Environmental linkage of in-port emissions of PM, their chemical analysis and health effects in Cork Harbour, Ireland

I. P. O'Connor*, A. Allanic, S. Hellebust, E. Peré-Trepat, D. Healy, J. Wenger and J. R. Sodeau

Centre for Research into Atmospheric Chemistry, Department of Chemistry,

University College Cork, Cork, Ireland.

**e mail : i.p.oconnor@.ucc.ie*

Introduction

The chemical/biological composition of particulate matter (PM) in aerosols can be complex and varies spatially – between rural and urban environments and between continental and marine environments *[1]*. One source of PM that contributes to air pollution is that derived from ship emissions. Seagoing ships are not subject to the stringent air quality legislation which is applied to land-based transport. Emission estimates demonstrate the fact that ships make significant contributions to the pollution inventories of SO_2, CO_2, NO_x, organic compounds, and PM (especially $PM_{2.5}$ – fine particulates). The average sulfur content of marine heavy fuel oil ("bunker fuel") used in European waters is 27,000 ppm and it is estimated that by 2010 emissions from ships will equal three-quarters of the EU total for sulfur *[2]*. In-port emissions of PM may be considerably more acidic due to the high sulphur content of bunker fuel Between 20% to 30% of secondary inorganic particles in coastal areas are thought to be formed from such emissions *[3]*.

Aims

Project ELIPSE is a wide-ranging ambient air monitoring study. The main aim of this study is to assess the contribution that a range of products associated with marine diesel (bunker fuel) combustion in-port make to the ambient air pollution of Cork City and Harbour. Receptor modelling techniques will be performed in order to identify and apportion pollution sources in the Cork Harbour region. Chemical characterisation and physico-toxicological assessment will identify the most toxic aerosol components.

Preliminary Sampling Campaign Cork Harbour – Winter 2007/08

Sampling Equipment

High Volume Cascade Impactor *(Chem Vol Model 2000):*

- Collection of PM onto inert polyurethane foam substrate with high mass loading capacity.
- Size fractionation of PM into PM $_{10\text{-}2.5}$ and PM $_{2.5\,-\,0.1}$.
- Sampler flow-rate 900 L min^{-1} .

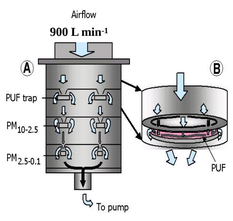


Figure 1. High Volume Cascade impactor

Chemical Analysis

- Total Metals by ICP- OES (Perkin & Elmer Optima 2000 series – UV/Vis detector).
  - Extraction by microwave acid digestion (HNO_3: HF).
- Soluble Inorganic Ions - IC (Dionex ICS 2000)
  - Aqueous extraction (shaking & sonication).
- Total mass loading of ambient PM $_{2.5\text{-}0.1}$ by gravimetric analysis.

Preliminary Results

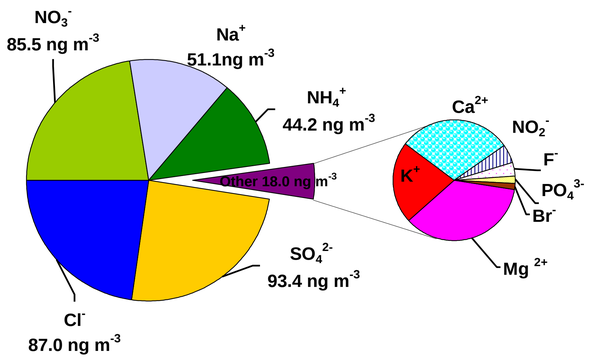


Figure 2. Mean ambient concentration of inorganic ions for Winter 2007/08.

The mean ambient concentration of water soluble inorganic ions shows a high degree of variation between ionic species. Sulfate, chloride and nitrate were the most prominent components of $PM_{2.5\text{-}0.1}$ having concentrations of 93.4 ng m^{-3}, 87.0 ng m^{-3} and 85.5 ng m^{-3} respectively. Sodium and ammonium ions were also present in the fine fraction in relatively significant concentrations (**Figure 2**).

Mean Ambient Concentration of $PM_{2.5\text{-}0.1}$

The mean ambient concentration of metals shows a high degree of variation between metallic species. Magnesium, calcium, zinc, silicon and iron were the most prominent components of PM $_{2.5\text{-}0.1}$. Lead, mercury, nickel, chromium, titanium and vanadium were present but in less significant quantities. Lead, nickel and vanadium are oil soluble metals and are contaminants of bunker fuels. (**Figure 3**).

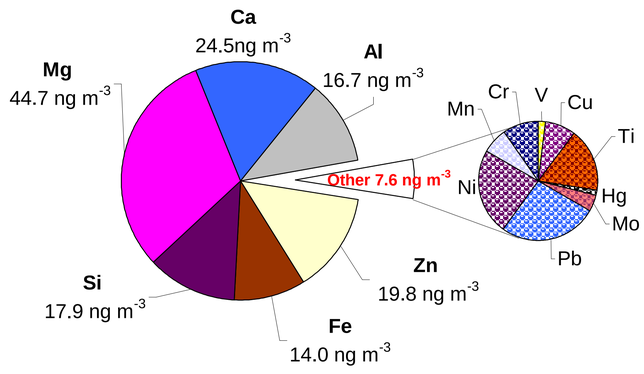


Figure 3. Mean ambient concentration of trace metals for Winter 2007/08.

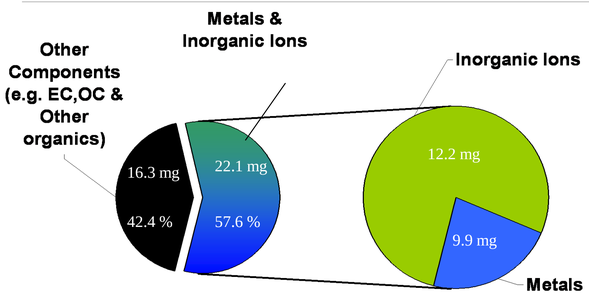


Figure 4. Mass loading of inorganic ion & metal component of $PM_{2.5\text{-}0.1}$.

The inorganic ions and metals analysed for composed 58% of the mass of the $PM_{2.5\text{-}0.1}$ collected during the entire winter sampling campaign. 45% of the mass of $PM_{2.5\text{-}0.1}$ was inorganic ions and metals accounted for 13% of the mass of the fine fraction (**Figure 4**).

Table 1. Summary of correlation coefficients between selected species in $PM_{2.5}$ collected in Cork Harbour Ireland.

	Mg	Ca	Zn	Si	Al	Fe	Pb	Ni	Na	Cl	NH_4^+	NO_3^-	SO_4^{2-}
Mg	1.0000												
Ca	**0.6949**	1.0000											
Zn	-0.6133	-0.2821	1.0000										
Si	-0.0489	0.3755	-0.0088	1.0000									
Al	0.1498	0.4310	0.2302	0.2519	1.0000								
Fe	-0.4868	0.2688	0.4921	0.5192	0.2835	1.0000							
Pb	-0.6872	-0.1394	**0.8264**	0.1292	0.5089	**0.7050**	1.0000						
Ni	-0.4310	0.3163	0.5247	0.4176	0.1806	**0.9714**	0.6713	1.0000					
Na	**0.9896**	**0.6918**	-0.5993	-0.0558	0.2405	-0.4616	-0.6443	-0.4302	1.0000				
Cl	**0.9631**	**0.7406**	-0.5784	0.1202	0.3549	-0.3732	-0.5758	-0.3731	**0.9804**	1.0000			
NH_4^+	**-0.7931**	-0.3594	**0.8519**	0.0100	0.3968	0.5984	**0.9716**	0.5527	**-0.7446**	**-0.6950**	1.0000		
NO_3^-	-0.6899	-0.0645	**0.7561**	0.2279	0.4612	**0.7817**	**0.9816**	**0.7551**	-0.6621	-0.5842	**0.9272**	1.0000	
SO_4^{2-}	-0.5353	-0.4565	**0.8005**	-0.2743	0.4724	0.1542	**0.7683**	0.1090	-0.4687	-0.4531	**0.8492**	0.6382	1.0000

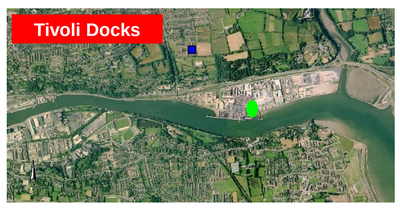
Correlations between selected species were determined as a preliminary step for statistical analysis (**Table 1**).

High correlation coefficients were observed for:

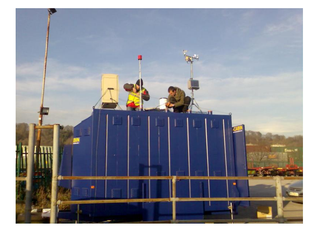
- Ca^{2+}, Mg^{2+}, Na^+, Cl^- suggesting a sea spray source
- NH_4^+/ SO_4^{2-} and NH_4^+/ NO_3^- suggesting a secondary sulfate/nitrate source
- Zn and Pb and finally Fe with Ni or Pb suggesting anthropogenic sources.

Further receptor modelling techniques will be performed in order to identify and apportion pollution sources in the Cork Harbour region.

ELIPSE Project - Sampling Campaign 2008



- Collection of high amounts of PM (mg) for toxicological studies using high volume cascade impactor and polyurethane foam (PUF) substrate.



- High time resolution PM collection using high volume sampler (300-1200 L min^{-1}) with quartz fibre filter collection substrate. Collection of PM in sufficient quantities for chemical analysis of inorganic ions and metals.
- Real-time aerosol analysis:
  - Particulate sulphate analyser: using UV fluorescence after catalytic conversion to SO_2.
  - Elemental & Organic Carbon analyser (EC/OC): collection onto quartz filters and measurement by NDIR detector system.
  - Gas phase monitoring of SO_2 using UV fluorescence.

- Collection of high amounts of PM (mg) for toxicological studies using high volume cascade impactor and polyurethane foam (PUF) substrate.
- Chemical analysis of PM $_{2.5\text{-}0.1}$ for metals and inorganic ions.

- Tapered Element Oscillating Microbalance (TEOM) system for determination of mass loading of PM in ambient.
- Collection of PM 2.5 on quartz fibre filters for chemical analysis of metal and inorganic ions.

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[1] Finlayson-Pitts, B. J.; Pitts, J. N., Jr. Chemistry of the Upper and Lower Atmosphere; Academic Press: New York, 2000.

[2] "Air pollution from ships". (European Environmental Bureau, Swedish NGO Secretariat on Acid Rain). 2004.

[3] World Health Organisation 2004; Health Aspects of Air Pollution : Report on a WHO working group meeting, Bonn, Germany: January 2004.