



## Introduction

The chemical/biological composition of **particulate matter (PM)** in aerosols can be complex and varies spatially – between continental and marine environments [1]. **Sulfur dioxide** is a primary inorganic pollutant that undergoes gas to particle conversion (heterogeneous reactions) and can take part in gas-phase (homogeneous) reactions to form secondary inorganic pollutants. These secondary pollutants formed in the atmosphere include acidic sulfate aerosols. Acidic aerosols including bisulfate and sulfate aerosols can react with gaseous ammonia to form ammonium salt [2]. Hence aerosol acidities are known to be lower in atmospheric regions where ready neutralisation of sulfates by reaction with ammonia occurs [3].



Figure 1 Satellite image of ship stack emissions, showing "Ship Tracks".

Figure 2 Relative contributions of sulfur made from automobiles and sea-going vessels.



Ships make significant contributions to the pollution inventories of SO<sub>2</sub>, CO<sub>2</sub>, NO<sub>x</sub>, organic compounds, and PM (especially PM<sub>2.5</sub> – fine particulates). **Marine residual fuel oil**, the residual from crude oil refinement, typically contains **sulfur up to 3.5% and vanadium 0.02%**. It is estimated that by 2010 emissions from ships will equal three-quarters of the EU total for sulfur [4]. Ships burning the residual fuel are more likely to produce cloud condensing nuclei and produce "ship tracks" (Fig. 1).

## Cork Harbour

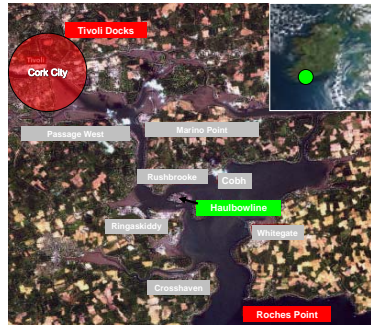


Figure 3 Map of Cork Harbour – showing in-port facilities and monitoring sites (red and green)

## Sampling Site & Equipment



Figure 4 Mid-harbour monitoring site.

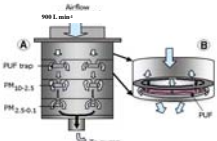


Figure 5 Particulate collection system.

### Chem Vol Model 2400 High Volume Cascade Impactor

The collection instrument was set up as follows:

- A two stage configuration mode with two acceleration platforms for PM<sub>10-2.5</sub> and PM<sub>2.5-0.1</sub> collections was used.



- Air passed through 32 cm circular nozzles before PM was trapped on polyurethane collection substrate on the platforms.

- A high capacity vacuum pump maintained a constant flowrate of 900 litres per minute (48m<sup>3</sup>.hr<sup>-1</sup>).

## Project ELIPSE

The **Environmental Linkage of In-Port Shipping Emissions** project is a wide-ranging ambient monitoring study. The main aims of this project are to identify and apportion pollution sources in the Cork Harbour region.

- Phase I** – Collection and chemical characterisation of inorganic component of PM at Haulbowline (HNB) and Tivoli docks (TP)
  - Phase II** – Source apportionment using various methods including receptor modelling
- Particular attention will be given to assessing correlations between the sulfate ions, nitrate ions and soluble metal indicators with the toxicological endpoints.

## Project TACCO

The **Toxicological Analysis and Chemical Correlation for PM<sub>2.5</sub> in transit to Cobh** a one-year desk study will provide a toxicological assessment of the airborne particulate matter (PM<sub>2.5</sub>) seasonally present in Cork Harbour and in transit to Cobh.

- Phase I** - Identify the most toxic aerosol components and will be compared to those previously found for samples collected in two Cork City sites (city centre & in-port).

## Methodology

### Chemical Analysis

- Total Metals by ICP-OES (Perkin & Elmer Optima 2000 series – UV/Vis detector).
  - Extraction by microwave acid digestion (HNO<sub>3</sub>: HF).
- Soluble Inorganic Ions - IC (Dionex ICS 2000)
  - Aqueous extraction (shaking & sonication).
- Total mass loading of ambient PM<sub>10-2.5</sub> & 2.5-0.1 by gravimetric analysis.

### Source Apportionment

**Receptor modeling** techniques will be performed in order to identify and apportion pollution sources in the Cork Harbour region.

**Refer to poster – Ambient levels of PM<sub>2.5</sub> in Cork Harbour, Ireland. T02A046P Tuesday poster session**

## Results - Sampling Campaign at Haulbowline (HNB) (2006- 2007)

### Aerosol Acidity – Ammonium to Sulfate Ratio for Cork Harbour (HNB)

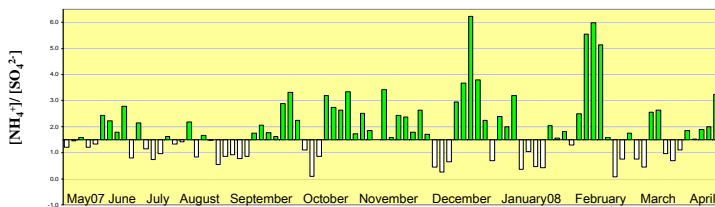


Figure 5. An indication of the degree of neutralisation of aerosols at Haulbowline, Cork.

The **ammonium to sulfate ratio** is an index used to identify the degree of neutralisation of acid sulfate in aerosols. Ammonium Rich particles ( $2 \geq [\text{NH}_4^+] / [\text{SO}_4^{2-}] \geq 1.5$ ) are mostly dominant in air at Haulbowline but with significant exceptions at times (Fig. 5)

### Aerosol Acidity – Strong Acidity ([H<sup>+</sup>] per m<sup>3</sup>) of air for Cork Harbour (HNB)

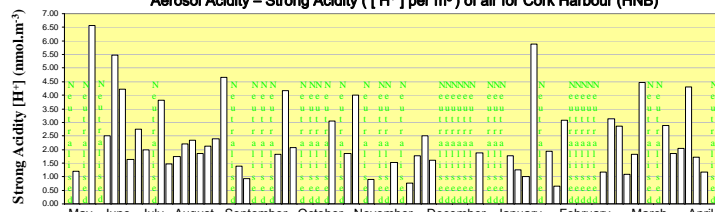


Figure 6. An indication of the degree of strong acidity of aerosols at Haulbowline, Cork.

The **strong acidity** in terms of nmol of H<sup>+</sup> per m<sup>3</sup> of air can be a useful indicator of the absolute acidity of atmospheric aerosols. It is estimated using an ionic balance of the inorganic ionic species. Using this index it was found that acidic aerosols were associated with the summer season with a greater degree of variation existing during winter (Fig. 6).

## Future Work

A short field campaign has been undertaken at Tivoli Docks using an **ATOFMS** (Aerosol Time-Of-Flight Mass Spectrometer TSI 3800).

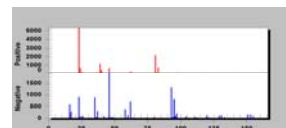


Figure 6. Positive and Negative Mass Spectra from a particle analysed at Tivoli docks. Sea-salt particles were readily collected, characterised by Na, Mg, Ca & Cl content.

The ATOFMS will provide information on the composition of single particles as a function of size range.

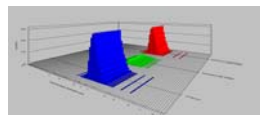


Figure 7. Size distribution and composition of a single particle.

Further intensive field campaigns will take place at harbour sites during 2008 & 2009. These will include chemical analysis of PM<sub>2.5</sub> for inorganics, organics and metals.

### And

- Real-time aerosol analysis:
  - Particulate sulphate analyser: using UV fluorescence after catalytic conversion to SO<sub>2</sub>.
  - Elemental & Organic Carbon analyser (EC/OC): collection onto quartz filters and measurement by NDIR detector system.
  - Gas phase monitoring of SO<sub>2</sub> using UV fluorescence.

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