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Characterisation of single particles from in-port ship emissions

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ABSTRACT

Emissions from shipping traffic may impact severely upon air quality in port cities. In this study, the size and composition of freshly emitted individual ship exhaust particles has been investigated using an aerosol time-of-flight mass spectrometer (ATOFMS) co-located with a suite of real-time instrumentation at a site in the Port of Cork, Ireland. The collected spectra were clustered using the *K*-means algorithm and a unique ship exhaust class containing internally mixed elemental and organic carbon, sodium, calcium, iron, vanadium, nickel and sulfate was identified. Over twenty sharp emission events were observed for this particle type during the three week measurement period in August 2008. Coincident increases in mass concentrations of sulfate, elemental carbon and particles below 2.5 μm in diameter ($PM_{2.5}$) were also observed during these events. Simultaneous scanning mobility particle sizer (SMPS) measurements indicate that the vast majority of freshly emitted ship exhaust particles lie in the ultrafine mode (<100 nm diameter). A second particle class consisted of internally mixed organic carbon, elemental carbon, ammonium and sulfate, and is tentatively attributed to aged or regionally transported ship exhaust. The results suggest that ATOFMS single particle mass spectra, when used in conjunction with other air quality monitoring instrumentation, may be useful in determining the contribution of local shipping traffic to air quality in port cities.

1. Introduction

Globally, ship exhaust is estimated to contribute 1.2–1.6 Tg particulate matter with aerodynamic diameter less than 10 μm (PM_{10}), 4.7–6.5 Tg sulfur oxides (SO_x as S) and 5.0–6.9 Tg nitrogen oxides (NO_x as N) annually (Corbett and Koehler, 2003; Corbett et al., 2007; Eyring et al., 2005). International shipping has been linked with increased mortality in coastal regions, with an estimated 60 000 deaths from cardiopulmonary and lung cancer per annum attributed to emissions from ship exhaust (Corbett et al., 2007; Lubick, 2007). Ships typically burn residual fuel oil with high sulfur content (up to 4.5% m/m) containing polycyclic aromatic hydrocarbons and transition metal impurities (Fridell et al., 2008; Murphy et al., 2009). Emissions of particulate matter (PM) are of particular concern, and it is estimated that premature mortalities arising from exposure to PM from ship exhaust could increase by 40% by 2012 if emissions are not controlled (Corbett et al., 2007). Particles emitted from ship exhaust have also been shown to contribute significantly to marine cloud formation, both directly (Hobbs et al., 2000), and indirectly by acting as condensation sites for biogenic and anthropogenic sulfur-containing species (Phinney et al., 2009).

Airborne measurements have been used to calculate emission factors of 15–89 and 2–25 g kg^{-1} for SO_2 and NO respectively and particle fluxes of 4×10^{15}–1.5×10^{16} particles s^{-1} for diesel powered ships burning residual fuel oil (Hobbs et al., 2000). The emitted particles exhibited a nucleation mode (0.01–0.1 μm radius) with relatively few particles larger than 0.1 μm in radius. Off-line analysis by ion chromatography revealed a composition of organic carbon and sulfuric acid formed from gas-particle conversion of SO_2 (Hobbs et al., 2000). More recently, a series of ship plumes were detected in Vancouver with a range of real-time instruments (Lu et al., 2006). Plumes were characterised by an increase in levels of SO_2, NO_x, NO, CO, VOCs, black carbon, particle counts (5–200 nm diameter) and $PM_{2.5}$ and were attributed to shipping traffic approximately 5 km from the sampling site. The composition of particles from one ship plume was investigated in detail using an aerosol mass spectrometer (AMS) (Lu et al., 2006). During that event, a quantitative increase in ultrafine (<100 nm) particle phase organic carbon and sulfate was observed. However, the AMS is not capable of measuring refractory material such as black carbon or metals that may be present in ship exhaust particles. A very recent comprehensive joint shipborne and airborne study focused on the chemical composition and hygroscopicity of freshly emitted ship exhaust particles (Murphy et al., 2009). In-stack ship-based particle

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measurements were performed using micro-orifice uniform deposit impactors (MOUDI) with off-line analysis. Freshly emitted ship exhaust particles were found to be comprised of approximately 30% organic carbon and 70% sulfuric acid by mass (Murphy et al., 2009). A recent off-line study of PM emitted from the main engine of an ocean going container vessel involving X-ray fluorescence, ion chromatography and thermal-optical carbon aerosol analysis estimated the mass composition to be approximately 80% sulfate and 15% organic carbon (Agrawal et al., 2008). Vanadium, nickel, calcium and iron were also observed in that case. The internal mixing of sulfuric acid and transition metals in ship exhaust particles raises additional concerns for human health as increased particle acidity may enhance the bioavailability of surface-bound metals (Sodeau et al., 2009). Although the main engine of a ship produces the highest emissions, these are typically used at sea. When approaching ports ships generally switch to auxiliary engines for power generation and manoeuvring. A short term maximum in auxiliary engine emissions is observed when bow and stern thrusters are operating when approaching or departing from berths (Cooper, 2003), and these are the most likely events to be observed at an in-port sampling site.

Single particle mass spectrometry is a useful tool for determining the internal mixing state of ambient particles, allowing simultaneous detection of organic carbon, ionic species and refractory material (Sullivan and Prather, 2005). Previous aerosol time-of-flight mass spectrometry (ATOFMS) studies have successfully obtained "signature" single particle mass spectra taken directly from diesel exhaust and industrial stacks to identify these sources in ambient datasets (Reinard et al., 2007; Shields et al., 2007). A recent ATOFMS study involved the identification of regionally transported single particles arriving at San Diego (Ault et al., 2009). Two different particle types were attributed to aged ship exhaust (or possibly oil refining); internally mixed elemental and organic carbon particles and internally mixed vanadium, nickel and iron particles. Both types were also internally mixed with nitrate and sulfate. The aim of this study was to identify a unique ATOFMS mass spectral signature for local freshly emitted ship exhaust particles and to investigate the applicability of these spectra as a possible marker for calculating the impact of in-port shipping emissions on local air quality.

2. Experimental

2.1. Sampling site

The sampling site was located at Tivoli Docks in the Port of Cork (51°54′5 N, 8°24′38 W), approximately 3 km east of Cork city centre and adjacent to a container terminal, liquid bulk storage facility and gas jetty. A berth for liquid bulk ships is located approximately 150 m to the southwest and berths for container ships are located 400–600 m to the west-southwest (Fig. 1). The prevailing winds are south-westerly.

2.2. Equipment and data analysis

A suite of real-time instrumentation was located at the site for the duration of the campaign; SO_2, SO_4^{2-}, NO/NO_x and O_3 were monitored using Thermo Electron models 43i, 5020 SPA, 42i and 49i respectively. Elemental carbon and organic carbon (EC/OC) mass concentrations were measured using a thermal-optical carbon aerosol analysis instrument (Sunset Laboratory Inc., field model 3rd generation) fitted with a cyclone to remove particles larger than 2.5 μm in diameter. The ATOFMS (TSI model 3800) was fitted with an aerodynamic lens (TSI model AFL100) for the measurement of particles in the size range 100–3000 nm in real time. The instrument is described in detail elsewhere (Dall'Osto et al., 2004). Briefly, particles are sampled through an orifice and accelerated through the aerodynamic lens to the sizing region of the instrument. Here, the aerodynamic diameter of particles is calculated based on their time-of-flight between two orthogonally positioned continuous wave lasers (Nd:YAG, 532 nm). Particles are then transmitted to the mass spectrometry region of the instrument and ionised using a Nd:YAG laser (266 nm). The resulting positive and negative ions are finally analysed using two collinear time-of-flight mass spectrometers. The scanning mobility particle sizer (SMPS, TSI model 3081) collected particle number concentrations in the size range 20–600 nm (mobility diameter) every 3 min. A TEOM (tapered element oscillating microbalance, Thermo Electron model 1400a) was also located on-site for the measurement of $PM_{2.5}$ mass concentrations (averaged every 30 min). Wind speed, wind direction, temperature, humidity and rainfall were

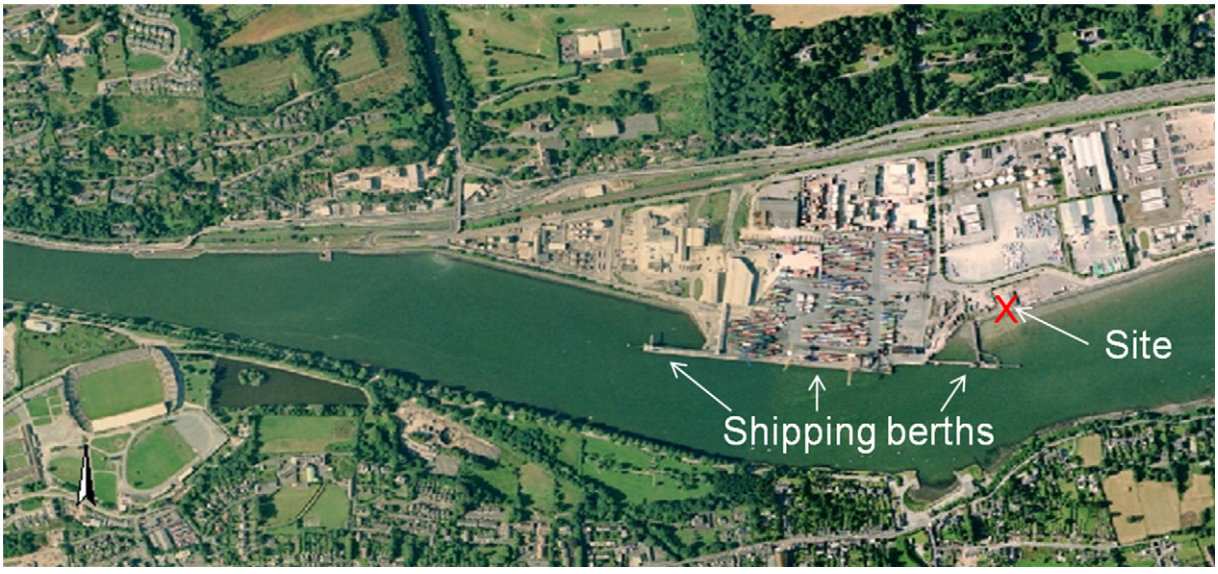

Fig. 1. Location of sampling site and shipping berths at Tivoli Docks, Port of Cork.