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Emission factors of inorganic ions from road traffic: A case study from the city of Naples (Italy)

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ABSTRACT

PM_{10} samples were collected in the urban tunnel of Naples (southern Italy) during a monitoring campaign on March 2015. Two sets of samples were collected at both sides of the tunnel, each set representing the daily cycle at a 1 h time resolution. Distance-based – mass per kilometer – emission factors (EFs) were calculated using mass concentrations, traffic flow rates and wind speed as a function of fleet composition. Samples were analysed for mass and water-soluble inorganic ions (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^- and SO_4^{2-}) with the aim of investigating the influence of road traffic on the contribution of these species to PM levels.

Road traffic directly emits inorganic ions, both from the exhaust and non-exhaust components. Analysis of ionic composition highlighted the increase in calcium concentration, which may derive from non-exhaust sources (road dust, wear of brake pads, clutches, tires) and calcium sulfonates, phenates or salicylates, often added to motor oils. Sulphate, added to lubricant oils, is also directly emitted at a rate higher than the gaseous sulphur dioxide emission.

According to our analysis, nearly 10% of PM mass is composed by water-soluble inorganic ions, most of which directly emitted by automobiles. This suggests that an important contribution to PM emissions may derive from the inorganic component and more efforts should be devoted to constrain these emissions if PM concentration had to effectively comply with air quality standards.

1. Introduction

The effects of particulate matter (PM) on the atmosphere, climate and health are among the central topics in current environmental research (Pöschl, 2005; Lohmann and Feichter, 2005). Road traffic is one of the major contributors to atmospheric pollution in urban areas (Negral et al., 2008; Pey et al., 2009; Lonati et al., 2011; Riccio et al., 2016). Automobiles both directly emit particles (primary PM) and gaseous precursors, e.g. SO_2, NO_x, organic compounds and NH_3, leading to the formation of secondary particles. Direct emissions account for approximately 40–50% of the observed PM mass and gas to particle transformation processes account for the remaining 50–60% (Seinfeld and Pandis, 2006). Despite the constant developments on environmentally friendlier fuels and the reduction of pollutant emissions, 30–40% of the European urban

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population was exposed at concentrations above allowable EU air quality standards for PM from 2000 to 2012 (Guerreiro et al., 2014).

To understand the health effects and formation/emission of PM, it is essential to unravel its chemical characteristics and mechanisms of formation. PM characterization from road traffic is often based on the content of heavy metals and carcinogenic components (Adachi and Tainosho, 2004; Amato et al., 2011; Deng et al., 2006; Hjortenkrans et al., 2007; Huang et al., 2012; Johansson et al., 2009; Riccio et al., 2016), but less attention has been devoted to inorganic reactions. Most of the inorganic reactions are complex and competing with each other: ammonia plays a primary role in neutralising atmospheric acids, such as nitric, sulphuric and hydrochloric acid to form ammonium sulphate $(NH_4)_2SO_4$, ammonium bisulphate (NH_4HSO_4), ammonium nitrate (NH_4NO_3), and ammonium chloride (NH_4Cl) aerosols (Seinfeld and Pandis, 2006). These reactions depend on ambient air temperature, relative humidity, solar radiation and concentration of the precursor gases to a large extent; moreover, the long-range transport of these salts, joined to the reversible equilibrium with their gaseous precursors, facilitates the transport and release of inorganic salts to areas far from the emission sources.

Automobiles greatly influence inorganic chemistry, emitting NO_x, NH_3 and SO_2. Nowadays, the introduction of the Euro V fuel standard (<20 ppmS) drastically reduced SO_2 emissions in many European countries, although sulphates are added to lubricant oils, so that road vehicles must be considered as primary emitters for sulphate, too (Stepina and Vesely, 1992). Ammonia is mainly emitted from agriculture practices, which contributes for more than 90% to the total European emission (http://www.eea.europa.eu/data-and-maps/indicators/eea-32-ammonia-nh3-emissions-1/assessment-4), but road traffic is the most important non-agricultural source (Sutton et al., 2000; Sapek, 2013). Specifically, the introduction of catalysts has much increased ammonia emissions. For example, it is estimated that gasoline passenger cars may emit up to 40 mg km^{-1} vec^{-1} in Italy (http://www.sinanet.isprambiente.it/it/sia-ispra/fetransp/fattori-emissione-trasporto-stradale/view). Therefore, road traffic is now recognised as an important source of ammonia in the urban environment, and as a result, the production of ammonium salts from this source may have an important role in the build up of particles. Recently, highway tunnel (Emmenegger et al., 2004; Cui et al., 2016; Kean et al., 2009) and chassis dynamometer studies (Durbin et al., 2002; Huai et al., 2003) indicate that ammonia emissions from vehicles may be larger than previously estimated. Livingston et al. (2009) estimated that mobile sources might be responsible for as much as 18% of total NH_3 emissions in the South Coast Air Basin of California. US EPA concluded that mobile sources contributed 3% of NH_3 emissions nationwide in 2014 (EPA, 2015).

Road tunnels are excellent locations to measure vehicle emissions as the influence of meteorological conditions is minimised and the emissions undergo 'real world' dilution effects with minimal interference from other sources, enabling the vehicle emission factors to be determined. More importantly, road tunnel studies provide emissions from a large number of vehicles under 'real world conditions', that is, vehicles operating at stable conditions when going through a road tunnel. Tunnel measurements have been frequently used in the past to validate model EFs. Weingartner et al. (1997), Abu-Allaban et al. (2002) and Gertler and Pierson (1996) describe the methodology for calculation of emission factors using tunnel measurements. Pant and Harrison (2013) reviewed all these methods and their applications.

Unfortunately, the emission of inorganic ions in particles and their precursor gases from vehicle exhaust are rarely measured and estimated. To better characterise the inorganic ion content from automobiles and their emission factors, a sampling campaign was performed in an urban tunnel in the city of Naples, with particulate matter samplers, meteorological instrumentation and traffic counters. This paper presents data on the inorganic content of atmospheric aerosols sampled at the two sides of an urban tunnel in Naples (South Italy) and the corresponding emission factors (EFs).

2. Experimentals

2.1. Sampling

The '4 giornate' tunnel is a main thoroughfare connecting two densely populated districts in the urban area of Naples and has a length of about 800 m. The number of vehicles passing through the tunnel is relatively high, with more than 25,000 vehicles crossing the tunnel per day. The speed limit is 50 km/h with a traffic light at the beginning of the tunnel. During the time in which measurements have taken place, the traffic in the tunnel was unidirectional with two lanes in a single hole (a second separate hole operates in the opposite direction). The lane roadway shows different gradients, a rise of 2.6% in the first 400 m after the entrance, then a section with almost flat conditions up to the exit. The ventilation system was not active during the measuring campaign, so that the fresh air was mainly influenced by the 'piston effect' along the driving direction.

PM_{10} (particulate matter with an aerodynamic diameter less than 10 μm) samples were collected at both sides of the tunnel using two inter-calibrated low-volume gravimetric samplers (Tecora Bravo-H and Tecora Echo models) equipped with PM_{10} inlets. Filters (47 mm borosilicate glass Emfab filters TX40HI20 by PALL Life Sciences) were collected during a two days campaign on 25–26 March, 2015, at a 1 h time resolution, as already described in Riccio et al. (2016). The first day was devoted to instrument inter-calibration and the second day to the actual collection of samples. Before and after sampling, filters were pre-conditioned in a box with constant humidity (50%) and temperature (20 °C) for 24 h, electrostatically neutralised and weighted with a micro balance to determine the deposited aerosol mass, according to the EN 12341:2014 standard (CEN/TC 264).