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A chemometric investigation of aromatic emission profiles from a marine engine in comparison with residential wood combustion and road traffic: Implications for source apportionment inside and outside sulphur emission control areas

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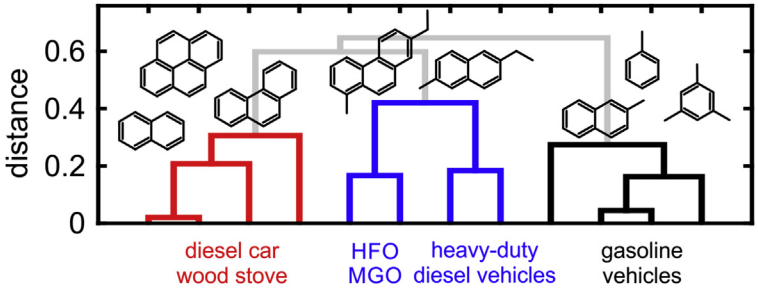
HIGHLIGHTS

- Aromatic emission profiles of twelve real-world emission sources.
- Temporal variability of emissions considered.
- Significant aromatic markers for ship emissions in-/outside SECAs.
- Prediction model for contribution of ship emissions.

GRAPHICAL ABSTRACT



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ABSTRACT

Ship emissions are known to cause severe impacts on human health, but are less restricted than land-based emissions. A regulation to improve air quality in coastal regions and frequented waterways is the limitation of fuel sulphur content to 0.1% in sulphur emission control areas (SECAs), which has caused a switch from heavy fuel oil (HFO) towards diesel-like marine gas oil (MGO) or marine diesel oil (MDO). The fraction of aromatic organic vapours in the exhaust from a marine engine, operating on HFO and MGO, was investigated by resonance-enhanced multi-photon ionisation time-of-flight mass spectrometry (REMPI-TOFMS). MGO with fuel sulphur content (FSC) below 0.1% and HFO with an average FSC of 2.7% denote representative marine fuels inside and outside SECAs, respectively. The obtained emission spectra were combined with data of previous REMPI-TOFMS studies of combustion engines and wood combustion in statistical analyses to derive marker substances for ship emissions inside and outside SECAs. A diagnostic ratio of C2-naphthalenes to methyl-naphthalenes was found to hold for a good discriminator between ship emissions on the one hand and road traffic and wood combustion on the other hand. Furthermore, random REMPI spectra from all emission sources were mixed with different

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proportions in a simulation to create a model based on partial least square (PLS) regression for the prediction of ship contribution to aromatic organic vapours. We point out that in particular PAHs with higher degree of alkylation are significant markers for primary ship emissions which may support source apportionment studies inside and outside SECAs to assess the benefits of fuel sulphur content regulation on air quality.

1. Introduction

Seaborne trade accounts for more than 90% of the global trade volume (IMO, 2012) and exceeds 10 billion tons per year (UNSTAD, 2016). Ships have been identified as a significant contributor to total anthropogenic emissions causing complex effects on climate and human health (Fuglestvedt et al., 2009). Substantial emissions of particulate matter, gaseous pollutants and greenhouse gases by ships can be addressed to the fact that off-shore emissions, especially in international waters, are less regulated than land-based emissions. The vast majority of the ships are operated on low-grade heavy fuel oil (HFO) with fuel sulphur content (FSC) allowed up to 3.5%. Significant correlations were found between increased mortality and hospitalisation and emitted PM from ships from a local to global scale (Corbett et al., 2007; Liu et al., 2016; Tian et al., 2013). Therefore, the identification and quantification of ship emissions in source apportionment studies is important to assess air quality and adopt measures for its improvement.

On that account, the International Maritime Organisation (IMO) decided to tackle ship emissions by limiting the FSC to 0.1% from 2015 on in European and North American coastal waters, called sulphur emission control areas (SECAs). Since 2010, this limit holds already for harbour areas within the European Union due to the European Directive 2005/33/EC. Moreover, the FSC will be generally restricted to 0.5% in international waters as well, starting from 2020 or 2025 (IMO, 2017).

Sulphur scrubber technology is available, but currently not economic. Thus the FSC restriction has currently led to a switch in marine fuel from HFO to marine gas oil (MGO) or marine diesel oil (MDO), which represent diesel-like middle distillates of the crude oil refinery with intrinsically lower FSC, instead of using sulphur-scrubber technology (Wan et al., 2016) since the economic efficiency depends on the crude oil price (Jiang et al., 2014). Although it was predicted that air quality will benefit from this legislation (Eyring et al., 2010; Lack et al., 2011; Winebrake et al., 2009), it has been demonstrated that even diesel fuel with an FSC below 10 ppm shows strong biological effects on human epithelia lung cells (Oeder et al., 2015) and macrophages (Sapcariu et al., 2016). Therefore, switching to low-sulphur fuel will likely not reduce the adverse effects of ship emissions to environment and health effectively.

As a consequence of the fuel switch, the composition of ship emissions from SECA-compliant fuels changed in terms of sulphur-containing species (mainly sulphur dioxide and sulphate), particle number and mass (Khan et al., 2012; Moldanová et al., 2013; Zetterdahl et al., 2016). However, it also affected the molecular composition of gaseous as well as particle-bound organic compounds (Radischat et al., 2015; Sippula et al., 2014; Streibel et al., 2017). In addition to these impacts on primary emissions, sulphur-containing compounds, metals, polycyclic aromatic hydrocarbons (PAHs), PM number and mass concentration were found to decline in ambient air of SECAs as well (Gregoris et al., 2016; Kotchenruther, 2017; Merico et al., 2016).

Substantially amounts of the emitted organic vapours belong to mono- and polyaromatic compounds (Kleeblatt et al., 2015; Radischat et al., 2015). In particular polycyclic aromatic hydrocarbons (PAHs) in both gas and particle phase have been frequently used in diagnostic ratios (DRs) to identify or discriminate between emission sources (Tobiszewski and Namieśnik, 2012). This study investigated the aromatic organic vapour emissions from a marine engine with resonance-enhanced multi-photon ionisation time-of-flight mass spectrometry (REMPI-TOFMS). REMPI refers to a selective and sensitive ionisation technique for aromatic compounds (Boesl, 2000), which has been frequently applied for process control and analytic, such as for combustion (Streibel and Zimmermann, 2014). Its high selectivity results from the combination of the optical properties of an analyte by UV-spectroscopy with a mass selective detection (Zimmermann et al., 2008). The obtained chemical information goes beyond fingerprinting and enables to strikingly shrink the number of possible molecular assignments per nominal m/z that REMPI-TOFMS can be regarded as a sensor for aromatic compounds.

The aromatic emission profiles of the marine engine emissions for SECA- and non-SECA-compliant fuels were compared with emission profiles of residential wood burning and road traffic from previous studies by several statistical techniques. Many of the detected aromatic constituents can be assigned more precisely to the fraction of intermediate-volatile organic compounds (IVOCs) with saturation concentration between 1 and 100 mg m^{-3} (Donahue et al., 2006). IVOCs released from motor vehicles have been described as substantial precursor of secondary organic aerosol (SOA) (Gentner et al., 2012), which has to be considered in air quality control. In the following, aromatic marker substances from the VOC/IVOC fraction and DRs for ship emissions from both HFO and MGO combustion are presented including their statistical significance. Finally, a partial least-square regression model was developed to predict the contribution of ships in simulated REMPI mass spectra of ambient air as a proof of concept.

2. Materials and methods

2.1. Marine engine, engine conditions and fuels

Emissions were analysed from a four-stroke one-cylinder research diesel engine (1 VDS 18/15 CR) on a test-bench with a maximum power of 80 kW. A detailed description of the engine can be found in (Sippula et al., 2014). Engines of these dimensions may be used on smaller ships as a main power supply and on larger ships for auxiliary power, but also as backup power supply in, e.g., hospitals. The engine was operated at different engine loads (11, 25, 50, 75 and 100%) on marine gas oil (MGO) and heavy fuel oil (HFO, HFO-380a in Table 1) with fuel sulphur contents of 0.078% and 2.3%, which refer to representative fuels in SECA and non-SECA, respectively. Each engine load of this study was once measured for 30–60 min at stable conditions. HFO, also called residual fuel oil, is mainly composed of the vacuum residue of the crude oil distillation blended by lighter refinery products such as kerosene to meet a maximum viscosity of e.g. 180 mm^2 s^{-1} (“HFO-180”) or 380 mm^2 s^{-1} (“HFO-380”) (Fahim et al., 2010). To cover the variability of the HFO emission depending of the crude oil origin and