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High contributions of vehicular emissions to ammonia in three European cities derived from mobile measurements

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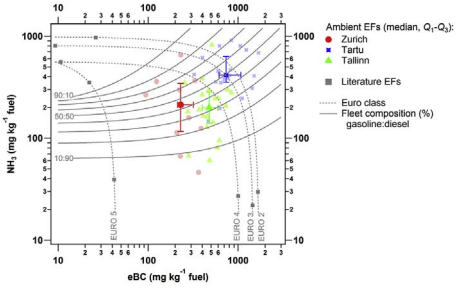
GRAPHICAL ABSTRACT



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ABSTRACT

Ambient ammonia (NH_3) measurements were performed with a mobile platform in three European cities: Zurich (Switzerland), Tartu (Estonia) and Tallinn (Estonia) deploying an NH_3 analyzer based on cavity ring-down spectroscopy. A heated inlet line along with an auxiliary flow was used to minimize NH_3 adsorption onto the inlet walls. In addition, a detailed characterization of the response and recovery times of the measurement system was used to deconvolve the true NH_3 signal from the remaining adsorption-induced hysteresis. Parallel measurements with an aerosol mass spectrometer were used to correct the observed NH_3 for the contribution of ammonium nitrate, which completely evaporated in the heated line at the chosen temperature, in contrast to ammonium sulfate. In this way a quantitative measurement of ambient gaseous NH_3 was achieved with sufficient time resolution to enable measurement of NH_3 point sources with a mobile sampling platform. The NH_3 analyzer and the aerosol mass spectrometer were complemented by an aethalometer and various gas-phase analyzers to enable a complete characterization of the sources of air pollution, including the spatial distributions and the regional background concentrations and urban increments of all measured components. Although at all three locations similar increment levels of organic aerosols were attributed to biomass burning and traffic, traffic emissions clearly dominated the city enhancements of NH_3, equivalent black carbon (eBC) and carbon dioxide (CO_2). Urban increments of 3.4, 1.8 and 3.0 ppb of NH_3 were measured in the traffic areas in Zurich, Tartu and Tallinn, respectively, representing an enhancement of 36.6, 38.3 and 93.8% over the average background

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concentrations. Measurements in areas strongly influenced by traffic emissions (including tunnel drives) were used to estimate emission factors (EF) for the traffic-related pollutants. The obtained median EFs range between 136.8-415.1 mg kg^{-1} fuel for NH_3, 157.1–734.8 mg kg^{-1} fuel for eBC and 39.9–324.3 mg kg^{-1} fuel for HOA. Significant differences were found between the EFs of certain components in the three cities, which were partially linked to an older vehicle fleet in Estonia compared to Switzerland. Using the determined EFs we show that traffic can fully explain the NH_3 enhancements in the three cities and also presents a non-negligible fraction of the background concentrations, which are mostly related to agricultural activities. Moreover, the estimated total contribution of traffic to NH_3 at all three locations is in good agreement with the available emission inventories.

1. Introduction

Ammonia (NH_3) is a major component of the total reactive nitrogen and the predominant gaseous basic compound in the atmosphere. Therefore, NH_3 has major environmental implications, including the eutrophication and acidification of natural ecosystems, which can lead to changes in the species composition (Fangmeir et al., 1994; Krupa, 2003; Bobbink et al., 2010). In the atmosphere, gaseous NH_3 will neutralize sulfuric and nitric acid leading to the formation of ammonium sulfate ($(NH_4)_2SO_4$), ammonium hydrogen sulfate (NH_4HSO_4) and ammonium nitrate (NH_4NO_3). These species are the most abundant secondary inorganic compounds in the atmospheric aerosols or $PM_{2.5}$ (particulate matter with aerodynamic diameter below 2.5 μm) and thus have significant implications for regional air quality, health effects, visibility, cloud formation and radiative balance. NH_3 can enhance particle nucleation by several orders of magnitude, which affects climate by increasing the number of potential cloud condensation nuclei (Kirkby et al., 2011). The accurate knowledge of NH_3 current atmospheric levels, emission sources and spatial distribution (compared to the pre-industrial era) is fundamental for the assessment of its influence on climate and other ecosystem aspects.

Current estimates of global NH_3 emissions vary between 35 and 65 Tg N $year^{-1}$ (Bouwman et al., 1997; Sutton et al., 2013). Combining emission inventories with global models, Sutton et al. (2013) modeled the spatial distributions of NH_3 emissions and reported the dominant sources in each region. NH_3 emissions vary strongly by region, with emission hotspots in China, India, central Africa and northern Europe. In most regions, the dominant NH_3 sources are livestock and crops, while biomass burning is the main NH_3 source across central Africa. However, in urban areas additional anthropogenic sources can be significant. These sources include road traffic, residential coal and biomass burning, industrial NH_3 and fertilizer production, waste management, and human and pets emissions (Sutton et al., 2000; Reche et al., 2012).

NH_3 emissions from gasoline vehicles equipped with a three-way catalyst (TWC) have been shown to be an important source of NH_3 in areas with heavy traffic (e.g. Perrino et al., 2002; Reche et al., 2015). In the TWC, NH_3 is generated as a side product in the NO_x reduction process (Huai et al., 2003). Remote sensing in London showed a strong increase in traffic-derived NH_3 emission factors (from 520 to 970 mg_{NH3} kg_{fuel}^{-1}) when catalyst-equipped vehicles were introduced in the UK fleet in 1992, while since the introduction of Euro 3 vehicles in the year 2000, NH_3 emissions have monotonically decreased, reaching in 2012 similar values to the pre-catalyst times (Carslaw and Rhys-Tyler, 2013). Laboratory dynamometer studies have shown large variability in the EFs of NH_3 for various types of TWC equipped-vehicles, temperatures and driving cycles (e.g. Durbin et al., 2002; Heeb et al., 2006; Huai et al., 2005; Suarez-Bertoa et al., 2014). Furthermore, the recent introduction of the selective catalytic reduction system (SCR) with its addition of urea or NH_3 in heavy-duty vehicles (HDV) and more recently in diesel light-duty vehicles (LDVs) resulted in increased NH_3 emissions from traffic (Suarez-Bertoa and Astorga, 2016), which needs further investigation.

Real-time measurements of NH_3 are hindered by the adsorption of NH_3 on the sampling lines, which severely degrades the measurement time resolution. In this work, we use specially designed inlets and correction algorithms for a quantitative characterization of NH_3 point sources with a mobile sampling platform in three European cities: Zurich (Switzerland), Tartu (Estonia) and Tallinn (Estonia). Such mobile measurements enabled the characterization of the spatial distribution of NH_3 in the three cities, the determination of NH_3 regional background concentrations and urban increments and the calculation of emission factors (EFs) from specific sources under real world conditions. Traffic EFs were estimated for NH_3, equivalent black carbon (eBC) and hydrocarbon-like (HOA) and were used to assess the contribution of traffic to the measured NH_3 levels inside the cities.

2. Methodologies

2.1. Measurement campaigns and instrumentation

Mobile measurements were performed for approximately one week in Zurich (9–19 October 2013), Tartu (10–17 March 2014) and Tallinn (25 March to 1 April 2014). The mobile measurements were mostly performed during daytime, while stationary measurements were additionally performed overnight in Tartu and Tallinn. Driving routes were designed to include different areas of the cities and were covered repeatedly during the measurement campaign (20–30 times) in order to obtain statistically significant spatial distributions of the measured compounds. Meteorological parameters recorded at the NABEL station (Swiss National Air Pollution Monitoring Network) Zurich-Kaserne are reported in Fig. S1.

All details about the mobile laboratory set-up have been reported by Elser et al. (2016) and only a brief description follows. The Paul Scherrer Institute mobile platform (IVECO Turbo Daily Transporter, detailed description in Bukowiecki et al. (2002)) was used as rolling platform for the on-road measurements. An NH_3-Picarro analyzer (G1103-t) was used to measure real-time NH_3 concentrations. Additionally, the concentrations of CO_2, CO and CH_4 were measured with a Licor-7000 CO_2/H_2O monitor and a Picarro-G2401 $CO/CO_2/CH_4/H_2O$ analyzer (available only in Tartu and Tallinn). Regarding the PM measurements, a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc.) was deployed to investigate the size resolved chemical composition of the non-refractory (NR)-$PM_{2.5}$ aerosol (including nitrate (NO_3), sulfate (SO_4), ammonium (NH_4), chloride (Cl), and organic aerosols (OA)). In addition, a seven-wavelength Aethalometer (Magee Scientific, model AE33) was used to measure the light absorption from carbonaceous aerosols and determine the concentrations of equivalent black carbon (eBC) (Drinovec et al., 2015).

The measurement principle of the NH_3-Picarro analyzer is based on cavity ring-down spectroscopy (CRDS), i.e. the measurement of the absorption of a pulse of light of a specific wavelength trapped in an optical cavity is used to determine the concentration of the absorbing substance in the gas mixture in the cavity. Possible interferences from other gases in the NH_3 quantification are minimized by measuring at reduced pressure, so that absorption line widths are small, and selecting several spectral lines on the basis of its strength and absence of interference from other molecular species (Martin et al., 2016). When interferences are unavoidable, the interfering peaks can be measured and their contributions to the measurement of interest deconvolved and