## Aged ship emissions before and after the decrease of the sulphur fuel content

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Gaseous and particulate emissions from the marine transport sector contribute significantly to air pollution, climate and human health (Corbett et al., 2007). It has been estimated that for the year 2000, in the seas surrounding Europe,  $SO_2$  and  $NO_x$  emissions reached 2.3 and 3.3 million tonnes per year respectively, while particulate matter emitted reached 250,000 tonnes. Previous studies have shown that ship exhaust particles are dominated by organic species, sulphates and black carbon, while the organic to sulphate ratio is increasing the last years (Psichoudaki et al., 2015).

The International Maritime Organization has released a new legislation, applying from 1/1/2015 regarding the sulphur fuel content (SFC) of the ships fuel. According to that, sulphur content must be less than 0.1% in the fuel, while the previous limit was at 1%. In order to assess the impact of this change on the ship emissions, two intensive campaigns were conducted. One from 24 October to 12 November 2014, before the change of the legislation, and a second one after the new legislation applied, from 23 of September to 12 of November, 2015. The measurements were conducted at a sampling site located on a small peninsula at the entrance of the port of Gothenburg, Sweden.

While fresh ship emissions affect mostly coastal areas close to big ports, these emissions can also affect larger areas when they remain in the atmosphere and undergo photochemical aging, producing secondary aerosols and gases. Thus, the goal of this work was to simulate this photochemical aging and measure the long term products of the ship emissions. A Potential Aerosol Mass (PAM) flow reactor was employed in order to achieve the oxidation of the fresh ship emissions during the first campaign. In the second campaign, a modified PAM chamber was employed: This reactor operates in a laminar flow and the oxidation achieved in both of them is equivalent to a few days of atmospheric photochemical aging. Similar oxidation conditions were achieved in both flow reactors. A constant concentration of 500 ppb of ozone was present in the reactor, while the addition of water vapor assisted in the formation of OH under UV light, inside the reactor.

In order to monitor the concentration of the gaseous species produced from the oxidation of fresh ship plumes, an Aerodyne High Resolution Time-of-Flight Chemical Ionization Mass Spectrometer (HR-ToF-CIMS) was used. The concentrations of various organic and inorganic species present in the aged gas plumes were measured using negative (iodide and

acetate) ionization mode. Acids, alcohols, diols, oxygenated organics, nitrogen, sulphur and halogen containing species were identified using the above reagents in different time periods in both campaigns. During 2015 campaign, CIMS was employed with a particle inlet filter (FIGAERO), allowing for the semicontinuous measurement of the condensed phase. Particle emissions from multiple ships were collected on a filter, with a solenoid valve opening only when a sharp increase of the particle number was detected by a Condensation Particle Counter (CPC). Individual ship plumes were detected and identified by sharp increases in the particle number and  $CO_2$  levels measured by a CPC and a  $CO_2$  monitor respectively (Figure 1).



Figure 1. Increase of particle number (left) and CO<sub>2</sub> concentration (right) during a ship plume.

Each of these peaks was afterwards directly related to an individual ship so a classification of the ships and their emissions according to their type was achieved.

Based on the above, a comparison of the average gaseous chemical composition of different types of ships before and after the change of the SFC legislation was achieved. Additionally, ship emitted aerosol species were identified from 2015 campaign. Simultaneous  $CO_2$  measurements and calibrations for individual species allowed the calculation of emission factors that are also presented here.

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