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Emission fingerprint of inland navigation vessels compared with road traffic, domestic heating and ocean going vessels

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A B S T R A C T

Despite increasing need for cargo shipping, little knowledge exists on emissions from inland navigation. Here we characterized and compared patterns of metals, and parent-, thio- and alkylated PAHs in gaseous and particulate emissions from inland navigation vessels (INVs) with those of road traffic, domestic heating (solid fuels) and ocean going vessels (OGVs) using data from this study and the literature. Diagnostic tools for tracing the environmental impact of inland navigation are proposed. INV and diesel fueled road traffic emissions were differentiated from OGVs and coal combustion via V/Ni values. The PAH inventory of particulate INV emissions also differed significantly from other emitters via a higher proportion of three ring PAHs. The ratio of phenanthrene to dibenzothiophene distinguished diesel fueled road traffic, lignite combustion, OGVs and INVs from gasoline fueled road traffic and wood combustion. The 1,7/(1,7 + 2,6) and 1,7/(1,7 + x4) dimethylphenanthrene ratios (x4 = sum of 1,3-, 2,10-, 3,9- and 3,10-dimethylphenanthrene) separated INV, road traffic (diesel), domestic heating and OGV emissions and are recommended for future application in environmental quality studies.

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1. Introduction

Emissions from fuel combustion continue to affect environmental quality, releasing hazardous particulate matter (PM) and persistent organic pollutants like polycyclic aromatic hydrocarbons (PAHs), their S containing counterparts, and inorganic pollutants (e.g. Warnatz et al., 2006). To evaluate the degree and range of emissions specific compound patterns of exhaust have been described. However, little knowledge about the composition of emissions from inland navigation exists.

Emissions from inland navigation vessels (INVs) have been studied for climate-relevant gases like CO_2 and NO_x, and for their PM emissions (Klein et al., 2007; Hulskotte and Denier van der Gon, 2010; UBA, 2012). More studies have concentrated on emissions from ocean going vessels (OGVs), so a more detailed suite of pollutants has been reported, also including organic and inorganic C, elemental composition and PAHs (Cooper, 2001, 2003; Agrawal et al., 2008; Moldanova et al., 2009; Sippula et al., 2014). However, OGVs are fueled mainly with marine or residue oil, causing about 5× greater PM emissions than diesel fueled INVs

(Trozzi and Laurentis, 2013), so significantly lower metal and PAH emissions from INVs are likely.

INVs are driven by multifuel or diesel engines (BUND e.V., 2010) with average motor age of 40 yr; the latter likely have a negative effect on the average emission from inland navigation (Landesumweltamt NRW, 2001). Additionally, although particle filters are known to reduce emissions (Matti Maricq, 2007; Liu et al., 2008; Pakbin et al., 2009; Hu et al., 2013; Zhao et al., 2014), these filters are not installed in most INVs.

Organic pollutant emissions from road traffic have been investigated regarding different fuel and motor types such as diesel and gasoline (Cadle et al., 1999; Westerholm et al., 2001) or the use of catalyst/diesel particulate filters (Kado et al., 2005; Hu et al., 2013; Zhao et al., 2014). Emission rate and composition were found to be influenced by engine load and driving cycle (e.g. cold starts; Rogge et al., 1993; Kado et al., 2005), which also holds true for INVs (Keuken et al., 2014). Assuming that inland navigation would have fewer cold starts, and higher engine volume and load than road traffic, significantly different elemental and PAH patterns would be expected.

For domestic heating, particularly wood combustion, the influence of fuel and oven type on the amount and composition of emissions has been shown (Oros and Simoneit, 2001; Schauer et al., 2001; Eriksson et al., 2014; Bruns et al., 2015). The abundance of

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individual parent and alkylated PAHs depends on wood type, be it softwood or hardwood, and on combustion conditions (Benner et al., 1995; Bari et al., 2009; Pettersson et al., 2011; Vicente et al., 2015).

The use of characteristic ratios was introduced for attributing environmental metal and PAH abundance to emission sources (Bargagli, 1998; Yunker et al., 2002, 2014, 2015). For tracing emissions from different fossil fuels (e.g. from the combustion of marine or residue oil from OGVs) via metals, the ratio of V to Ni was used (Isakson et al., 2001; Viana et al., 2009; Zhao et al., 2013). It is likely that the ratio also enables tracing of INV emissions in environmental compartments along waterways.

In environmental studies PAHs are suitable tracers for source allocation of PM (e.g. Bandowe et al., 2014; Khan et al., 2015). Wood combustion residues and motor vehicle emissions have been differentiated by way of source diagnostic ratios of PAHs like fluoranthene to pyrene (Flua/(Flua + Py); Budzinski et al., 1997; Yunker et al., 2002, 2014, 2015) and the ratio of indeno[1,2,3-*cd*]pyrene to benzo[*ghi*]perylene (IP/(IP + B[*ghi*]P); Sicre et al., 1987; Yunker et al., 2002, 2014, 2015). Additionally, Benner et al. (1995) established dimethylphenanthrene (DMP) ratios to differentiate motor vehicles (liquid fuels) from domestic heating (solid fuels, e.g. wood, lignite and black coal combustion). DMP patterns share the advantage of being suitable for comparing emissions (i) collected via different sampling designs and (ii) of gas and particle phase, due to their close physicochemical properties (Benner et al., 1995). Also, the S containing PAH, dibenzothiophene (DBT), is often used as a marker for the combustion of diesel and lignite (e.g. Lehndorff and Schwark, 2009).

In this study we aimed at a first characterization of metal and PAH emissions from INVs. We hypothesized that emissions from INVs would differ from (i) those of road traffic due to differences in motor construction and running behavior and (ii) those of domestic heating (solid fuels) due to differences in fuel type (diesel vs. biomass and coal) and combustion conditions. Overall, fingerprints of INV emissions were evaluated for their potential in environmental studies dealing with the impact of inland navigation on urban and agricultural areas.

Therefore, exhaust from INVs (freight and passenger ships), one road heavy duty diesel engine (HDDE) and domestic heating (different solid fuels and ovens) were sampled and analyzed for concentrations of major and trace metals as well as parent and alkylated and thio-PAHs. The data were supported by a literature compilation of road diesel and gasoline and domestic heating and OGV emissions (Table 1).

2. Material and methods

2.1. Sampling

Two passenger ships, one container ship, one freight ship, one HDDE, and one lignite and wood (spruce) fired domestic chimney (Küppersbusch oven) were included in the experiment. Additionally, PM_{10} (PM with diameter < 10 µm) samples from combustion of different types of wood (beech, common oak, hornbeam, lignite and black coal; Table S1) and coal burned in small-scale stoves (collected at the emission test stand of TU Vienna with commercial appliances) were used.

Exhaust from INVs, the HDDE and the Küppersbusch oven was collected using a manual pump (Sensidyne, Gilian 5000; constant 2.5 l/min; total sample volume 75 l). The particle phase was collected on quartz filters (diameter 32 mm; Sigma Aldrich). The gas phase was sampled with a subsequent polyurethane foam cartridge (PUF, Sigma Aldrich). For each emitter four repetitions were sampled, with the exception of the HDDE (n = 3). Before sampling, equipment was pre-cleaned, i.e. quartz filters were heated for 2 h at 200 °C, PUF cartridges were pre-extracted via ultrasonic extraction with *n*-hexane (15 min). Distance to the tail pipe was 1–2 m for INVs, 10 cm for HDDE; the Küppersbusch oven samples were taken from the exhaust stream (Table S1). For the wood, pellet and coal fired ovens only the particle phase was sampled: PM_{10} was collected on quartz filters (diameter 47 mm, Pall Life Sciences) after dilution of exhaust, the size separation was done via a commercial low volume sampling head (Digitel AG, Switzerland) with a one stage impactor principle (separation efficiency 50% for particles with 10 µm aerodynamic diameter; as described by Schmidl et al., 2008 and Kistler et al., 2012).

2.2. Analytical methods

2.2.1. Major and trace metals

Fe, Ni, V, Sb, Cr and Cu were determined for the particle phase of manually sampled exhausts from INVs and the Küppersbusch oven. Quartz filters were extracted via aqua regia extraction (28 ml of HCl:HNO$_3$, 3:1, v/v,) using a Kjeldaltherm block digestion unit (Gerhardt GmbH, Königswinter, Germany) with the following temperature program: 70 °C (held 45 min), 110 °C (held 30 min), 120 °C (held 180 min). Elements were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES; Jobin Yvon Ultima 2, Horiba, Frankfurt, Germany).

2.2.2. Polycyclic aromatic hydrocarbons (PAHs)

Samples were extracted using accelerated solvent extraction (Dionex, ASE 350; 120 °C, heating time, 6 min, static time, 20 min, extraction cycles: 3). Quartz filters were extracted 4× with dichloromethane (DCM). PUF cartridges were extracted 3× using *n*-hexane. After extraction, samples were spiked with [^{2}H$_{10}$]acenaphthylene, [^{2}H$_{12}$]chrysene and [^{2}H$_{12}$]perylene (recovery 75%, 102% and 80%, respectively). Each extract was purified using solid phase extraction (SPE): a glass cartridge was filled with 2 g deactivated silica gel (0.063–0.2 mm; Macherey–Nagel, Düren; Germany) and conditioned with *n*-hexane. The extract was consecutively eluted with 4.5 ml *n*-hexane and 4 ml DCM:*n*-hexane (2:1, v/v), the latter fraction yielding aromatic compounds. After reducing the aromatic fraction close to dryness it was spiked with 10 ng/µl [^{2}H$_{10}$]phenanthrene as a recovery standard for quantification.

PAHs were quantified using gas chromatography (GC; Agilent Technologies 6890N Böblingen, Germany) coupled with mass selective detection (MSD; Agilent Technologies 5973) and equipped with an Optima 5 MS column (30 m × 0.32 mm i.d., 0.25 µm film thickness; Macherey & Nagel, Düren, Germany). He was the carrier gas at a constant 1.2 ml/min, oven temperature program: 70 °C (held 2 min), to 225 °C at 10 °C/min, then to 325 C at 7 °C/min. For PAH analysis, the routine limit of quantification (RLOQ, the smallest detectable concentration of the external standard) was used, i.e. 0.01 µg/ml. Since 1,3-, 2,10-, 3,9- and 3,10-DMPs co-elute on a Optima 5 MS column (Benner et al., 1995; Huang et al., 2004) this group of DMPs is abbreviated below as x4-DMP.

All equipment (filters and PUF cartridges) was analyzed for initial metal and PAH content; no target metal or PAH was detected. Laboratory blanks were processed with each batch of samples.

2.2.3. Statistics

Statistical data comparisons included a test for data distribution (Shapiro–Wilk, for all tests α = 0.05 was selected). Significant differences between two groups were determined from the following procedures: if the data set was normally distributed and showed an equal variance, a *t*-test was applied. If the set showed a normal distribution but no equal variance, the Welch test was conducted.