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## INTRODUCTION TO ELIPSE:

### ENVIRONMENTAL LINKAGES BETWEEN IN-PORT SHIP EMISSIONS OF PARTICULATE MATTER TO THEIR CHEMICAL CONTENT AND EFFECTS ON HEALTH



Airborne Particulate Matter (PM) is a mixture of solid and liquid particles suspended in the air. These particles are important in terms of impact of the environment and public health. International policy on air quality, protection of human health and the protection of the environment depends on research on ambient air particulate pollution. Knowledge on the origin of airborne particulate matter, the identification of particles hazardous to the quality of life and the chemistry of atmospheric aerosols is essential to understanding the sources and fates of particulate matter in the environment and their effects on human health.

Since the London Smog event in 1952, where acidic fog mixed with sulfurous smoke and a subsequent influenza epidemic caused about 4000 excess deaths in the winter of 1952/53 compared to the same period in the previous years, this has become a major environmental and epidemiological issue as industrial and population growth has increased and several monitoring networks and legislative measures have been put in place to reduce adverse effects of particulate matter pollution. However, emissions are increasing and abatement strategies need to become more effective in dealing with these problems. The first step in reducing emissions is to determine what measures are cost-effective and practical without curbing economic growth and development. This requires unequivocal knowledge of what the major sources are in different areas of the world.

It is known that transport and private vehicles are the main culprits in most parts of the world, by virtue of the sheer volume, although industrial activities can dominate in areas of high industrial activity. Ports in particular are economic and industrial hubs connecting air, road, shipping and air transport, while usually situated in areas of high population density. This fact should make them prime targets for research on air borne pollution, a fact which was overlooked for many years while the emphasis was on road traffic and space heating.

The fact that ports are associated with other forms of transport and economic activity means that emissions measured in-port are not all attributable to shipping. This also means that data linking with shipping and ambient levels of pollutants can not be made. Thus, the solution to the problem of high levels of air pollution in port areas is not necessarily to reduce shipping, because it is not known if the main source is shipping emissions or emissions from other associated economic activities. Thus, proper identification of sources to the air pollution measured in ports has to be carried out before abatement strategies can be effective. If shipping turns out to be a major source, effective measures can be taken without compromising economic growth and shipping volume, such as reduction of sulfur content in the fuel and provision of shore-power for loading and unloading of goods and handling, instead of keeping the ships engines running while alongside quay.



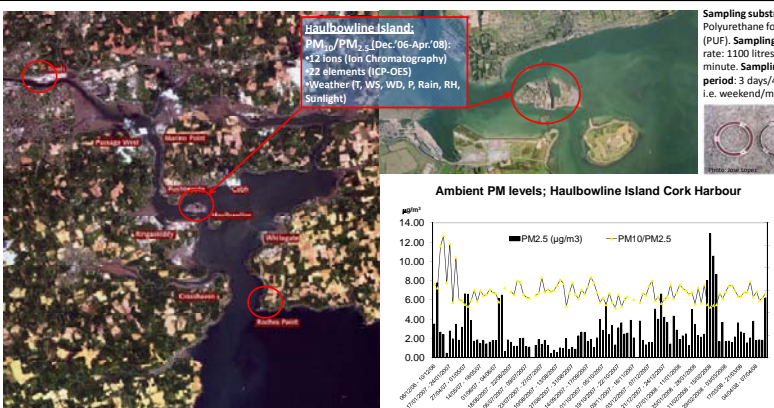
## AIMS, SAMPLING LOCATION AND RESULTS

The aims of this study are to collect and chemically characterize airborne particulate matter (PM<sub>10</sub>, PM<sub>2.5</sub> and other) present in Cork Harbour. The driving force for the studies is based on the world-wide recognition that ship emissions comprise a major, relatively unmeasured source of pollution with potentially adverse effects on human health.

PM collection programmes are operated at three Cork Harbour sites: Tivoli Docks (berth-side), Haulbowline Island (mid-harbour) and Roche's Point (Outer harbour) using a High Volume approach for capture of particles. Chemical analysis for inorganic compounds found in the PM<sub>2.5</sub> fraction employed ion chromatography and inductively coupled plasma – optical emission spectroscopy.

A "real-time" measurement programme for important atmospheric components such as Elemental and Organic carbon and the oxidation of Sulfur (IV), as SO<sub>2</sub> to Sulfur (VI), as sulfate ions is in operation since December 2007.

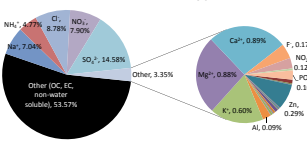
A second phase of the ELIPSE project is envisioned in which both toxicological and source apportionment issues associated with Cork Harbour will be thoroughly addressed.



### PM<sub>10</sub> and PM<sub>2.5</sub> mass per collection (mg) and ambient concentrations (µg/m³)

Collection	PM <sub>10</sub> Sample Weight (µg)	PM <sub>2.5</sub> Sample Weight (µg)	PM <sub>10</sub> / PM <sub>2.5</sub> (µg/m³)	PM <sub>10</sub> / PM <sub>2.5</sub> (µg/m³)	
					PM <sub>10</sub> (µg/m³)
2007-12-01	75.05	8.59	70.11	7.78	1.1
2007-12-02	81.21	7.26	28.89	2.84	1.1
2007-12-03	74.32	8.20	21.82	2.40	1.1
2007-12-04	6.86	0.66	5.24	0.67	1.1
2007-12-05	77.24	8.55	25.16	2.76	1.1
2007-12-06	9.48	0.88	20.78	2.05	1.1
2007-12-07	10.17	0.81	21.12	2.07	1.1
2007-12-08	6.85	1.00	14.83	1.65	1.1
2007-12-09	8.22	0.98	16.22	1.82	1.1
2007-12-10	10.24	2.41	14.85	4.43	1.1
2007-12-11	9.26	2.30	16.22	4.40	1.1
2007-12-12	10.34	2.17	18.39	3.86	1.1
2007-12-13	10.22	2.52	19.29	4.29	1.1
2007-12-14	10.02	2.52	18.82	4.18	1.1
2007-12-15	10.22	2.52	18.82	4.18	1.1
2007-12-16	10.22	2.52	18.82	4.18	1.1
2007-12-17	10.22	2.52	18.82	4.18	1.1
2007-12-18	10.22	2.52	18.82	4.18	1.1
2007-12-19	10.22	2.52	18.82	4.18	1.1
2007-12-20	10.22	2.52	18.82	4.18	1.1
2007-12-21	10.22	2.52	18.82	4.18	1.1
2007-12-22	10.22	2.52	18.82	4.18	1.1
2007-12-23	10.22	2.52	18.82	4.18	1.1
2007-12-24	10.22	2.52	18.82	4.18	1.1
2007-12-25	10.22	2.52	18.82	4.18	1.1
2007-12-26	10.22	2.52	18.82	4.18	1.1
2007-12-27	10.22	2.52	18.82	4.18	1.1
2007-12-28	10.22	2.52	18.82	4.18	1.1
2007-12-29	10.22	2.52	18.82	4.18	1.1
2007-12-30	10.22	2.52	18.82	4.18	1.1
2007-12-31	10.22	2.52	18.82	4.18	1.1

### Mass fraction of water soluble ions and metals in PM<sub>2.5-0.1</sub>



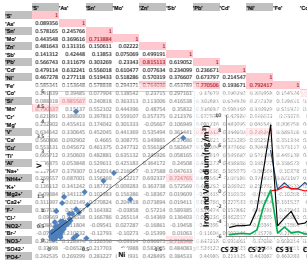
The main ions are SO<sub>4</sub><sup>2-</sup> (15% by mass), NO<sub>3</sub><sup>-</sup> (8%), NH<sub>4</sub><sup>+</sup> (5%), Na<sup>+</sup> (7%) and Cl<sup>-</sup> (9%)

The fluctuation between weekend and midweek samples in the values of PM mass and its chemical content suggests that there is a strong influence of anthropogenic sources in this mid-harbour location. Industrial and economic activities are reduced at weekends, but shipping activities are not.

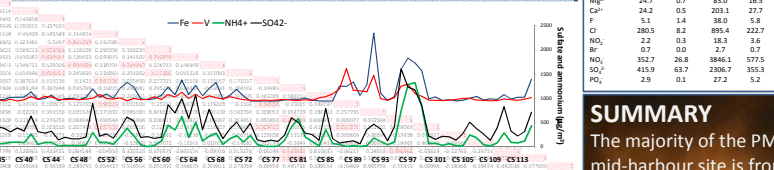
The high sulfate levels suggest a large component of secondary aerosols. Shipyards are a major emitter of SO<sub>2</sub>. Shipping related elements such as Vanadium and Nickel may be present in ultrafine particles that do not contribute significantly to total mass.

Levels of Vanadium, which is frequently used as a marker element for heavy bunker fuel, increase at weekends when there are regular arrivals of international passenger ferries and high levels of shipping activities in nearby cargo and cruise terminals. The V/Ni ratios in samples are typical of sites influenced by shipping emissions, with an average value of 3.4 and a median of 2.9.

## CORRELATIONS, PRINCIPAL COMPONENTS AND SOURCE APPORTIONMENT

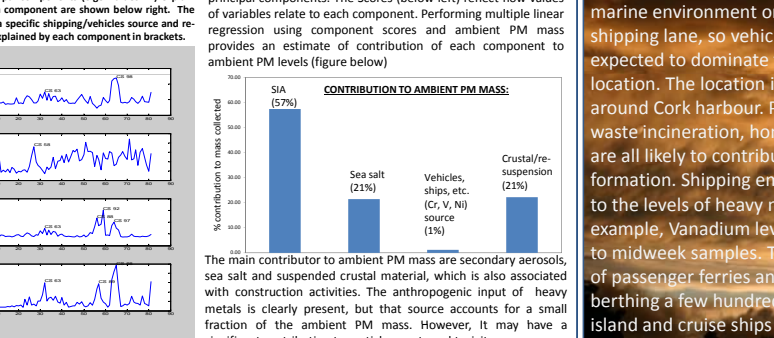
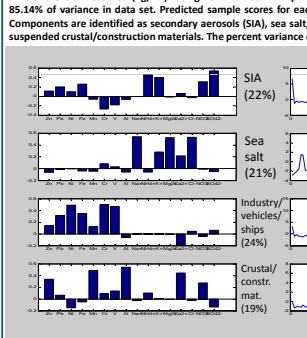


**WHAT IS CORRELATED?**  
Ions group 1: NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> (with K<sup>+</sup> and F<sup>-</sup>)  
Ions group 2: Na<sup>+</sup>, Mg<sup>2+</sup> and Cl<sup>-</sup>  
Metals group 1: Mn, Al, Ca, Zn and Cu  
Metals group 2: Pb, Fe, Ni, Cr, V and Ni



Orthogonally rotated principal components (PCA-Varimax) are shown below left. Analysis performed on ambient levels measured (µg/m³) using 16 variables. Four principal components (eigenvalues >1) explain 85.14% of variance in data set. Predicted sample scores for each component are shown below right. The Components are identified as secondary aerosols (SIA), sea salt, a specific shipping/vehicles source and re-suspended crustal/construction materials. The percent variance explained by each component in brackets.

The dimension of the dataset is reduced from 16 variables to 4 principal components. The Scores (below left) reflect how values of variables relate to each component. Performing multiple linear regression using component scores and ambient PM mass provides an estimate of contribution of each component to ambient PM levels (Figure below)



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## SUMMARY

The majority of the PM<sub>2.5-0.1</sub> fraction of aerosols at this mid-harbour site is from an anthropogenic, combustion related source. The site is located in a predominantly marine environment on an island in the middle of the shipping lane, so vehicle-related emissions are not expected to dominate to the same extent as in an urban location. The location is influenced by industrial activities around Cork harbour. Power plants, production plants, waste incineration, home heating and shipping emissions are all likely to contribute to secondary inorganic aerosol formation. Shipping emissions are also likely to contribute to the levels of heavy metals in ambient aerosols. For example, Vanadium levels increase at weekends relative to midweek samples. This may be due to weekend arrivals of passenger ferries and high tonnage cargo ships berthing a few hundred metres to the South West of the island and cruise ships berthing in Cobh cruise terminal opposite the receptor site.

## References

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