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REVIEW ARTICLE

Airborne emissions in the harbour and port of Cork

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Abstract
It is now accepted that the transport sector is responsible for a large and growing share of global emissions affecting both health and climate. The quantification of these effects requires, as an essential first step, a comprehensive analysis and characterization of the contributing subsectors, i.e. road transport, shipping, aviation and rail. The shipping contribution in dock/harbour areas is of particular interest because many vessels use old engines powered with old technology giving rise to high levels of particulate emissions mainly because the fuel employed contains high levels of sulphur, up to 4.5%. Large amounts of polyaromatic hydrocarbons and varying contents of transition metals are also detected. Few studies on the physicochemical composition of direct emissions from ship fuels have been performed; none have been compared to actual contents in local harbour or port atmospheres. The transformation of these ship-related materials to toxicologically active species may be much more efficient than corresponding road emission or domestic sources because of the expected highly acidic nature of the particulates. Surface, toxic material may therefore become readily bioavailable under such conditions but such studies have not been performed hitherto. This mini-review outlines in detail the issues raised above in the context of measurements made in Cork, Ireland.

Keywords: *Air quality monitoring; shipping emissions; V/Ni ratios; aerosols*

Introduction

A recent publication indicates that shipping-related emissions are responsible annually for ca. 60 000 cardiopulmonary and lung cancer deaths. Most of the deaths were reported to occur near coastlines in Europe, East Asia and South Asia. However it should also be remembered that many of the deaths, attributable to ship-related $PM_{2.5}$ within mainland Europe, were associated with inland-waterway regions. The study is important because maritime transport plays an indispensable role in sustaining the world's economy. In fact shipping accounts for some 90% of all goods carried worldwide, comprising some 30 000 billion tonnes-miles per year (Corbett et al. 2007).

Annually, ocean-going ships have been estimated to emit 1.2–1.6 million metric tons (Tg) of PM with aerodynamic diameters of 10 μm or less along with 4.7–6.5 Tg of sulphur oxides. Seventy per cent of these emissions occur within 400 km of land (Corbett et al. 1999). Indeed in a port such as Göteborg some 40% of PM emissions are ascribed to shipping sources whereas only some 20% takes a road-traffic origin (Fridell et al. 2008). The relationship between particulate formation and sulphur content is linear and so the recent amendment to the MARPOL agreement (Annex VI) makes a serious attempt to reduce S emissions from ships (although it pays little attention to PM itself). Hence it is expected that the current 26 000 ppm average sulphur content of shipping fuel will be capped globally to 5000 ppm by 2020 and that in so-called SECA (sulfur emission control areas) the cap will be 1000 ppm by 2015 (IMO MEPC57 2007).

Although Ireland might be considered a relatively pollution-free country it is predicted that the percentage contribution of shipping to sulphur emissions in Cork (South West) region will be some 40–50% of the total loading by 2020 (Cofala 2007). Therefore given the connection between sulphur and particulates and the fact that scientists have not been able to identify a threshold

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below which health effects do not occur for PM, then airborne emissions in the harbour and port of Cork are of considerable current concern to the Irish EPA.

Methodology

Several monitoring sites were used in the studies described here; they were chosen as good representatives of: a fully pristine environment (Mace Head Co. Galway); clean-marine (Roche's Point, Co. Cork); mid-harbour (Haulbowline Island, Co Cork); Tivoli Docks (Port of Cork); roadside (Old Station Road, Cork City); urban backgrounds (Heatherton Park Estate and University College Cork, UCC).

Three-day and 24-h collections of particulate matter were made (both $PM_{10-2.5}$ and $PM_{2.5-0.1}$). The collections (made with a high volume cascade impactor (Hi-Vol) on PUF filters) were subsequently taken back to the laboratory and analysed for mass, metals (ICP-AES Perkin-Elmer Optima 2000DV), anions/cations (ion chromatography Dionex IC-2000). Organic compounds were also measured using GC-MS-TPD but are not reported in this mini-review.

Real-time measurements of SO_2 (Thermo Electron Model 43i), SO_4^{2-} (Thermo Electron Model 5020 SPA), O_3 (Thermo Electron Model 49i), NO_x (Thermo Electron Model 42i) and EC/OC splits (Sunset carbon analyser field model) were also made along with TEOM mass measurements (Thermo Electron Model 1400a). Meteorological measurements were made using a Casella Nomad Weather Station. Finally, a second generation aerosol time of flight mass spectrometer (ATOFMS, TSI 3800-100) was used as a mobile single particle monitor for individual site comparison purposes.

Results and discussion

Comparisons between ship emission outputs and $PM_{2.5-0.1}$ collections made in Cork

Two main types of fuel are used in the shipping industry: (1) marine residual fuel oil (resid.), which contains large quantities of sulphur and water along with many pollutants including PAHs and the important metal 'markers', vanadium and nickel; on combustion it produces soot, char and ash with distinguishable morphology; and (2) diesel/distillate. This is a much cleaner fuel in terms of sulphur content than resid. but is more expensive and used less. Combusted diesel particles consist of an agglomerated carbonaceous core with an active surface consisting of SO_x/water, surface soluble organics and some metals (such as iron).

Recent studies of the size of primary emitted particles from ships along with XRF measurements of the bulk composition of ship fuel have been made and indicate that for resid., the following metals are found in the wt% order: Ca > V > Fe > Ni > S > Cr > Mn > Zn. By comparison, all the metals (other than Fe) were found in very small (or non-detectable) quantities with diesel/distillate (Popovicheva 2008, Fridell et al. 2008). This finding would have important consequences if translated to actual field measurements because transition metals have been shown to be good promoters of ROS (reactive oxygen species) generation in biological systems. Hence they are themselves good indicators of toxicological oxidative stress (Kelly 2003, Borm et al. 2007, Ayres et al. 2008).

In related ion chromatography experiments on the same fuels it was found that some 45% of the resid. water soluble fraction consisted of sulphate ions and 15% calcium ions. (These figures are equivalent to 20% of the *total* for sulphate and 6% for calcium ions because the 'water soluble fraction' (WSF) comprised some 44% of the total mass.) By comparison, the fractions of the total for diesel/distillate were 1% sulphate and 0.3% calcium ions with up to 20% as WSF. In both oil samples, magnesium ions are found at a level of about 0.04% of the total (Popovicheva 2008). For comparison, sea water contains about 8% of sulphate ions, 1% calcium ions and 4% magnesium ions; such figures allow the measurements of these materials made in airborne samples collected in Cork Harbour to be put into full context as will be described below.

Using $PM_{2.5-0.1}$ samples collected with the Hi-Vol at the Tivoli Docks, the mid-harbour and the city centre roadside sites along with ion chromatography for anion/cation analysis, it was observed that the dock sample comprised up to 16% sulphate (of the total), whereas the mid-harbour and roadside samples contained some 14–19% and 8.5–10%, respectively. The dock composition is clearly consistent with the ship resid. measurements described above. The calcium ion content was found to be 3.3% of the total at the docks and much lower at the other two sites (up to 1%). Several other metals and ions were analysed in the study but are not reported here (e.g. nitrate, chloride, ammonium, potassium, sodium, copper, zinc).

Metal analysis of the V/Ni content of the airborne samples was also undertaken using ICP-AES. At the dock and mid-harbour sites the ratio was found to be 2.3–2.7 and 1.5–2.1, respectively, which compares well with the figure found for ship resid., 2.3. In contrast the V/Ni ratio measured at the roadside site took values up to 3.1, measurements which can be rationalized by considering that vehicular traffic sources exhibit intrinsically higher V/Ni ratios (Espinosa et al. 2002).

Many chemical issues need to be clarified in dock/harbour areas regarding airborne pollutants. First and foremost they represent sites which are complex to source apportion because of the co-location of a variety of contributing emitters. Hence busy harbours often combine the presence of densely populated urban areas with energy-intensive industries, power plants alongside chemical and petrochemical companies. Furthermore ports also act as important, busy transport hubs linking road, rail and sea traffic. Hence only four, relatively simple, questions/issues will be outlined here from the perspective of the above results:

1. Why were high calcium ion levels observed in the docks and for the marine oil emissions? (The field measured levels are much higher than can be explained by resuspended crustal material or sea-water origins.) Of course, resid. fuel is both viscous and wet and therefore the use of lubricants (containing calcium-based detergents) is possible on ships. Could such fuel conditioner additives be responsible?
2. The sulphate levels found in the dock PM were higher than those found in the mid-harbour and roadside sites. Although sulphate ions may exert little direct toxicological damage (Reiss et al. 2007), increased sample acidity may lead to greater solubilization of important surface-located transition metals (such as copper, zinc, nickel) making them more bioavailable. Would ROS be generated by respiratory-based cells after exposure to PM more efficiently (and more damagingly) under such circumstances?
3. The sulphate levels found in the mid-harbour site were, on average, much lower than those found in the docks. However dispersion is very important in such an area with the prevailing south-westerly winds taking increasing importance. In fact a detailed analysis of the results shows that some very high levels and very low levels of sulphate ions were measured at this site.
4. Measurements of the V/Ni ratio do appear to be a good indicator of marine oil/shipping emissions in a harbour area as previously discussed (Ariola et al. 2006).

Although useful for source apportionment studies using PCA and PMF (especially when many species are measured over relatively short 12 h time spans), PM site collection does only provide ‘past-time’ average values of mass and composition. The question remains: is this information sufficient to really understand the complexity of a multi-emitter pollutant area such as a port? If not, what other complementary approaches can/should be undertaken?

Real-time measurements of airborne pollutants in Cork Harbour

One of the most modern and effective techniques for determining the nature of aerosols in the atmosphere is by use of ATOFMS. Such an instrument is mobile but generates positive and negative mass spectra from individual particles that are captured. Using such an approach generates an enormous amount of data, which can be statistically analysed to provide information on a variety of key airborne pollutant metrics. These include chemically-specific size distributions and the internal and external mixing state of the particles. An outline of the power of the method to provide contrasts between differing sites, which are not observable by ‘past-time’ techniques, is given below.

In our measurements obtained at Cork Harbour, Mace Head and UCC sites, it was clear the TSI Model 3800-100 ATOFMS could generate interpretable data that were complementary to our ‘past-time’ measurements. Hence at the docks the real-time aerosol measurements indicated that about 60% of the particles sampled by ATOFMS contained sulphate ions and 50% contained nitrate ions. (By comparison the ion chromatography results for PM indicated about 15/16%, by mass, sulphate content and about 13% nitrate ion content.) Furthermore the sulphate signal clearly correlated with the carbon signal as would be expected for particles with a ship combustion origin. Interestingly at the Tivoli Docks site, the ammonium ions were found to be present, almost entirely, in particles also containing sulphate, but not nitrate, ions. In contrast, the UCC site aerosols showed that the ammonium ions were about equally correlated with both the sulphate and nitrate ions. The observations indicate clear differences for the origins of the sulphate materials in the contrasting sites.

Finally, a comparison between the size distributions for aerosols containing chloride ions with pristine (Macehead) vs marine polluted (Tivoli) vs other polluted Cork sites was made. The second generation TSI 3800-100 instrument employed can, in principle, monitor particles in the 100–3000 nm range and with a suitable aerodynamic focusing lens extend to the 20–300 nm range. It was found that Macehead samples (obtained under westerly-wind conditions) gave exclusive monomodal, sea-salt, distributions centring on a 1.5 μm diameter. The Tivoli Dock material was dominated by sea salt with some evidence for chloride-containing material of smaller diameter. The urban site was clearly bi-modal with some sea-salt contribution but with a main component, 550 nm in diameter, presumably with pollutant, perhaps fly-ash, origin.

The concentration ratio of SO_2 to CO_2 measured from ship stacks is directly proportional to the sulphur content of the fuel. Remote measurements of these levels are being used increasingly to check whether vessels are compliant with SECA legislation. Hence at the Tivoli site we are carrying out a programme of real-time measurements of sulphur (as sulphur dioxide and sulphate particles) and carbon (as elemental carbon/organic carbon) to assess their relationship in a dock area.

A highly regular variation of EC/OC monitored on a semicontinuous basis, was observable in Tivoli between the months of December 2007 and April 2008; they peaked between 18:00 and 20:00, almost without exception. This variation was observed to be entirely decoupled from the day-of-week, wind direction, temperature, etc., but it did show high correlation with three other parameters: sulphur dioxide, sulphate particulate matter and the onset of darkness. The most likely source of this observed evening peak in ambient levels of EC/OC, SO_2 and sulphate particulate matter is electricity generation at the ESB Marina power station (south-west to the receptor site) or at the Aghada facility (east) further out in the harbour. Peak electricity consumption during the same period (December–April) occurs at 18:00 due to households requiring electricity for lights, heating, cooking, etc. at the end of the day and the end of daylight. This fact is true not just during the working week but also at weekends. Such a finding had not been apparent before and the issue is now being looked at by local authorities.

Figure 1 shows an example of a suite of real-time measurements obtained during a 24 h period at Tivoli Docks, on 25 February 2008. On this day the wind direction was such that the air parcels sampled would have passed directly over the main berths at Tivoli Docks only minutes, or seconds, before the measurements were taken, at the receptor site. The figure shows a series of brief, but clear, peaks in the levels of sulphur dioxide (SO_2), nitrogen oxides (NO_x) and elemental carbon, or soot (EC). These are all very strong markers for high temperature combustion processes, involving high sulphur-content fuel. These events are therefore likely to be associated with fresh ship plumes, detected before significant oxidation and dispersal of the primary emissions has occurred. The times of day at which they occur (e.g. early morning/late night) and the direction of the wind excludes the possibility of them being attributable to a road traffic-related source. There is the possibility that the air parcels picked up the pollutants before passing over the shipping channel. However, the short duration of the events and the high concentrations measured strongly suggest a source near to the receptor site. Furthermore the log for ship arrivals and departures obtained from the port of Cork show good matching between vessel activity and the chemical measurements (allowing for travel time between berths and monitoring station).

The real-time values of PM_{10} from a TEOM instrument on the same day showed two maxima, at 09:00

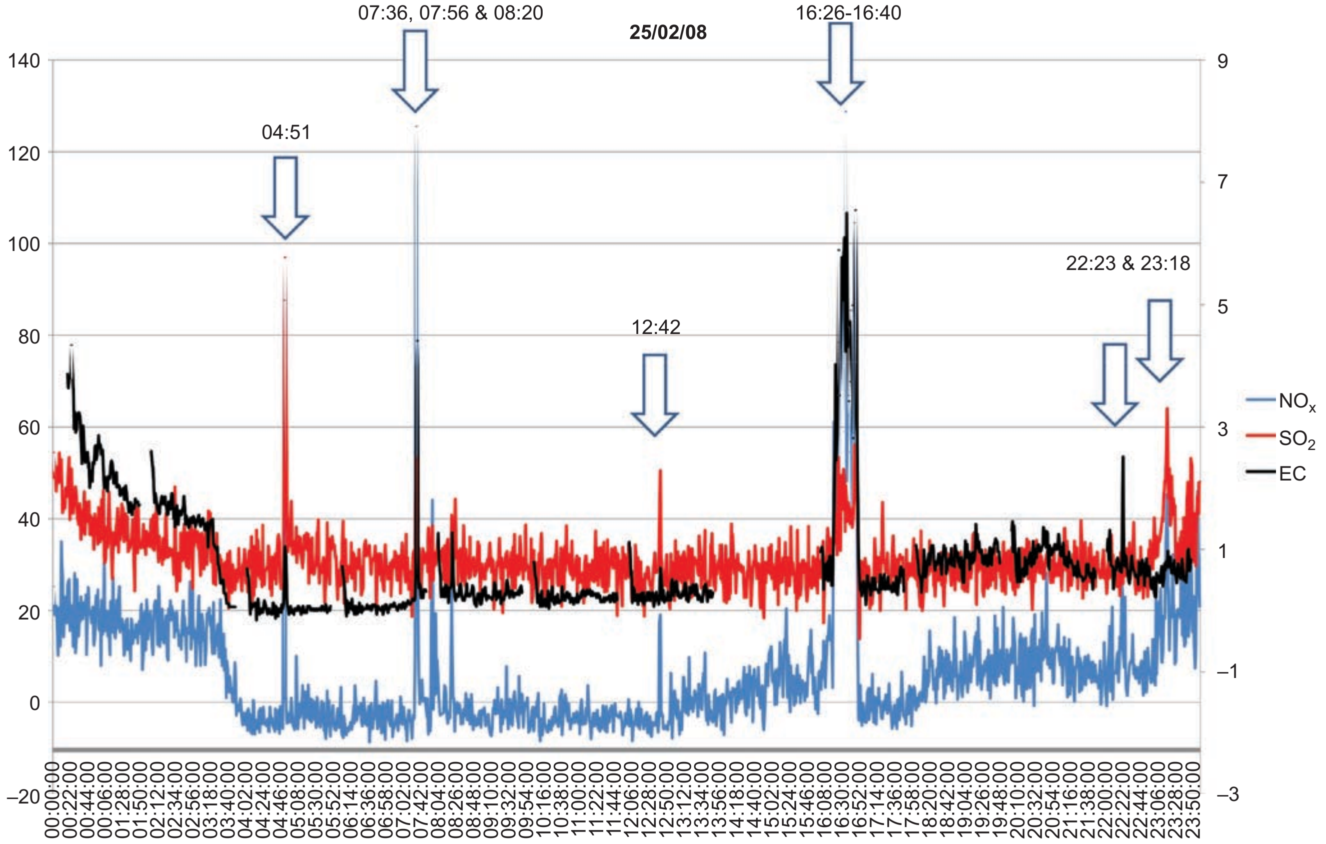

Figure 1. Real-time concentration values for NO_x, SO_2 and EC measured at Tivoli Docks, Cork on 25 February 2008, at a temporal resolution of 1 min. The baseline drop corresponds to a change in wind direction from easterly to southwesterly.

and 20:30, with each event lasting 1–2 h. Transient maxima (as shown in Figure 1) were not observed for PM_{10} measurements but primary ship particulates are emitted in the fine and ultrafine fractions. As such they consequently make little contribution to the total mass of the PM_{10}, even if particle counts can be of the order of several millions per cubic metre.

Conclusion

Although there have been an increasing number of studies investigating the traditional capture and analysis of particulate matter in port/harbour regions (Isakson et al. 2001, Ariola et al. 2006) there have been none performed in tandem with the deployment of a suite of real-time, continuous instrumentation. The methodology allows us to investigate, in great depth, the crucial chemical features that underpin the time-averaged measurements. The approach may also prove to be of key importance when the toxicological assays are performed for the dockside materials and the results compared with those obtained for city centre roadside collections.

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References

Ariola V, D'Alessandro A, Lucarelli F. (2006). Elemental characterization of PM_{10}, $PM_{2.5}$ and PM_1 in the town of Genoa (Italy). *Chemosphere* 62:226–32.

Ayres JG, Borm P, Cassee FR, Castranova V, Donaldson K, Ghio A, Harrison RM, Hider R, Kelly F, Kooter IM, Marano F, Maynard RL, Mudway I, Nel A, Sioutas C, Smith S, Baeza-Squiban A, Cho A, Duggan S, Froines J. (2008). Evaluating the toxicity of airborne particulate matter and nanoparticles by measuring oxidative stress potential – a workshop report and consensus statement. *Inhal Toxicol* 20:75–99.

Borm P, Kelly F, Kunzli N, Schins R, Donaldson K. (2007). Oxidant generation by particulate matter: from biologically effective dose to a promising, novel metric. *Occup Environ Med* 64:73–7.

Cofala J, et al. (2007). Analysis of policy measures to reduce ship emissions in the context of the revision of the national emissions ceilings directive. EC IIASA contract April 2007. Available at: http://ec.europa.eu/environment/air/pdf/06107_final.pdf

Corbett J, Winebrake J, Green E, Kasibhatla P, Eyring V, Lauer A. (2007). Mortality from ship emissions: a global assessment. *Environ Sci Technol* 41:8512–18.

Corbett J, Fischbeck P, Pandis S. (1999). Global nitrogen and sulphur inventories for oceangoing ships. *J Geophys Res-Atmos* 104:3457–70.

Espinosa A, Rodriquez M, de la Rosa F, Sanchez J. (2002). A chemical speciation of trace metals for fine urban particles. *Atmos Environ* 36:773–80.

Fridell E, Steen E, Peterson K. (2008). Primary particles in ships emissions. *Atmos Environ* 42:1160–8.

IMO MEPC. (2007). 57th session amendment to Annex VI of MARPOL 73/78: International Convention for the prevention of pollution from ships.

Isakson J, Persson T, Lindgren E. (2001). Identification and assessment of ship emissions and their effects on the harbour of Goteborg, Sweden. *Atmos Environ* 35:3659–66.

Kelly F. (2003). Oxidative stress: its role in air pollution and adverse health effects. *Occup Environ Med* 60:612–16.

Popovicheva O. (2008). Abstracts of the HAQCC 2nd International Conference on Harbours, Air Quality and Climate Change, Rotterdam, 2008.

Reiss R, Anderson E, Cross C. (2007). Evidence of health impacts of sulfate- and nitrate-containing particles in ambient air. *Inhal Toxicol* 5:419–49.