x} of 48 ± 2 and EI_{PM₁} $2.7 \pm 1.2 \text{ g kg}^{-1}$ were derived, which are in a good agreement with the present study.

In order to comply with the limit values of the current RheinSchUO guideline for inland water navigation for NO_x with 29–37 g kg⁻¹, a further significant reduction of NO_x emission is necessary. This can be achieved by using exhaust gas aftertreatment systems, whose functional capability have been demonstrated in recent studies (Cooper, 2001; Schweighofer and Blaauw, 2009; BMVBS, 2012; Future Carrier, 2012; Hallquist et al., 2013; Pirjola et al., 2014). For example, the European project “Cleanest Ship” (Schweighofer and Blaauw, 2009) shows that NO_x and PM emissions of a ship diesel engine equipped with an SCR (selective catalytic reduction) system and particle filter can be reduced to 4 and 0.02 g kg⁻¹ respectively.

4 Summary and conclusion

The present study shows that the measurement site on the Rhine river provided representative real world emission data from inland navigation. Emissions of NO, NO₂, CO₂ and particulate matter from a large number of individual ships

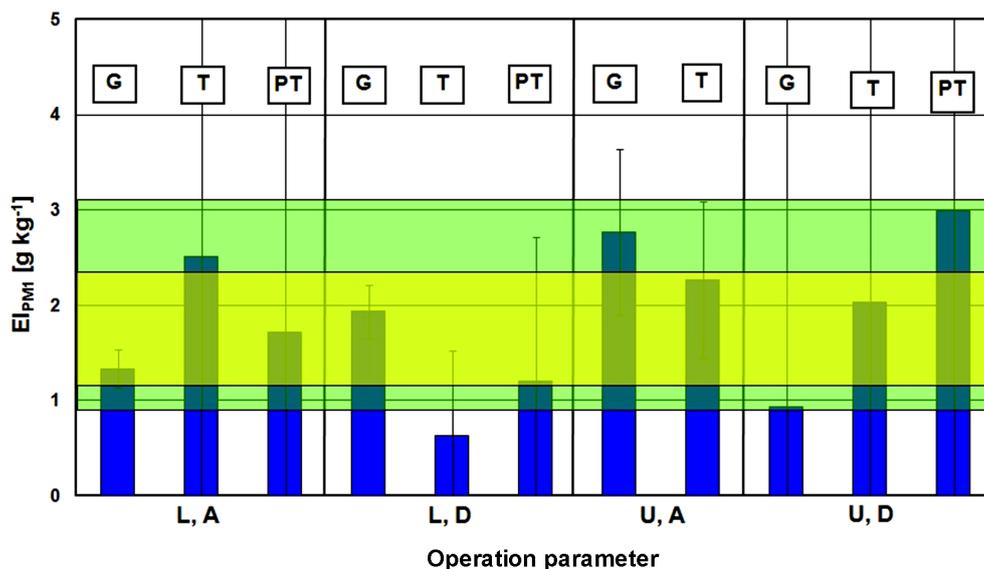


Figure 9. Weighted average lower limit emission index for PM₁ (EI_{PM_1}) in $g\ kg^{-1}$ burnt fuel for different motor ship types (G = goods, T = tanker and PT = push-tow) at different operation parameters (L = loaded, U = unloaded, A = upstream and D = downstream), in comparison with German guidelines (BinSchAbgasV, 2005 (yellow) and RheinSchUO, 2011 (green)).

Table 1. Emission indices NO_x and PM₁ in $g\ kg^{-1}$ burnt fuel calculated from the measured values in comparison with different literature data from inland water transportation.

Reference	Location	Sampling period	EI_{NO_x} ($g\ kg^{-1}$)	EI_{PM_1} ($g\ kg^{-1}$)	Ship types
(a) field measurements (inland, engine without exhaust gas aftertreatment system)					
This study	Germany, Rhine (inland)	2013	54 ± 4	$\geq 2.0 \pm 0.3$	different
Kesgin and Vardar (2001)	Turkey, Bosphorus (inland)	1998	57	1.2	domestic passenger ships (a)
Trozzi and Vaccaro (1998)	Italy, Tyrrhenian Sea (inland)	1998	51	1.2	domestic passenger ships (a)
Van der Gon and Hulskotte (2010)	Netherlands (inland)	2010	45	1.9	different
Schweighofer and Blaauw (2009)	inland	2009	39	0.73	research vessel (b)
(b) field measurements (inland, engine with exhaust gas aftertreatment system)					
BMVBS (2012)	inland	2011	n.d.	0.08–0.48	research vessel
Futura Carrier (2010)	inland	2009	n.d.	0.29 ± 0.01	research vessel
Schweighofer and Blaauw (2009)	inland	2009	11–39	0.02	research vessel (c)
(c) inventories					
Rohacs and Simongati (2007)	Average EU (inland)	2007	47	3.2	inventory
Van der Gon and Hulskotte (2010), CBS (2009)	Netherlands (inland)	2008–2009	46	1.9	inventory
Klimont et al. (2002)	RAINS, EU (inland)	2002	51	4.0	inventory
UBA (2013)	TREMOD, Germany (Inland)	2013	49 ± 6	1.5 ± 0.2	inventory

Remarks: n.d. is no data, (a) domestic passenger ships with diesel engine (medium speed), (b) without exhaust gas aftertreatment system, (c) with exhaust gas aftertreatment system.

were monitored and analysed. Particulate emissions measured in the ship plumes were dominated by PM₁. An av-

erage NO₂/NO_x emission ratio of 0.08 ± 0.02 was obtained, which is typical for ship diesel engines without af-

terreatment systems such as oxidation catalysts or PM filter systems. The emission indices for emitted mass of pollutant per kg burnt fuel for NO_x (EI_{NO_x}) and PM₁ (EI_{PM₁}), which were determined for different motor ship types (goods, petroleum tanker and push-tow) and for different operation parameters (L = loaded, U = unloaded, A = upstream and D = downstream), exhibited a large variation and were almost independent of the ship types and operation parameters. For the motor ship types and operation conditions investigated, a weighted average EI_{NO_x} of $54 \pm 4 \text{ g kg}^{-1}$ and lower limit EI_{PM₁} of $\geq 2.0 \pm 0.3 \text{ g kg}^{-1}$ were obtained with minimum and maximum values ranging from 20 to 161 g kg⁻¹ for NO_x and ≥ 0.2 to 8.1 g kg⁻¹ for PM₁ respectively. The EI_{NO_x} and EI_{PM₁} from the present study are in a good agreement with literature data. The comparison of emission indices for NO_x and PM₁ with limit values of the German guidelines (BinSchAbgasV, 2005; RheinSchUO, 2011) showed that NO_x emissions of all motor ship types investigated were above the limit values, whereas the obtained lower limit PM₁ emissions for almost all motor ship types were just within the limit values. In order to meet the limit values for NO_x and PM, the NO_x emissions in particular have to be reduced significantly, e.g. by the introduction of specific exhaust gas aftertreatment systems, some of which have proven to be very effective.

Future campaigns should include PM size distribution and also CO, SO₂ and NMVOC measurements. Campaigns should be carried out different seasons to study a potential impact of water level and river streaming on the emissions.

5 Data availability

All data are available upon request to the authors.

The Supplement related to this article is available online at doi:10.5194/acp-16-14285-2016-supplement.

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References

- Alföldy, B., Lööv, J. B., Lagler, F., Mellqvist, J., Berg, N., Beecken, J., Weststrate, H., Duyzer, J., Bencs, L., Horemans, B., Cavalli, F., Putaud, J.-P., Janssens-Maenhout, G., Csordás, A. P., Van Grieken, R., Borowiak, A., and Hjorth, J.: Measurements of air pollution emission factors for marine transportation in SECA, *Atmos. Meas. Tech.*, 6, 1777–1791, doi:10.5194/amt-6-1777-2013, 2013.
- Atkinson, R.: Atmospheric chemistry of VOCs and NO_x, *Atmos. Environ.*, 34, 2063–2101, 2000.
- Beecken, J., Mellqvist, J., Salo, K., Ekhol, J., and Jalkanen, J.-P.: Airborne emission measurements of SO₂, NO_x and particles from individual ships using a sniffer technique, *Atmos. Meas. Tech.*, 7, 1957–1968, doi:10.5194/amt-7-1957-2014, 2014.
- Binnenschiffahrt Abgasverordnung (BinSchAbgasV9, 2005): Richtlinie EU2004/26/EG, <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2004:225:0003:0107:DE:PDF> (last access: 4 November 2016) 2005.
- BMVBS: Bundesministerium für Verkehr, Bau und Stadtentwicklung: Erprobung von Partikelfilter für den Einsatz in der Binnenschiffahrt, Projektbericht, <http://www.bmvbs.de> (last excess: 4 November 2016), Berlin, Germany, 2012.
- Browning, L. and Bailey, K.: Current Methodologies and Best Practices for Preparing Port Emission Inventories, ICF Consulting and EPA, Fairfax, Virginia, USA, Final Report for US, 2006.
- Bundesverband der Deutschen Binnenschiffahrt e.V. (BDA): Daten und Fakten 2014/2015, <http://binnenschiff.de/content/wp-content/uploads/2015/08/150827-Daten-Fakten-2014-2015.pdf> (last excess: 4 November 2016), Duisburg, Germany, 2015a.
- Bundesverband der Deutschen Binnenschiffahrt e.V. (BDA): Pressemitteilung http://bdbev.de/aktuell/2015/150205_Binnenschiffahrt_boomt_im_Rheinkorridor.pdf (last excess: 4 November 2016), Duisburg, Germany, 2015b.
- Carslaw, D. C. and Rhys-Tyler, G.: New insights from comprehensive on-road measurements of NO_x, NO₂ and NH₃ from vehicle emissions remote sensing in London, UK, *Atmos. Environ.*, 81, 339–347, 2013.
- CBS, StatLine.: Luchtverontreiniging, emission naar luct, CBS, Den Haag/Heerlen, the Netherlands, 2009.
- Chameides, W. L., Fehsenfeld, F., Rodgers, M. O., Cardelino, C., Martinez, J., Parrish, D., Lonneman, W., Lawson, D. R., Rasmussen, R. A., Zimmerman, P., Greenberg, J., Middleton, P., and Wang, T.: Ozone Precursor Relationships in the Ambient Atmosphere, *J. Geophys. Res.*, 97, 6037–6055, 1992.
- Chen, G., Huey, L. G., Trainer, M., Nicks, D., Corbett, J., Ryerson, T., Parrish, D., Neuman, J. A., Nowak, J., Tanner, D., Holoway, J., Brock, C., Crawford, J., Olson, J. R., Sullivan, A., Weber, R., Schauffler, S., Donnelly, S., Atlas, E., Roberts, J., Flocke, F., Hübler, G., and Fehsenfeld, F.: An investigation of the chemistry of ship emission plumes during ITCT 2002, *J. Geophys. Res.*, 110, D10S90, doi:10.1029/2004JD005236, 2005.
- Clapp, L. J. and Jenkin, M. E.: Analysis of the relationship between ambient levels of O₃, NO₂ and NO as a function of NO_x in UK, *Atmos. Environ.*, 35, 6391–6405, 2001.
- Cooper, D. A.: Exhaust emissions from high speed passenger ferries, *Atmos. Environ.*, 35, 4189–4200, 2001.
- Cooper, A. D.: Exhaust emissions from ships at berth, *Atmos. Environ.*, 37, 3817–3830, 2003.
- Cooper, D. A. and Andreasson, K.: Predictive NO_x emission monitoring on board a passenger ferry, *Atmos. Environ.*, 33, 4637–4650, 1999.
- Cooper, D. A. and Ekström, M.: Applicability of the PEMS technique for simplified NO_x monitoring on board ships, *Atmos. Environ.*, 39, 127–137, 2005.
- Cooper, D. A., Peterson, K., and Simpson, D.: Hydrocarbon, PAH and PCB emissions from ferries: a case study in the Skagerak-Kattegatt-Oresund region, *Atmos. Environ.*, 30, 2463–2473, 1996.

- Dutch Transport Research Centre (DTRC): Inland Shipping Emissions Protocol, EMS-protocol – emissies door de binnenvaart: verbrandingsmotoren versie 3, Rotterdam 22 November 2003, the Netherlands, 2003.
- European Commission: White paper 2011, 52011DC0144: Roadmap to a Single European Transport Area – Towards a competitive and resource efficient transport system, SEC(2011)391 final, <http://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1433420196688&uri=CELEX:52011DC0144> (last access: 4 November 2016), 2011.
- European Commission Transport (ECT): Inland waterways, What do we want to achieve?, http://ec.europa.eu/transport/modes/inland/index_en.html (last access 4 November 2016), 2015.
- Eyring, V., Köhler, H. W., van Aadenne, J., and Lauer, A.: Emissions from international shipping: 1. The last 50 years, *J. Geophys. Res.*, 110, D17305, doi:10.1029/2004JD005619, 2005.
- Eyring, V., Isaksen, I. S. A., Bernsten, T., Collins, W. J., Corbett, J. J., Endresen, O., Grainger, R. G., Moldanova, J., Schlager, H., and Stevenson, D. S.: Transport impact on atmosphere and climate: Shipping, *Atmos. Environ.*, 44, 4735–4771, 2010.
- FUTURE Carrier: New Logistics® GmbH: <http://www.new-logistics.de/new-logistics/pdf/uebersichtsbroschuere.pdf> (last access: 2 November 2015), 2012.
- Grice, S., Stedman, J., Kent, A., Hobson, M., Norris, J., Abbott, J., and Cooke, S.: Recent trends and projections of primary NO₂ emissions in Europe, *Atmos. Environ.*, 43, 2154–2167, 2009.
- Hallquist, A. M., Fridell, E., Westerlund, J., and Hallquist, M.: Onboard Measurements of Nanoparticles from a SCR-Equipped Marine Diesel Engine, *Environ. Sci. Technol.*, 47, 773–780, 2013.
- International Maritime Organisation (IMO): Nitrogen Oxides – Regulation 13, [http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Nitrogen-oxides-\(NOx\)-%E2%80%93-Regulation-13.aspx](http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Nitrogen-oxides-(NOx)-%E2%80%93-Regulation-13.aspx) (last access: 4 November 2016), London, United Kingdom, 2012.
- Jonsson A. M., Westerlund, J., and Hallquist, M.: Size-resolved particle emission factors for individual ships, *Geophys. Res. Lett.*, 38, L13809, doi:10.1029/2011GL047672, 2011.
- Kesgin, U. and Vardar, N.: A study on exhaust gas emissions from ships in Turkish Straits, *Atmos. Environ.*, 35, 1863–1870, 2001.
- Klimont Z., Cofala, J., Bertok, I., Aman, M., Heyes, C., and Gyatfas, F.: Modelling Particulate Emissions in Europe, A Framework to Estimate Reduction Potential and Control Costs, Intermin Report IR-02-076, IIASA, Laxenburg, 2002.
- Kousoulidou, M., Nitzichristos, L., Mellios, G., and Samaras, Z.: Road-transport emission projections to 2020 in European urban environments, *Atmos. Environ.*, 42, 7465–7475, 2008.
- Kurtenbach, R., Becker, K. H., Gomes, J. A. G., Kleffmann, J., Lörzer, J. C., Spittler, M., Wiesen, P., Ackermann, R., Geyer, A., and Platt, U.: Investigations of Emissions and Heterogeneous Formation of HONO in a Road Traffic Tunnel, *Atmos. Environ.*, 35, 3385–3394, 2001.
- Lack, D. A., Cappa, Ch. D., Langridge, J., Bahreini, R., Bufaloe, G., Brock, Ch., Cerully, K., Coffman, D., Hyden, K., Holloway, J., Lerner, B., Massoli, P., Li, Sh.-M., Middlebrook, A. N., Moore, R., Nenes, A., Nuaaman, I., Onasch, Th. B., Peischl, J., Perring, A., Quinn, P. K., Ryerson, T., Schwartz, J. P., Spackman, R., W. St. C., Worsnop, D., Xiang, B., and Williams, E.: Impact of Fuel Quality Regulation and Speed Reductions on Shipping Emission: Implications for Climate and Air Quality, *Environ. Sci. Technol.*, 45, 9052–9060, 2011.
- Moldanova, J., Fridell, E., Popovicheva, O., Demirdjian, B., Tishkova, V., Faccinnetto, A., and Focsa, C.: Characterisation of particulate matter and gaseous from a large ship diesel engine, *Atmos. Environ.*, 43, 2632–2641, 2009.
- Murphy, S. H., Agrawal, H., Sorooshian, A., Padro, L. t., Gates, H., Hersey, S., Welch, W. A., Jung, H., Miller, J. W., Cocher III, D. R., Nenes, A., Jonsson, H., Flagan, R. C., and Seinfeld, J. H.: Comprehensive Simultaneous Shipboard and Airborne Characterization of Exhaust from a Modern Container Ship at Sea, *Environ. Sci. Technol.*, 43, 4626–4640, 2009.
- Petzold, A., Hasselbach, J., Lauer, P., Baumann, R., Franke, K., Gurk, C., Schlager, H., and Weingartner, E.: Experimental studies on particle emissions from cruising ship, their characteristic properties, transformation and atmospheric lifetime in the marine boundary layer, *Atmos. Chem. Phys.*, 8, 2387–2403, doi:10.5194/acp-8-2387-2008, 2008.
- Pirjola, L., Pajunoja, A., Walden, J., Jalkanen, J.-P., Rönkkö, T., Kousa, A., and Koskentalo, T.: Mobile measurements of ship emissions in two harbour areas in Finland, *Atmos. Meas. Tech.*, 7, 149–161, doi:10.5194/amt-7-149-2014, 2014.
- RheinSchUO: Zentralkommission für die Rheinschifffahrt: http://www.ccr-zkr.org/files/documents/reglementRV/rv1a_122015.pdf#search=%22Emissionsgrenzwerte%20NOx%22 (last access 4 November 2016), Strasbourg, France, 2011.
- Rohacs, J. and Simongati, G.: The role of inland water navigation in a sustainable transport system, *TRANSPORT – 2007*, Vol XXII, 148–153, doi:10.1080/16484142.2007.9638117, 2007.
- Schlager, H., Baumann, R., Lichtenstern, M., Petzold, A., Arnold, F., Speidel, M., Gurk, C., and Fischer, H.: Aircraft-based trace gas measurements in a primary European corridor, in: *Proceedings of the International Conference on Transport, Atmosphere and Climate (TAC)*, Oxford, UK, 83–88, 2008.
- Schrooten, L., De Vlieger, I., Panis, L. I., Chiffi, C., and Pastori, E.: Emission of maritime transport: A European reference system, *Sci. Total Environ.*, 408, 318–323, 2009.
- Schweighofer, J. and Blaauw, H.: The Cleanest Ship, Final Report, Österreichische Wasserstraße GmbH and Maritime Research Institute Netherlands, https://www.researchgate.net/publication/273447753_FINAL_REPORT_THE_CLEANEEST_SHIP_PROJECT (last access 4 November 2016), Wageningen, the Netherlands, 2009.
- Sinha, P., Hobbs, P. V., Yokelson, R. J., Christian, T. J., Kirchstetter, T. W., and Brintjes, R.: Emissions of trace gases and particles from two ships in southern Atlantic Ocean, *Atmos. Environ.*, 37, 2139–2148, 2003.
- Trends: Calculation of indicators of environmental pressure caused by transport: main report. European Commission, Office for Official Publications of European Communities, Luxembourg, 2003.
- Trozzi, C. and Vaccaro, R.: Methodologies for estimating air pollutant emissions from ships, Technical Report MEET. (Methodologies for Estimating Air Pollutant Emissions from Transport) RF98, European Community, 1998.
- Tzannatos, E.: Ship emissions and their externalities for the port of Piraeus – Greece, *Atmos. Environ.*, 44, 400–407, 2010.

- UBA: Aktualisierung der Emissionsberechnung für die Binnenschifffahrt und Übertragung der Daten in TREMOD, Umweltbundesamt, Endbericht, 371145105, Berlin, Germany, 2013.
- US Environmental Protection Agency: Compilation of air pollutant emission factors-AP42, 5th Edn. (Chapter 3.4 Large Stationary Diesel Engines) Office of the Federal Register National Archives and Records Administration, US Government Printing Office, Washington, DC, USA, 1996.
- Van der Gon, H. D. and Hulskotte, J.: Methodologies for estimating shipping emissions in the Netherlands, A documentation of currently used emission factors and related activity data, BOP report, Netherlands Environmental Assessment Agency, Bilthoven, the Netherlands, 2010.
- Van der Werf, H.: LNG as Fuel in Inland Navigation. Secretary General. Central Commission for the Navigation of the Rhine (CCNR), http://www.mariko-leer.de/cms_uploads/files/hans-van-der-werf-zkr.pdf (last access 4 November 2016), Strasbourg, France, 2013.
- Versuchsanstalt für Binnenschifffahrt e. V. (VBD): Emissionen luftverunreinigender Stoffe durch den Schiffverkehr in Nordrhein-Westfalen – Ein Modell zur Berechnung der Schadstoffverteilung auf Wasserstraßen, in Schleusen und Häfen, 2001.
- Westerlund, J., Hallquist M., and Hallquist A. S.: Characterization of fleet emissions from ships through multi individual determination of size-resolved particle emissions in a coastal area, *Atmos. Environ.*, 112, 159–166, 2015.
- Williams, E. J., Lerner, B. M., Murphy, P. C., Herdon, S. C., and Zahniser, M. S.: Emissions of NO_x, SO₂, CO, and HCHO from commercial marine shipping during Texas Air Quality Study (TexAQS) 2006, *J. Geophys. Res.*, 114, D21306, doi:10.1029/2009JD012094, 2009.