

# **ELEMENTAL ANALYSIS AND SOURCE APPORTIONMENT OF AIRBORNE PARTICLES AT AN INDUSTRIAL AREA IN WELLINGTON, NEW ZEALAND**

Perry K. Davy<sup>1</sup>, Andreas Markwitz<sup>2</sup>, William J. Trompetter<sup>2</sup> and David C. Weatherburn<sup>1</sup>

<sup>1</sup>School of Chemical and Physical Sciences, Victoria University of Wellington, PO Box 600, Wellington, New Zealand, <sup>2</sup>Institute of Geological and Nuclear Sciences, PO Box 31-312, 30 Gracefield Road, Lower Hutt, New Zealand.

## **ABSTRACT**

Traditional gravimetric analysis of airborne particulate matter is unable to provide information on the sources contributing to air particulate concentrations. Ion Beam Analysis has been used to identify the elemental composition of air particulates for source apportionment and determining the relative contribution of biogenic and anthropogenic sources to air particulate pollution. Information on source contributions to ambient air particulate concentrations is a vital tool for air quality management. Analysis of ambient air particulates in New Zealand provides a challenge due to a strong maritime influence and a marked difference in particle composition compared to continental air masses. PM<sub>10</sub> and PM<sub>2.5</sub> have been collected at the industrial area of Seaview, Wellington over the past two years using a GENT stacked filter unit sampler. Concentrations of elements with atomic mass above neon were determined using Ion Beam Analysis and elemental carbon concentrations were determined using a reflectometer. Specific ambient source elemental 'fingerprints' were then determined by factor analysis and the relative contributions of various local and regional sources were assessed. The significant factors (sources) were determined to be: seasalt, soil, industry, and combustion sources. Local industry was found to contribute to ambient lead concentrations.

## **INTRODUCTION**

Measuring the total mass of air particulate provides no information on the identity of the contributing sources. In areas where the air resource is degraded by high concentrations of particulate matter, it is important that environmental management authorities and key policy decision-makers have information available that helps pinpoint the major contributing sources to that air pollution. The major contributors can then be targeted to reduce particulate emissions in order to improve air quality.

Air particulate matter has been collected at various locations in the Wellington Region since 1996 using GENT stacked filter units. The GENT sampler effectively collects two different size fractions, PM<sub>2.5</sub> or fine particulate matter and PM<sub>10-2.5</sub> or coarse particulate matter on to 47mm polycarbonate filters [1]. This paper presents the results of air particulate sampling carried out at the Seaview industrial area, Wellington from April 2002 to November 2003. The purpose of the monitoring programme was to characterise the elemental composition of ambient particles and then use the results for source apportionment of ambient particulate matter in the industrial area.

The concentrations of PM<sub>2.5</sub> and PM<sub>10-2.5</sub> collected by the GENT sampler at Seaview were determined gravimetrically and then the elemental composition of particulate matter on the filters was analysed at the New Zealand Ion Beam Analysis facility. The fingerprints of the contributing sources were determined by performing factor analysis on the elemental concentrations of air particulate on the filters collected at the Seaview industrial estate.

## MONITORING LOCATION

The Seaview industrial area covers approximately 1 km<sup>2</sup> and is located on the eastern side of the Hutt Valley where it meets Wellington Harbour. Wellington City is 10 km to the southwest across the harbour and immediately adjacent to the Seaview industrial area is the city of Lower Hutt with a population of 100,000. Figure 1 shows the location of the industrial area.

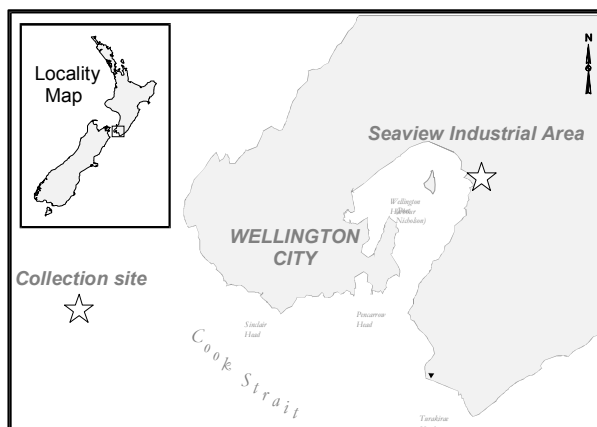


Figure 1. Map of monitoring location

Industrial activities range from light manufacturing and engineering facilities, freight storage, oil and fuel tank farms to wastewater treatment.

## PARTICULATE MATTER CONCENTRATIONS AT SEAVIEW

The monitoring programme at Seaview ran from April 2002 to November 2003. A total of 80 each of PM<sub>2.5</sub> and PM<sub>10-2.5</sub> filters were collected. The samples were collected over a 3-5 day sampling period in order to collect sufficient mass for elemental analysis. Figure 2 shows the gravimetric results for GENT PM<sub>2.5</sub> and PM<sub>10-2.5</sub>.

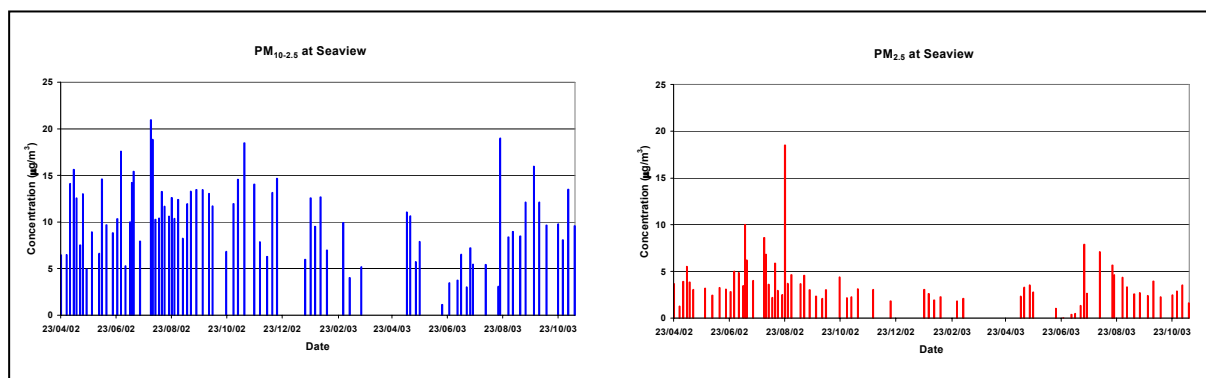


Figure 2. Ambient concentrations (µg/m<sup>3</sup>) of coarse and fine particles at Seaview

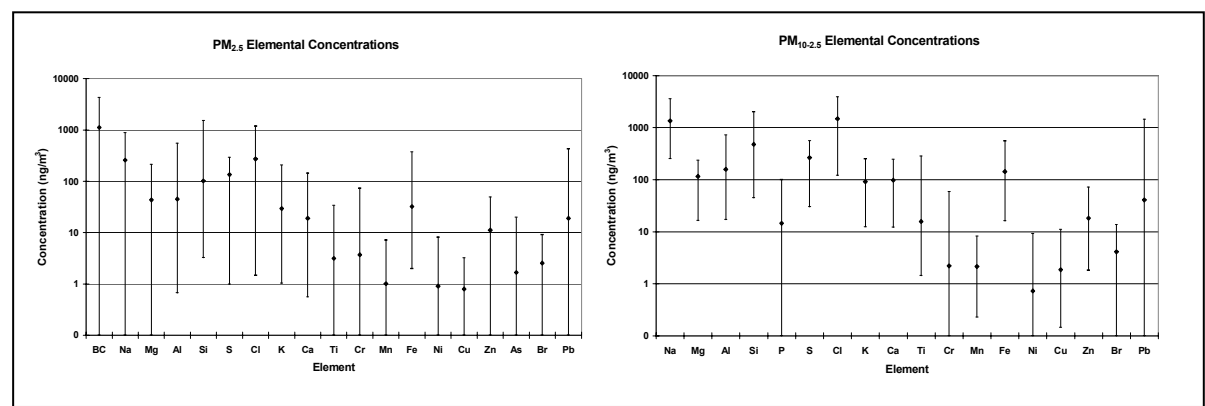
In general, the PM<sub>10-2.5</sub> concentrations (mean = 10 µg/m<sup>3</sup>) were higher than PM<sub>2.5</sub>. (mean = 4 µg/m<sup>3</sup>) concentrations. Fine particle concentrations were found to be at their highest during the winter months, which is consistent with monitoring results elsewhere in the Wellington Region and throughout New Zealand. Cold, calm weather under inversion conditions during the winter result in the stagnation of local air masses coupled with emissions from combustion

sources from such as solid fuel fires for domestic heating can lead to elevated fine particle concentrations [2].

While the GENT sampler is not a reference method for air particulate monitoring and the length of sampling times differ from the 24-hour average used to compare monitoring results with human health guidelines, comparison with a nearby ambient air quality monitoring station indicate that the ambient air quality PM<sub>10</sub> standard of 50 µg/m<sup>3</sup> was unlikely to have been exceeded at Seaview during the monitoring period.

### ELEMENTAL ANALYSIS

Elemental analysis of the particulate collected on the filters was carried out using IBA at the New Zealand Ion Beam Analysis facility, Lower Hutt, Wellington. Sodium was measured using proton induced gamma-ray emission (PIGE) and elements above sodium were measured using proton induced x-ray emission (PIXE). Elemental carbon concentrations were determined using a light reflectance device. A more in-depth description and discussion of the techniques used is presented in [3]. Figure 3 displays the range of elements and their respective concentrations detected on the polycarbonate filters.



**Figure 3. Range of elemental concentrations (ng/m<sup>3</sup>) for PM<sub>2.5</sub> and PM<sub>10-2.5</sub> respectively**

The elements included in Figure 3 are those that were present in concentrations above the limit of detection in each size fraction for IBA analytical techniques.

### SOURCE APPORTIONMENT – FINGERPRINT DETERMINATION

The elements that make up a fingerprint for each source of ambient air particulate are determined by statistically analysing the elemental composition of the particulate over a large number of samples. The statistical package SYSTAT was used to perform Factor Analysis (Principal Components) to determine the grouping of elements that vary together and therefore determine the components of a factor or ‘fingerprint’ for each different source. In reality the factor analysis is performed in several reiterations with statistical checks at each stage to ensure that sample matrix variance accounted for is due to real world phenomena rather than an artefact of uncertainty in the analytical process.

#### PM<sub>10-2.5</sub>

Table 1 lists the fingerprints or factors identified for the PM<sub>10-2.5</sub> fraction at Seaview

Element	Factor 1 'Soil'	Factor 2 'Seasalt'	Factor 3 'Lead'
Fe	<b>0.98</b>	-0.02	0.08
Si	<b>0.98</b>	-0.03	0.12
Al	<b>0.97</b>	-0.05	0.10
Ti	<b>0.96</b>	0.03	0.13
K	<b>0.89</b>	0.41	0.04
Ca	<b>0.86</b>	0.46	0.08
Zn	<b>0.72</b>	0.16	-0.13
Cl	-0.08	<b>0.96</b>	-0.08
Br	-0.02	<b>0.90</b>	0.20
Na	0.04	<b>0.87</b>	-0.09
Mg	0.52	<b>0.78</b>	0.11
S	0.32	<b>0.77</b>	0.27
Pb	0.10	0.13	<b>0.97</b>

**Table 1. Sources of ambient PM<sub>10-2.5</sub> identified by Factor Analysis**

Three significant factors were determined for the coarse particle fraction at Seaview, these have been labelled 'Soil', 'Seasalt' and 'Lead' respectively for factors 1, 2 and 3 as shown in Table 1. The 'name 'Soil' has been used as the elements present in the factor are typical of those found in crustal matter. Similarly the 'Seasalt' factor contains elements that are major components of seasalt. Some elements such as Mg, Ca and K are common to both factors, but tend to be more highly associated with one particular factor, in this case, K and Ca with the "Soil" factor and Mg with the 'Seasalt' factor. Both the 'Soil' and 'Seasalt' factors are most likely from natural sources. The 'Lead' factor is of interest due to the toxic nature of the metal and that it is likely to be from a local industrial source.

#### **PM<sub>2.5</sub>**

Table 2 lists the factors determined for the PM<sub>2.5</sub> fraction at Seaview.

Element	Factor 1 'Soil'	Factor 2 'Combustion'	Factor 3 'Seasalt'	Factor 4 'Lead'
Fe	<b>0.96</b>	0.21	0.07	0.06
Si	<b>0.95</b>	0.25	0.04	0.04
Ca	<b>0.89</b>	0.27	0.32	0.05
Ti	<b>0.87</b>	-0.01	0.01	0.07
Al	<b>0.85</b>	<b>0.50</b>	-0.02	0.04
K	<b>0.82</b>	<b>0.49</b>	0.18	0.06
Zn	<b>0.67</b>	0.38	0.29	0.01
BC	0.37	<b>0.83</b>	-0.17	0.24
Mg	0.27	<b>0.89</b>	0.21	0.07
S	0.27	<b>0.60</b>	<b>0.57</b>	0.23
Na	0.20	0.07	<b>0.93</b>	0.08
Cl	-0.01	0.01	<b>0.95</b>	-0.04
Pb	0.06	0.21	0.06	<b>0.97</b>

**Table 2. Sources of ambient PM<sub>2.5</sub> identified by Factor Analysis**

Four significant sources were established from the factor analysis, three of them, 'Soil',

‘Seasalt’ and ‘Lead’ are the same as for the PM<sub>10-2.5</sub> fraction and are likely to also be from the same sources. The ‘Combustion’ source has been so named by virtue of the inclusion of elemental or black carbon that is usually associated with combustion sources (soot particles). The inclusion of Mg, Al, K and S in the combustion factor is consistent with source apportionment work elsewhere in the Wellington Region [4] and the use of solid fuel fires for domestic heating during the winter is likely to be the predominant contributor to this factor.

The elemental composition of the PM<sub>2.5</sub> fraction collected at the Seaview site is compared with the average elemental concentrations measured in other studies in Table 3 (reproduced from Choong-Min Kang *et al*) [5].

Element	This study	Seoul <sup>a</sup>	Ch'ongju <sup>b</sup>	Barcelona <sup>c</sup>	Beijing <sup>d</sup>	Los Angeles <sup>e</sup>	Mexico City <sup>f</sup>
Al	0.045 (1.1)	0.556 (1.1)	0.183 (0.4)	0.244 (0.7)	0.8 (0.7)	0.035 (0.1)	0.47 (1.2)
Si	0.102 (2.6)	1.361 (2.8)	0.36 (0.8)	0.49 (1.4)	2.39 (2.1)	0.052 (0.1)	1.63 (4.2)
S	0.135 (3.4)	3.163 (6.5)	1.136 (2.6)	1.937 (5.5)	6.57 (5.7)	2.832 (6.9)	1.88 (4.9)
Cl	0.272 (6.8)	1.925 (4.0)	0.459 (1)	0.59 (1.7)	2.05 (1.8)	0.093 (0.2)	0.23 (0.6)
K	0.029 (0.7)	0.781 (1.6)	0.214 (0.5)	0.48 (1.4)	2.83 (2.5)	0.041 (0.1)	0.33 (0.9)
Ca	0.019 (0.5)	0.535 (1.1)	0.097 (0.2)	0.51 (1.5)	1.23 (1.1)	0.022 (0.1)	0.62 (1.6)
Ti	0.003 (0.1)	0.080 (0.2)	0.021 (0.1)	0.02 (0.1)	<sup>g</sup> NA	0.005 (0)	0.04 (0.1)
Mn	0.001 (0.0)	0.036 (0.1)	0.015 (0)	0.014 (0)	0.097 (0.1)	0.016 (0)	0.02 (0.1)
Fe	0.032 (0.8)	0.555 (1.1)	0.146 (0.3)	0.26 (0.7)	1.14 (1)	0.099 (0.2)	0.56 (1.4)
Cu	0.011 (0.0)	0.035 (0.1)	0.013 (0)	0.052 (0.1)	0.035 (0)	0.063 (0.2)	0.02 (0.1)
Zn	0.002 (0.3)	0.198 (0.4)	0.055 (0.1)	0.178 (0.5)	0.48 (0.4)	0.09 (0.2)	0.26 (0.7)
Pb	0.019 (0.5)	0.187 (0.4)	0.063 (0.1)	0.13 (0.4)	0.304 (0.3)	0.038 (0.1)	0.1 (0.3)
Mass	4.0	48.5	44.2	35	115	41.1	38.7

Note: Values in (µg/m<sup>3</sup>). Numbers in parentheses are percentages of contribution to the mass; <sup>a</sup>PM<sub>2.5</sub> samples were measured from April 2001 to February 2002 in the eastern-central part of Seoul; <sup>b</sup>PM<sub>2.5</sub> samples were measured from October 1995 to August 1996; <sup>c</sup>PM<sub>2.5</sub> was continuously monitored from June 1999 to June 2000; <sup>d</sup>PM<sub>2.5</sub> samples were measured from July 1999 to September 2000; <sup>e</sup>PM<sub>2.5</sub> samples were measured during summer and fall 1987; <sup>f</sup>PM<sub>2.5</sub> was measured over 24-hr intervals at 6 core sites from February 23 to March 22, 1997; <sup>g</sup>Not available.

**Table 3. Comparison of elemental composition of PM<sub>2.5</sub> (µg/m<sup>3</sup>) from various studies**

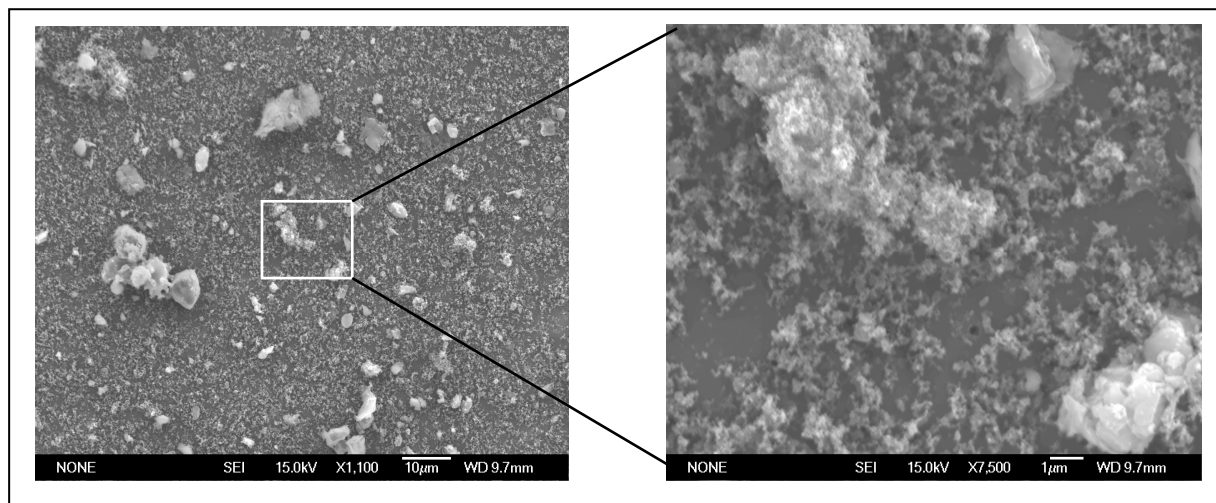
The most marked difference between this study and those others listed in Table 3 is that the average concentration of the PM<sub>2.5</sub> fraction is lower by an order of magnitude. The concentrations of the elements themselves are also lower by at least an order of magnitude, however, their percentage contributions are similar apart from a higher Cl component. This is likely a reflection of the fact that Al, Si, Ca, Ti and Fe are from crustal origins. Choong-Min Kang *et al.* identify S, Cl and Pb as anthropogenic in origin whereas in this study, the source of Cl is most definitely natural due to the high relative contribution of seasalt to ambient particulate levels. Our results suggest that sulfur is from both natural and anthropogenic sources and lead is most definitely anthropogenic in origin. It is important to note that lead was phased out of petrol in New Zealand in 1996 and average background environmental concentrations are now less than 0.05 µg/m<sup>3</sup> [6].

## DISCUSSION

The gravimetric dominance of the coarse (PM<sub>10-2.5</sub>) fraction at the Seaview site is perhaps the most telling factor in attributing sources of particulate matter at that location. Soil and seasalt sources in the Wellington region of New Zealand invariably dominate the PM<sub>10-2.5</sub> fraction [6]. The presence of these two sources in the PM<sub>2.5</sub> fraction is a result of ‘break-through’ of the

finer particles from the coarse fraction.

The factor analysis of elemental composition can also provide a 'Factor Score' for each individual sample filter that indicates the relative contribution of a particular factor to the particle loadings on each filter. Scanning electron microscopy (SEM) images of PM<sub>2.5</sub> filters from the Seaview site show particles of soil and seasalt dispersed across the filter (particle diameter in the 1-3 µm range), the density of particles depending on the relative contribution from each source to the loadings on the filter in question. Particle composition for source attribution was by energy dispersive spectroscopy. In contrast particles from combustion sources are in the sub-micron range, tend to be filamentous in nature (most likely due to particle agglomeration) and are always in the PM<sub>2.5</sub> fraction. Figure 4 is a SEM image from a filter that had a high factor score for 'Soil' and 'Combustion'. The contrast in particle morphology is striking.



**Figure 4. SEM image of filter with a high 'Soil' and 'Combustion' loading**

The Seaview industrial site is comprised of significant areas of unsealed lots, mainly covered in aggregates. Vehicle movements and wind action on these areas can lead to airborne particulate matter. The industrial area also lies at the mouth of the Hutt River which is a source of alluvial fines and loess, it is therefore unsurprising that the 'Soil' factor features strongly in the source apportionment. Similarly, 'Seasalt' features due to the proximity of the location to Wellington Harbour and the southern Pacific Ocean in general.

Combustion sources in the area are motor vehicles (petrol and diesel fuelled), gas and diesel fired boilers for heat energy production and, further afield, emissions from solid fuel fires used for domestic heating during the winter.

The only major local source of lead at Seaview is a lead-acid battery manufacturing plant some 200m from the monitoring site. While ambient levels of lead at Seaview were below the New Zealand human health guideline of 0.2 µg/m<sup>3</sup> (3-month average), several peaks in the lead concentration (max 1.8 µg/m<sup>3</sup>) during 2002 give some cause for concern. Further investigation into the reasons for these lead 'spikes' are currently underway.

## CONCLUSION

Coarse (PM<sub>10-2.5</sub>) and fine (PM<sub>2.5</sub>) ambient particulate matter fractions were collected during 2002-2003 at Seaview, an industrial area near Wellington City, New Zealand. The gravimetric results showed ambient particle loadings at the monitoring site to be relatively low, particularly in the fine fraction. IBA was used to analyse the elemental composition and factor analysis was performed to elucidate source contributions to ambient particulate matter concentrations. It was found that 'Seasalt' and 'Soil' sources dominated the coarse fraction and were also major source contributors to the fine fraction. Sources of 'Combustion' particles were an important contributor to the fine fraction, particularly in the sub-micron particle size range. The study found that local industrial sources do not have a major influence on particle concentrations at Seaview, however, a local source of lead was identified in both the coarse and fine fractions.

In contrast to similar studies carried out at locations subject to continental air masses, it was found that seasalt is an important contributor to ambient particle loadings due to New Zealand's isolated oceanic location.

## REFERENCES

- [1] Hopke, P. K., Xie, Y., Raunemaa, T., Biegalski, S., Landsberger, S., Maenhaut, W., Artaxo, P., Cohen, D., 1997. 'Characterisation of the Gent Stacked Filter Unit PM<sub>10</sub> Sampler', *Aerosol Science and Technology* **27**:726-735.
- [2] New Zealand Ministry for the Environment, 2003. 'Health effects of PM<sub>10</sub> in New Zealand', *Air Quality Technical Report No. 39*, Ministry for the Environment.
- [3] Trompetter W.J., Markwitz A. Davy P. 2000, 'Using Ion Beam Analysis to characterise sources of air particulates in the Wellington region of New Zealand', *Proceedings of the 15th International Clean Air and Environment Conference, Sydney, 2000*, Clean Air Society of Australia & New Zealand, Eastwood, NSW, Australia, pp. 382-386.
- [4] Davy P., Markwitz A., Trompetter W.J., 2002, 'Elemental Analysis and Source Apportionment of Ambient Particulate Matter in the Wellington Region of New Zealand', *Proceedings of the 16th International Clean Air and Environment Conference, Christchurch, 2002*, Clean Air Society of Australia & New Zealand, Eastwood, NSW, Australia
- [5] Choong-Min Kang; Young Sunwoo, Hak Sung Lee, Byung-Wook Kang, Sang-Kwun Lee, 2004, 'Concentrations of PM<sub>2.5</sub> Trace Elements in the Seoul Urban Area of South Korea', *Journal of the Air and Waste Management Association*, Volume 54, Number 4.
- [6] New Zealand Ministry for the Environment 2003, 'GEMS Air Monitoring Program Annual Report 2002', Ministry for the Environment.