Air Quality Monitoring Technical Report

Perry Davy
Resource Investigations Department
Greater Wellington Regional Council

Contents

Executive Summary

The Air Quality Monitoring Technical Report presents the results of ambient air quality monitoring that has been carried out in the Wellington Region since 1999. Ambient air quality monitoring was undertaken at Central Wellington, Upper Hutt, Lower Hutt, Masterton, Otaki and Wainuiomata.

The contaminants that have been monitored in the Wellington Region to date include fine particulate matter (PM_{10}), carbon monoxide (CO), and nitrogen dioxide (NO_2). These pollutants are known to adversely affect human health and well-being, as well as to have other adverse environmental effects. Air quality monitoring has focused on these pollutants as they are discharged to the atmosphere in the greatest quantities from a variety of sources.

Upper Hutt

A mobile ambient air quality monitoring station has been located at Trentham Fire Station in Upper Hutt since June 2000. The monitoring data confirms that the Upper Hutt area continues to be susceptible to wintertime pollution episodes of fine particulate matter (PM_{10}).

Particulate matter, carbon monoxide and nitrogen dioxide concentrations were found to be higher during the winter. Research has shown that domestic fires are the main cause of the particulate pollution and, a combination of motor vehicles and domestic fires, are responsible for the elevated levels of carbon monoxide and nitrogen dioxide.

Lower Hutt

A permanent ambient air quality monitoring station has been operating at Birch Lane in Lower Hutt since February 2001.

The results indicate that nitrogen dioxide and carbon monoxide levels were higher during the winter than in summer in Lower Hutt, although there were no exceedences of any guidelines or standards. The peak winter time levels are likely to be due to the combined effects of motor vehicle emissions and combustion emissions from residential and commercial heating, combined with cold calm meteorological conditions. Peak levels occurred at similar times as those recorded at Upper Hutt, indicating the predominant influence of the weather on air pollution levels.

Wainuiomata

PM_{10} has been monitored at Wainuiomata Bowling Club from since September 2000. Fine particulate concentrations were found to exceed the National Environmental Standard for Air Quality on a number of occasions each winter. Peaks in air pollution occurred during cold calm weather conditions when dispersion of air pollutants was poor. The use of solid fuel fires for domestic heating is thought to be the main source of air pollution in Wainuiomata.

Masterton

A permanent ambient air quality monitoring station was established at Wairarapa College in Masterton during October 2002. The highest air pollution levels in

Masterton were recorded during winter. A number of exceedences of the National Environmental Standard for particulate matter (PM_{10}) occurred each year. Research has shown that the cause of the high particulate matter concentrations is likely to be emissions from domestic solid fuel fires.

Vivian and Victoria Streets, Central Wellington

The monitoring station at the corner of Vivian and Victoria Streets was established in February 2004. Monitoring air quality at that location is aimed at tracking the influence of motor vehicle emissions on local air quality and would be classed as a 'Peak' site whereas, all other Greater Wellington sites are oriented towards background/neighbourhood air quality monitoring.

Air quality monitoring at Vivian and Victoria Streets indicates that long-term average carbon monoxide and particulate matter concentrations are higher than other sites around the region but peak levels have not exceeded National Environmental Standards or the National Ambient Air Quality Guidelines. Several years of monitoring at that site will be required to provide a fully informed picture of air quality on the streets of Central Wellington.

Rural Otaki

PM_{10} was monitored at Otaki from September 1998 through to February 2000. There was one result that equalled the National Environmental Standard value.

The results indicate that PM_{10} concentrations tend to be highest during dry summer weather with moderate to strong winds. Further research has shown that the source of the majority of PM_{10} is likely to be fine alluvial matter from the Otaki River floodplain.

Conclusion

The results of the ambient air quality monitoring carried out in the Wellington Region since 1999 have indicated that the highest concentrations of air pollutants occurred during the winter. The higher winter time air pollution levels are the consequence of periods of cold, calm weather and a greater quantity of emissions to atmosphere from combustion sources. Cool, calm conditions restrict the dispersion of air pollutants. The major pollution sources have been shown to be emissions from motor vehicles and domestic solid fuel fires.

Ambient air quality monitoring at various locations within the Wellington Region showed that air quality is generally good during the summer months at suburban locations. However, at times, certain areas experience degraded air quality due to a combination of meteorological conditions and local emission sources exerting pressure on the air resource to the extent that it may pose a risk to the health of local communities. With the establishment of a permanent air quality monitoring network, clear trends in air pollution levels are becoming evident. Winter is the most likely time for pollution episodes to occur, the extent and severity of which are primarily dependent on the type of winter we experience.

1. Introduction

This Air Quality Monitoring Technical Report reports on all ambient air quality monitoring that has been carried out in the Wellington Region since 1999. Ambient air quality is the general quality of the air that surrounds us. Ambient air quality reflects the cumulative effects of discharges to the atmosphere from both human activities and natural sources.

Greater Wellington (the Council) has the responsibility to monitor the state of the environment pursuant to section 35 of the Resource Management Act 1991. Part of this responsibility includes monitoring ambient air quality.

The Regional Air Quality Management Plan requires the collection of information on particular aspects of air quality so that the effectiveness and appropriateness of policies, objectives and rules can be assessed.

The cumulative effects of emissions from domestic fires, motor vehicles and certain industrial production processes can be evaluated by monitoring the ambient concentrations of key air pollutants. We need good information about these pollutants to make any management decisions necessary to maintain and enhance air quality within the Region

The Regional Air Quality Management Plan contains Regional Ambient Air Quality Guidelines (see Table 2.1). Air quality within the Wellington Region needs to be monitored in order to assess whether these guidelines are being met. It is important to note that these guideline levels are intended only for the protection of human health, based on current medical and scientific knowledge, and may not provide adequate protection for the wider environment, such as sensitive ecosystems.

Greater Wellington has now established permanent air quality monitoring stations at Wainuiomata, Masterton, Lower Hutt and Central Wellington. A new permanent monitoring station is under construction for Upper Hutt, and a mobile air quality monitoring station is about to be commissioned with the specific target of monitoring the air pollution caused by motor vehicle emissions.

2.   Air quality monitoring

2.1   Monitoring strategy

Ambient air quality monitoring is necessary for assessing many of the issues identified in the Regional Policy Statement and the Regional Air Quality Management Plan. In particular, the relative concentrations of various air pollutants have adverse effects on human health and amenity values.

There is insufficient information and data available to fully characterise the state of ambient air quality (for state of the environment reporting) in the Wellington Region. This was one of the issues identified in the Region's State of the Environment Report "*Measuring Up*" (Wellington Regional Council 1999). A series of air quality screening investigations was undertaken from 1997-2001 in order to prioritise potential sites for permanent air quality monitoring stations. These investigations have identified areas where air quality is, or can intermittently become, degraded to the extent that it may affect human health. It is in these areas that permanent ambient air quality monitoring will be undertaken.

Permanent monitoring stations are required to assess trends in air quality and the state of the resource. At least three years continuous data is necessary before any trends become evident and useful comparisons can be made between sites.

The Wellington Region is divided into a series of airsheds, delineated by valleys in between steep hills or mountains. This produces unique microclimates and meteorological conditions for each of these sub-regional airsheds. Each location has differing pressures on the air quality resource and the resultant effects on air quality cannot be inferred from one site to another. The main airsheds that have been identified as subject to air quality pressures are Wellington City, Lower Hutt Valley, Upper Hutt Valley, Wairarapa Valley, Porirua, Kapiti Coast, Karori and Wainuiomata.

The *Wellington Regional Air Quality Monitoring Strategy 2000-2005* (Resource Investigations Technical Publication WRC/RINV-T-00-20 June 2000) identifies the sites where permanent monitoring stations are appropriate and where further screening investigations need to be undertaken.

2.2   Air pollutants monitored

The contaminants that are being monitored in the Wellington Region are particulate matter (PM_{10}), carbon monoxide (CO) and nitrogen oxides (NOx). These compounds are three of the air pollutants identified in the Resource Management (National Environmental Standards Relating to Certain Air Pollutants, Dioxins, and Other Toxics) Regulations 2004 (NES). The Regulations were Gazetted on 8 October 2004. National environmental standards are mandatory technical environmental regulations. They have the force of regulation and are implemented by agencies and parties with responsibilities under the Resource Management Act 1991 (the Act). The standards are prepared in accordance with sections 43 and 44 of the Act. The

NES require that air quality is monitored for the specified pollutants wherever the general population may be exposed to elevated concentrations.

The CO, NO_2 and PM_{10} air pollutants are also three of the air pollutants identified in the Regional Ambient Air Quality Guidelines (reproduced as Table 2.1), the *National Ambient Air Quality Guidelines* (Ministry for the Environment 1994) and in *Ambient Air Quality Guidelines: 2002 Update* (Ministry for the Environment 2002).

CO, NOx and PM_{10} are also national State of the Environment Indicators for air quality. These contaminants have been monitored as they are emitted in the greatest concentrations from a variety of sources throughout the Wellington Region. They were chosen as they are known to have adverse effects for human health and well-being, and to have other adverse environmental effects.

2.2.1 Nitrogen oxides (NOx)

Nitrogen oxides principally consist of nitric oxide (NO) and nitrogen dioxide (NO_2). NO and NO_2 have the potential to cause adverse human health effects and NO_2 contributes to poor visibility. Both compounds form acidic species when in aqueous solution (hence they are a component of acid rain) and can attack the human body's mucous membranes and the respiratory system. Nitrogen dioxide forms a brown gas in the atmosphere and can be seen as a haze over cities during periods of calm weather and heavy traffic congestion (e.g. during *rush hours*).

Sources include:

- Motor vehicles
- Domestic fires
- Industrial combustion processes.

NO_2 is not usually discharged from these sources in significant concentrations, but is more likely to form in the atmosphere by chemical transformation of NO. For the purposes of this report, the monitoring stations were considered to be of sufficient distance away from major local NOx sources for the formation of NO_2 to be representative of general ambient NO_2 concentrations. Only NO_2 has been reported in this document. The NES for NO_2 is 200 $\mu g/m^3$ (1-hour average) and the NAAQG for NO_2 is 100 $\mu g/m^3$ (24-hour average).

2.2.2 Particulate matter (PM_{10})

PM_{10} is that portion of particulate matter with an aerodynamic cross-section less than 10 micrometers. This fine particulate matter is small enough to enter the smaller more vulnerable passages of the respiratory system. The health effects associated with inhalation of fine particulate matter have been established from epidemiological studies overseas. The NES for PM_{10} is 50 $\mu g/m^3$ (24-hour average).

An interim ambient air quality guideline for $PM_{2.5}$ of 25 $\mu g/m^3$ (24-hour average) has been recommended. $PM_{2.5}$ is that portion of particulate matter

with an effective aerodynamic cross-section less than 2.5 micrometers. Recent medical research suggests that $PM_{2.5}$ may be a better indicator of potential adverse human health effects. By definition $PM_{2.5}$ is a subset of PM_{10}.

PM_{10} is associated with the following issues in the Wellington Region:

- Adverse human health effects
- Winter time "smog" events
- Reduction in atmospheric visibility (haze)
- Dust nuisance

Sources of PM_{10} include:

- Domestic fires
- Motor vehicles
- Industrial combustion processes
- Quarrying activities
- Natural sources such as sea salt and soil particles

Densely populated residential areas, solid fuel heating appliances, adverse meteorological conditions (temperature inversions), and the dispersion limiting effect of topography can all combine to produce high ambient concentrations of particulate matter.

The ambient air quality monitoring results for PM_{10} at the various sites within the Wellington Region have been assessed in this report using the NES of 50 $\mu g/m^3$.

2.2.3   Carbon monoxide (CO)

Carbon monoxide is principally a concern because of its potential to replace oxygen molecules in haemoglobin resulting in adverse health effects. CO is produced from the following sources:

- Domestic fires
- Industrial combustion sources
- Motor vehicles

Wellington's main shopping areas are along streets that suffer from traffic congestion. The combination of traffic emissions, complex topography (i.e. streets enclosed by tall buildings) and adverse meteorological conditions, such as evening inversions in the winter, can result in carbon monoxide concentrations rising to levels that may affect public health.

High carbon monoxide concentrations have also been measured in built up residential areas and, in this case, are usually the result of emissions from motor vehicles and/or domestic fires. The NES for CO is 10 mg/m^3 (8-hour average) and the NAAQG for CO is 30 mg/m^3 (1-hour average).

2.3   Ambient air quality guidelines

Regional Ambient Air Quality Guidelines are reproduced in Table 2.1. The Regional Guidelines are based on National Ambient Air Quality Guidelines (Ministry for the Environment 2002).

The National Guidelines and the Regional Maximum Acceptable Level (MAL) Guidelines are recommended only as minimum standards of air quality to protect public health. The guidelines were developed from World Health Organisation Standards and international epidemiological research. They are **not** maximum permissible concentrations of pollutants in air or limits that can be polluted 'up to' safely as the more sensitive members of the population to air pollution may experience adverse health effects below these levels.

The Maximum Desirable Level (MDL) is defined as the level that will provide maximum protection to the environment (including soil, water, flora, fauna, structures, and amenity values), taking into account existing air quality, community expectations, economic implications, and the purpose and principles of the Resource Management Act 1991. Desirable levels are appropriate guidelines or targets in rural or residential areas, and in other areas where good air quality is considered a priority.

The MDL's set in the Regional Ambient Air Quality Guidelines are based on Canadian and World Health Organisation Standards. These guidelines include a factor for the protection of sensitive flora and fauna (ecosystems) as well as human health.

The National Ambient Air Quality Guidelines include guidelines for a range of toxic organic compounds such as benzene and formaldehyde and heavy metals such as mercury and chromium. Some of these toxic pollutants may be of concern at certain locations in the Wellington Region and Greater Wellington will consider screening surveys of for these air pollutants in the future.

Table 2.1: Regional and national air quality guidelines

Indicator	Maximum Desirable Level (Regional)	Maximum Acceptable Level (Regional /National)	Averaging Times	Techniques for Measurement
Particulates PM$_{10}$		50 µg/m³	24 hours	AS3580.9.6-1990
	40 µg/m³	40 µg/m³	Annual	AS3580.9.7-1990
PM$_{2.5}$		25 µg/m³	24 hours	US 40 CFR Part50
Carbon Monoxide		30 mg/m³	1 hour	AS3580.7.1-1992
	6 mg/m³	10 mg/m³	8 hours	AS3580.7.1-1992
Lead		0.2 µg/m³	3 months	AS2800-1985
Nitrogen Dioxide	95 µg/m³	200 µg/m³	1 hour	AS3580.5.1-1995
	30 µg/m³	100 µg/m³	24 hours	
Fluoride	**Special Land Use**			
		1.8 µg/m³	12 hours	AS3580.1.13.1-1993
		1.5 µg/m³	24 hours	AS3580.13.2-1991
		0.8 µg/m³	7 days	
		0.4 µg/m³	30 days	
		0.25 µg/m³	90 days	
	General Land Use			
	1.8 µg/m³	3.7 µg/m³	12 hours	AS3580.13.1-1993
	1.5 µg/m³	2.9 µg/m³	24 hours	AS3580.13.2-1991
	0.8 µg/m³	1.7 µg/m³	7 days	
	0.4 µg/m³	0.84 µg/m³	30 days	
	0.25 µg/m³	0.5 µg/m³	90 days	
	Conservation Areas			
		0.1 µg/m³	90 days	
Hydrogen Sulphide	1 µg/m³	7 µg/m³	30 minutes	AS3580.8.1-1990
Ozone	100 µg/m³	150 µg/m³	1 hour	AS3580.5.1-1993
		100 µg/m³	8 hours	
Sulphur Dioxide		350 µg/m³	1 hour	AS3580.8.1-1990
		120 µg/m³	24 hours	

µg - micrograms
mg - milligrams
AS - Australian Standard

A useful method to illustrate the significance of ambient air quality monitoring results is to depict the percentage of time that the monitoring results fall into certain categories. This method is described by the Ministry for the Environment in the discussion document on Environmental Performance Indicators (Ministry for the Environment, October 1997). Table 2.2 provides a description of these categories.

Table 2.2: Air quality categories

Category	Maximum Measured Value	Comment
Action	Exceeds Guideline	Completely unacceptable by national and international standards.
Alert	Between 66% and 100% of the guideline	A warning level which can lead to guidelines being exceeded if trends are not curbed.
Acceptable	Between 33% and 66% of the guideline	A broad category, where maximum values might be of concern in some sensitive locations, but are generally at a level that does not warrant dramatic action.
Good	Between 10% and 33% of the guideline	Peak measurements in this range are unlikely to affect air quality.
Excellent	Less than 10% of the guideline	Of little concern.

The main intention of the air quality categories is to present the results of ambient monitoring in a manner that assists in setting goals for air quality management. Greater Wellington has set the goal that "Air quality throughout the Region is always 'acceptable' (i.e. minimal health risk)" as part of its Long Term Council Community Plan.

2.4 National environmental standards for air quality

The Ministry for the Environment promulgated a series of National Environmental Standards, including standards for Air Quality. National environmental standards have the force of regulation. The standards are presented as a package consisting of:

- **ambient standards** for carbon monoxide (CO), particles (PM_{10}), nitrogen dioxide (NO_2), sulphur dioxide (SO_2) and ozone (O_3);
- **prohibitive standards**, which prohibit various activities that discharge unacceptable quantities of contaminants into the air;
- **an emission standard** for the design of small, domestic solid-fuel-burning appliances.

Agencies responsible for managing emissions to air under the Resource Management Act 1991 (RMA) will need to implement policies and rules to achieve the National Standards.

The NES for Air Quality are similar to the national guidelines, except that provision for an 'allowable' number of exceedences has been included. The implementation of National Standards will have implications for Greater Wellington. For example;

- all exceedences of the Standard will need to be publicly notified;
- Greater Wellington will need to develop strategies to improve air quality in areas that are in non-compliance with the Standard.

The ambient air quality monitoring results presented in the following sections have been compared to the NES, or where the relevant averaging period has not been included as an NES, the monitoring results are compared to National Ambient Air Quality Guidelines for the protection of human health and categorised using the air quality categories in Table 2.2.

3.   Air quality monitoring technical details

3.1   Mobile ambient air quality monitoring station

The mobile ambient air quality monitoring station is a small (1.8 x 1.8 x 2.4 m high) insulated and air-conditioned shed with a 6 metre meteorological mast and sampling ports. The air-conditioning is maintained at 23-24°C. Figure 3.1 is a photograph of the mobile monitoring station.

Figure 3.1: Mobile air quality monitoring station

3.2   Permanent monitoring stations

3.2.1   Birch Lane, Lower Hutt

Greater Wellington established its first permanent air quality monitoring station at Birch Lane in Lower Hutt. This monitoring station monitors background air quality in order to assess trends in air pollution levels and the exposure risks for the population of the Lower Hutt Valley. Figure 3.2 is a photo of the Birch Lane site.

Figure 3.2: Birch Lane air quality monitoring station

The Birch Lane monitoring station houses similar monitoring equipment to the mobile station and the instrumentation is included in the general description section 3.3. The only real difference is that the permanent station is a little larger and the meteorological mast is 10 metres instead of six. Additional parameters monitored are solar radiation (global) and rainfall.

3.2.2   Wairarapa College, Masterton

Greater Wellington established its second permanent air quality monitoring station at Wairarapa College in Masterton. This monitoring station monitors background air quality and meteorology in order to assess trends in air pollution levels and the exposure risks for the population of Masterton. An air quality screening survey undertaken in 1999-2000 indicated that Masterton was subject to high pollution episodes during the winter. Figure 3.3 is a photo of the Wairarapa College site.

Figure 3.3: Wairarapa College air quality monitoring station

Air pollutants monitored include CO, NOx, and particulate matter. The monitoring station is adjacent to a 15 metre meteorological mast; parameters monitored include wind speed, wind direction, temperature, solar radiation, relative humidity, soil moisture and temperature, and rainfall.

3.2.3 Corner of Vivian and Victoria Streets, Central Wellington

In February 2004, a new permanent site was established at the corner of Vivian and Victoria Streets in Central Wellington. The monitoring site is primarily aimed at monitoring the effects of motor vehicle emissions on local air quality in the area. Figure 3.4 is a photo of the monitoring station.

Air pollutants monitored include CO and PM_{10} with NOx, monitoring to be added in early 2005. temperature, relative humidity, wind speed and direction are also monitored at the site.

Figure 3.4: Central Wellington air quality monitoring station

3.3   Monitoring instruments

3.3.1   Nitrogen oxides (NOx)

Nitrogen oxides are continuously monitored using NOx Chemiluminescence Analysers. The instruments have an internal zero air scrubber for zero checks and a NO_2 permeation tube (supplying *ca*. 500 ppb NO_2) for span checks. The sample inlet for the instrument is approximately 3 m above ground level in a rain protected outlet. All NOx data is recorded as parts per billion (ppb).

Only the monitoring results for NO_2 have been assessed in this document, as NO_2 is included in the ambient air quality guidelines. NO is slowly converted to NO_2 in the atmosphere by oxidative processes.

3.3.2   Particulate matter (PM_{10})

PM_{10} is continuously monitored with a Rupprecht & Patashnick Co. Ltd. TEOM Series 1400AB Ambient Particulate Monitor or a ThermoElectron Corp FH62 C14 Beta Attenuation Monitor.

The TEOM cap, case and air temperatures were set at 40 ^{O}C in line with national ambient air quality monitoring protocols. The TEOM PM_{10} size selective inlet was 3 m above ground level. The instrument is set to record

particulate matter concentrations as μg/m^3 at 0°C and 1 atmosphere pressure. As recommended in the *Good Practice Guide for Air Quality Monitoring and Data Management* (MfE 2000) a high volume sampler has been collocated at the Masterton site since April 2003 in order to provide a baseline comparison.

3.3.3 Carbon monoxide (CO)

Carbon monoxide is continuously monitored using a CO Gas Filter Correlation Infrared Analysers. The instrument has an internal zero air scrubber with a zero air supply for zero checks and a span gas for span checks. Span gas (40 ppm CO) is supplied using BOC Gases Limited β–Grade CO gas. The sample inlets for the instrument are approximately 3 m above ground level alongside the NOx inlet. All CO data is recorded as parts per million (ppm).

3.3.4 Meteorological parameters

A 6 m meteorological mast is attached to the mobile monitoring station and the Birch Lane station has an associated 10 m mast, while the new Masterton station has a 15 m mast. Various meteorological parameters are monitored continuously. Wind speed, wind direction, relative humidity and temperature are all monitored at mast top. Temperature is also monitored at 1.5 m for atmospheric stability assessments. North or 0° for the wind direction indicator is aligned with true north.

3.3.5 Data acquisition

The CO, NOx and PM$_{10}$ instruments were connected by a digital interface to an Iquest DS 4483 DOLogger dataloggers. All logged data was stored as 10 minute averages. Data was downloaded to a central archive four times a day via a radio modem or GPRS system.

3.3.6 Quality assurance

Greater Wellington's Resource Information Section, which collects, checks and archives all the air quality data, is an ISO 9002 registered supplier. The methodologies used for collecting and archiving data, as well as the maintenance schedules and record sheets are all documented, as part of the ISO 9002 registered quality system. The air quality monitoring methods used by the Regional Council are either Australian Standard methods or (in the case of the TEOM and Beta-Gauge) United States EPA equivalent methods. All maintenance and instrument inspections are carried out as per manufacturers' instructions and recommendations and/or to the appropriate Australian Standard.

All incoming data for the air quality monitoring stations was inspected on a daily basis to ensure that the monitoring instruments were operating within expected parameters. The monitoring stations were visited at least once a week in order to carry out a diagnostics check on all instruments. Site visits and any operations carried out on the monitoring instruments were recorded in a carbon-copy site log book, which are kept at the monitoring stations at all times.

Multipoint calibrations were performed monthly out on the CO and NOx instruments.

The data used in this report has been corrected for zero drift of more than ±2% for CO and NOx. For the purposes of analysis in this report, ppm CO has been converted to mg/m^3 at 0^oC and 101.3 kPa pressure (i.e. $mg/m^3 = 1.25$ x ppm). NO_2 has been converted from ppb to $\mu g/m^3$ at $0\ ^oC$ and 101.3 kPa pressure (i.e. $\mu g/m^3 = 2.05$ x ppb). All data manipulation and analyses in this report has been performed using Hilltop, a software package designed to store and provide analyses of time dependent data.

3.4 PM_{10} high volume sampler

The high volume particulate sampling utilises a gravimetric method for monitoring PM_{10}. The instrument itself is a Lear Siegler Australasia Pty Limited Flow-Set High Volume Air Sampler. Ambient air is passed through a size selective inlet and then through a pre-weighed conditioned filter that is removed after 24 hours continuous sampling, conditioned and then reweighed. The results are expressed as the 24-hour average for that time period.

This ambient air quality monitoring method is an Australian and USEPA Standard method and the high volume sampler is operated accordingly. Two instruments are currently operated on a one-day-in-three 12:00 pm to 12:00 pm sampling basis. One high volume sampler has been located at Wainuiomata Bowling Club since September 2000 and the other has been co-located alongside the monitoring station at Wairarapa College, Masterton. Figure 3.5 shows the high-volume sampler at Wainuiomata Bowling Club.

Figure 3.5: High volume sampler at Wainuiomata Bowling Club

3.4.1   Quality assurance

The high volume samplers were calibrated on a two-monthly basis using an Orifice Calibration Plate as per AS 3580.9.6-1990. The calibrations showed <3% drift in the flow rates.

4. Monitoring results

4.1 Trentham Fire Station, Upper Hutt

4.1.1 Site description

The monitoring station was located within the grounds of Trentham Fire Station, off Fergusson Road in Upper Hutt (Grid Reference E2681464; N6006446, elevation 40m). Figure 4.1 shows a map of the area and Figure 4.2 details the site layout.
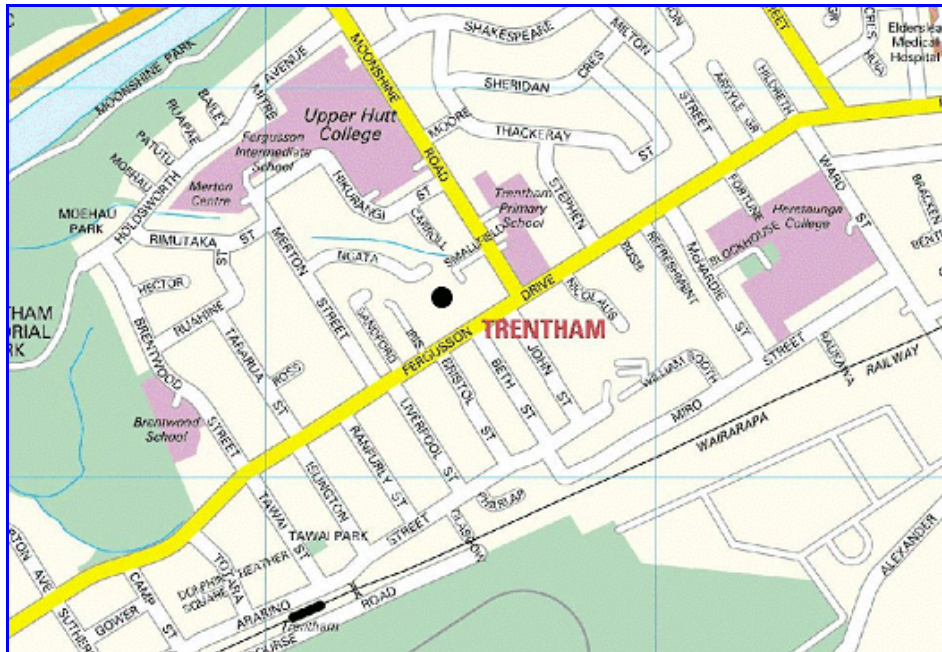

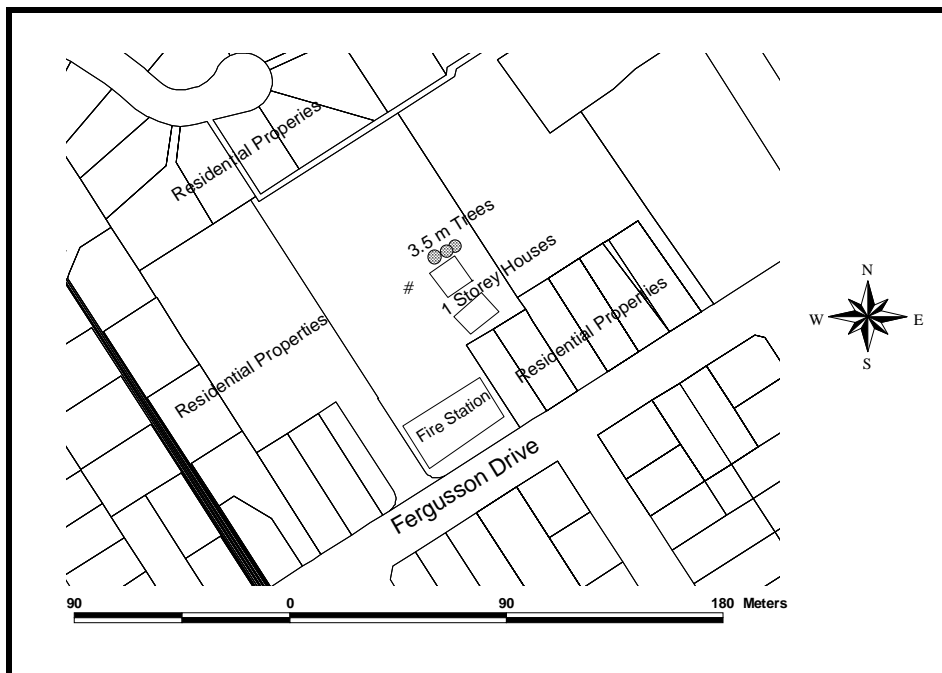Figure 4.1: Map showing location of monitoring site (●)

Figure 4.2: Monitoring site (●) layout at Trentham Fire Station, Upper Hutt

The northern side of the monitoring station was up against a 2m fence and beyond that, approximately 20 m away, were two one-storey residential houses. 70m to the east was the one-storey high Trentham Fire Station. To the west were open fields and beyond that were residential properties. To the south of the monitoring station (30 metres) was a practice tower for fire drills and then beyond that were residential properties.

The land around the site at Trentham Fire Station was flat and surrounded by open space or residential buildings no more than 2 storeys high. The nearest large structure to the monitoring station was the practice tower, which was also two storeys high.

The Trentham Fire Station site is approximately 3 kilometres southwest from the central business district of Upper Hutt City. Upper Hutt City is located in the Hutt Valley, 30km northeast of Central Wellington and has a population of about 37,000. Land use in the area is predominantly residential with some light industrial activities.

The main urban area lies in a valley basin surrounded by hills up to 500 metres high. The Hutt River flows in through the top end of Upper Hutt and out through Taita Gorge which forms a natural topographical constriction at the southern end of the Upper Hutt basin. At times the atmospheric dispersion of pollutants discharged from various activities in Upper Hutt is severely limited and can lead to a build up of pollutants. Figure 4.3 is an aerial view of Upper Hutt City with the hills and farmland on either side of the river valley.

Figure 4.3: Aerial view of Upper Hutt urban area and monitoring site (●)

The predominant wind directions are from the northerly and southerly quarters as shown by the wind roses in Appendix 1.

4.1.2   Nitrogen dioxide (NO$_2$)

Table 4.1 contains summary statistics of nitrogen dioxide concentrations for the monitoring period. The National Environmental Standard (NES) or the National Ambient Air Quality Guideline (NAAQG) where an NES has not been set is also indicated.

Table 4.1: Summary statistics for NO$_2$ at Trentham Fire Station, Upper Hutt

Parameter	NO$_2$ (g/m^3)							
Averaging Time	1 Hour (NES=200)				24 Hour (NAAQG=100)			
Year	2001	2002	2003	2004	2001	2002	2003	2004
Maximum	106	59	60	117	46	29	29	27
99.9 Percentile	78	57	54	58	42	28	28	25
99.5 Percentile	61	47	48	43	39	26	25	23
75 Percentile	16	12	12	12	15	13	12	13
Mean (annual)	11	8.7	8.6	8.8	11	8.7	8.3	9.1
Median	7.0	4.9	4.5	5.8	8.7	7.4	7.4	7.9
25 Percentile	2.7	1.7	1.4	2.7	4.7	3.9	3.3	4.1

1-hour moving average

Figure 4.4 is a graph of the 1-hour moving average of NO$_2$ concentrations at Trentham Fire Station for the monitoring period. The NES of 200 $\mu g/m^3$ for NO$_2$ is also shown.

Upper Hutt AQ <Nitrogen Dioxide (ppb)>*2.05 from 20-May-2000 00:00:00 to 01-Jan-2005 00:00:00 - 1 Hour Moving Average
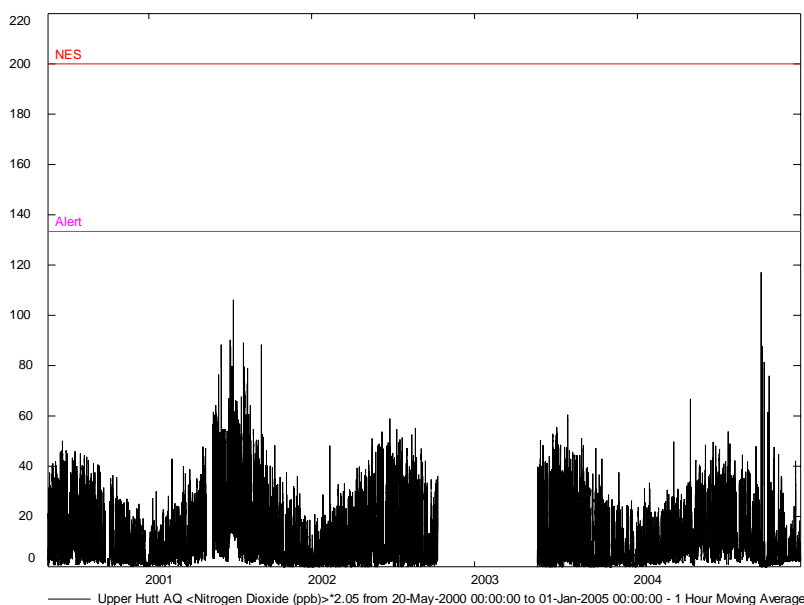
Figure 4.4: 1-hour moving average NO$_2$ ($\mu g/m^3$) at Trentham Fire Station, Upper Hutt

24-hour moving average

Figure 4.5 is a graph of the 24-hour moving average of NO_2 concentrations at Trentham Fire Station for the monitoring period. The graph also indicates the NAAQG of 100 $\mu g/m^3$.
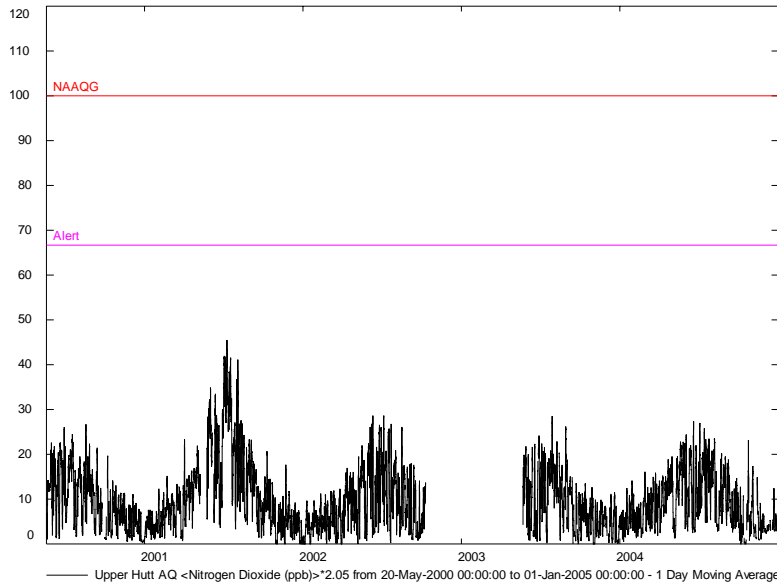

Figure 4.5: 24-hour moving average NO_2 ($\mu g/m^3$) at Trentham Fire Station, Upper Hutt

Analysis of NO_2 monitoring results

There were no exceedences of the NO_2 1-hour NES of 200 $\mu g/m^3$ or the 24-hour NAAQG of 100 $\mu g/m^3$ during the monitoring period. Winter time is when the highest levels of NO_2 were recorded.

Data from the Wellington Regional Emissions Inventory indicates that motor vehicles are the major contributor to NO_2 emissions on a typical winter's day. Figure 4.6 provides a comparison of the NO_2 monitoring results with the relative ambient air quality guidelines using the categories described in Table 2.2.
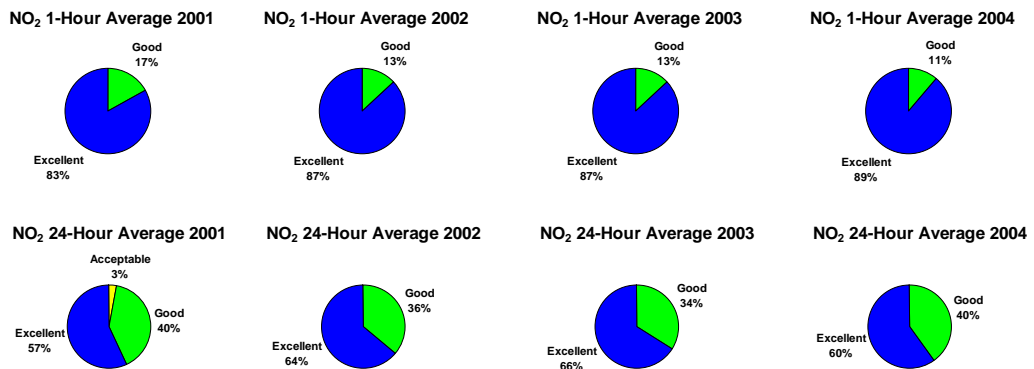

Figure 4.6: NO_2 monitoring results at Trentham Fire Station, Upper Hutt compared to air quality categories

Figure 4.6 indicates that the NO_2 monitoring results at Trentham Fire Station compare favourably with both the NES and NAAQG.

4.1.3 Particulate matter (PM_{10})

Table 4.2 contains summary statistics of PM_{10} concentrations for the monitoring period. The National Environmental Standard (NES) is also indicated.

Table 4.2: Summary statistics for PM_{10} at Trentham Fire Station, Upper Hutt

Parameter	PM_{10} ($\mu g/m^3$)			
Averaging Time	24 Hour (NES=50)			
Year	2001	2002	2003	2004
Maximum	61	55	39	49
99.9 Percentile	50	46	34	44
99.5 Percentile	49	39	33	34
75 Percentile	16	17	17	16
Mean (annual)	14	15	15	12
Median	12	14	14	11
25 Percentile	9.4	11	11	6.1

24-hour moving average

Figure 4.7 is a graph of the 24-hour moving average of PM_{10} concentrations at Trentham Fire Station for the monitoring period. The graph also indicates the 24-hour NES of 50 $\mu g/m^3$.
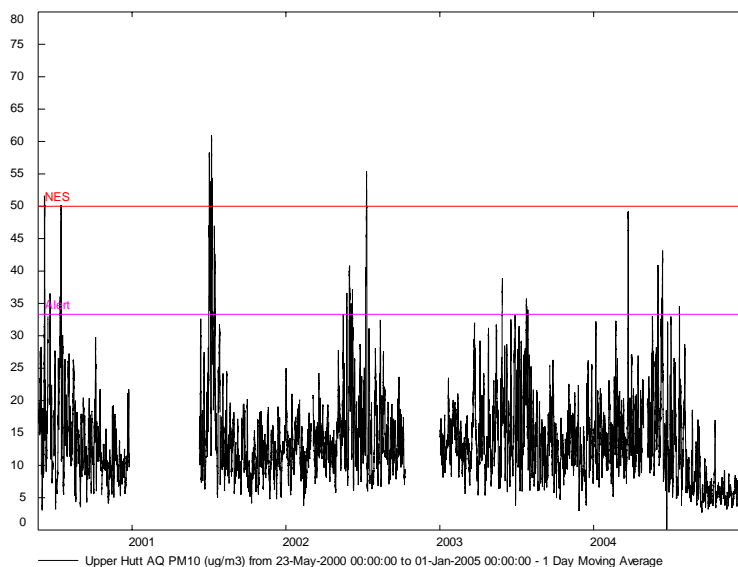

Figure 4.7: 24-hour moving average PM_{10} ($\mu g/m^3$) at Trentham Fire Station, Upper Hutt

Analysis of PM$_{10}$ monitoring results

The highest 24-hour moving average concentrations for PM$_{10}$ at Upper Hutt were recorded in June and July 2001 during extended periods of cold frosty weather. The peak PM$_{10}$ levels during the winters of 2003 and 2004 were lower than those recorded for the previous winters and there were no exceedences of the NES. This is most likely due to milder weather for the winters of 2003 and 2004.

Figure 4.8 shows the monitoring results compared with the relevant ambient air quality guidelines using the air quality categories described in Table 2.2. The NES for PM$_{10}$ (50 µg/m^3) was not exceeded during the past year.
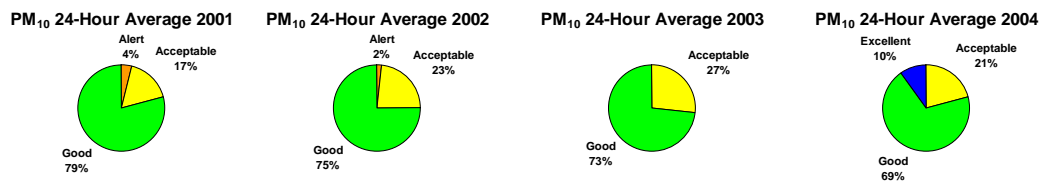

Figure 4.8: PM$_{10}$ monitoring results at Upper Hutt compared to air quality categories

Monitoring and research work on fine particulate matter at Upper Hutt has shown that during PM$_{10}$ pollution episodes, smoke emissions from domestic solid fuel heating appliances are the main contributor to ambient concentrations. Appendix 5 provides an in-depth analysis of elemental composition and source apportionment for particulate matter at Upper Hutt.

4.1.4 Carbon monoxide (CO)

Table 4.3 contains summary statistics of carbon monoxide concentrations for the monitoring period. The National Environmental Standard (NES) or the National Ambient Air Quality Guideline (NAAQG) where an NES has not been set is also indicated.

Table 4.3: Summary statistics for CO at Trentham Fire Station, Upper Hutt

Parameter	CO (mg/m³)							
Averaging Time	1 Hour (NAAQG=30)				8 Hour (NES=10)			
Year	2001	2002	2003	2004	2001	2002	2003	2004
Maximum	7.0	8.0	5.7	6.0	3.9	4.1	2.7	3.4
99.9 Percentile	5.3	4.6	4.6	4.6	3.3	2.8	2.1	2.4
99.5 Percentile	3.8	3.6	3.0	3.1	2.7	2.7	1.9	2.0
75 Percentile	0.38	0.38	0.31	0.21	0.44	0.39	0.37	0.24
Mean (annual)	0.35	0.32	0.21	0.25	0.35	0.34	0.20	0.25
Median	0.16	0.15	0.08	0.05	0.19	0.19	0.12	0.07
25 Percentile	0.01	0.04	0.01	0.01	0.03	0.07	0.01	0.01

1-hour moving average

Figure 4.9 is a graph of the 1-hour moving average of CO concentrations at Trentham Fire Station for the monitoring period. The 1-hour NAAQG of 30 mg/m^3 for CO is also shown.
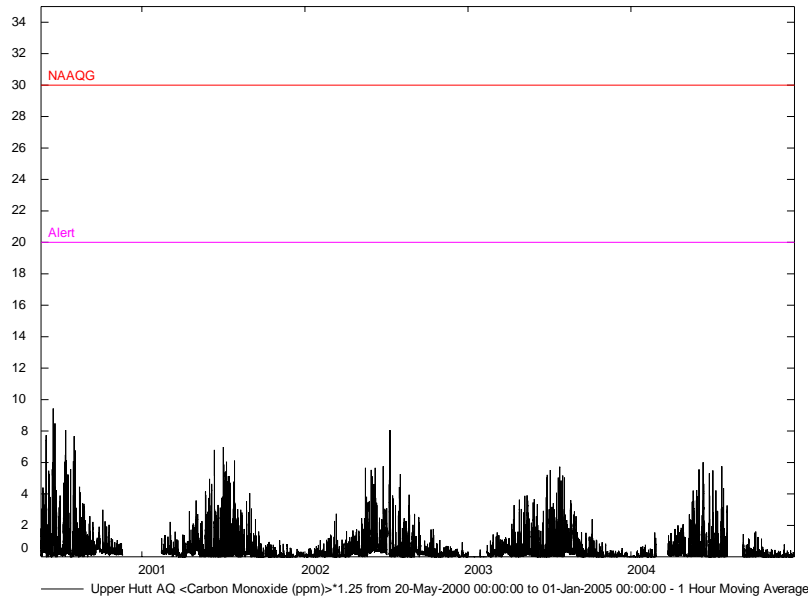

Figure 4.9: 1-hour moving average CO (mg/m³) at Trentham Fire Station from 1/10/03 to 1/10/04

8-Hour moving average

Figure 4.10 is a graph of the 8-hour moving average of CO concentrations at Trentham Fire Station for the monitoring period. The graph also indicates the 8-hour NES of 10 mg/m^3.
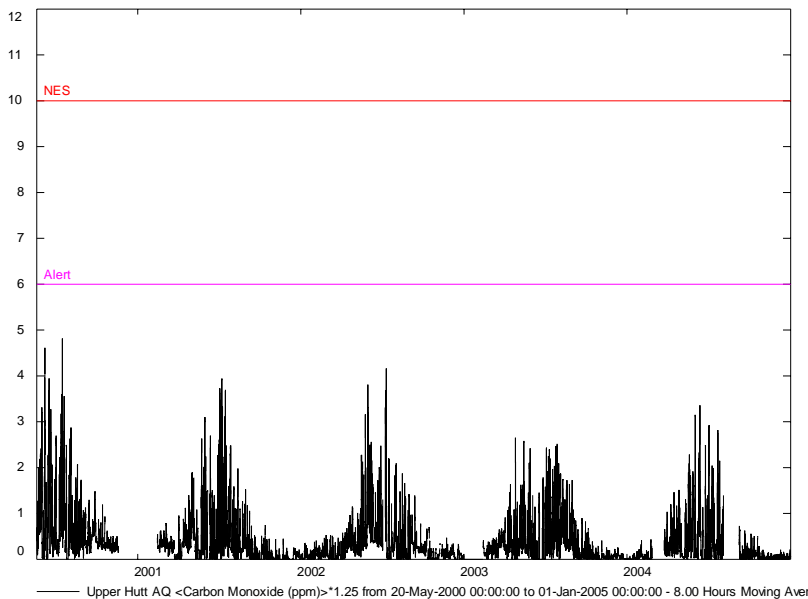

Figure 4.10: 8-hour moving average CO (mg/m³) at Trentham Fire Station from 1/10/03 to 1/10/04

Analysis of CO monitoring results

There were no exceedences of either the NES or the NAAQG during the monitoring period. The peaks in CO are likely to be due to a combination of motor vehicle exhaust emissions and emissions from domestic solid fuel heating appliances.

Figure 4.11 illustrates the comparison of the monitoring results with the relative ambient air quality guidelines using the air quality categories described in Table 2.2.

CO 1-Hour Average 2001	CO 1-Hour Average 2002	CO 1-Hour Average 2003	CO 1-Hour Average 2004
Good 1%	Good 1%		
Excellent 99%	Excellent 99%	Excellent 100%	Excellent 100%

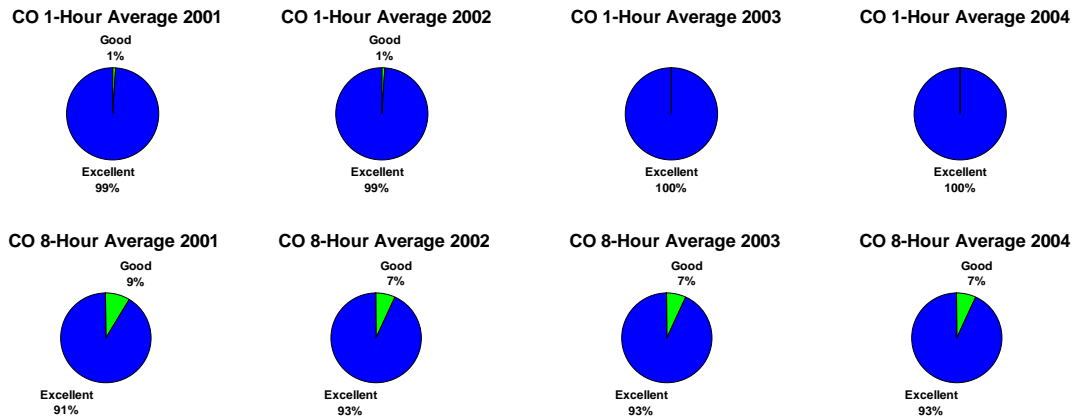| CO 8-Hour Average 2001	CO 8-Hour Average 2002	CO 8-Hour Average 2003	CO 8-Hour Average 2004
Good 9%	Good 7%	Good 7%	Good 7%
Excellent 91%	Excellent 93%	Excellent 93%	Excellent 93%

Figure 4.11: CO monitoring results compared to air quality categories

Overall, the levels of CO recorded during the monitoring period were not at concentrations that could be considered a concern to human health based on the current standards and guidelines. CO concentrations showed a variation similar to NO_2 and PM_{10} with higher levels being recorded during the winter months.

4.2   Birch Lane, Lower Hutt

4.2.1   Site description

The Birch Lane Air Quality Monitoring Station is located within the grounds of Phil Evans Reserve, off Birch Lane in Lower Hutt (Grid Reference E2671059; N5997570, elevation 15m). Figure 4.12 shows a map of the area and Figure 4.13 details the site layout.
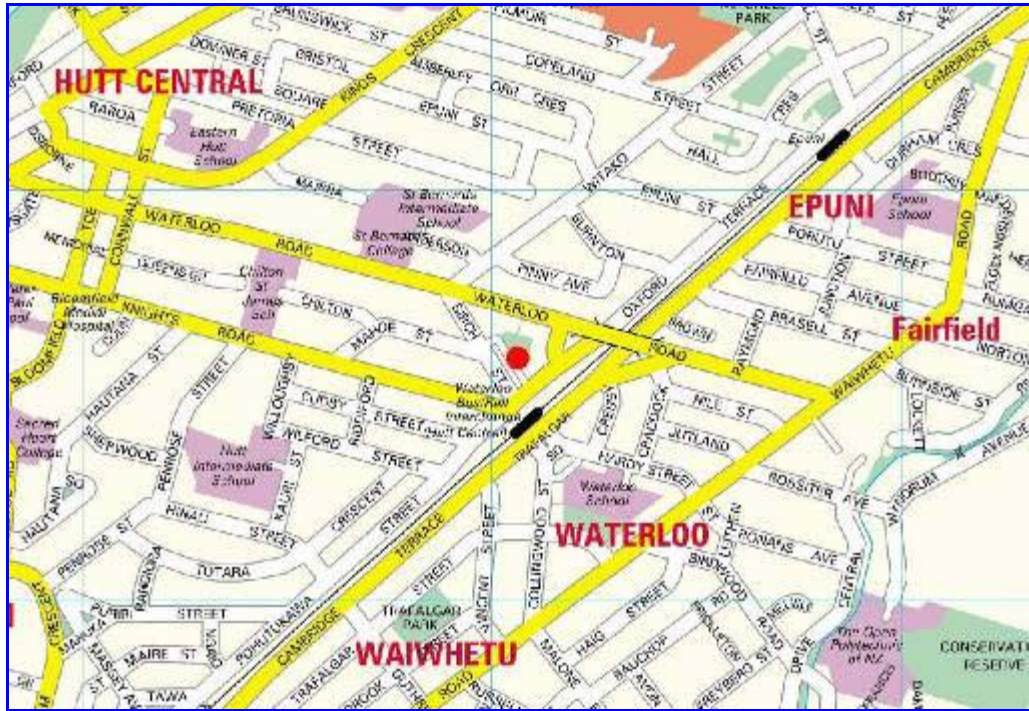
Figure 4.12: Map showing location of monitoring site (●)

The western side of the monitoring station is up against a one-storey building that serves as clubrooms for the local Scout Group. To the east, approximately 60m away, are a number of one-storey residential houses. 30m to the south are some one- and two-storey commercial buildings. To the north is an open grassed area that forms part of Phil Evans Reserve and beyond that are residential properties.

The land around the site at Birch Lane is flat and surrounded by open space or residential buildings. The nearest large structures to the monitoring station are some commercial buildings 50m to the south, these are up to two storeys high.
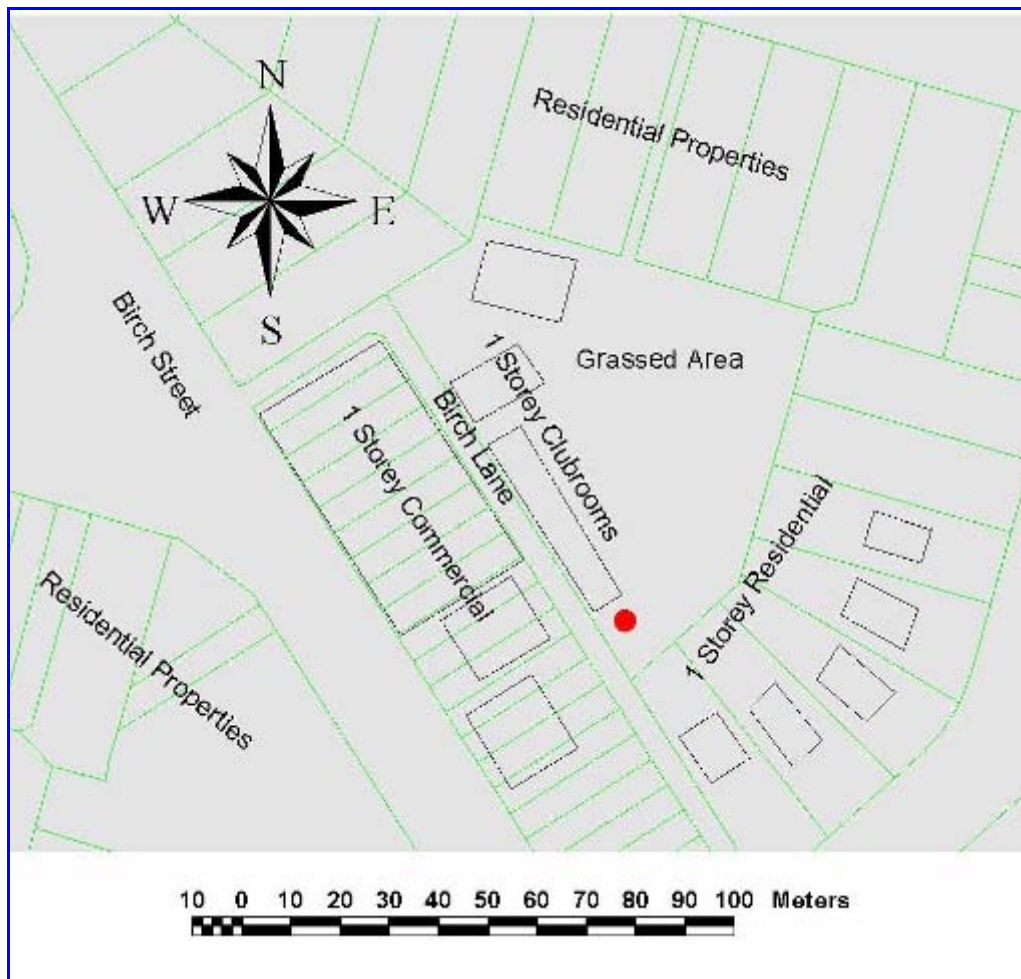
Figure 4.13: Monitoring site (●) layout at Birch Lane, Lower Hutt

The Birch Lane site is approximately 1 kilometre east of the central business district of Lower Hutt City. Lower Hutt City has a population of about 100,000 and is located in lower reaches of the Hutt Valley 15km northeast of central Wellington. Land use in the area is predominantly residential with some light industrial activities. Three kilometres to the south of the central business district is the industrial area of Seaview where a number of light to medium scale industrial activities operate.

The main urban area of Hutt City lies in a valley basin with hills up to 500 metres high on either side. The Hutt River runs through the middle of Lower Hutt and discharges into Wellington Harbour. The Hutt Valley is about 5km wide where it meets Wellington Harbour.

Figure 4.14 shows an aerial view of the Lower Hutt Valley and the Hutt City urban area.
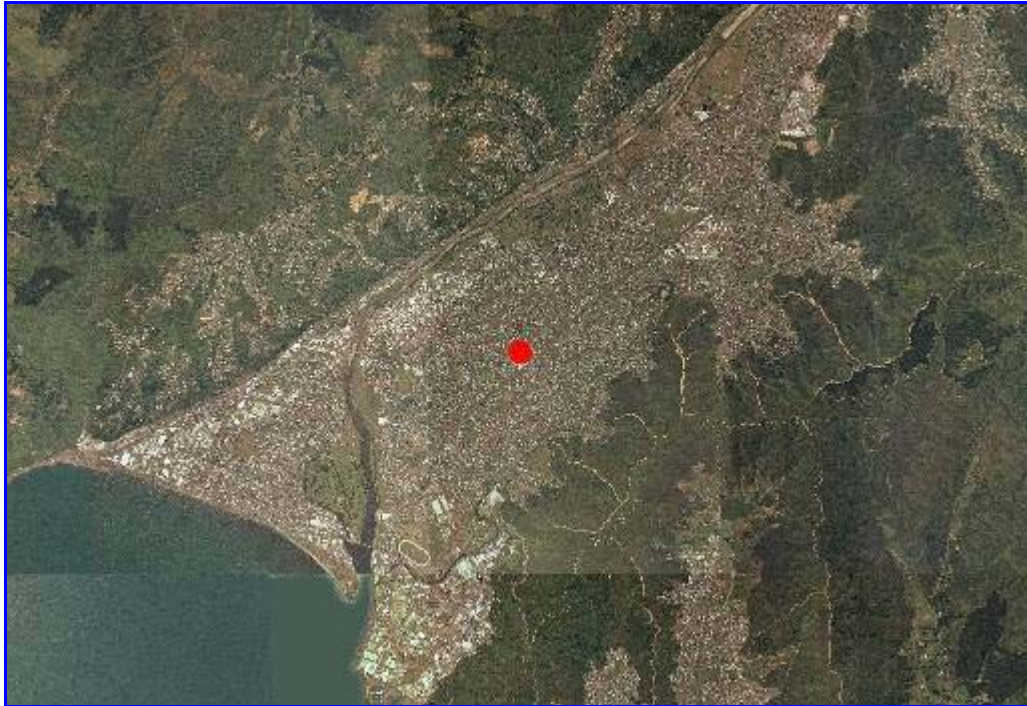
Figure 4.14: Aerial photograph of Hutt City urban area and monitoring site (●)

The predominant wind directions at Lower Hutt are from the northerly and southerly quarters as shown by the wind rose in Appendix 2.

4.2.2   Nitrogen dioxide (NO$_2$)

Table 4.4 contains summary statistics of nitrogen dioxide concentrations for the monitoring period. Also shown is the NES or NAAQG where an NES has not been set.

Table 4.4: Summary statistics for NO$_2$ at Birch Lane, Lower Hutt

Parameter	NO$_2$ (µg/m³)					
Averaging Time	**1 Hour (NES=200)**			**24 Hour (NAAQG=100)**		
Year	2002	2003	2004	2002	2003	2004
Maximum	69	85	91	35	40	36
99.9 Percentile	62	71	63	32	37	31
99.5 Percentile	51	63	54	27	36	30
75 Percentile	14	18	14	15	19	15
Mean (annual)	11	13	11	11	13	11
Median	7.6	8.8	7.4	9.7	11	8.9
25 Percentile	4.4	4.1	4.0	6.4	6.0	5.5

1-hour moving average

Figure 4.15 is a graph of the 1-hour moving average of NO_2 concentrations at Birch Lane for the monitoring period. Also shown is the 1-hour NES of 200 $\mu g/m^3$ for NO_2.
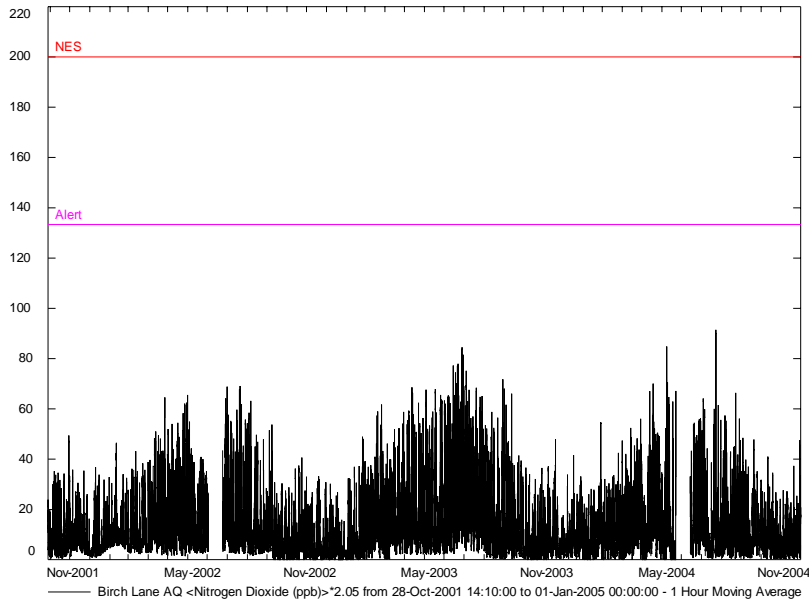

Figure 4.15: 1-hour moving average NO_2 ($\mu g/m^3$) at Birch Lane

24-hour moving average

Figure 4.16 is a graph of the 24-hour moving average of NO_2 concentrations at Birch Lane for the monitoring period. The graph also indicates the 24-hour NAAQG of 100 $\mu g/m^3$.
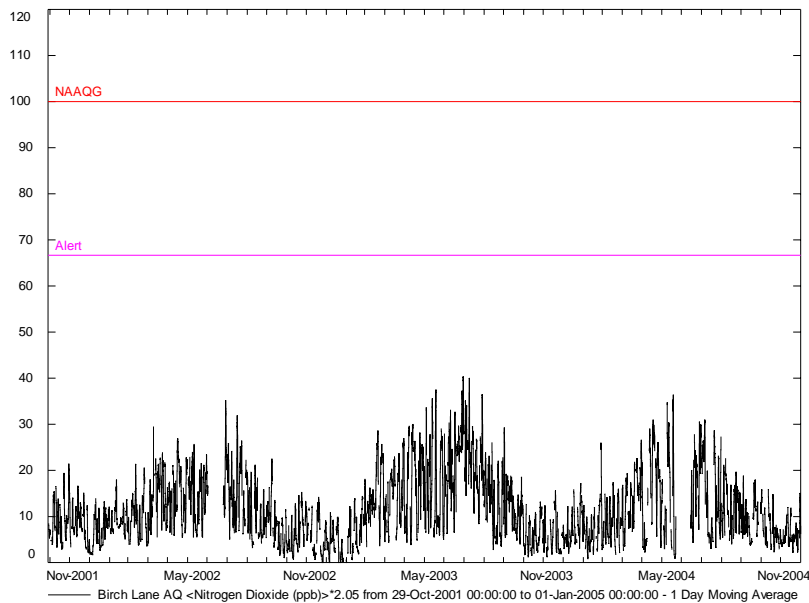

Figure 4.16: 24-hour moving average NO_2 ($\mu g/m^3$) at Birch Lane, Lower Hutt

Analysis of NO2 monitoring results

Data from the Wellington Regional Emissions Inventory indicates that motor vehicles are the major contributor to NO_2 emissions on a typical winter's day.

Figure 4.17 provides a comparison of the monitoring results with the relative ambient air quality guidelines using the categories described in Table 2.2.
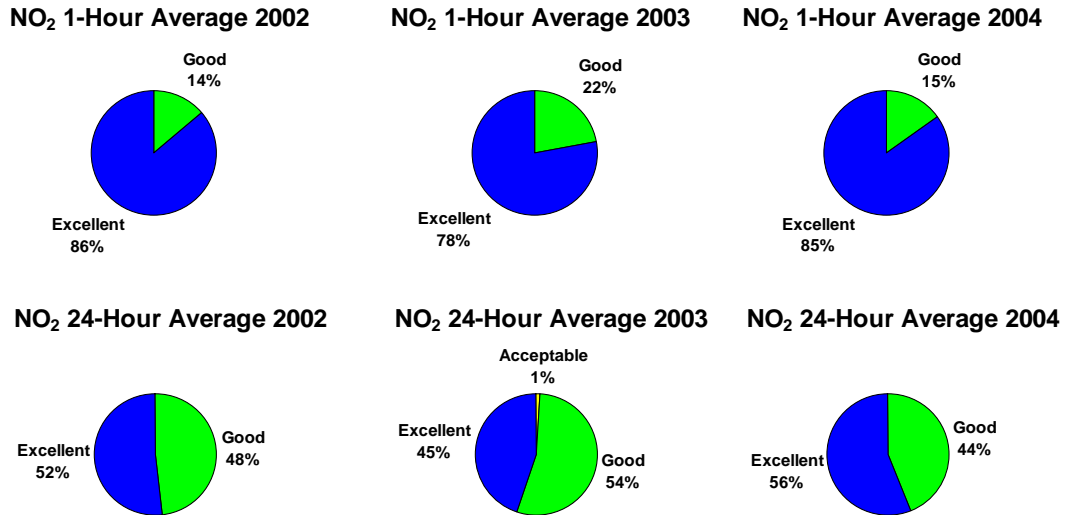
NO₂ 1-Hour Average 2002

Good
14%

Excellent
86%

NO₂ 1-Hour Average 2003

Good
22%

Excellent
78%

NO₂ 1-Hour Average 2004

Good
15%

Excellent
85%

NO₂ 24-Hour Average 2002

Excellent
52%

Good
48%

NO₂ 24-Hour Average 2003

Acceptable
1%

Excellent
45%

Good
54%

NO₂ 24-Hour Average 2004

Excellent
56%

Good
44%

Figure 4.17: NO₂ monitoring results at Birch Lane, Lower Hutt compared to air quality categories

Figure 4.17 indicates that the NO_2 monitoring results at Birch Lane compare favourably with the National Ambient Air Quality Guidelines and the National Environmental Standards.

4.2.3 Particulate matter (PM₁₀)

Table 4.5 contains summary statistics of PM_{10} concentrations for the monitoring period. Also shown is the NES.

Table 4.5: Summary statistics for PM_{10} at Birch Lane, Lower Hutt

Parameter	PM_{10} ($\mu g/m^3$)		
Averaging Time	24 Hour (NES=50)		
Year	2002	2003	2004
Maximum	42	38	46
99.9 Percentile	37	33	42
99.5 Percentile	29	29	36
75 Percentile	17	17	18
Mean (annual)	14	14	15
Median	14	13	14
25 Percentile	11	11	12

24-hour moving average

Figure 4.18 is a graph of the 24-hour moving average of PM_{10} concentrations at Birch Lane for the monitoring period. The graph also indicates the 24-hour NES of 50 $\mu g/m^3$.
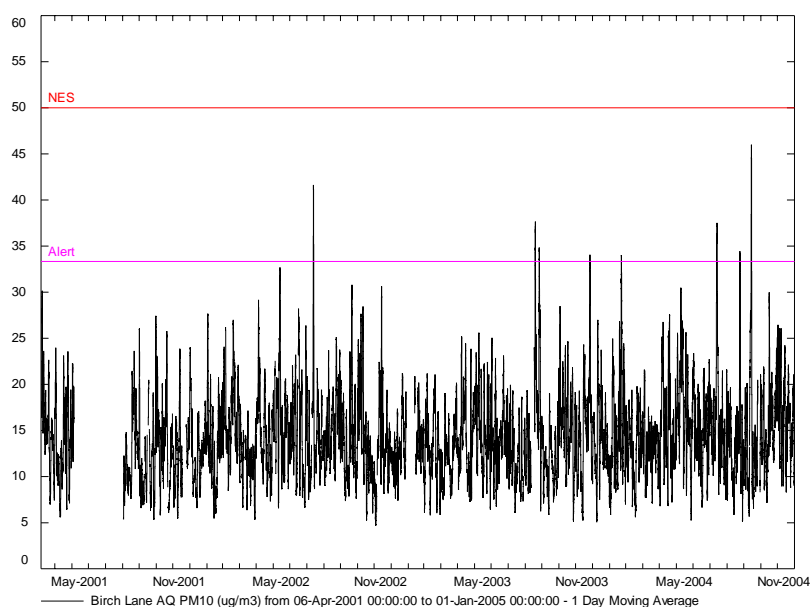

Figure 4.18: 24-hour moving average PM_{10} ($\mu g/m^3$) at Birch Lane, Lower Hutt

Analysis of the PM_{10} data would suggest that peak fine particulate matter concentrations at Lower Hutt are slightly elevated during the winter. Although no exceedences of the NES were recorded.
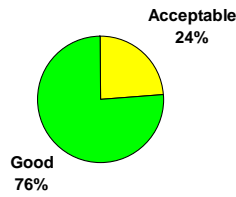
Analysis of PM_{10} monitoring results

Figure 4.19 shows of the monitoring results compared with the relevant ambient air quality guideline using the air quality categories described in Table 2.2, and with the NES for PM_{10} (50 $\mu g/m^3$).
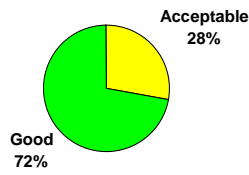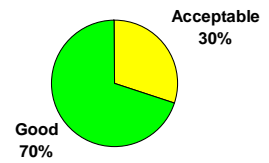
Figure 4.19: PM$_{10}$ Monitoring Results at Birch Lane, Lower Hutt Compared to Air Quality Categories

Research on the elemental composition and source apportionment of air particulate matter collected in Lower Hutt indicated that the major sources are likely to be motor vehicles, domestic fires (particularly during winter) and natural source such as seasalt and wind blown soil particles (dust). However, unlike Upper Hutt, smoke from domestic fires plays a less important role and this is borne out by the lack obvious difference between summer and winter peaks in PM$_{10}$ concentrations. Appendix 6 contains a more in-depth analysis of particulate matter composition and sources contributing to ambient concentrations in Lower Hutt.

4.2.4 Carbon Monoxide (CO)

Table 4.6 contains summary statistics of carbon monoxide concentrations for the monitoring period. Also shown is the NES or NAAQG where an NES has not been set.

Table 4.6: Summary statistics for CO at Birch Lane, Lower Hutt

Parameter	CO (mg/m³)					
Averaging Time	1 Hour (NAAQG=30)			8 Hour (NES=10)		
Year	2002	2003	2004	2002	2003	2004
Maximum	6.1	5.5	5.3	2.6	2.8	2.7
99.9 Percentile	3.6	3.8	3.9	2.0	2.7	2.5
99.5 Percentile	2.3	2.5	2.7	1.5	1.8	2.0
75 Percentile	0.14	0.33	0.25	0.17	0.35	0.28
Mean (annual)	0.08	0.20	0.20	0.08	0.20	0.20
Median	0.01	0.07	0.11	0.03	0.11	0.13
25 Percentile	0.01	0.01	0.01	0.01	0.01	0.02

1-Hour Moving Average

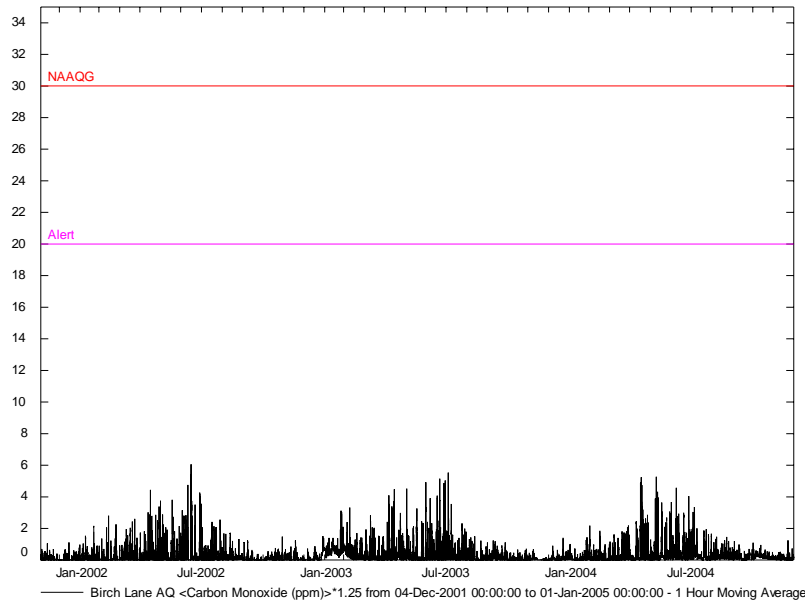Figure 4.20 is a graph of the 1-hour moving average of CO concentrations at Birch Lane for the monitoring period.

Figure 4.20: 1-hour moving average CO (mg/m³) at Birch Lane, Lower Hutt

8-hour moving average

Figure 4.21 is a graph of the 8-hour moving average of CO concentrations at Birch Lane for the monitoring period. The graph also indicates the 8-hour NES of 10 mg/m³.
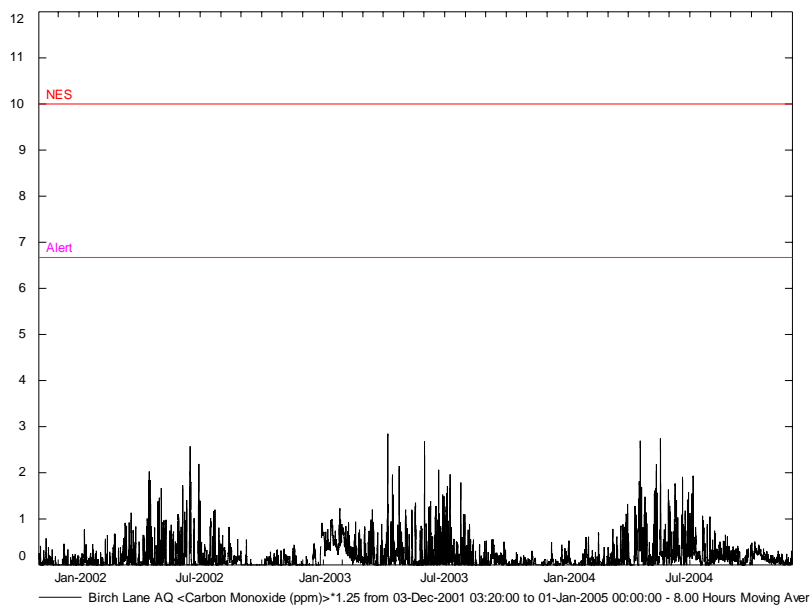

Figure 4.21: 8-hour moving average CO (mg/m³) at Birch Lane, Lower Hutt

Analysis of CO monitoring results

There were no exceedences of either the NAAQG or the NES during the monitoring period. Figure 4.22 illustrates the comparison of the monitoring results with the relative ambient air quality guidelines using the air quality categories described in Table 2.2.

CO 1-Hour Average 2002

Excellent
100%

CO 1-Hour Average 2003

Excellent
100%

CO 1-Hour Average 2004

Excellent
100%

CO 8-Hour Average 2002

Good
2%

Excellent
98%

CO 8-Hour Average 2003

Good
2%

Excellent
98%

CO 8-Hour Average 2004

Good
3%

Excellent
97%

Figure 4.22: CO monitoring results at Birch Lane, Lower Hutt compared to air quality categories

Overall, the levels of CO recorded during the monitoring period were not at concentrations that could be considered a concern to human health based on the NAAQG and the NES.

CO concentrations showed a variation similar to NO_2 with higher levels being recorded during the winter months.

4.3   Wainuiomata PM_{10} monitoring

4.3.1   Site description

A high volume sampler has been located at the Wainuiomata Bowling Club in Wainuiomata since 20 September 2000. (NZMS Grid Reference E2673668; N5991398, elevation 80m). The instrument is currently operating on a one-day-in-three sampling regime.

The sampler is located on a flat area of land at the Wainuiomata Bowling Club. Figures 4.23 and 4.24 show the site location and the site layout respectively.
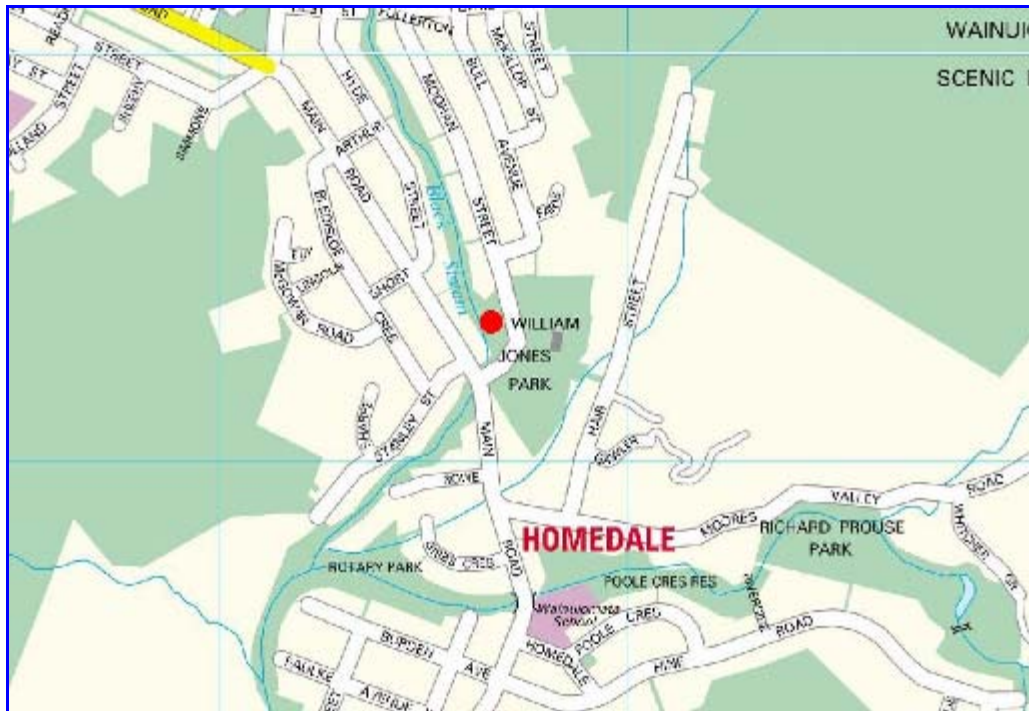
Figure 4.23: Location of Wainuiomata site (●)

The Wainuiomata Bowling Club site lies approximately 1km southeast of the main shopping centre. Wainuiomata has a population of about 16,500. The Wainuiomata valley is located east of the Hutt Valley and 20km northeast of central Wellington. The predominant land use around the site is residential with some adjacent recreational activities such as a swimming pool complex and rugby fields.

Wainuiomata lies in a basin shaped valley that has a narrow exit at the southern end through which the Wainuiomata River flows. The valley is surrounded by hills that are 300m high to the west, 600m high to the north and 800m high to the east. During the winter the valley is subject to frosts and meteorological inversion conditions. Many residential dwellings use solid fuel fires as a source of heating in the winter.
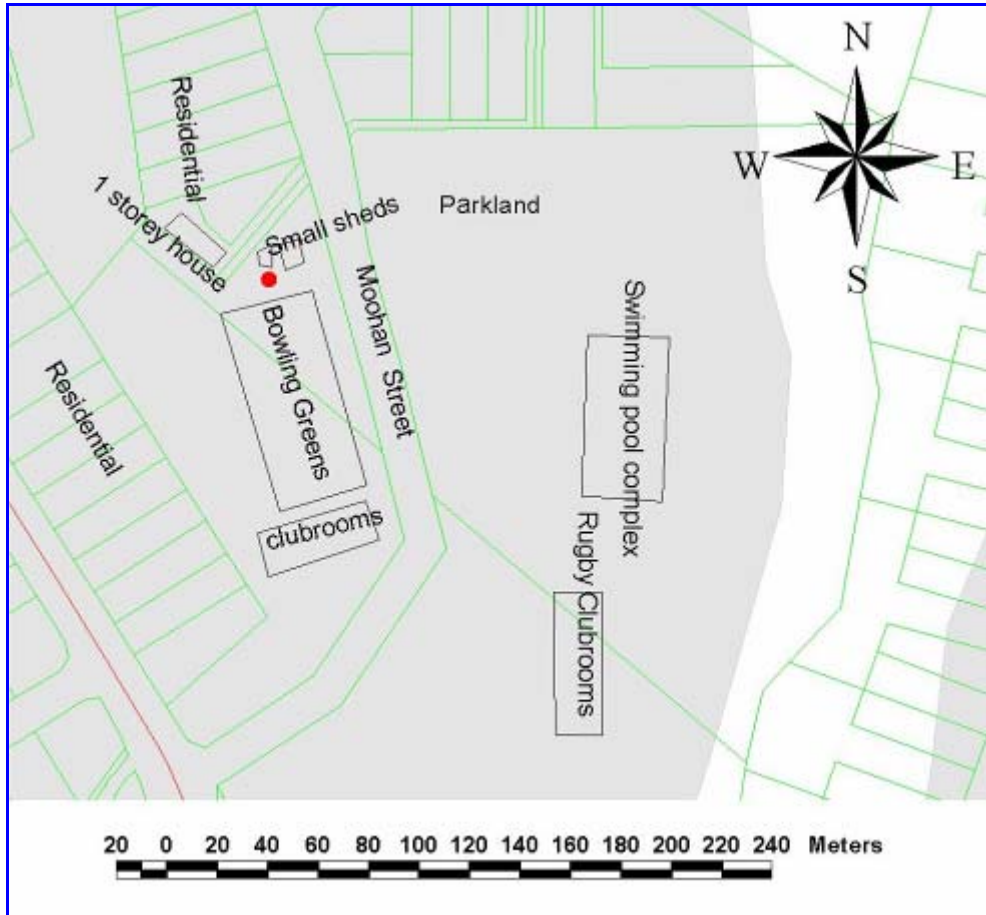
Figure 4.24: Site layout at Wainuiomata and hi-vol location (●)

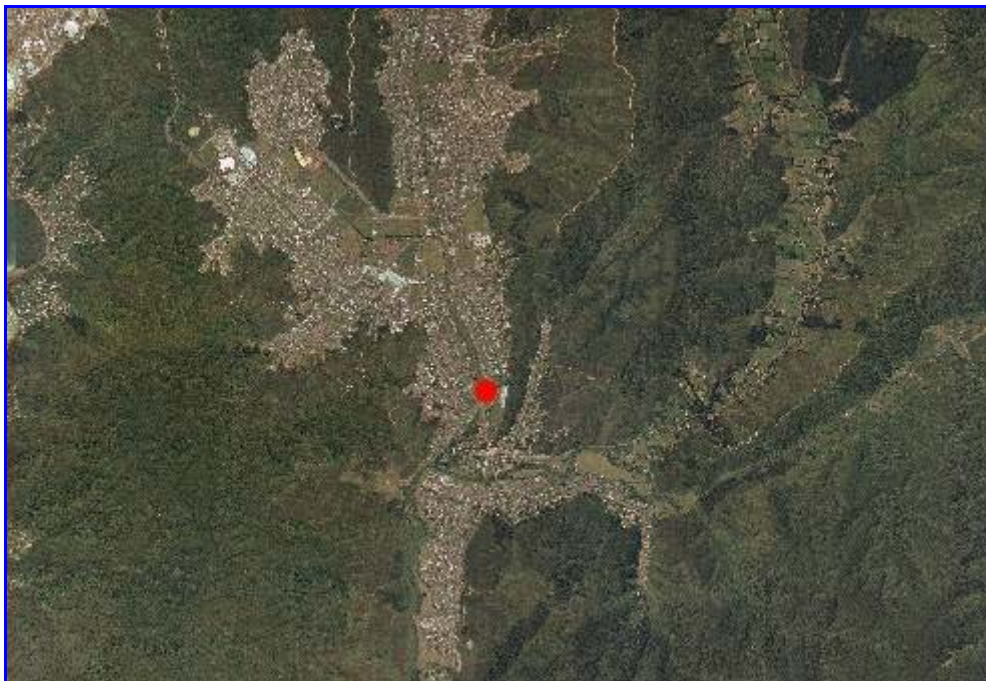Figure 4.28 is an aerial photograph of the Wainuiomata urban area and the monitoring site location.

Figure 4.25: Aerial photo of Wainuiomata Urban area showing site location (●)

Technical parameters and meteorology

The high volume sampler is a gravimetric method for monitoring PM_{10}. Ambient air is passed through a size selective inlet and then through a pre-weighed filter that is removed after 24 hours of continuous sampling of ambient air at 70 m^3/hr and then reweighed. The results are expressed as the 24 hour average for that time period. The 24-hour monitoring period used for this study was 12:00 to 12:00 the following day. The high volume sampler is an Australian and USEPA Standard method.

The nearest meteorological station was at Shandon Golf Club, Lower Hutt approximately 5 km west of this site. Wainuiomata is predominately affected by northerly and southerly winds. Wind direction at the sampling site would have been be similar to that experienced at Shandon Golf Club, however, wind speed and temperature would vary somewhat as the Wainuiomata Valley is decoupled from the Hutt Valley by a range of hills 300m high. Greater Wellington has now established (late 2004) meteorological monitoring (10 metre mast) at Wainuiomata Bowling Club in order to provide appropriate meteorological parameters for air pollution studies.

4.3.2 Monitoring results for PM_{10} at Wainuiomata

Table 4.7 contains summary statistics of PM_{10} concentrations for the monitoring period. Also shown is the NES.

Table 4.7: Statistical summary of PM_{10} monitoring data at Wainuiomata

Parameter	PM_{10} ($\mu g/m^3$)			
Averaging Time	24 Hour (NES=50)			
Year	2001	2002	2003	2004
Maximum	57	50	57	47
99.9 Percentile	56	49	56	46
99.5 Percentile	55	47	53	44
75 Percentile	13	11	12	11
Mean	13	11	11	11
Median	10	8.9	9.1	8.2
25 Percentile	7.0	6.6	6.4	6.2

The maximum 24-hour average PM_{10} concentration measured at Wainuiomata was 57 μg/m³ for the 24 hour period ending at 12:00 on 8 July 2001 and also on 26 July 2003. The higher PM_{10} concentrations occurred during periods of cold, calm weather in the winter. Similar to research findings in both Upper Hutt and Masterton, it is likely that the winter peaks in PM_{10} concentrations at Wainuiomata are due to the use of solid fuel fires for domestic heating.

Figure 4.26 shows the discrete results for each 24 hour period monitored by the high volume sampler.
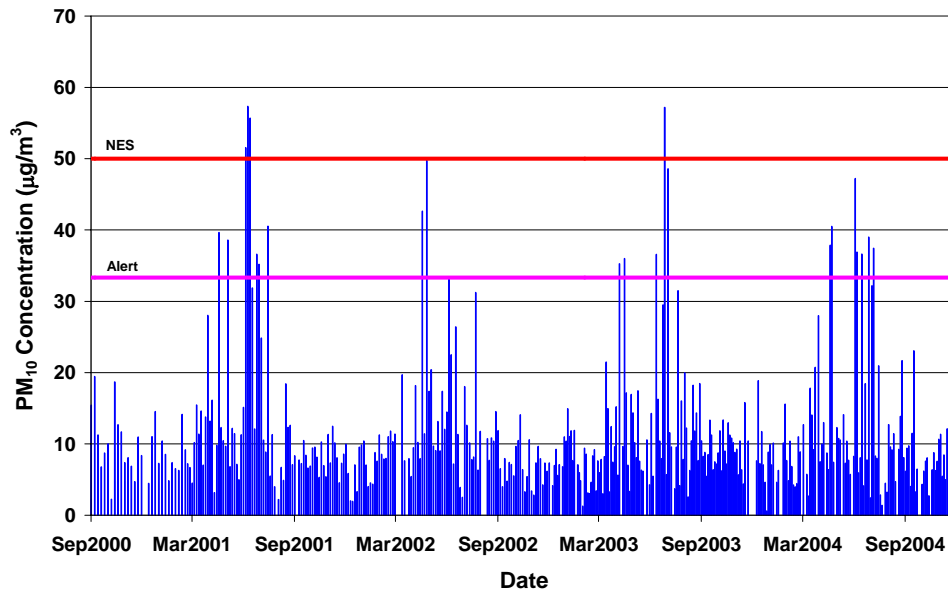
Figure 4.26: 24-hour average PM10 at Wainuiomata Bowling Club

4.3.3 Analysis of PM$_{10}$ monitoring results

Wainuiomata continues to have elevated levels of PM$_{10}$ air pollution during the winter. The use of solid fuel fires for domestic heating is suspected as the main source of air pollution. A meteorological monitoring station is to be established alongside the high volume sampler to provide meteorological data for air pollution studies.

Figure 4.27 provides a comparison of the monitoring results with the relative ambient air quality guidelines using the assessment categories described in Table 2.2
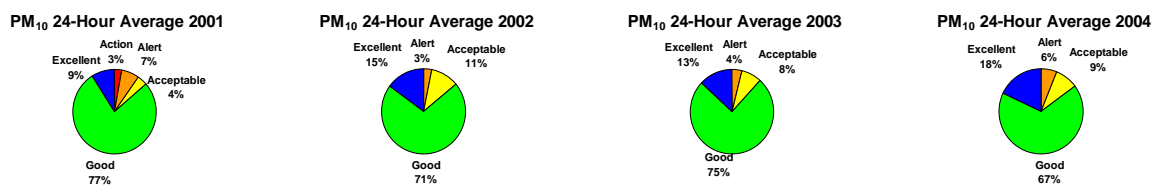

Figure 4.27: PM$_{10}$ monitoring results at Wainuiomata compared to air quality categories

The higher results suggest there are air quality issues and potential for adverse human health effects in Wainuiomata during the winter. The likely sources of particulate pollution are domestic fires.

4.4 Wairarapa College, Masterton

4.4.1 Site description

The monitoring station was located within the grounds of Wairarapa College, off Cornwall Street in Masterton (Grid Reference E2732770; N6024885, elevation 100m) from October 2002 until October 2003. Co-located at the site

were continuous CO, NOx and PM_{10} (TEOM) analysers and a PM10 high-volume sampler as a reference, various meteorological parameters were also monitored at the site. Figure 4.28 shows an aerial photo of Masterton.

Figure 4.28: Aerial photo of Masterton showing monitoring site (●)

Masterton is a rural town with a population of approximately 20,000. The town services the surrounding farming community. There are no major industries in Masterton itself and the predominant source of particulate matter emissions is from domestic solid fuel fires in the winter. Masterton is located on the flat river plain of the Wairarapa Valley which is approximately 20 kilometres wide. Figure 4.29 is a map of the local area surrounding the monitoring site.

Figure 4.29: Local map of area around Wairarapa College monitoring site (●)

The Wairarapa College site was approximately one kilometre from the central business district of Masterton. The land around the school site was flat and surrounded by open space or school and residential buildings no more than two storeys high. Figure 4.30 shows the site layout.
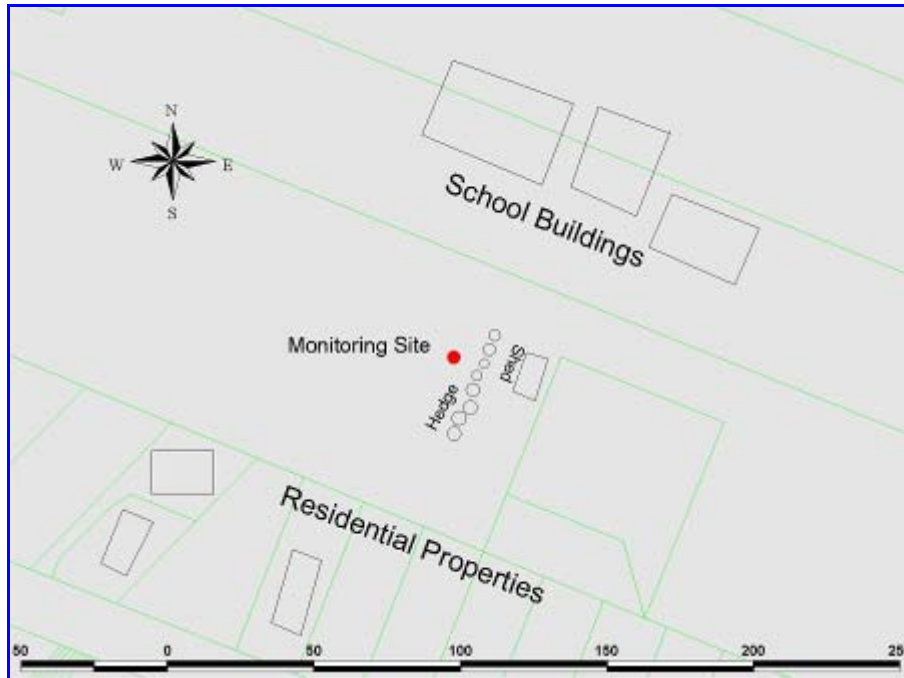

Figure 4.30: Site (●) layout around Wairarapa College monitoring station

The predominant wind directions at Wairarapa College are from the northerly and southwesterly quarters as shown by the wind rose in Appendix 3.

4.4.2   Nitrogen dioxide (NO₂)

Table 4.8 contains summary statistics of nitrogen dioxide concentrations for the monitoring period. Also shown is the NES or NAAQG where an NES has not been set.

Table 4.8: Summary statistics for NO₂ at Wairarapa College, Masterton

Parameter	NO₂ (µg/m³)			
Averaging Time	1 Hour (NES=200)		24 Hour (NAAQG=100)	
Year	2003	2004	2003	2004
Maximum	67	64	30	27
99.9 Percentile	58	52	28	26
99.5 Percentile	51	43	26	25
75 Percentile	13	11	14	12
Mean (annual)	11	9.6	11	9.6
Median	7.7	7.1	9.3	8.2
25 Percentile	5.1	5.2	6.9	6.4

1-hour moving average

Figure 4.31 is a graph of the 1-hour moving average of NO_2 concentrations at Wairarapa College for the monitoring period.
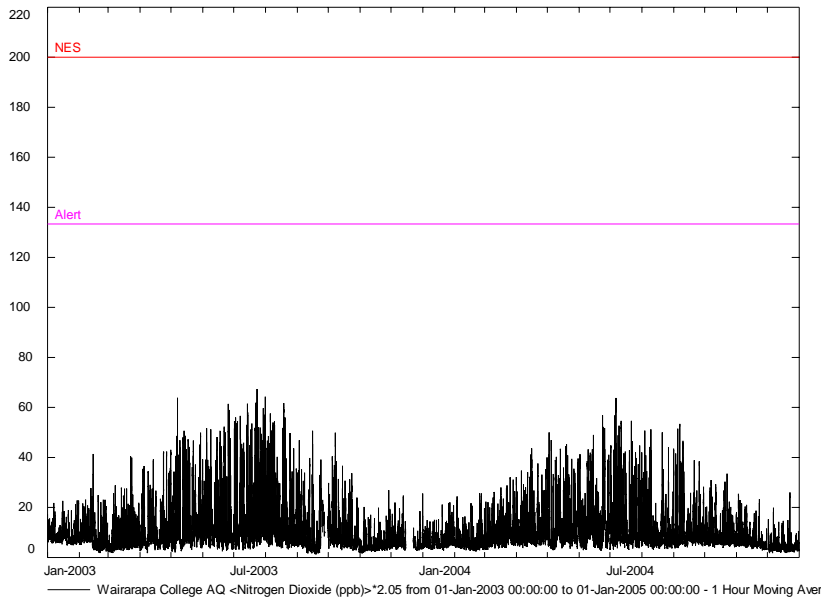

Figure 4.31: 1-hour moving average NO_2 ($\mu g/m^3$) at Wairarapa College, Masterton

24-hour moving average

Figure 4.32 is a graph of the 24-hour moving average of NO_2 concentrations at Wairarapa College for the monitoring period. The graph also indicates the 24-hour national ambient air quality guideline of 100 $\mu g/m^3$.
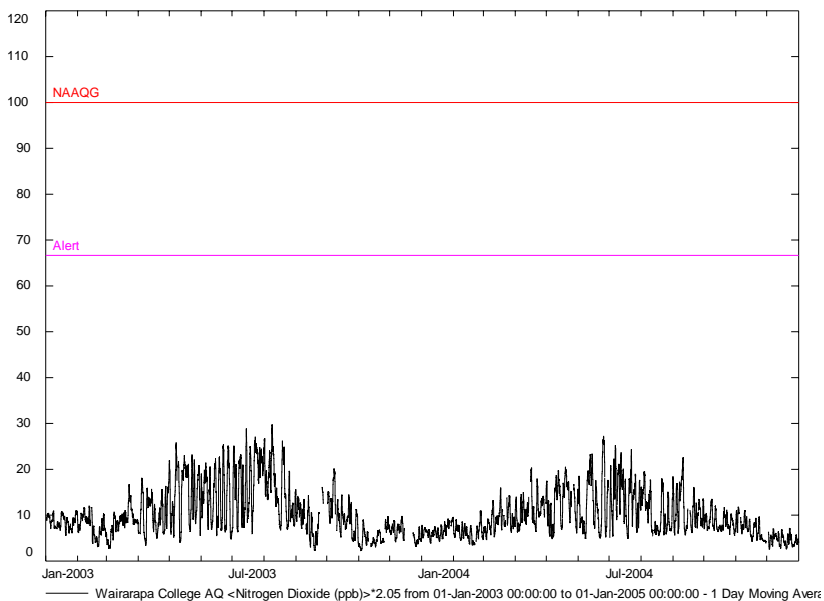

Figure 4.32: 24-hour moving average NO_2 ($\mu g/m^3$) at Wairarapa College, Masterton

Analysis of NO2 monitoring results

Figure 4.33 provides a comparison of the monitoring results with the relative ambient air quality guidelines using the categories described in Table 2.2.
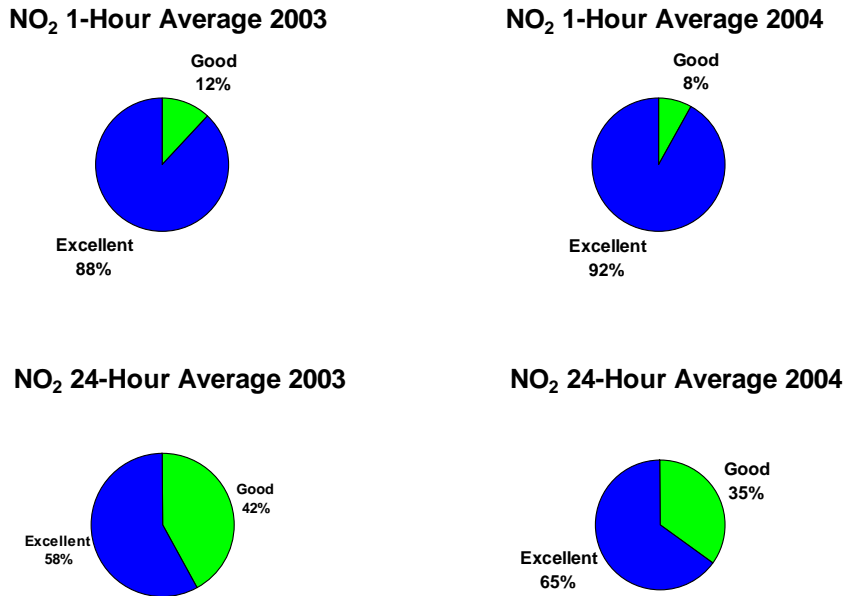
NO$_2$ 1-Hour Average 2003

NO$_2$ 1-Hour Average 2004

NO$_2$ 24-Hour Average 2003

NO$_2$ 24-Hour Average 2004

Figure 4.33: NO$_2$ monitoring results at Masterton compared to air quality categories

Figure 4.33 indicates that the NO$_2$ monitoring results at Wairarapa College compare favourably with the National Environmental Standards and National Ambient Air Quality Guidelines.

4.4.3 Particulate matter (PM$_{10}$)

Table 4.9 contains summary statistics of PM$_{10}$ concentrations for the monitoring period. Also shown is the NES.

Table 4.9: Summary statistics for PM$_{10}$ at Wairarapa College, Masterton

Parameter	PM$_{10}$ (g/m^3)	
Averaging Time	24 Hour (NES=50)	
Year	2003	2004
Maximum	64	60
99.9 Percentile	60	54
99.5 Percentile	51	53
75Percentile	18	17
Mean(annual)	16	15
Median	14	13
25 Percentile	11	10

24-hour moving average

Figure 4.34 is a graph of the 24-hour moving average of PM_{10} concentrations at Wairarapa College for the monitoring period. The graph also indicates the 24-hour NAAQG of 50 $\mu g/m^3$.
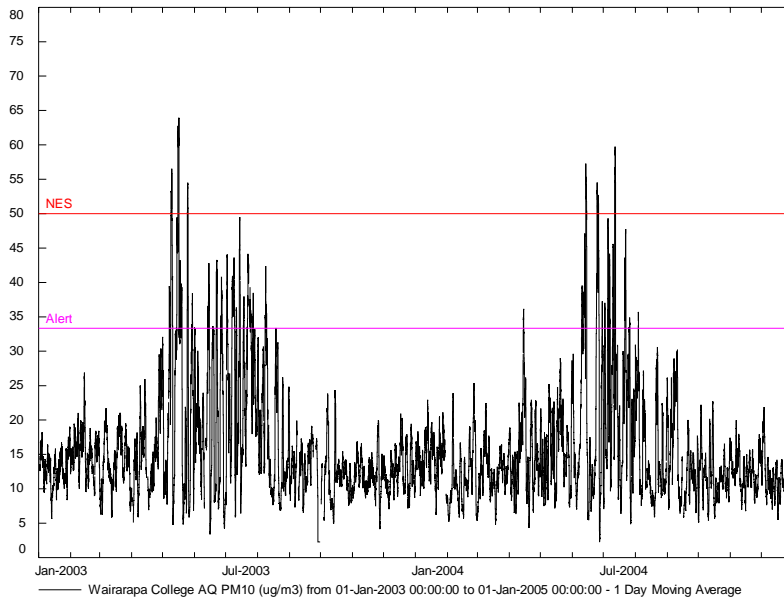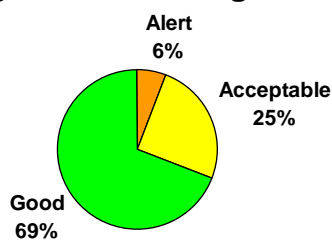

Figure 4.34: 24-hour moving average PM_{10} ($\mu g/m^3$) at Wairarapa College, Masterton

Analysis of PM10 monitoring results

Figure 4.35 shows of the monitoring results compared with the relevant ambient air quality guideline using the air quality categories described in Table 2.2, and with the National Environmental Standard for PM_{10} (50 $\mu g/m^3$).
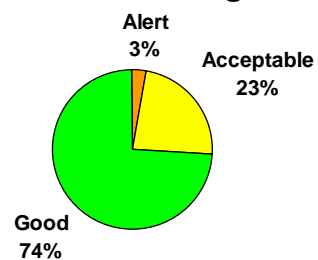

Figure 4.35: PM_{10} monitoring results at Masterton compared to air quality categories

The particulate matter monitoring results at Masterton suggest that there are air pollution episodes during the winter that may be of concern for community health. Further research into the composition and sources of particulate matter in Masterton was undertaken from May 2002 to November 2004. The analysis has shown that soil and seasalt sources dominate during the summer months

(when PM_{10} concentrations are generally low) but during the winter combustion sources (namely solid fuel fires for domestic heating) dominate ambient particle loadings and are responsible for the winter time pollution episodes. A detailed analysis of air particulate matter in Masterton is presented in Appendix 7.

As an example, Figure 4.36 shows the relative contribution of sources to ambient particle loadings during an air pollution episode which occurred on 12 July 2004.
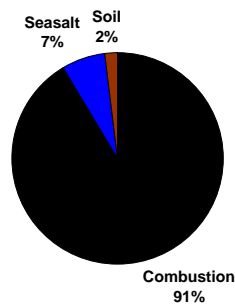
12 July 2004 PM_{10} = 77µg/m³

Figure 4.36: Relative contribution of sources to ambient PM_{10} concentrations during a pollution episode on 12 July 2004

4.4.4   Carbon monoxide (CO)

Table 4.10 contains summary statistics of carbon monoxide concentrations for the monitoring period. Also shown is the NES or NAAQG where an NES has not been set.

Table 4.10: Summary statistics for CO at Wairarapa College, Masterton

Parameter	CO (mg/m³)			
Averaging Time	1 Hour (NAAQG=30)		8 Hour (NES=10)	
Year	2003	2004	2003	2004
Maximum	7.2	5.3	3.5	3.6
99.9 Percentile	4.4	3.9	2.7	2.9
99.5 Percentile	3.30	2.9	2.4	1.9
75 Percentile	0.06	0.06	0.12	0.09
Mean (annual)	0.20	0.15	0.20	0.15
Median	0.01	0.01	0.02	0.02
25 Percentile	0.01	0.01	0.01	0.01

1-hour moving average

Figure 4.37 is a graph of the 1-hour moving average of CO concentrations at Wairarapa College for the monitoring period.
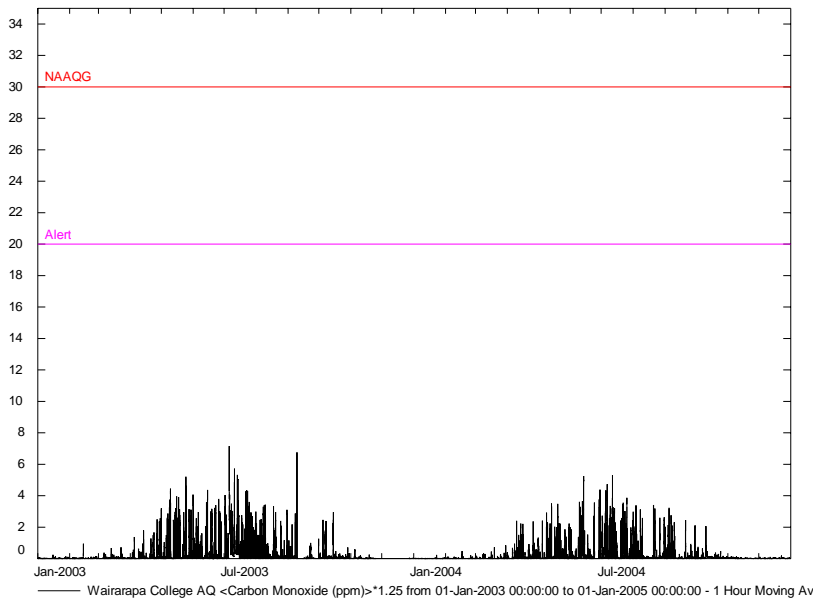

Figure 4.37: 1-hour moving average CO (mg/m³) at Wairarapa College, Masterton

8-hour moving average

Figure 4.38 is a graph of the 8-hour moving average of CO concentrations at Wairarapa College for the monitoring period. The graph also indicates the 8-hour NES of 10 mg/m³.
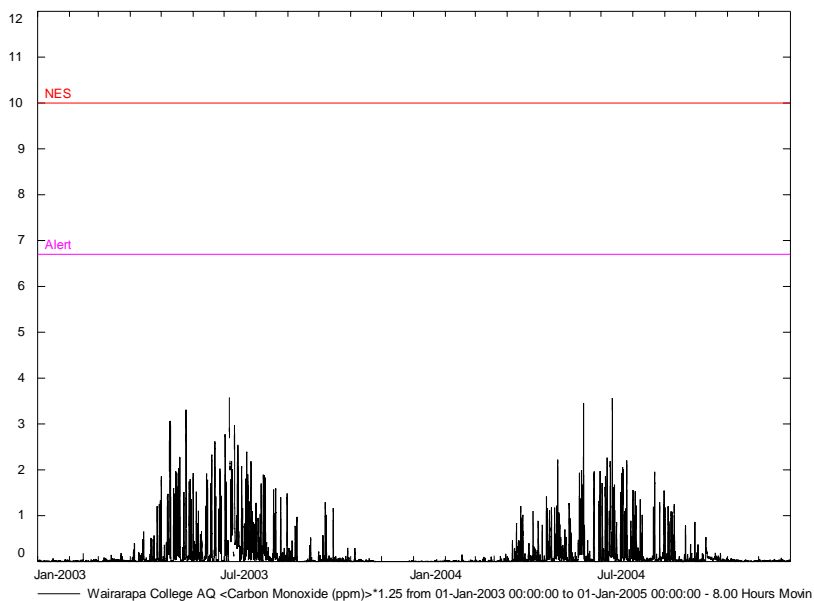

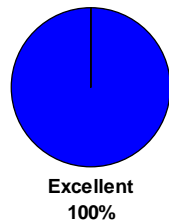**Figure 4.38: 8-hour moving average CO (mg/m³) at Wairarapa College, Masterton**

Analysis of CO monitoring results

There were no exceedences of either the NES or the NAAQG during the monitoring period.

Figure 4.39 illustrates the comparison of the monitoring results with the relative ambient air quality guidelines using the air quality categories described in Table 2.2.
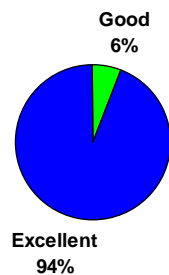
CO 1-Hour Average 2003

Excellent
100%

CO 1-Hour Average 2004

Excellent
100%

CO 8-Hour Average 2003

Good
6%

Excellent
94%

CO 8-Hour Average 2004

Good
4%

Excellent
96%

Figure 4.39: CO monitoring results at Masterton compared to air quality categories

Overall, the levels of CO recorded during the monitoring period were not at concentrations that could be considered a concern to human health based on the current guidelines.

4.5   Vivian and Victoria Streets, Central Wellington

4.5.1   Site description

The central Wellington monitoring station (CNR V) has been located on the corner of Vivian and Victoria Streets. (Grid Reference E2658477; N5988791, elevation 10m) since March 2004. Co-located at the site were continuous CO and PM_{10} (B-Gauge) analysers and various meteorological monitors. Figure 4.40 shows an aerial photo of the monitoring site.

Figure 4.40: Aerial photo of central Wellington monitoring site (●)

Central Wellington has a population of approximately 100,000. There are no major industries in central Wellington itself and the predominant source of air pollutants are motor vehicles emissions and domestic activities. Central Wellington is surrounded by hills to the North, west and south and the east is open to the harbour. Figure 4.41 is a map of the local area surrounding the monitoring site.

Figure 4.41: Local map of area around the monitoring site at Vivian and Victoria Streets (●)

4.5.2 Particulate matter (PM$_{10}$)

Table 4.11 contains summary statistics of PM$_{10}$ concentrations for the monitoring period. Also shown are the NES of 50 μg/m^3.

Table 4.11: Summary PM$_{10}$ statistics for Central Wellington at Vivian and Victoria Streets

Parameter	PM$_{10}$ (g/m^3)
Averaging Time	24 Hour (NES=50)
Year	2004
Maximum	49
99.9 Percentile	42
99.5 Percentile	32
75 Percentile	19
Mean	17
Median	16
25 Percentile	13

24-hour moving average

Figure 4.42 is a graph of the 24-hour moving average of PM$_{10}$ concentrations at CNR-V for the monitoring period. The graph also indicates the 24-hour NES of 50 μg/m^3. A peak 24-hour average concentration of 49 μg/m^3 was measured on 10 October 2004 and as can be seen from the graph below this peak stands well above other peak levels. Comparison with monitoring results at other monitoring sites around the region show similar peaks on the same day suggesting that the elevated particle concentrations were due to a regional event.
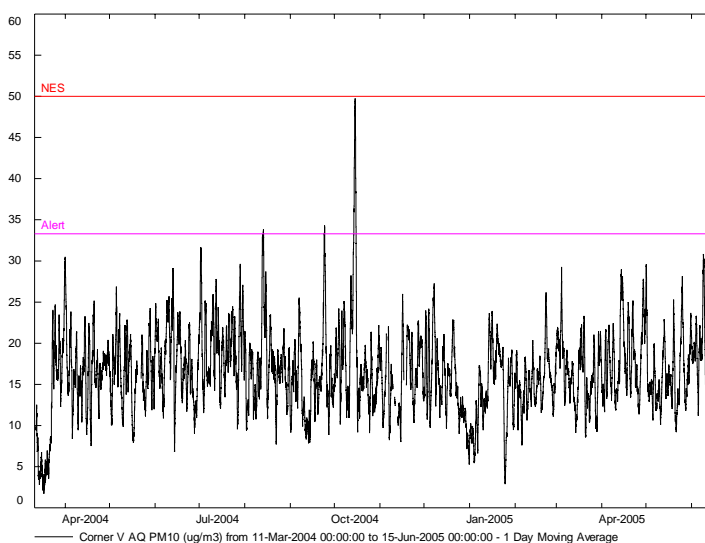

Corner V AQ PM10 (ug/m3) from 11-Mar-2004 00:00:00 to 15-Jun-2005 00:00:00 - 1 Day Moving Average

Figure 4.42: 24-hour moving average PM$_{10}$ (μg/m^3) for Central Wellington at Vivian and Victoria Streets

The PM$_{10}$ monitoring results indicate that there were no exceedences of the NES.

Analysis of PM10 monitoring results

Figure 4.43 shows of the monitoring results compared with the relevant ambient air quality guideline using the air quality categories described in Table 2.2, and with the NES for PM$_{10}$ (50 μg/m^3).
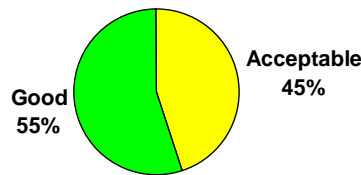
PM$_{10}$ 24-Hour Average 2004

Figure 4.43: PM$_{10}$ monitoring results for Central Wellington at Vivian and Victoria Streets compared to air quality categories

4.5.3   Carbon monoxide (CO)

Table 4.12 contains summary statistics of carbon monoxide concentrations at Vivian and Victoria Streets. Also shown is the NES or NAAQG where an NES has not been set.

Table 4.12: Summary CO statistics for Central Wellington at Vivian and Victoria Streets

Parameter	CO (mg/m³)	
Averaging Time	1 Hour (NAAQG=30)	8 Hour (NES=10)
Year	2004	2004
Maximum	7.8	4.3
99.9 Percentile	6.2	3.4
99.5 Percentile	4.9	2.8
75 Percentile	1.3	1.3
Mean	0.92	0.92
Median	0.68	0.75
25 Percentile	0.30	0.43

1-hour moving average

Figure 4.44 is a graph of the 1-hour moving average of CO concentrations at CNR-V for the monitoring period.
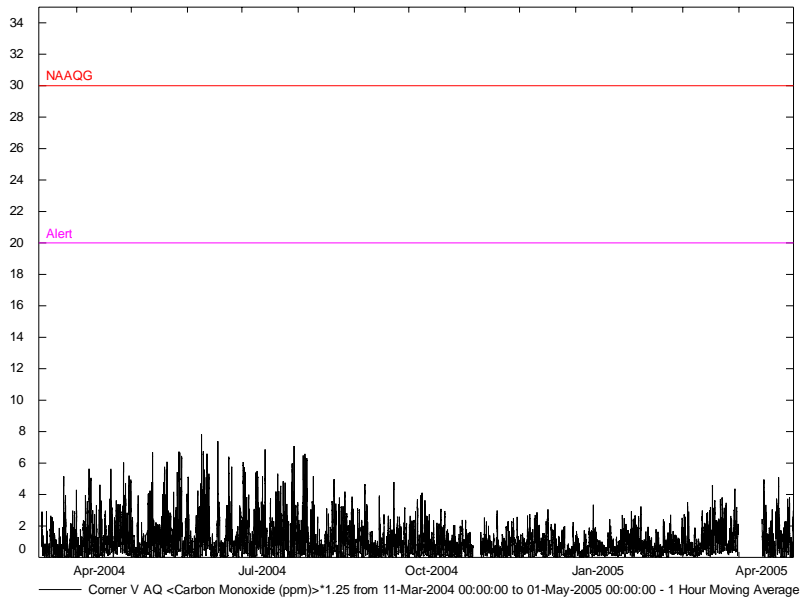
Figure 4.44: 1-hour moving average CO (mg/m³) for Central Wellington at Vivian and Victoria Streets

8-hour moving average

Figure 4.45 is a graph of the 8-hour moving average of CO concentrations at CNR-V for the monitoring period. The graph also indicates the 8-hour NES of 10 mg/m³.
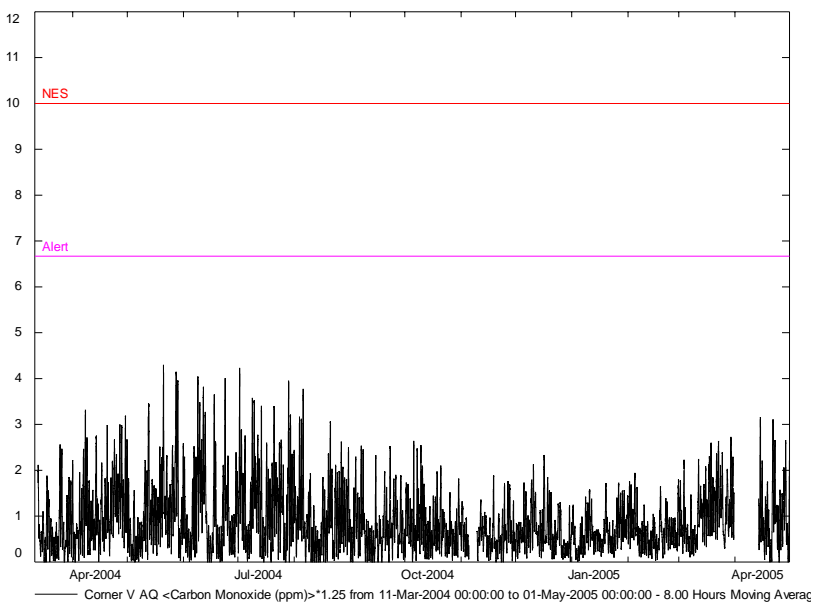

Figure 4.45: 8-hour moving average CO (mg/m³) for Central Wellington at Vivian and Victoria Streets

Analysis of CO monitoring results

There were no exceedences of either the NES or the NAAQG since the monitoring site was established in March 2004, however, CO concentrations were generally higher at CNR-V than measured elsewhere in the region. This is to be expected since it is a peak transport emissions monitoring site. Distinct diurnal peaks in concentrations were evident, coincident with the morning and evening 'rush hour' peaks in traffic density.

Figure 4.46 illustrates the comparison of the monitoring results with the relative ambient air quality guidelines using the air quality categories described in Table 2.2.

CO 1-Hour Average 2004   CO 8-Hour Average 2004
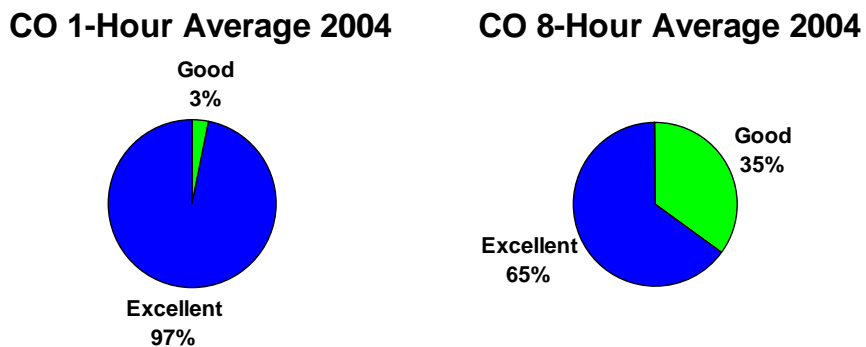
Figure 4.46: CO monitoring results for Central Wellington at Vivian and Victoria Streets compared to air quality categories

Overall, the levels of CO recorded during the monitoring period were not at concentrations that could be considered a concern to human health based on the current guidelines.

4.6   Otaki - Rural PM$_{10}$ monitoring

4.6.1   Site description

The high volume sampler was located at the Regional Council's Otaki depot (NZMS Grid Reference E2691005; N6046390, elevation 17m)on the Kapiti Coast from October 1998 to February 2000. The instrument was operated on a one-day-in-six sampling regime. Figures 4.47 and 4.48 show the site location and the site layout respectively.

Figure 4.47: Location of Otaki site (●)

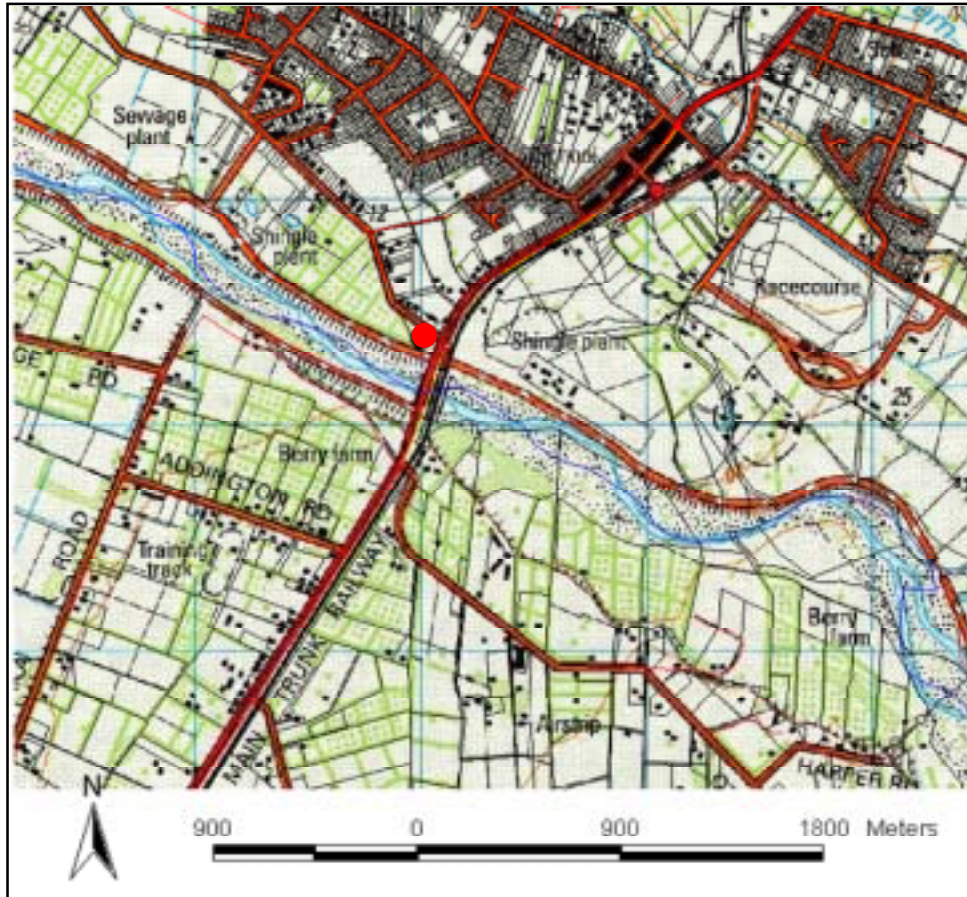The Otaki site was located next to the Otaki River, south of Otaki township itself and was not in an urbanised area. To the west of the site (1.5 km) is Otaki Beach and the Tasman Sea. South of the site is rural land and to the east the land rises to the foothills of the Tararua Range.
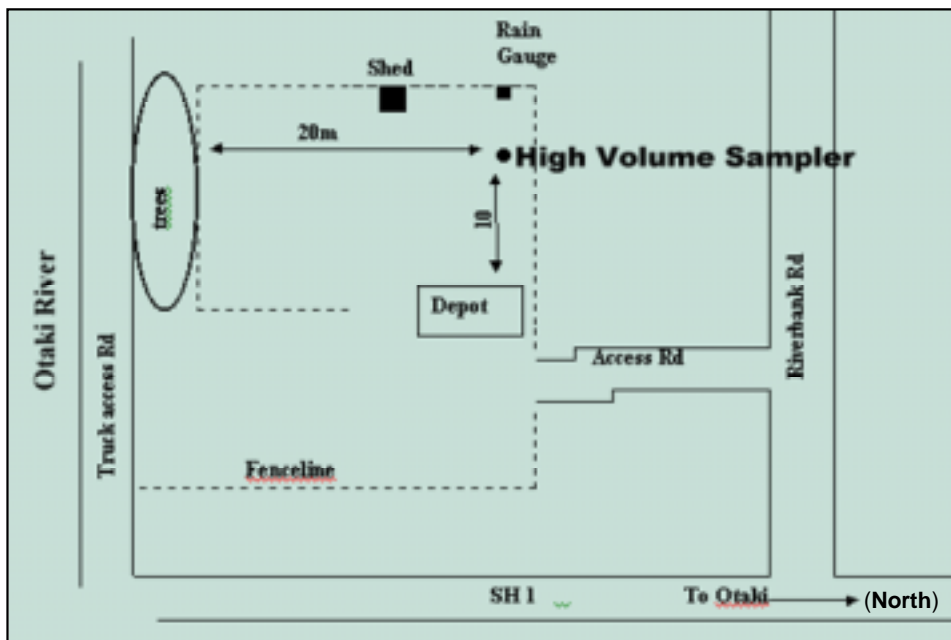

Figure 4.48: Site layout at Otaki and hi-vol location (●)

Figure 4.49 is an aerial photograph of the Wainuiomata urban area and the monitoring site location.

Figure 4.49: Aerial photo of Otaki rural area showing site location (●)

Technical parameters and meteorology

The high volume sampler is a gravimetric method for monitoring PM_{10}. Ambient air is passed through a size selective inlet and then through a pre-weighed filter that is removed after 24 hours of continuous sampling of ambient air at 70 m^3/hr and then reweighed. The results are expressed as the 24 hour average for that time period. The 24-hour monitoring period used for this study was 12:00 to 12:00 the following day. The high volume sampler is an Australian and USEPA Standard method.

The nearest meteorological station to the monitoring site is at Paraparaumu Aerodrome which is approximately 20 km south of this site. The Kapiti Coast is predominately affected by west to north-west winds. Wind speed and direction at the sampling site will be similar to that experienced at Paraparaumu Aerodrome.

4.6.2 Monitoring results for PM_{10} at Otaki

Table 4.13 contains summary statistics of PM_{10} concentrations for the monitoring period. Also shown is the NES.

Table 4.13 : Statistical summary of PM_{10} monitoring data at Otaki

Parameter	PM_{10} ($\mu g/m^3$)
Averaging Time	24 Hour (NES=50)
Year	1999
Maximum	50
99.9 Percentile	49
99.5 Percentile	48
75 Percentile	21
Mean	17
Median	14
25 Percentile	9

The maximum 24-hour average PM_{10} concentration measured was 50 $\mu g/m^3$ for the 24 hour period ending at 12:00 on 11 February 1999.

Figure 4.50 shows the discrete results for each 24 hour period monitored by the high volume sampler.
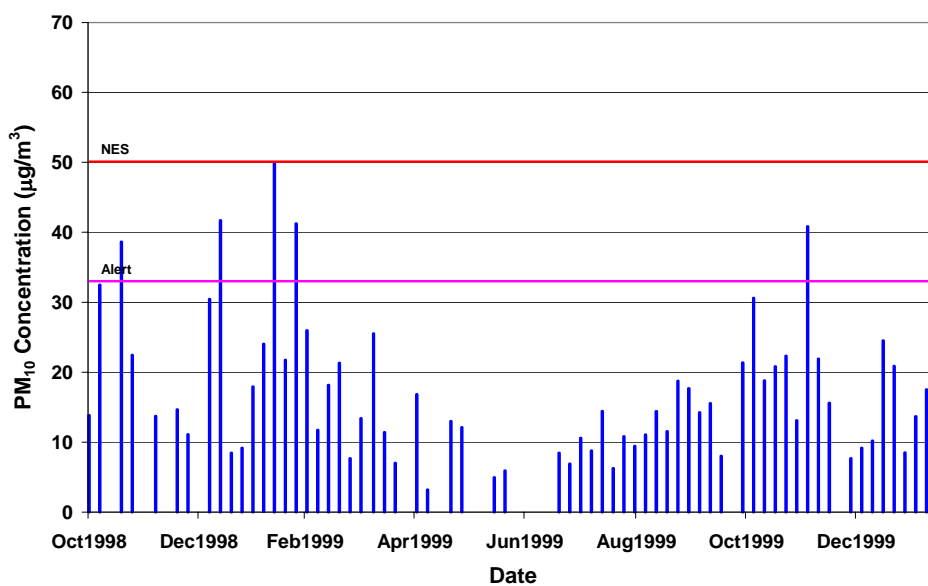
Figure 4.50: 24-hour average PM_{10} at Otaki 30/4/02 to 11/8/03

4.6.3 Analysis of PM_{10} monitoring results

Figure 4.51 provides a comparison of the monitoring results with the relative ambient air quality guidelines using the assessment categories described in Table 2.2

PM₁₀ 24-Hour Average 1999
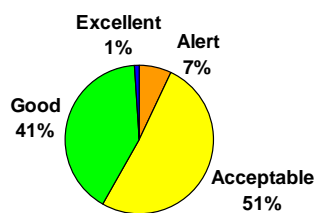
Figure 4.51: PM$_{10}$ monitoring results at Otaki compared to air quality categories

A full analysis of sources contributing to particulate matter concentrations at Otaki and those sources responsible for elevated concentrations is provided in **Appendix 8**

5.   Conclusion

The results of the ambient air quality monitoring carried out in the Wellington Region since 1999 have indicated that the highest concentrations of air pollutants generally occur during the winter. The reasons for the higher winter time air pollution levels are periods of cold, calm weather when pollutant concentrations increase in the local air mass rather than being dispersed, coupled with a greater quantity of emissions to atmosphere from combustion sources such as solid fuel fires for residential heating and motor vehicle emissions.

Statistical analysis of the data indicates that peak concentrations of carbon monoxide and nitrogen dioxide are not currently reaching levels that would be of concern for human health.

Fine particle concentrations were found to exceed the National Environmental Standard for PM_{10} during winter months at Wainuiomata, Upper Hutt and Masterton. Research and analysis of fine particle composition and source contributions has shown that the pollution episodes are primarily a result of domestic fire emissions coupled with adverse meteorological and topographical effects.

Long term averages of PM_{10} are relatively low across the Region indicating that acute health effects from peaks in fine particle concentrations are more likely than chronic effects.

References

Ministry for the Environment, October 1997. *Environmental Performance Indicators: Proposals for Air, Fresh Water and Land*

NIWA, June 1995. *National Ambient Air Quality Monitoring Network for New Zealand* NIWA Report AK95001

Ministry for the Environment, 1994. *National Ambient Air Quality Guidelines*

Ministry for the Environment, May 2002. *Ambient Air Quality Guidelines*

Ministry for the Environment, December 2000. *Good Practice Guide for Air Quality Monitoring and Data Management*

Wellington Regional Council, June 2000 *Wellington Regional Air Quality Monitoring Strategy 2000-2005* Wellington Regional Council Technical Report WRC/RINV-T-00/20.

Appendix 1

Wind Roses for the Monitoring Period at Trentham Fire Station, Upper Hutt
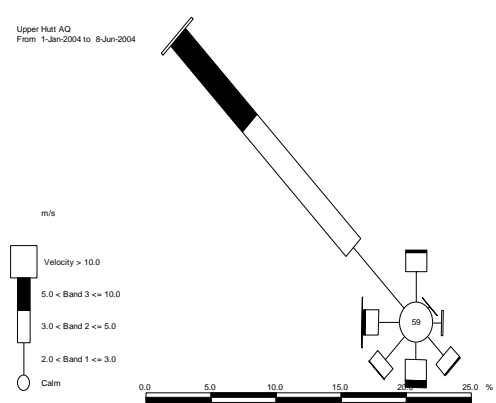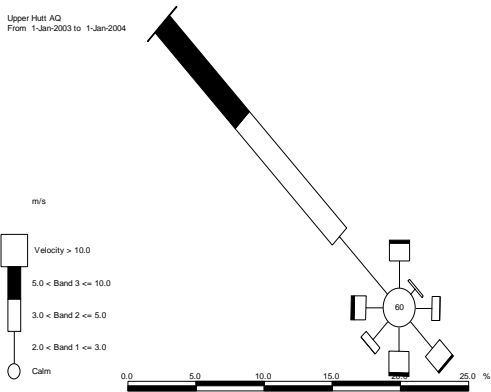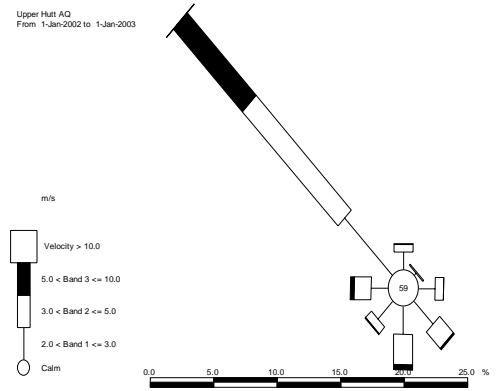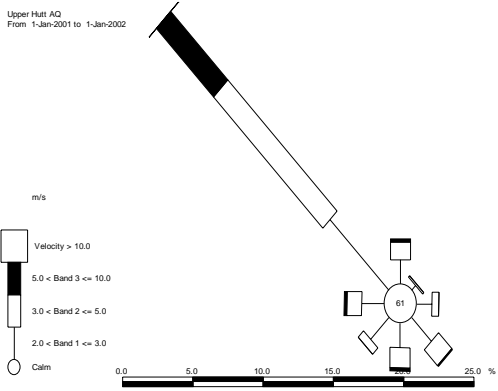
Appendix 2

Wind Roses for the Monitoring Period at Birch Lane, Lower Hutt

Appendix 3

Wind Roses for the Monitoring Period at Wairarapa College, Masterton

Wairarapa College AQ
From 1-Jan-2003 to 1-Jan-2004

m/s

Velocity > 10.0

5.0 < Band 3 <= 10.0

3.0 < Band 2 <= 5.0

2.0 < Band 1 <= 3.0

Calm

0.0   5.0   10.0   15.0 %
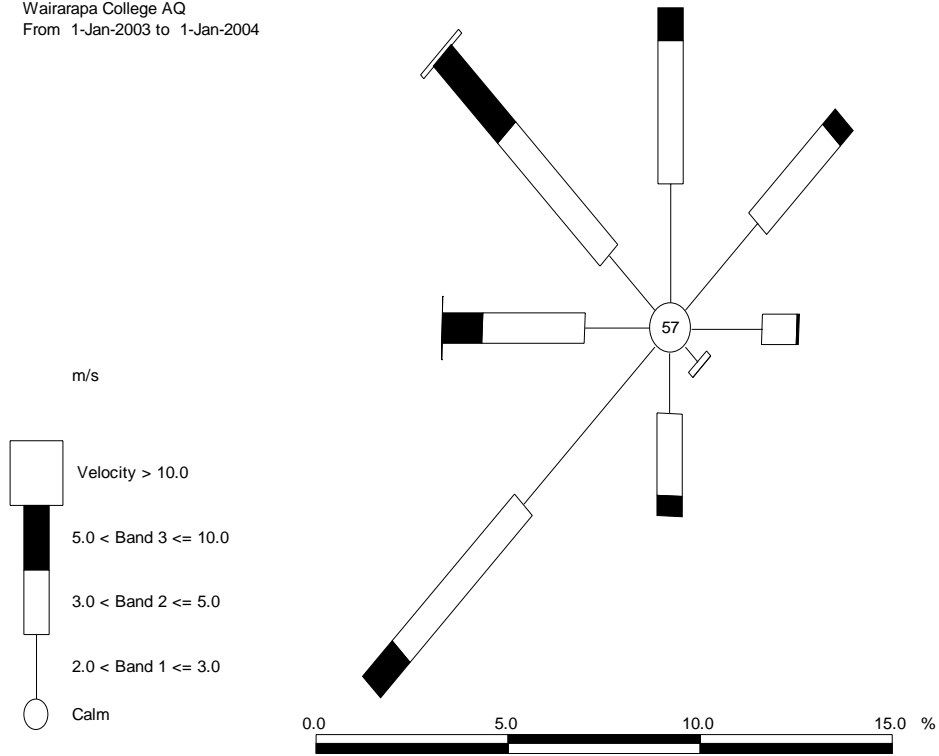
Wairarapa College AQ
From 1-Jan-2004 to 1-Jan-2005

m/s

Velocity > 10.0

5.0 < Band 3 <= 10.0

3.0 < Band 2 <= 5.0

2.0 < Band 1 <= 3.0

Calm

0.0   5.0   10.0   15.0 %
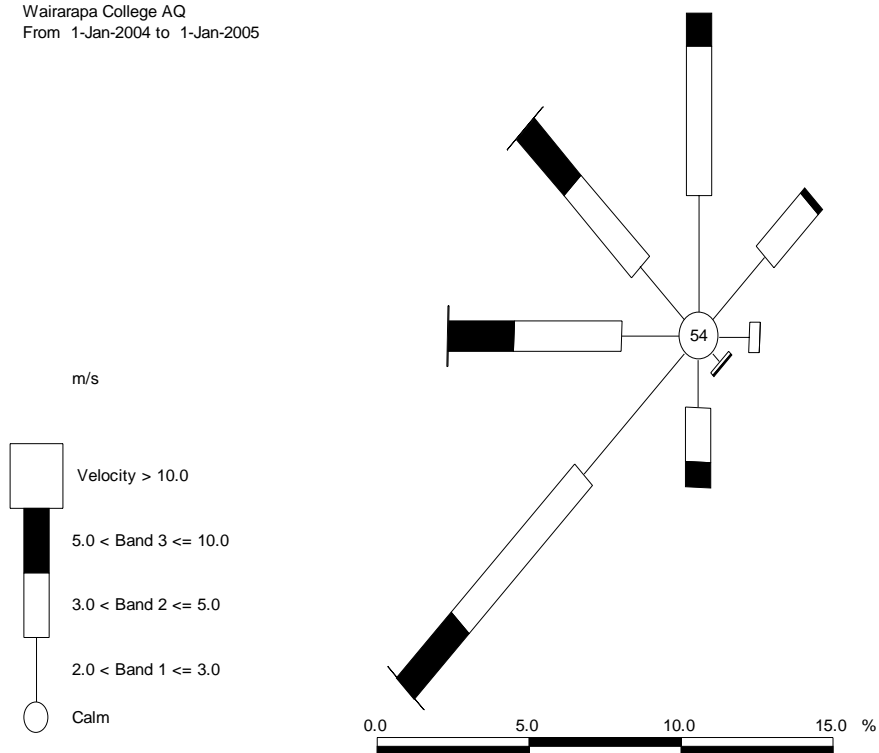
Appendix 4

Wind Rose for the Monitoring Period at Vivian and Victoria Streets, Central Wellington

Corner V AQ
From 1-Apr-2004 to 1-Apr-2005
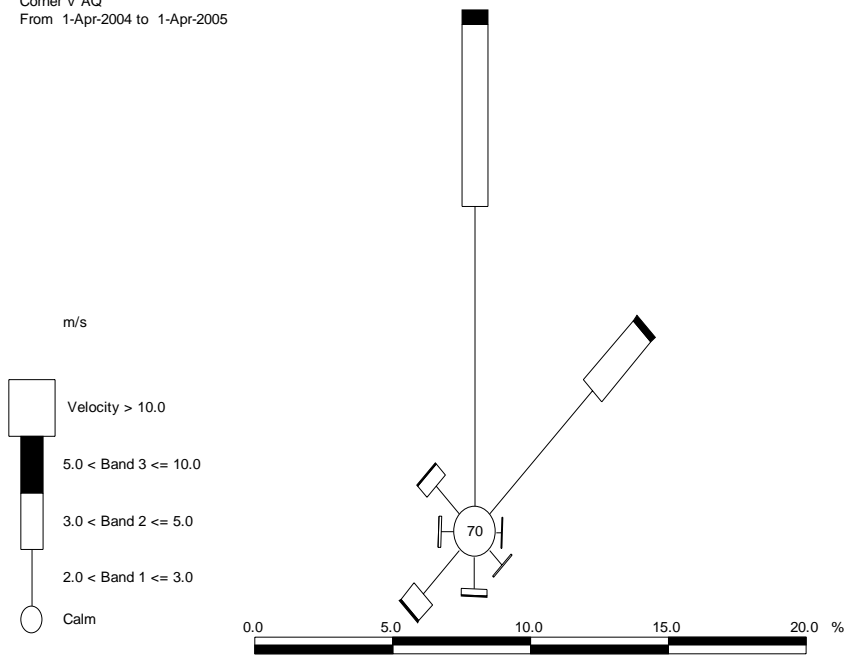
Appendix 5

Analysis of sources contributing to air particulate matter concentrations at Upper Hutt

Elemental analysis and source apportionment of ambient particulate matter In the Wellington region of New Zealand

P. Davy[1], A. Markwitz[2] and W. J. Trompetter[2]

[1]Wellington Regional Council, PO Box 11-646, 142-146 Wakefield Street, Wellington, New Zealand and
[2]Institute of Geological and Nuclear Sciences, PO Box 31-312, 30 Gracefield Road, Lower Hutt, New Zealand

Summary

At certain locations in the Wellington Region pollution episodes due to air particulate matter are known to occur from time to time. Ion Beam Analysis (IBA) is one of the few non-destructive techniques that can be used to identify the elemental composition of air particulates on a filter sample. IBA has been used to characterise airborne particulate matter in two size fractions, $PM_{2.5}$ and $PM_{10-2.5}$, collected at a monitoring station in Upper Hutt, Wellington, New Zealand. Elements with atomic mass above neon were measured using IBA. Elemental carbon was measured with a light reflectance device. Elemental 'fingerprints' of contributing sources were determined by performing factor analysis of the elemental composition. The results indicate that 'Sea Salt' and 'Soil' sources are major contributors to the coarse ($PM_{10-2.5}$) fraction and 'Combustion' sources dominate the fine ($PM_{2.5}$) fraction of air particulate. Analysis of seasonal differences was a useful tool in elucidating source profiles. The factor analysis of particulate matter was relatively unchanged by inclusion of gaseous pollutants and meteorological variables.

Keywords: Particulate Matter, Ion Beam Analysis, Factor Analysis, Source Apportionment, New Zealand

1.   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.

Since 1996, air particulate matter has been collected at various locations in the Wellington Region using a GENT stacked filter unit. The GENT sampler effectively collects two different size fractions, $PM_{2.5}$ or fine particulate matter and $PM_{10-2.5}$ or coarse particulate matter on to 47mm polycarbonate filters (Hopke et al, 1997). This paper presents the results of 18 months of air particulate monitoring at Upper Hutt, Wellington. Some of the results for other locations in the Wellington Region were presented at a previous Clean Air and Environment Conference in Sydney (Trompetter et al, 2000).

The concentrations of $PM_{2.5}$ and $PM_{10-2.5}$ collected by the GENT sampler at Upper Hutt were determined gravimetrically and then the elemental composition of particulate matter on the filters was analysed at the New Zealand Ion Beam Analysis facility. Elements with atomic mass above neon were measured using ion beam analysis and elemental carbon (EC) was measured with a light reflectance device. A more in-depth description and discussion of the analysis techniques involved is being presented in another paper at this conference (Trompetter and Markwitz, 2002). The fingerprints of the contributing sources were determined by performing factor analysis on the elemental concentrations in air particulate on the filters collected at Upper Hutt. To date, the significant $PM_{2.5}$ factors (sources) determined from several NZ locations are: Sea salt, Soil, Industry, Smoke and Vehicle sources. The significant $PM_{10-2.5}$ sources are: Sea Salt, Soil and Industry.

2.   Particulate matter concentrations at Upper Hutt

2.1   Sampling site location

The Upper Hutt site is located approximately 30 kilometres north-east of central Wellington City in a residential area of Upper Hutt City. Upper Hutt City has a population of about 37,000 and land use in the area is predominantly residential with some light industrial activities. Figure 1 shows the sampling site location.
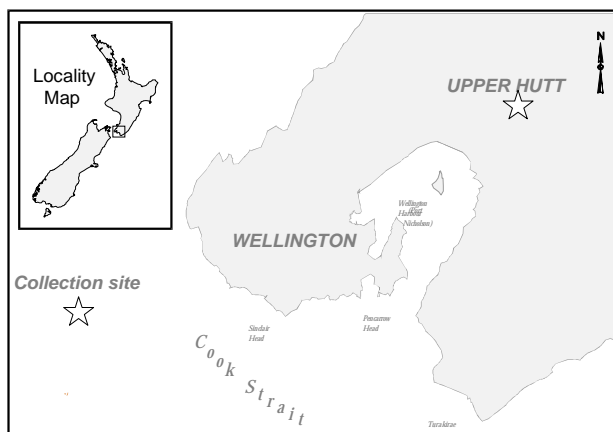
Figure 1: Map showing the sampling location

Upper Hutt lies in a valley basin that can be subject to significant temperature inversions during the winter, which can reduce the dispersion of air pollutants and effectively trap them in the valley.

2.2   PM$_{2.5}$ and PM$_{10\text{-}2.5}$ sampling results

The monitoring station at Upper Hutt was established in June 2000. The GENT sampler was used to collect particulate matter until February 2002. A total of 142 PM$_{2.5}$ and PM$_{10\text{-}2.5}$ filters were collected. Co-located at the site were continuous CO, NOx and PM$_{10}$ (TEOM) analysers, as well as various meteorological instruments. Figure 2 shows the gravimetric results for the GENT PM$_{2.5}$ and PM$_{10\text{-}2.5}$ filters.
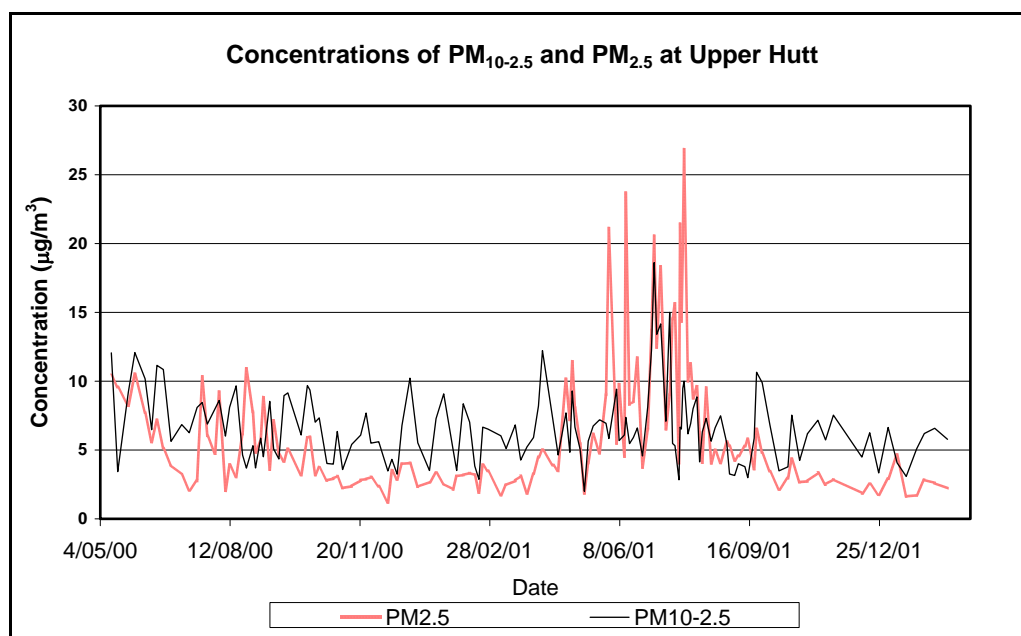
Figure 2: PM2.5 and PM10-2.5 sampling results

The GENT gravimetric results show that particulate matter concentrations are generally highest in the winter months (May-August) and that, at times, PM$_{2.5}$ can dominate gravimetrically.

Note that the GENT sampler was run to optomise the particulate loading on the filters and not a 24-hour regime. Therefore, during the summer the sampler may have run continuously for a week and during peak ambient particulate concentrations in the winter, the sampler may only run for a day. PM_{10} monitoring with a TEOM co-located at Upper Hutt shows that each year there are several exceedences of the New Zealand ambient air quality guideline for PM_{10} of 50 $\mu g/m^3$ (24-hour average).

3. Elemental analysis and source apportionment

Elemental analysis of the particulate collected on the filters was carried out using Particle Induced X-ray Emission (PIXE) at the New Zealand Ion Beam Analysis facility, Lower Hutt, Wellington. Figures 3 and 4 show the range of elements and their respective concentrations detected on the polycarbonate filters.
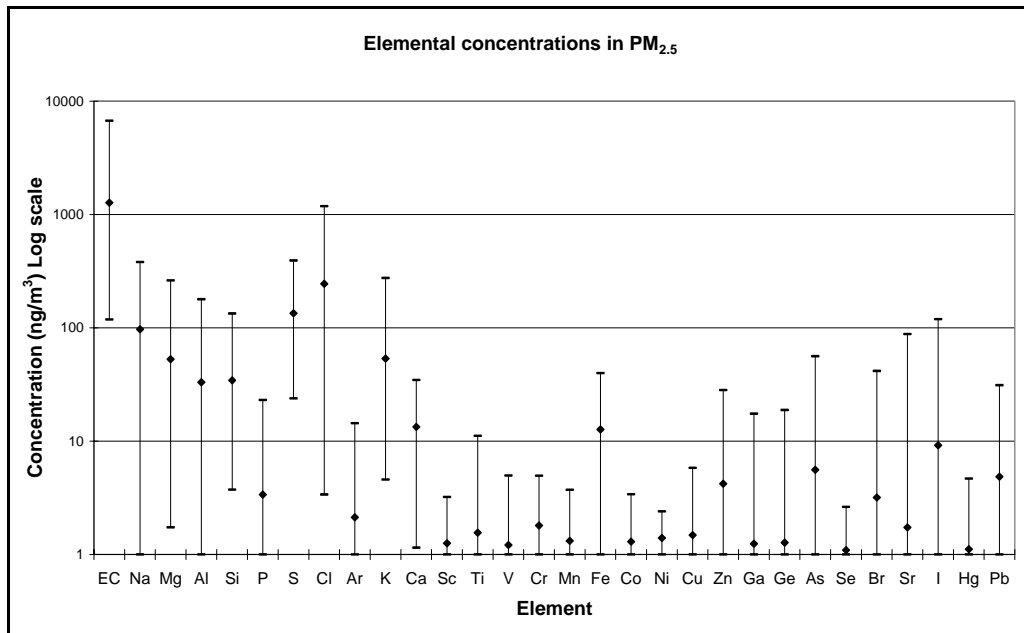
Figure 3: Elemental concentrations in $PM_{2.5}$ at Upper Hutt
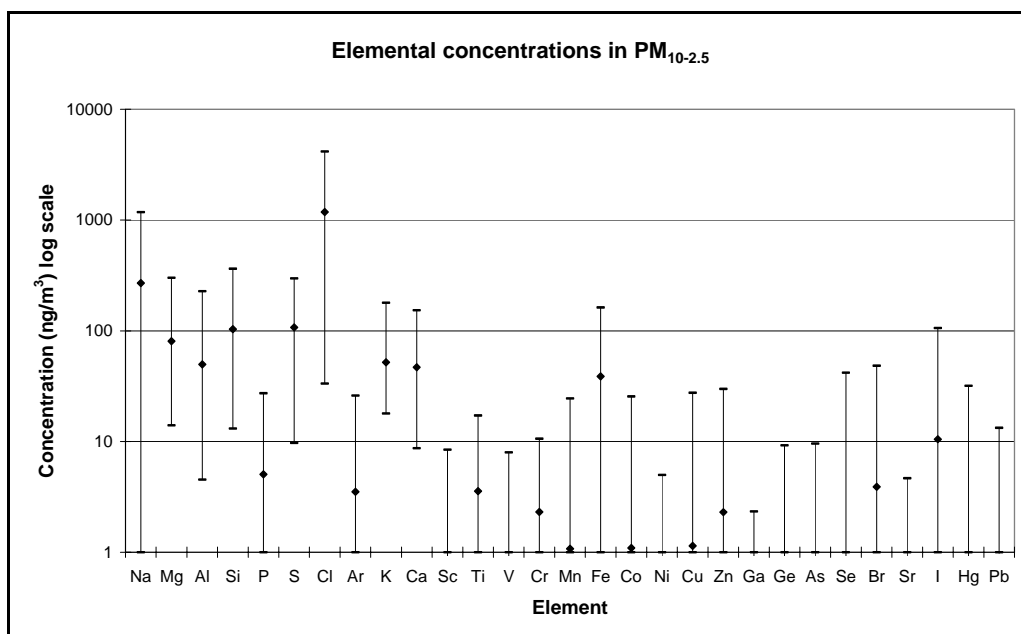
Figure 4: Elemental concentrations in PM$_{10-2.5}$ at Upper Hutt

3.1 Source apportionment – fingerprint determination

The elements that make up a fingerprint for each source of air particulate are determined by statistically analysing the elemental composition of the particulate over a large number of air filters. A statistical package such as SYSTAT or STATGRAPHICS, was used to perform Factor Analysis or Principal Components Analysis to determine the grouping of elements that vary together and therefore determine the components of a fingerprint.

3.1.1 PM$_{10-2.5}$

Table 1 lists the fingerprints or factors identified for the PM$_{10-2.5}$ fraction at Upper Hutt.

Table 1: Factor analysis loadings determined for PM$_{10-2.5}$

Element	Factor 1 'Soil'	Factor 2 'Sea Salt'
Al	0.82	0.28
Si	0.90	0.14
Ti	0.82	0.08
Fe	0.89	0.13
Cu	0.72	0.22
Zn	0.81	0.12
Na	0.09	0.92
S	0.09	0.94
Cl	-0.02	0.98
Ca	0.53	0.80
Mg	0.39	0.77
K	0.58	0.75

Only two significant fingerprints were determined for the coarse particle fraction at Upper Hutt, these have been labelled 'Soil' and 'Sea Salt' respectively for factors 1 and 2 as shown in Table 1. The 'Soil' factor has been named as the elements present are typical of those found in crustal matter. Similarly the "Sea Salt' factor contains elements that are major components of sea salt. 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, the 'Sea salt' factor.

The statistical analysis of elemental compositions can also provide a 'score' for the presence of each factor on a particular filter. The percentage contribution of each element in a fingerprint is determined from specific filters that are identified as principally containing air particulate from a specific source. From these individual filters the elemental ratios were calculated and are listed in Table 2.

Table 2: Contribution of elements to each fingerprint

Element	Factor 1 'Soil'	Factor 2 'Sea salt'
Al	18%	
Si	39%	
Ti	2%	
Fe	16%	
Cu	1%	
Zn	2%	
Na		16%
S		5%
Cl		71%
Ca	11%	2%
Mg		4%
K	12%	2%

Table 2 shows that the 'Sea salt' factor can make up a significant proportion of the measured elemental mass on a filter. This is illustrated graphically in Figure 5.
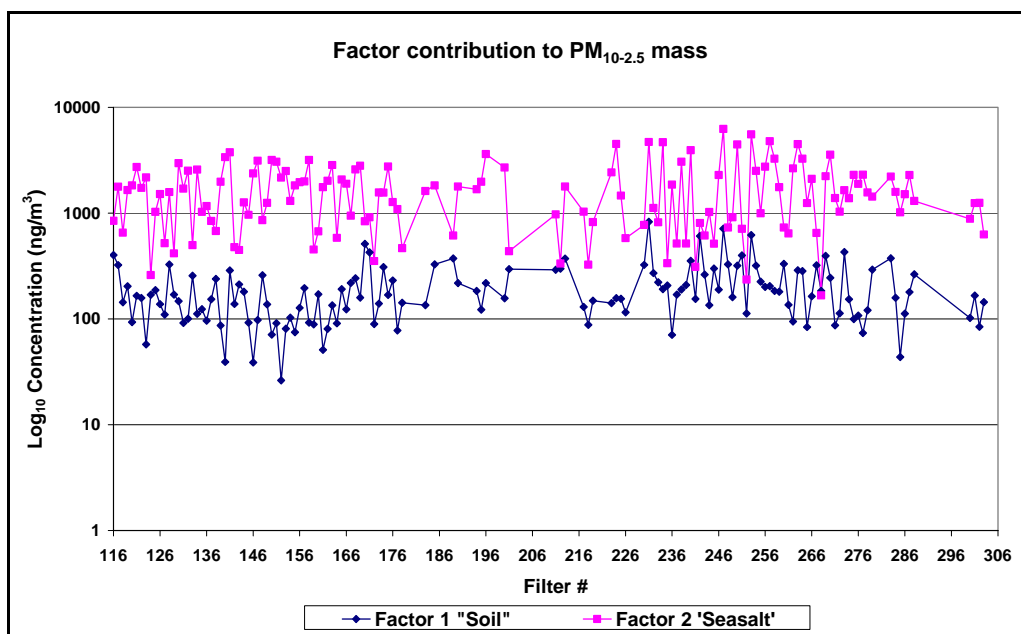
Figure 5: Contribution of factors to each $PM_{10-2.5}$ filter

The contribution of the 'Sea salt' factor to the measured elemental mass on each coarse filter is generally an order of magnitude greater than the contribution of the 'Soil' factor. Average contribution and standard deviations of the two sources to particulate loadings are given in Table 3. The 'Soil' mass contribution was calculated using the formula described by Malm (Malm et al 1996).

Table 3: Average $PM_{10-2.5}$ source concentrations

	Soil (ng/m^3)	Sea salt (ng/m^3)
Average	544	1738
Std Deviation	325	1189

This result is consistent with Wellington's maritime location and results obtained at a Lower Hutt site (see Trompetter et al 2000).

3.1.2 $PM_{2.5}$

Factor analysis was applied to identify elemental compositions of the fine particulate filters. Table 4 lists the fingerprints or factors identified for the $PM_{2.5}$ fraction at Upper Hutt.

Table 4: Factor loadings for $PM_{2.5}$ fingerprints

	Factor 1 'Combustion'	Factor 2 'Sulphur'	Factor 3 'Sea salt'
EC	**0.93**	0.13	-0.01
Na	0.22	-0.18	**0.81**
Mg	**0.91**	0.03	0.28
Al	**0.93**	0.04	0.15
Si	**0.83**	0.25	0.25
S	-0.08	**0.60**	0.38
Cl	-0.06	0.06	**0.84**
K	**0.88**	0.19	0.07
Ca	0.07	0.34	**0.85**
Cr	0.25	**0.78**	0.03
Fe	0.38	**0.79**	0.01
Ni	0.12	**0.71**	-0.04
Cu	**0.70**	0.17	-0.17
Zn	**0.81**	0.23	-0.13

Three significant fingerprints were derived by factor analysis of the fine particle fraction at Upper Hutt; these have been labelled 'Combustion', 'Sulphur' and 'Sea salt' respectively for factors 1, 2 and 3 as shown in Table 4. The 'Combustion' factor has been named as such due to strong presence of EC and K. The 'Sulphur' factor contains S and a trace of metals, the most significant being Fe. The fine 'Sea salt' factor contains elements that are major components of sea salt and is similar in profile to the coarse 'Sea salt' factor.

The statistical analysis of elemental compositions can also provide a 'score' for the presence of each factor on a particular filter and this can be used to determine the relative mass contribution of each element to a fingerprint. In this case we have used an aggregate of contributions from filters on which a particular factor predominates (high factor score for that filter). This can assist in deducing the significance of element(s) in a fingerprint. Table 5 shows the relative mass contributions of each element to a fingerprint. Table 5 indicates that EC dominates the 'Combustion' factor (which in turn dominates $PM_{2.5}$ at times). The 'Sulphur' factor is a relatively minor constituent even on filters that have a high factor score for the 'Sulphur' factor. 'Sea salt' is less predominant in the $PM_{2.5}$ fraction than the $PM_{10-2.5}$ fraction as would be expected from the size distribution of sea salt particles.

Table 5: Contribution of elements to PM$_{2.5}$ fingerprints

	Factor 1 'Combustion'	Factor 2 'Sulphur'	Factor 3 'Sea salt
EC	88.2%		
Mg	3.4%		
Al	2.6%		
Si	1.8%		
K	3.7%		
Cu	0.1%		
Zn	0.3%		
S		86.1%	
Cr		1.6%	
Fe		11.7%	
Ni		0.6%	
Cl			73.6%
Na			23.5%
Ca			2.9%

Average contribution and standard deviations of the different sources to particulate loadings are given in Table 6.

Table 6: Average PM$_{2.5}$ source concentrations

	Combustion (ng/m^3)	Sulphur (ng/m^3)	Sea salt (ng/m^3)
Average	1440	147	352
Std Deviation	1325	82	323

4.   Discussion

PM$_{2.5}$ and PM$_{10-2.5}$-monitoring and subsequent elemental analysis has revealed a number of sources responsible for ambient particulate matter concentrations at Upper Hutt. The composition of the coarse fraction is comprised largely of sea salt and crustal matter (soil). The fine fraction appears to be more complex to resolve into contributing sources.

A time series plot of EC concentrations, as shown in Figure 6, indicates that EC can dominate PM$_{2.5}$ and that the highest concentrations are recorded during the winter months. This is consistent with the fact that the Upper Hutt Valley is subject to inversion conditions during the winter and many households in the area use solid fuel burners (with wood mainly used as the fuel) as a heating source.
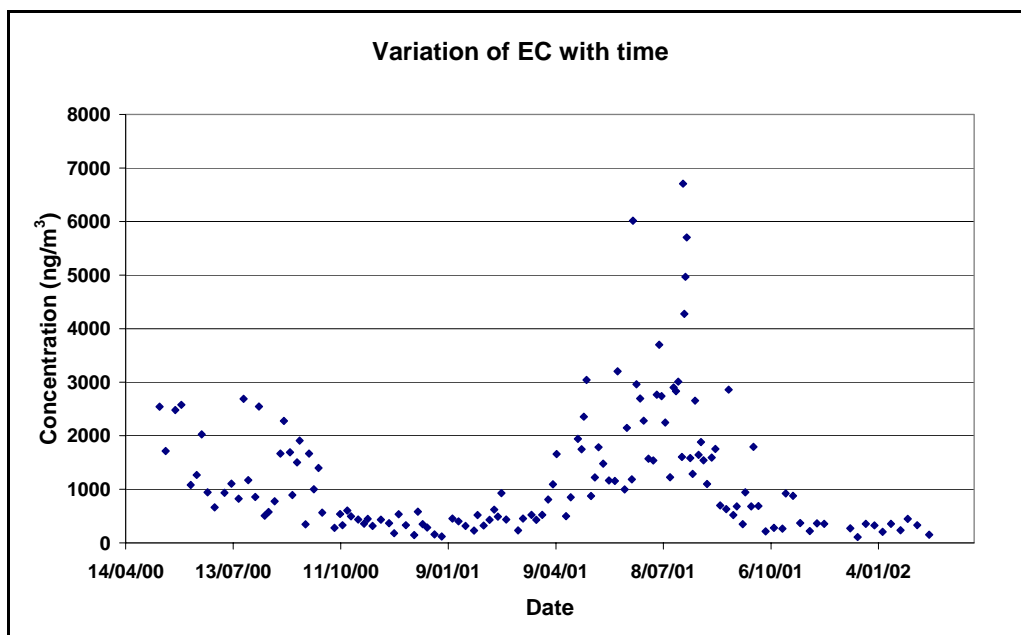
Figure 6: Variation of elemental carbon concentrations with time

An elemental profile for wood burner emissions in New Zealand has been compiled (Wilton and Spronken-Smith 2002), and workers overseas have reported similar groupings of elements (Fine et al. 2002) found in wood smoke discharges. The percentage contribution of various elements to the wood burning profile is shown in Table 7, along with the 'Combustion' factor derived from the Upper Hutt data.

Table 7: Comparison of ambient combustion profile with wood burner emissions

	Upper Hutt 'Combustion'	Wood Burner (after Wilton 2002)
EC	76.8%	52%
Mg	2.9%	~
Al	2.2%	3%
Si	1.6%	21%
K	3.2%	1%
Cu	0.1%	~
Zn	0.2%	5%
Na		3%
S		3%
Ca		6%
Fe		1%
I		2%
Sc		3%

Table 7 shows that while the 'Combustion' and wood burner elemental profiles are similar in composition there is a difference in percentage mass contribution of the elements. This difference is likely to be due to atmospheric transformations of wood burner emissions and the sensitivity and resolution of the factor analysis. Motor vehicle emissions are also likely to be a contributing source but perhaps not significant enough to resolve two different EC sources. The dominant factor may be the meteorological conditions.

In an attempt to improve the resolution of the fine source fingerprints, the data was divided into summer (October-April) and winter (May-September) periods, also delineated by the peaks in EC concentrations (see Figure 6). The intention was to see if source profiles differed between the two seasons. The winter factor loading matrices remain unchanged, although the "Sulphur' factor was a little less well defined as more S appeared to be partitioned into the 'Sea salt' factor. The summer data yielded four distinct factors after factor analysis. Two of the factors are essentially the same as previously found (i.e. 'Sea salt' and 'Sulphur''), whereas the 'Combustion' source profile appeared to resolve into two, one that contains mainly EC and K with some Cu and Zn which are again attributed to combustion sources. The other source profile contained Mg, Al and Si, which represents particulate matter derived from soil. This suggests that the main differences between the summer and winter data are meteorological factors and a lower contribution to particulate concentrations from combustion sources. Significant combustion sources in the summer are likely to be motor vehicles and biomass burning such as backyard fires and land clearance activities as opposed to solid fuel fires for domestic heating.

The Upper Hutt air quality monitoring station where the GENT sampler was located, also monitored gaseous air pollutants (NOx and CO) and meteorological parameters. We have examined the effect of meteorological influences on our source profiles by incorporating various meteorological parameters (temperature, wind speed, relative humidity) into our factor analysis and seeing how the gaseous air pollutants vary with the source profiles. This was done by taking the average data for these parameters over the same time period that the GENT sampler was collecting particulate matter. This may be a relatively insensitive method, in that the Upper Hutt airshed may experience several different synoptic weather patterns in during a sampling interval (up to 7 days in the summer). However, this would help provide indicative trends in the source profiles.

Factor analysis was performed on data that included elemental concentrations, and average CO, NO, NO_2, temperature and wind speed over the same sampling period for each filter. The source profiles obtained were relatively unchanged compared to factor analysis of the elemental components alone, except that a new source profile (factor) was present. This new factor contained CO, NO, NO_2, a positive correlation with calm meteorological conditions (wind speed<1m/s) and negative correlations with mean temperature and mean wind speed i.e. the gaseous pollutants tend to become elevated under cold, calm conditions.

The 'Combustion' factor appears to be negatively correlated with mean temperature but not particularly dependent on the other meteorological variables. That is, combustion particulate levels are higher in cooler conditions, which is confirmed by the winter peaks in EC and $PM_{2.5}$.

The 'Sulphur' factor remained relatively unchanged throughout the subsequent factor analyses. Further to our work in a road tunnel in central Wellington (Davy et al 2002), we had thought that S and trace metals (e.g. Fe, Ni, Cr) may help to provide a marker for motor vehicle emissions due to its presence in fuel (mainly diesel) or in tunnel emissions. However, the factor analysis would suggest that there is some other independent source of S that dominates (i.e.

not sea salt or soil). A time series plot of S concentrations as shown in Figure 7 indicates that sulphur levels are higher in summer than in winter.
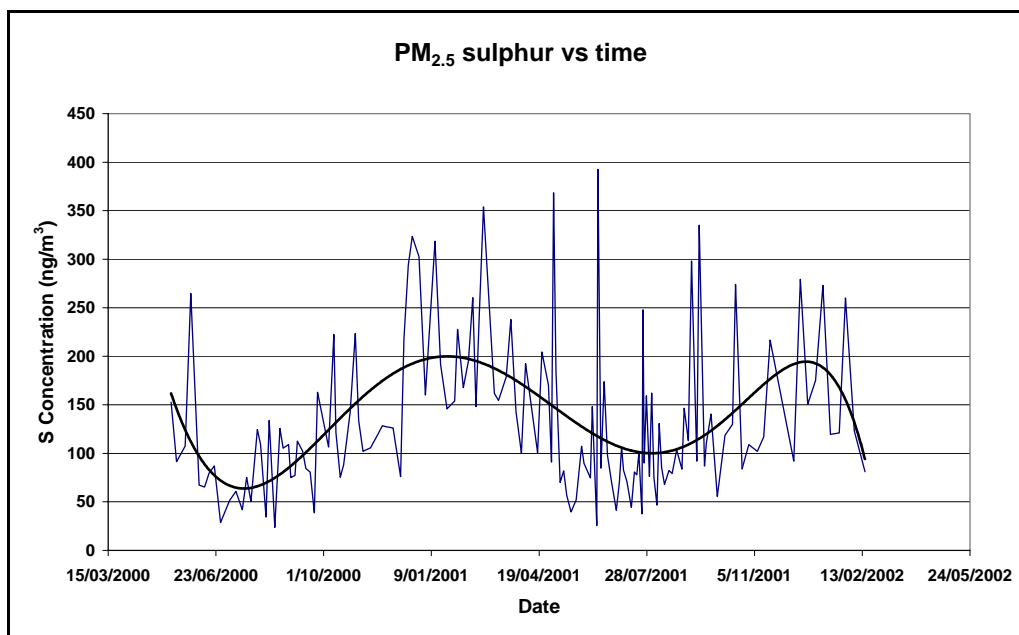

Figure 7: PM$_{2.5}$ sulphur concentrations vs time (with trend line)

Work by other researchers (Allen et al 1996, Wylie and De Mora 1996) indicates that there are significant sources of sulphur aerosol species other than sea salt (e.g. methane sulphonic acid and non-sea-salt-SO_4^{2-}) present in South Pacific marine air samples. The sulphur content from these sources was found to peak in summer. Wellington is essentially in a maritime location and sources such as the marine environment could conceivably dominate the sulphur source profile.

5. Conclusions/Summary

Two size fractions of ambient particulate matter PM$_{10-2.5}$ and PM$_{2.5}$ have been collected onto polycarbonate filters at an air quality monitoring station in Upper Hutt, New Zealand. The elemental composition of the particulate was determined using PIXE.

Source apportionment using factor analysis of the elemental composition of particulate was carried out to determine particle source 'fingerprints'. The PM$_{10-2.5}$ fraction was found to have two factors that were attributed to 'Sea salt' and 'Soil' sources. The PM$_{2.5}$ fraction was comprised of three factors attributed to 'Combustion', 'Sea salt' and 'Sulphur'. The evidence for a source of the 'Sulphur' factor is inconclusive, suggesting dominance of S concentrations by non-sea salt maritime emissions.

The PM$_{2.5}$ data from a seasonal perspective (winter and summer) revealed another factor. 'Soil' was identified as a significant contributor to particulate collected during the summer. The winter profile remained unchanged. Analysis of seasonal differences is a useful tool to help elucidate source profiles and contributions to ambient particulate concentrations.

The source profiles obtained for particulate were relatively unchanged by inclusion of gaseous pollutants and meteorological variables in the factor analysis.

Acknowledgments

References

Allen A. G., Dick, Alan L. Davison, Brian M., 1996, 'Sources of atmosphere methanesulfonate, non-sea-salt sulfate, nitrate and related species over the temperate South Pacific', Atmospheric. Environment. 31(2) 191-205.

Davy P., Markwitz A., Trompetter W.J., 2002, 'Source Characterisation of Air Particulate Emissions from a Road Tunnel in Wellington, New Zealand', *Proceedings of the 16th International Clean Air and Environment Conference, Christchurch, 2002*, Clean Air Society of Australia & New Zealand, Eastwood, NSW, Australia, in press.

Fine P. M., Cass G. R., Simoneit B. R. T. 2002, 'Chemical Characterisation of Fine Particle Emissions from the Fireplace Combustion of Woods Grown in the Southern United States', Environmental Science and Technology 36: 1442-1451

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_{10} Sampler', *Aerosol Science and Technology* **27**:726-735.

Malm W.C., Sisler J.F., Huffman D., Eldred R.A., and Cahill T.A., 1994. 'Spatial and seasonal trends in particle concentration and optical extinction in the United States', Journal of Geophysical Research., 99, 1347-1370.

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.

Wilton E., Spronken-Smith R., 2002, 'Assessing Sources of Visibility Degradation in Christchurch', *Proceedings of the 16th International Clean Air and Environment Conference, Christchurch, 2002*, Clean Air Society of Australia & New Zealand, Eastwood, NSW, Australia, in press.

Wylie D J., De Mora S J., 1996, 'Atmospheric dimethyl sulfide and sulfur species in aerosol and rainwater at a coastal site in New Zealand', Journal of Geophysical Research [Atmos.] 101 D15 21041-21049.

Appendix 6

Analysis of sources contributing to air particulate matter concentrations at Lower Hutt

Using ion beam analysis to characterise sources of air particulates in the Wellington region of New Zealand

William Trompetter[1] Andreas Markwitz[1] and Perry Davy[2]

[1]Institute of Geological and Nuclear Sciences, PO Box 31-312, 30 Gracefield Road, Lower Hutt, New Zealand

[2]Wellington Regional Council, PO Box 11-646, 142-146 Wakefield Street, Wellington, New Zealand

Summary

Measuring the total mass of air particulate provides no information on the identity of the contributing sources. Ion beam analysis can characterise air particulates. This is a key tool for identifying the elements in each sources as well as determining the proportions of the air particulate that originate from a variety of natural and manmade sources.

Air particulate of size fraction $PM_{2.5}$ and $PM_{10-2.5}$ have been detected and measured in the Wellington Region over the previous 4 years using a GENT sampler. Elements with atomic mass above neon were measured using ion beam analysis and elemental carbon was measured with a light reflectance device.

The fingerprints of the contributing sources were determined by performing factor analysis on the elemental concentrations of air particulate on filters from the different sites. The significant $PM_{10-2.5}$ factors (sources) were determined to be: Seasalt, Soil, Industry, Smoke and a source associated with vehicle sources. The concentrations of the air particulate from the Wellington Region are presented.

Keywords: Air particulate, Ion Beam analysis, Source apportionment, New Zealand

1.   Collecting and measuring air particulate

The purpose of this paper is to identify the elemental composition and concentrations of the major air particulate sources in the Wellington region of New Zealand.

1.1   Collecting Air Particulate on Filters

Air particulate of two size fractions were collected using a GENT sampler. The two size fractions are: $PM_{2.5}$ which include particles of a 2.5 micron diameter or less and $PM_{10-2.5}$ which include particles with a diameter from 2.5 to 10 microns.

The GENT sampler sucks air through a stacked filter unit and a gas meter to measure the volume and flow rate. The stacked filter unit is a size selective inlet mounted 4 m above ground level. The size selective inlet prevents air particulate larger than 10 microns from entering the stacked filter unit if the flow rate is kept above 15 lpm. The air particulate encounter the stacked filter unit, which has a coarse filter on the top, designed to allow air particulate smaller than 2.5 microns to pass through and to capture the larger air particulate. The second and final filter called the 'fine' filter is designed to capture all the fine (smaller than 2.5 microns) air particulate that passed through the 'coarse' filter. Air was passed through the filters at an initial rate of 18 lpm to collect particulate until there were enough air particulates collected on the filter to reduce the flow rate to 15 lpm. In general, collection of air particulate took 2-4 days to sample approximately 50 m^3 of air.

1.2   Collection sites

Air particulate has been collected from two sites in the Wellington region (figure 1). From April 1996 to March 1998 air particulate were collected from Baring Head, which is a Clean Air Research station on the south eastern entrance to Wellington Harbour, and approximately 20km southeast of central Wellington. The filters collected from this site contained air particulate that were mostly seasalt. For this reason the sampler was moved to an urban location at Huia Pool in Lower Hutt, 14km northeast of Wellington. Filters were collected at this site from June 1998 to June 1999.
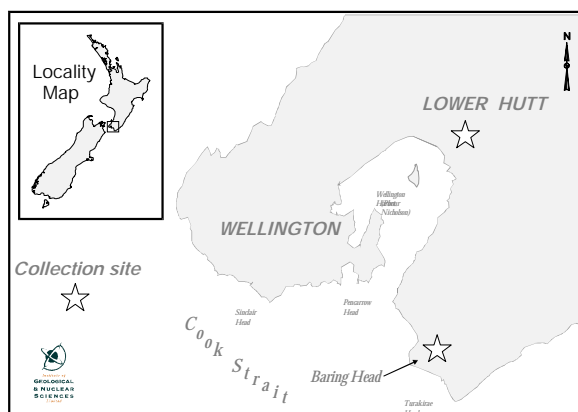

Figure 1: A map showing the sampling locations

1.3   Measuring elemental concentrations

The elemental concentrations on the filters were measured using Ion Beam Analysis (IBA). When a beam of particles hit air particulate sitting on a filter, a variety of interactions and reaction products result. From these interactions it is possible to determine elemental concentrations. Further details of these experimental methods are given in Cohen (1996a, 1996b, 2000). Figure 2 shows the range of air particulate concentrations measured in Lower Hutt between May 1998 and June 1999.
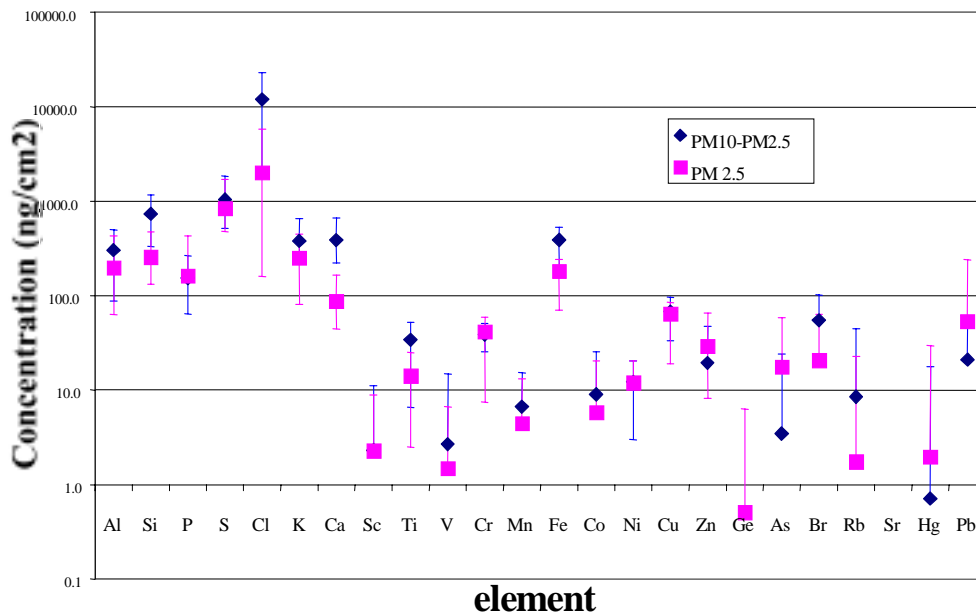
Figure 2: Range of air particulate concentrations

The generally accepted method for measuring PM$_{2.5}$ elemental carbon (soot) or Black Carbon (BC) in filters is by light reflection/transmission. Light from a light source is reflected from the filter onto a photocell to yield a value that is a measure of the reflectance for the filter. The reflectance is inversely proportional to the elemental carbon on the filter. A good correspondence ($r^2 = 0.94$) was achieved on a range of prepared standards using this method using a specially built light reflectance device.

2.   Source apportionment

2.1   Fingerprint determination

Each air filter will have a different mix of air particulate from different sources. The elements that make up a fingerprint for each source of air particulate are determined by statistically analysing the elemental composition of the particulate over a large number of air filters. A statistical package, such as STATGRAPHICS or SPLUS, can perform Factor Analysis or Principal Components Analysis to determine the grouping of elements that vary together and therefore determine the elements of a fingerprint. Table 1 lists the elemental correlations for five significant factors from the Wellington region.

Table 1: Factor analysis scores

	Factor1	Factor2	Factor3	Factor4	Factor5
	"Seasalt"	"Soil"	"Industry"	"Smoke"	"Bromine"
Cl	**0.94**	-0.07	0.04	0.00	0.13
Na	**0.90**	0.17	0.25	0.02	0.06
Ca	**0.88**	**0.40**	0.01	0.05	0.09
Mg	**0.85**	**0.40**	0.20	0.10	0.11
Si	0.20	**0.92**	0.13	0.04	0.10
Al	0.14	**0.91**	0.22	0.02	0.05
S	**0.40**	**0.77**	0.00	-0.10	-0.05
P	-0.55	**0.64**	0.20	0.28	-0.01
Sc	-0.07	-0.04	**0.79**	-0.03	-0.34
Cr	0.25	0.18	**0.79**	**0.27**	0.31
Fe	0.22	0.32	**0.73**	**0.32**	0.35
Ti	0.24	0.35	**0.67**	-0.11	0.13
Pb	0.04	0.00	-0.03	**0.89**	0.06
C	-0.09	-0.05	**0.48**	**0.59**	0.03
K	0.28	0.27	0.11	**0.42**	**0.46**
Br	0.09	-0.03	0.05	0.03	**0.91**

The five factors were given a name based on their composition (table 1).

1. Factor 1 contains all the Cl, most of the Na, Ca, Mg and some of the S. The main source of salt is the sea, so this factor is labelled "Seasalt".

2. Factor 2 contains all the Si and Al, most of the S and P, some Ca, Mg, Ti, Fe and K. This is typical of the composition of soil, hence this Factor is labeled "Soil".

3. Factor 3 has all the Sc, most of the Cr and Fe, and some elemental C. The most likely source of heavy metals is industry, hence this factor is labeled "Industry".

4. Factor 4 contains all the Pb and some of the K, Fe, Cr and elemental C. The K and elemental C are associated with smoke. Hence this Factor is labeled "Smoke".

5. Factor 5 is a Br, K mixture. Br and K can be associated with vehicles but two elements do not identify a factor strongly enough. In many countries lead is added to petrol which provides an additional element to fingerprint vehicle sources. New Zealand petrol has been lead free since 1996 hence we have simply labeled this factor "Bromine". Our future work will include sampling in locations where vehicle emissions are high in an effort to confirm that this fingerprint is from vehicles.

a) Sodium PM$_{2.5}$ (ng/m^3) versus Chlorine (ng/m^3)

Legend:
◆ Na (seasalt)
+ Na (mixture)
— Linear Fit

b) Magnesium PM$_{2.5}$ (ng/m^3) versus Chlorine (ng/m^3)

Legend:
■ Mg (seasalt)
+ Mg (mixture)
— Linear Fit
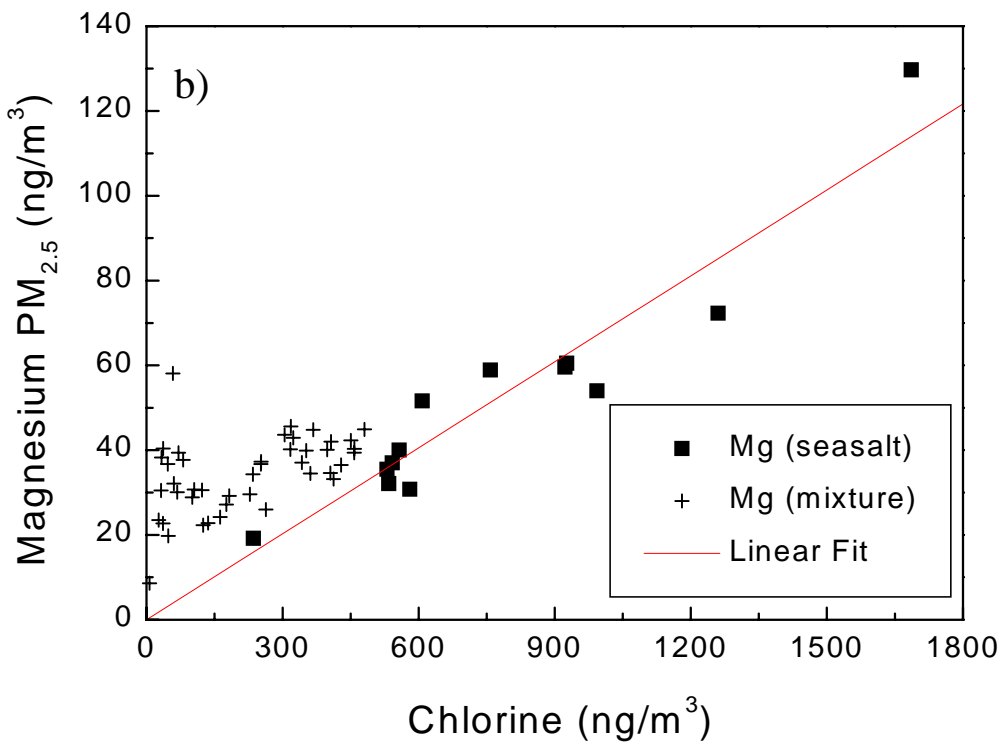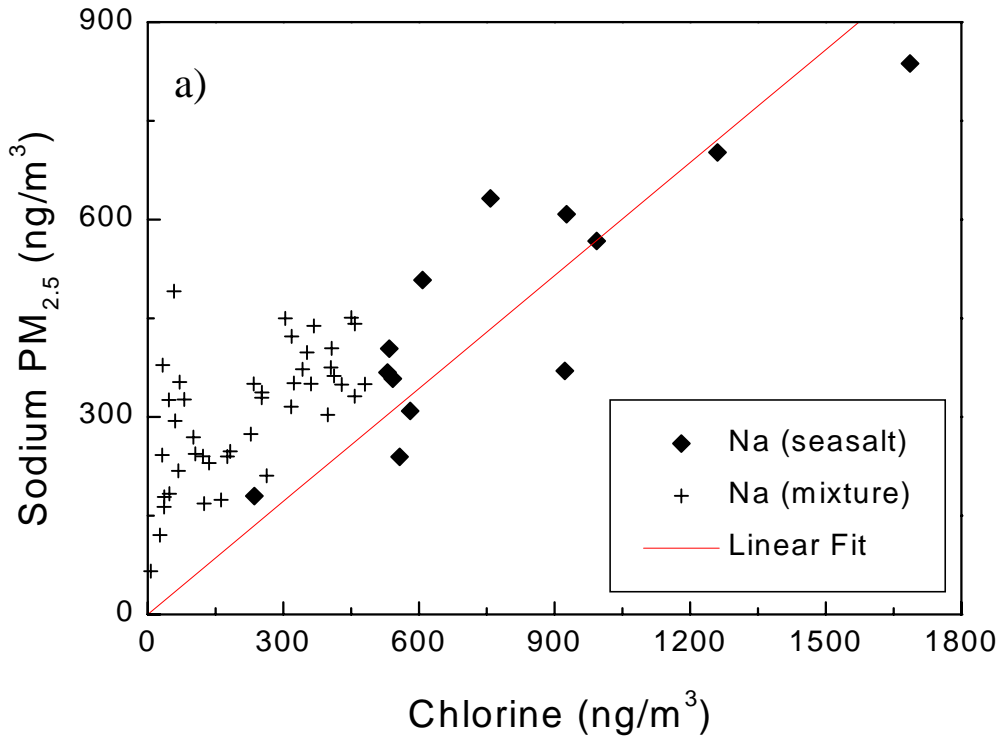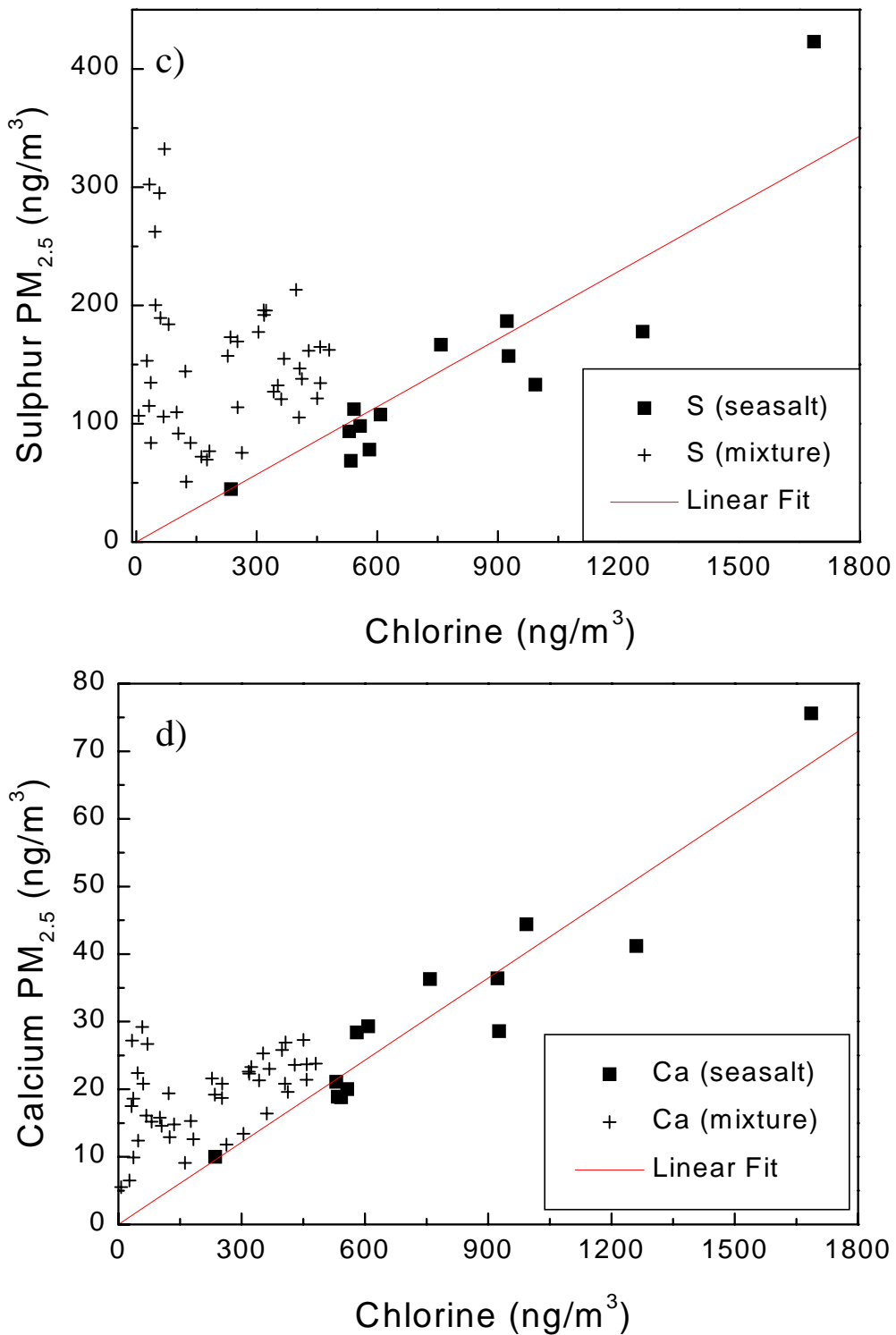
Figure 3: Major elements in seasalt; a)Na, b)Mg, c)S, d)Ca

To show how the air filters can have a different mix of air particulates from different possible sources, some elemental plots are shown in Figure 3. The plots are based on Cl (bottom axis) which is principally associated with Factor 1 ("Seasalt"). The filters which are principally "Seasalt" typically have a lower elemental ratio with Cl whereas higher elemental ratios with Cl also contain elements from other sources. The Na vs Cl plot shows that Na from seasalt has an elemental ratio of 0.57 to Cl. Filters with additional Na from other sources

occur above this line. Similarly Ca, Mg and S are plotted against Cl and the elemental ratios with respect to Cl are determined. Sodium, Ca, Mg and S can also occur in significant amounts in the "Soil" factor.

The percentage contribution of each element in a fingerprint is determined from specific filters that are identified as principally containing air particulates from a specific source. From these specific filters the elemental ratios were calculated and listed in Table 2.

Table 2: Composition of fingerprints

| Element | Fingerprints | | | | |
	"Seasalt"	"Soil"	"Smoke"	"Industry"	"Bromine"
C			95.6%	68.4%	
Na	20.4%			14.3%	
Mg	4.2%	7.3%			
Al		5.5%			
Si		17.5%			
P		2.0%			
S	9.3%	63.0%			
Cl	63.6%				
K			2.8%		27.2%
Ca	2.6%	4.8%			
Sc				0.2%	
Ti				0.4%	
Cr				4.0%	14.7%
Fe				12.6%	53.5%
Br					4.5%
Pb			1.6%		
Total	100.0%	100.0%	100.0%	100.0%	100.0%

2.2 Estimation of source contribution

Once the sources were identified and their fingerprints determined, the origin of the air particulates on individual filters was estimated. The variation of the different air particulate sources collected on filters in Lower Hutt from June 1998 – June 1999 are shown in Figure 4. Interestingly, "Smoke" air particulates show a seasonal variation with peaks during the winters (Mar-Aug) and a trough in summer (Oct-Jan). This can be explained with the use of domestic fires for heating requirements during winter.
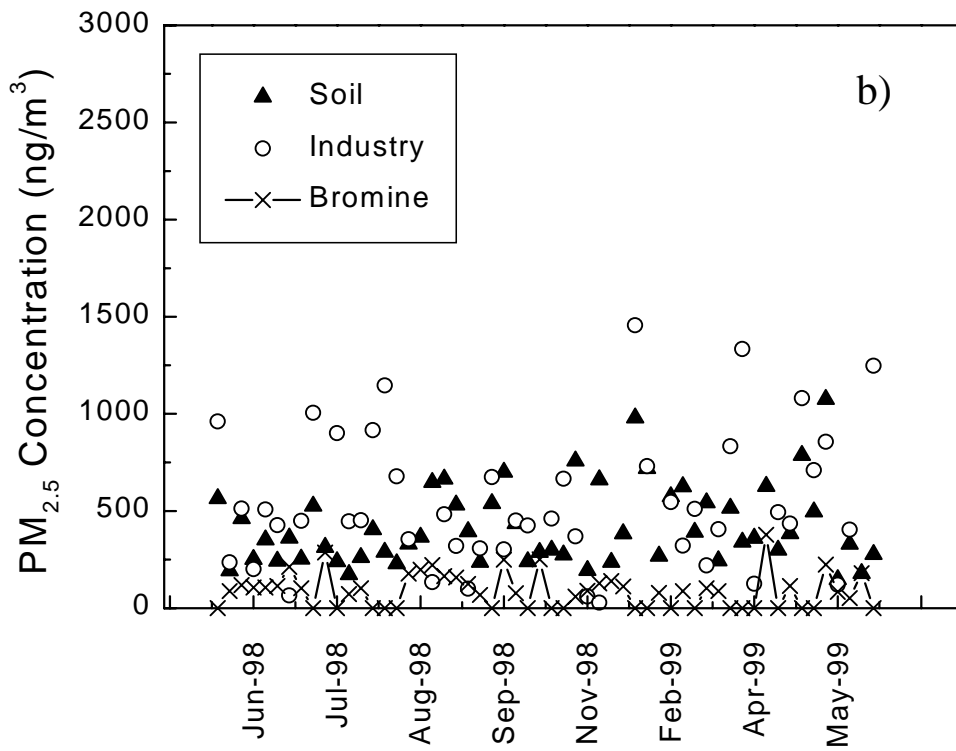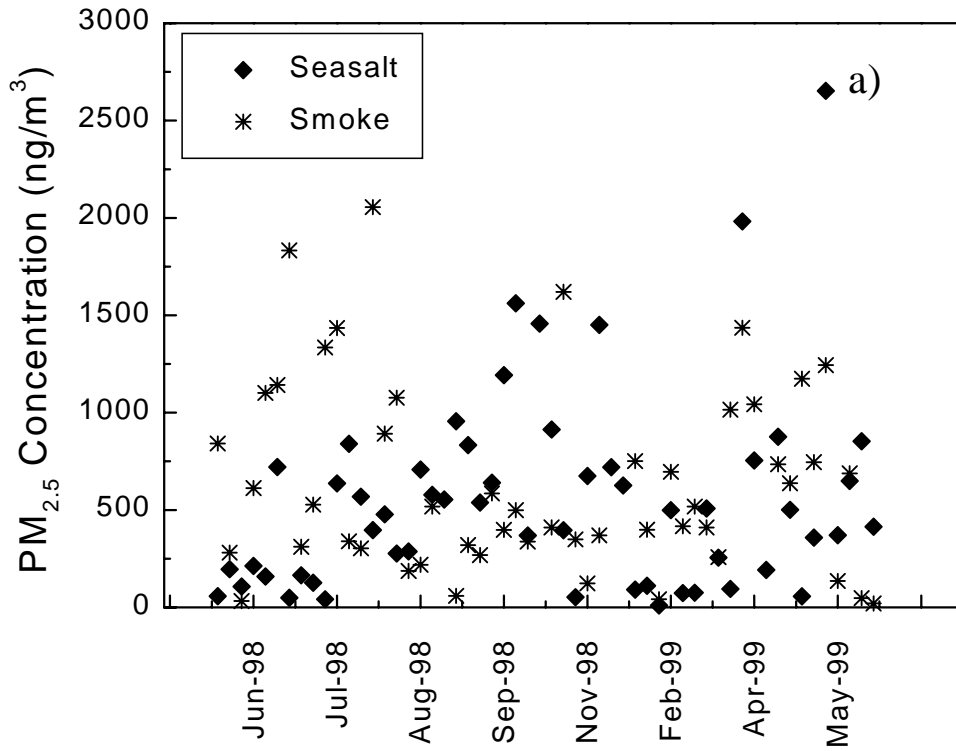
Figures 4a and 4b: PM$_{2.5}$ Source concentrations of five fingerprints

Table 3: Average PM$_{2.5}$ source concentrations

Fingerprint	Concentration (ng/m^3)	Std deviation (ng/m^3)
Seasalt	552	512
Soil	418	205
Smoke	572	552
Industry	443	695
Bromine	88	90

As can be seen in Figure 4 and the table of average source concentrations (Table 3), large variations in the concentration of air particulates occur from the various identified sources. This is to be expected as a wide range of source activities and meteoric conditions act as sources and sinks of air particulates. This is the subject of a second paper also being presented at this conference. (Trompetter, Markwitz & Davy CASANZ 2000)

2.3   PM$_{10-2.5}$ results

The same analysis procedures were carried out on PM$_{10-2.5}$ air particulate filters (Table 4). PM$_{10-2.5}$ air particulates are created principally from mechanical grinding or movement type processes and generally do not contain particulates from combustion processes. These activities occur in the production of seasalt (wind & waves), soil (wind blown soil) and some industry particulates. The concentrations from central Lower Hutt from June 1998 – June 1999 (Figure 5 & Table 5) show that PM$_{10-2.5}$ is mainly correlated with the "Seasalt" air particulates.

Table 4: Composition of PM$_{10-2.5}$ fingerprints

Element	"Seasalt"	"Soil"	"Industry"
Na	28.9%		69.4%
Mg	2.5%		
Al		10.0%	
Si		34.3%	
S	4.4%	14.0%	8.2%
Cl	59.4%		
K	2.0%	8.6%	
Ca	2.5%	12.5%	
Cr			3.8%
Fe		20.4%	16.1%
Total	100.0%	100.0%	100.0%
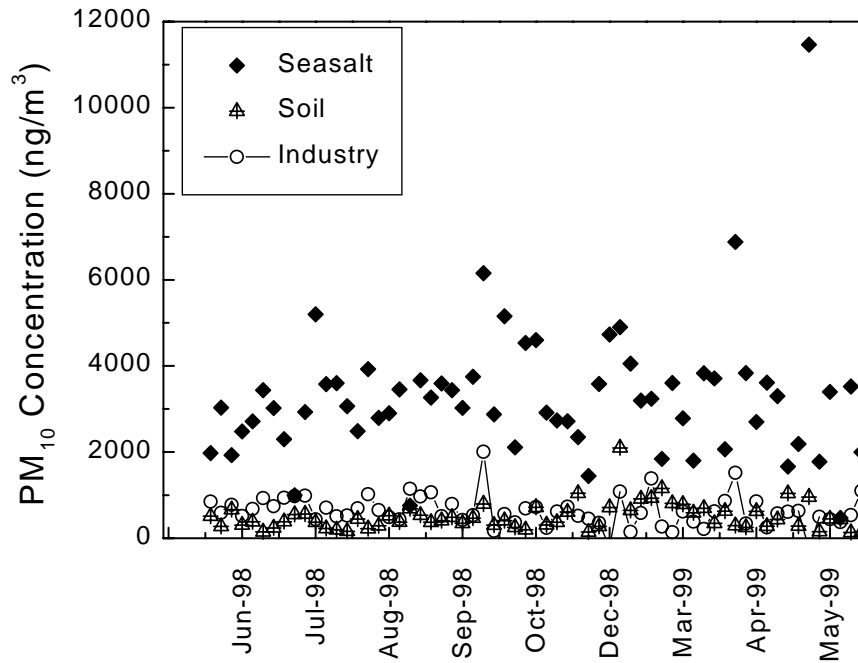
Figure 5: PM$_{10\text{-}2.5}$ source concentrations

Table 5: Average PM$_{10\text{-}2.5}$ source concentrations

Fingerprint	Concentration (ng/m^3)	Std deviation (ng/m^3)6
Seasalt	3255	1572
Soil	496	325
Industry	634	370

3.   Conclusions

- The elemental composition of the major air particulate sources in the Wellington region of New Zealand were determined using Ion Beam Analysis.

- Significant PM$_{2.5}$ sources were determined to be: Seasalt, Soil, Industry, Smoke and a source associated with vehicles (labeled "Bromine"). The significant PM$_{10\text{-}2.5}$ sources were determined to be: Seasalt, Soil and Industry.

- The average PM$_{2.5}$ source concentrations of the air particulates from an urban site in the Wellington Region were:

Fingerprint	Concentration (ng/m^3)	Std deviation (ng/m^3)
Seasalt	552	512
Soil	418	205
Smoke	572	552
Industry	443	695
Bromine	88	90

- The average PM10-2.5 source concentrations of the air particulates from an urban site in the Wellington Region were:

Fingerprint	Concentration (ng/m³)	Std deviation (ng/m³)
Seasalt	3255	1572
Soil	496	325
Industry	634	370

Acknowledgments

References

DD Cohen et al, 1996a, *Nuclear Instruments and Methods in Physics Research B 109/110* 1996 pp218-226

DD Cohen 1996b, *Proceedings of an International Symposium on Harmonization of Health Related Environmental Measurements Using Nuclear and Isotope Techniques* Organised by the IAEA Hyderabad India 4-7 November 1996, IAEA-SM-344/23.

DD Cohen et al, 2000, *Nuclear Instruments and Methods in Physics Research B 161-163* 2000 pp775-779.

Air particulate analysis in New Zealand with ion beam analysis: correlation of elemental fingerprints with meteorological data in the Wellington region

William J. Trompetter[1], Andreas Markwitz[1] and Perry Davy[2]

[1]Institute of Geological and Nuclear Sciences, PO Box 31-312, 30 Gracefield Road, Lower Hutt, New Zealand

[2]Wellington Regional Council, PO Box 11-646, 142-146 Wakefield Street, Wellington, New Zealand

Summary

Air particulates of size fraction $PM_{2.5}$ and $PM_{10-2.5}$ have been collected on filters using a GENT sampler in the Wellington Region over the previous 2 years. Ion beam analysis was used to identify the elements comprising the air particulate matter on these filters and to determine the contributions to atmospheric particulate concentrations from both natural and manmade sources. The significant factors (sources) were determined to be: Seasalt, Soil, Industry, Smoke and Bromine.

The concentrations of particulate from different sources were observed to fluctuate over time and it was thought that various meteorological conditions would have an influence. To test this hypothesis we analysed our data to include the influence of meteorological conditions on air particulates.

Keywords: Air particulate, Ion beam analysis, Source apportionment, Meteorological data, Wellington, New Zealand.

1.   Introduction

The purpose of this paper is to investigate how different sources of air particulates are influenced by meteorological conditions in the Wellington region.

Air particulates have been collected from two different sites in the Wellington region (Figure 1). From April 1996 to March 1998 air particulates were collected from Baring Head which is a clean air research station on the south eastern entrance to Wellington Harbour, and approximately 20 km south east of central Wellington City. The filters collected from the Baring Head site showed the signature of Seasalt, mostly. For this reason the sampler was moved to an urban location at Huia Pool in Lower Hutt, 14 km northeast of Wellington City. At the Lower Hutt location, filters were collected from June 1998 to June 1999. Average, minimum and maximum values for wind speed, wind direction and temperature were obtained from continuous monitors at the same site as the GENT sampler. Hourly rainfall data was obtained from a continuous monitor nearby.

Meteorological conditions in the Hutt Valley are influenced by the local topography. Hills and mountains, ranging from 500 m to 1500 m above sea level surround the valley on three sides, while to the south the valley opens out into Wellington Harbour. This topography acts to confine air pollutants within the valley during periods of calm wind conditions, especially during winter when significant temperature inversions can occur which further restrict pollution dispersion. Predominant winds are from the northerly and southerly quarters with higher average wind speeds experienced during spring and autumn. Temperature inversions and calm conditions are often experienced on cold winter mornings when air pollutants can build-up in the stagnant air mass.
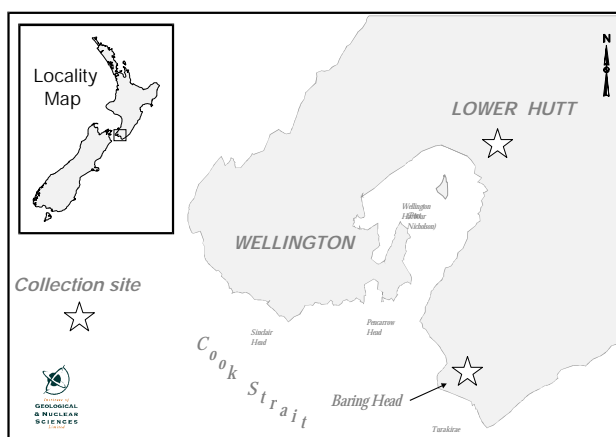
Figure 1: A map showing the sampling locations

Air particulate of two size fractions were collected using a GENT sampler. The two size fractions are: $PM_{2.5}$ which include particles of a 2.5 micron diameter or less and $PM_{10-2.5}$ which is comprised of particles with a diameter between 2.5 micron and 10 microns. Details of the GENT sampler are given in Hopke (1997). The $PM_{10-2.5}$ particulate concentrations measured with the GENT sampler was found to agree reasonably well with PM_{10} particulate

concentrations measured with a TEOM sampler for the monitoring period 8/5/98 to 1/6/99 with an average concentration over this period of 12 µg/m^3.

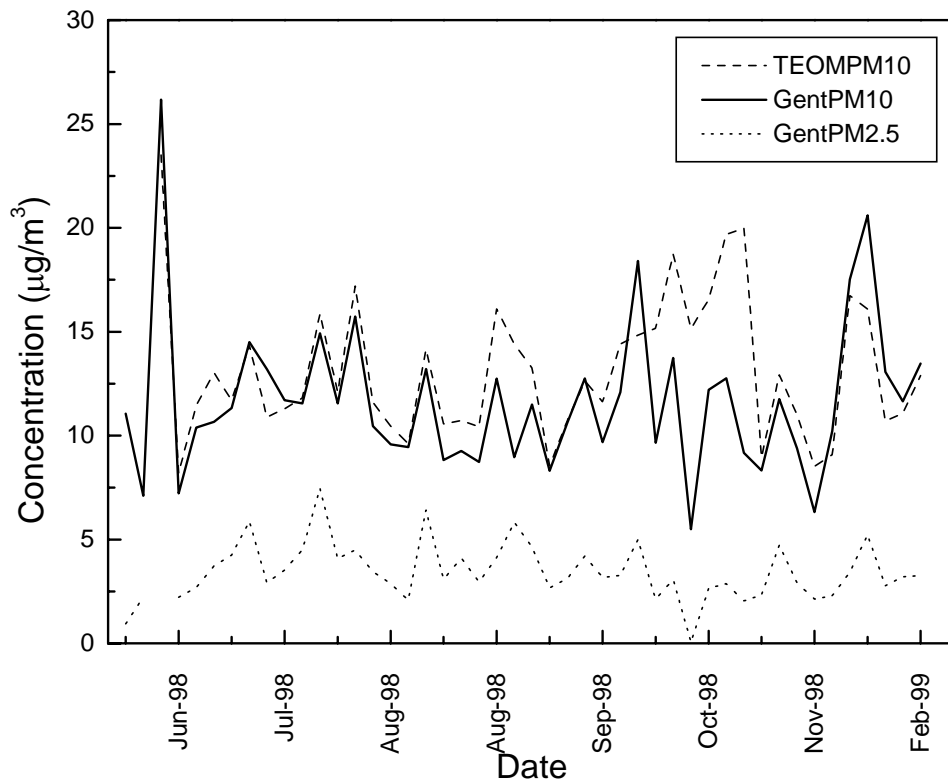Figure 2: Comparison of PM$_{10}$ TEOM with GENT PM$_{10-2.5}$ and PM$_{2.5}$ particulate concentrations

The elemental concentrations of the air particulates sitting on the filters were measured using ion beam analysis (IBA). When a beam of particles strikes the air particulate matter on a filter, a variety of interactions and reaction products can occur. From these interactions it is possible to determine the elemental composition and concentrations of the particulate matter on a filter. Further details of these experimental methods are given for example in Cohen (1996a, 1996b, 2000).

Naturally, each air filter has a different mix of air particulates from different sources. The elements that make up a finger print for each source of air particulates are determined by statistically analysing the elemental variations of the filters over a large number of air filters. Statistical packages such as STATGRAPHICS or SPLUS can be used to perform factor analysis or principal components analysis to determine the grouping of elements that vary together and thus determine the elements that form a fingerprint. This follows the approach of numerous others, for example Motallebi (1999) and Cohen (1996a, 1996b, 2000). In our first paper at this conference (Trompetter, Markwitz & Davy, CASANZ 2000), factor analysis of the elemental concentrations from the Wellington Region revealed five fingerprints: "Seasalt", "Soil", "Industry", "Smoke" and "Bromine". Once the sources were identified and their fingerprints determined, the origin of the air particulates on individual filters was estimated. The variation of the different PM$_{2.5}$ air

particulate sources collected on filters in Lower Hutt from June 1998 – June 1999 are shown in Figures 3a and 3b. The average concentrations are shown in Table 1.
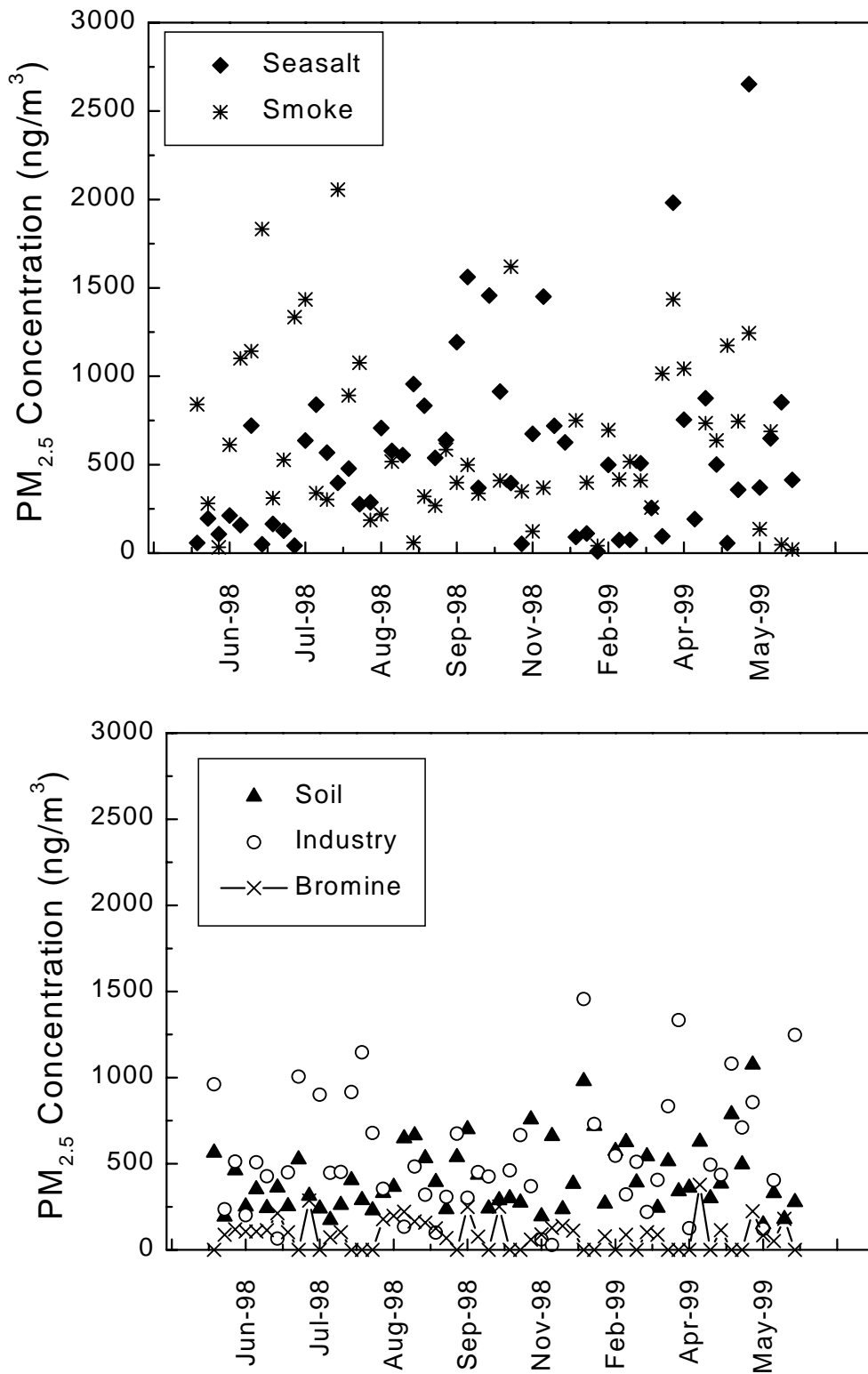
Figures 3a and 3b: PM$_{2.5}$ source concentrations of the five fingerprints

Table 1: Average PM$_{2.5}$ source concentrations

Fingerprint	Elements	Conc. (ng/m³)	Std dev. (ng/m³)
Seasalt	Na,Mg,S,Cl,Ca	552	512
Soil	Mg,AlSi,P,S,Ca	418	205
Smoke	El.C,K,Pb	572	552
Industry	El.C,Na,Sc,Ti,Cr,Fe	443	695
Bromine	K,Cr,Fe,Br	88	90

PM$_{10-2.5}$ air particulates are created principally from mechanical grinding or movement type processes and generally do not contain particulates derived from combustion processes. Mechanical processes are involved in the production of seasalt (wind and waves), soil (wind blown soil) and some industry air particulates. The PM$_{10-2.5}$ concentrations of "Seasalt", "Soil" and "Industry" are shown in Figure 4. The concentrations from central Lower Hutt from June 1998 – June 1999 (Table 2) show that PM$_{10-2.5}$ is mostly "Seasalt" air particulates.
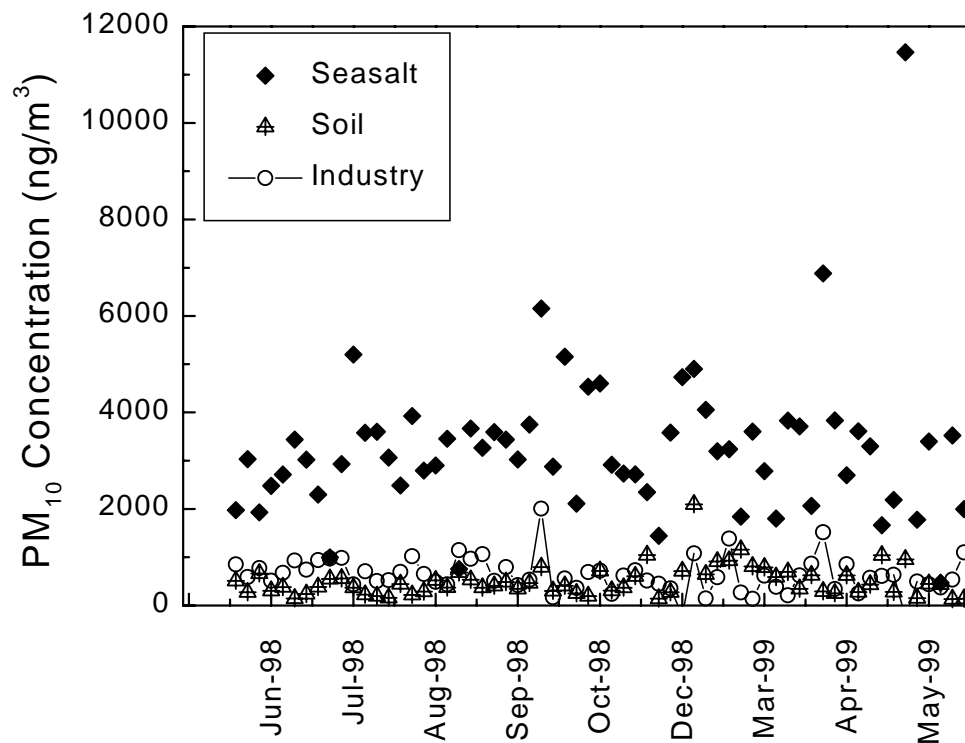

Figure 4: PM$_{10-2.5}$ source concentrations of 3 fingerprints

Table 2: Average PM$_{10-2.5}$ source concentrations

Finger Print	Element composition	Conc. (ng/m³)	Std dev (ng/m³)
Seasalt	Na,Mg,S,Cl,K,Ca	3255	1572
Soil	Al,Si,S,K,Ca,Fe	496	325
Industry	Na,S,Cr,Fe	634	370

2. Trends between air particulate and meteorological conditions

To investigate the dependence of meteorological factors on sources of air particulates, correlations are used from statistical software and spreadsheet analysis to determine statistically significant relationships between meteorological conditions and air particulate sources. The results are shown in tables 3 and 4. The bold typed values show significant relationships that are used for interpretation purposes in this paper. In addition, various meteorological factors on a source of air particulates are shown in x-y plots to illustrate these relationships in the data.

2.1 Seasalt

Both $PM_{2.5}$ and $PM_{10-2.5}$ "Seasalt" particulates were observed to be principally dependent on the wind speed. (Figures 5 and 6). This is consistent with the understanding of seasalt particulates being created from the mechanical action of the wind on the sea. There was also a slight negative correlation with easterly winds which is due to winds from the easterly quarter being of lower wind speed on average.

Table 3: $PM_{2.5}$ Meteorological and source correlations

	Seasalt	Soil	Industry	Smoke	Bromine
$PM_{2.5}$	**0.41**	**0.61**	**0.49**	**0.65**	0.04
PM_{10}	**0.74**	**0.47**	-0.08	0.20	0.23
$PM_{10-2.5}$	**0.81**	**0.47**	0.01	0.14	0.30
Rainfall	0.03	**-0.69**	-0.10	-0.10	-0.30
Wind North	-0.06	**0.70**	0.08	-0.17	0.06
Wind East	**-0.84**	0.02	-0.07	-0.03	-0.19
Wind South	-0.25	0.22	-0.04	0.32	0.11
Wind West	-0.02	0.15	0.08	0.20	-0.06
WindS. Min	0.15	-0.62	0.07	-0.08	-0.18
WindS. Avg	**0.84**	0.02	0.08	-0.13	0.08
WindS. Max	**0.80**	-0.29	-0.25	-0.11	0.31
Temp Min	-0.08	0.12	0.12	-0.45	-0.19
Temp Avg	-0.20	0.17	0.01	-0.39	-0.28
Temp Max	-0.22	0.38	0.10	-0.15	-0.36

Table 4: $PM_{10-2.5}$ meteorological and source correlations

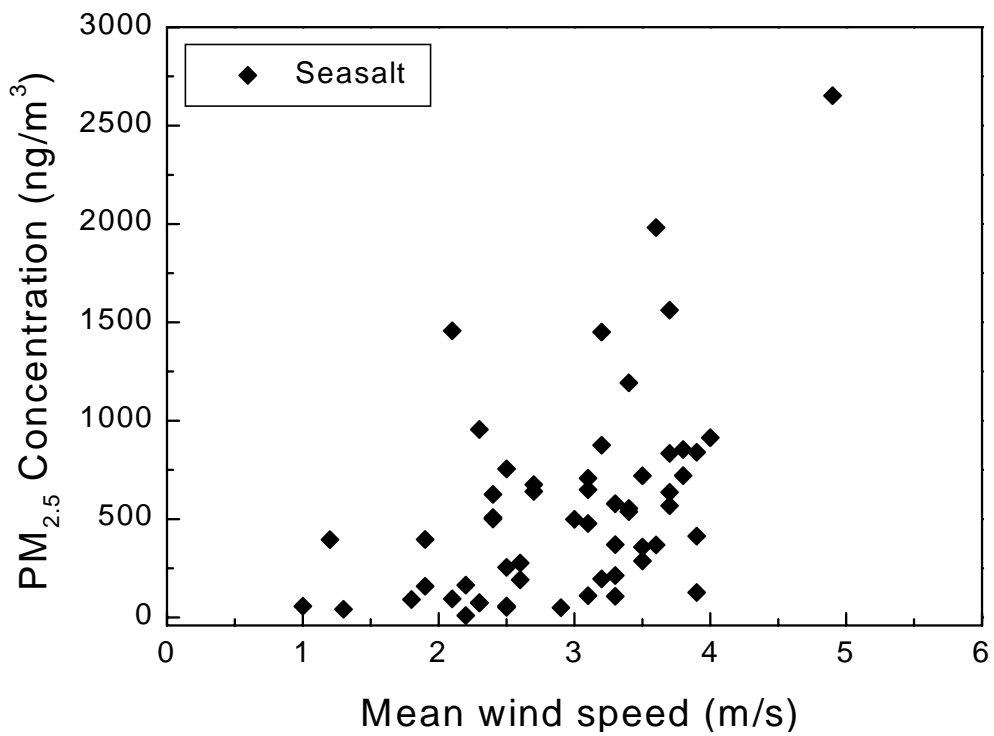|	Seasalt	Soil	Industry
$PM_{2.5}$	0.46	0.35	0.37
PM_{10}	**0.96**	**0.96**	0.13
$PM_{10-2.5}$	**0.88**	**0.94**	-0.06
Rainfall	-0.17	**-0.58**	-0.13
Wind North	0.00	-0.12	0.13
Wind East	-0.06	**0.84**	-0.32
Wind South	0.02	-0.04	-0.02
Wind West	0.04	0.12	0.05
WindSp. Min	0.01	-0.11	0.38
WindSp. Avg	0.29	**-0.79**	-0.13
WindSp. Max	0.20	**-0.71**	-0.26
Temp Min	0.03	-0.07	0.25
Temp Avg	0.11	0.11	-0.06
Temp Max	0.26	-0.33	-0.16

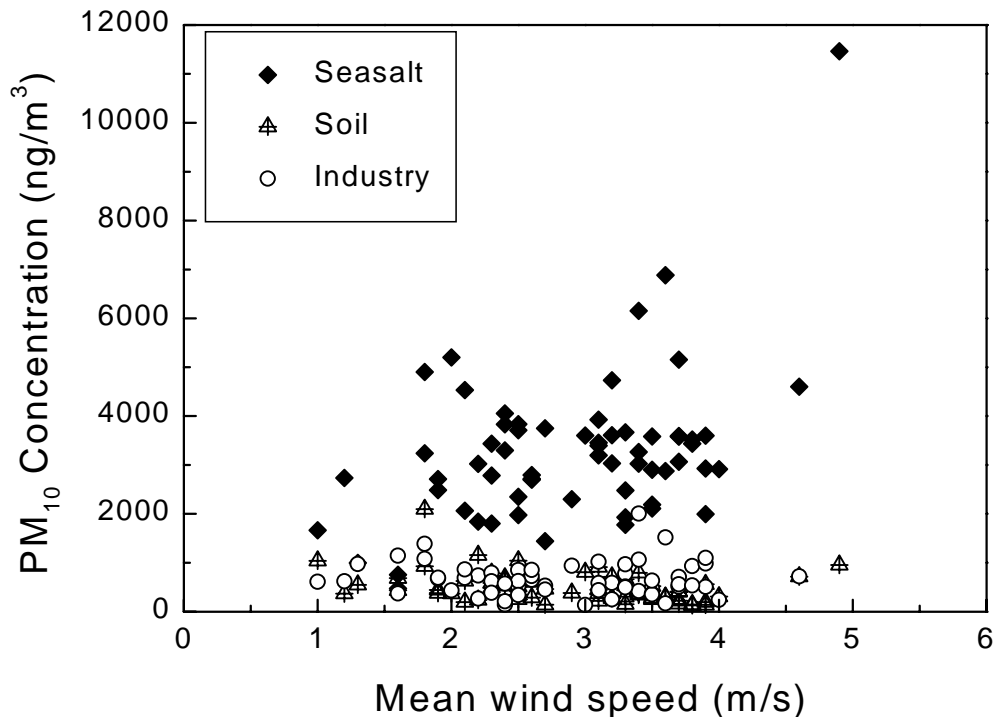Figure 5: $PM_{2.5}$ "Seasalt" and mean wind speed

Figure 6: PM$_{10-2.5}$ sources and mean wind speed

2.2 Soil

Soil particulates are also created from the mechanical action of the wind similar to the creation of seasalt particulates. For this reason, no positive correlation between soil particulate concentrations and wind speed for the Lower Hutt data came as a surprise. Instead the data showed an inverse correlation with wind speed (Figures 7 and 8) and a correlation with easterlies. Synoptic weather patterns in the Wellington Region are such that air masses originate over the ocean no matter what the wind direction. For higher wind speeds an air mass travels over more ocean and entrains a greater amount of seasalt particulate. Any soil particulates produced by higher wind speeds tend to be diluted/dispersed into a larger volume of air as the air mass crosses land. This results in a lower proportion of the 'soil factor' comprising particulate concentration.

Conversely, with lower wind speeds, the air mass will spend a greater percentage of its time over land resulting in a greater entrainment of soil particulates in the air mass. This is observed additionally in the PM$_{10-2.5}$ data for soil (Figure 9).

An obvious property of soil is that the amount of particles is reduced with increased moisture in the soil (ei less dusty when wet). This property is confirmed by the results for both PM$_{2.5}$ and PM$_{10-2.5}$ soil particulates. Plotting the soil particulate concentration against rainfall in Figure 10, an inverse relation is observed where higher soil particulate concentrations occur for lower rainfalls, or conversely, lower soil particulate concentrations occur during wetter periods.
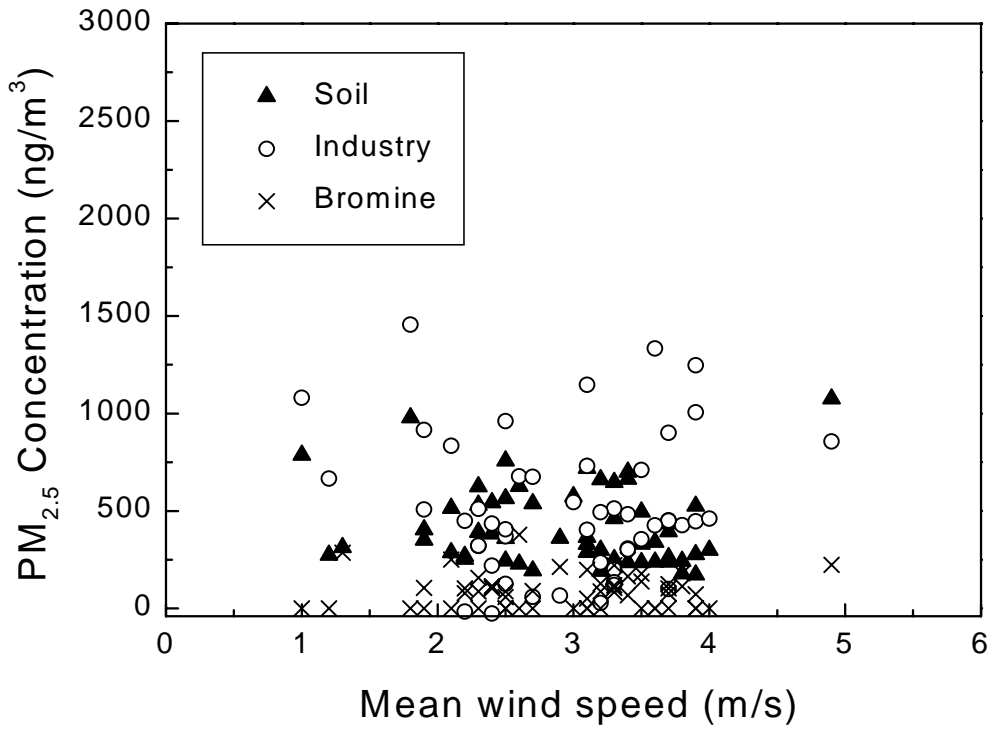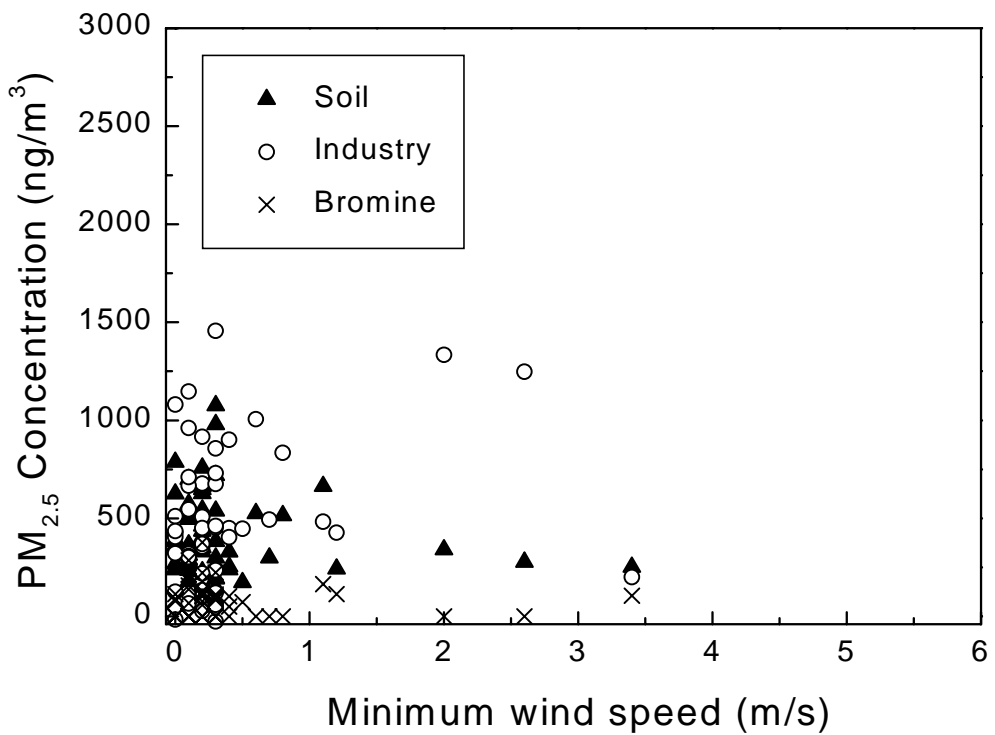
Figure 7: PM2.5 sources and mean wind speed
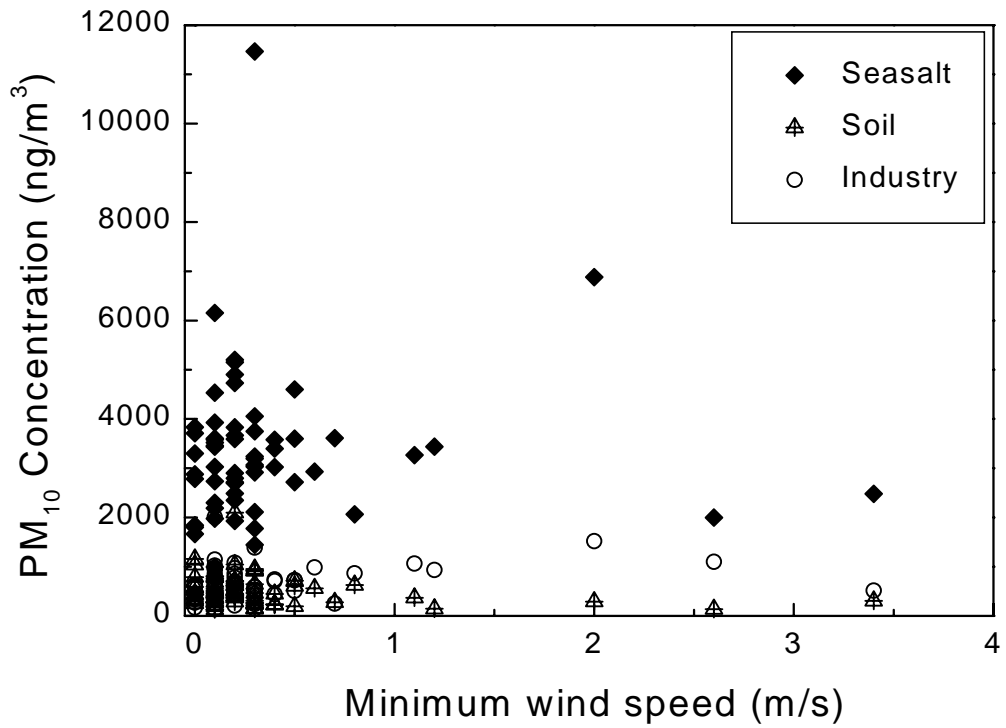

Figure 8: PM2.5 sources and minimum wind speed

Figure 9: PM10-2.5 sources and minimum wind speed
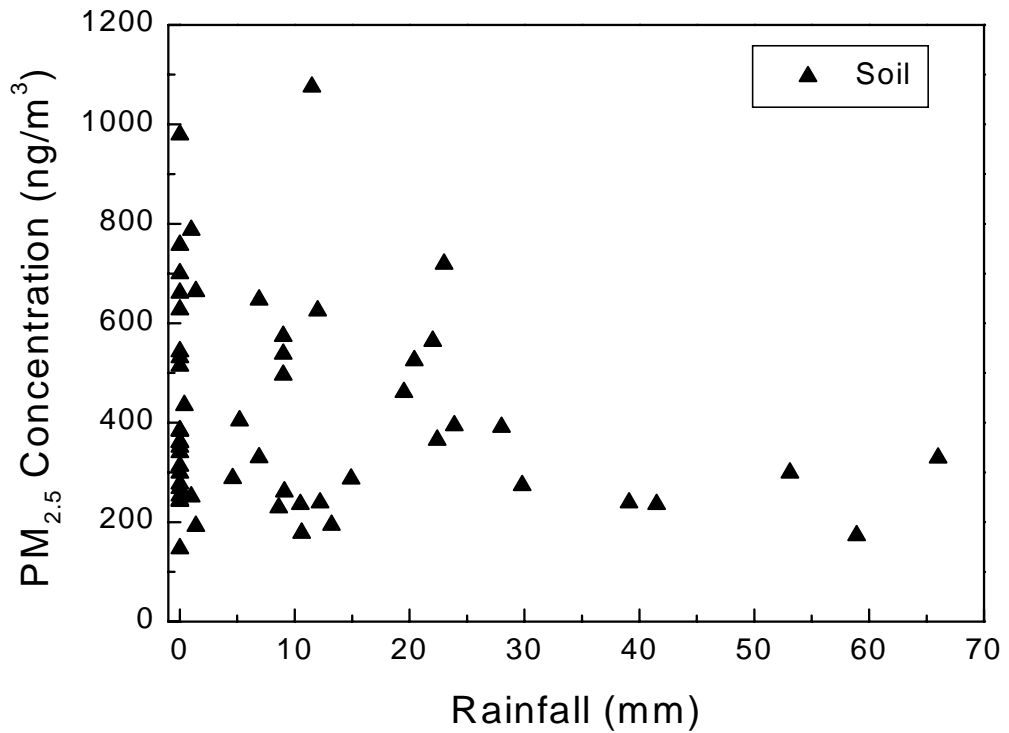

Figure 10: PM2.5 "Soil" and rainfall

2.3   Smoke, industry & bromine

The smoke and industry sources showed no significant relationships with the meteorological data (tables 3 and 4, Figures 6-9). This is because the Wellington region has very few large industrial type activities and production of particulate from these sources is independent of the meteorological conditions. Natural sources of air particulate such as seasalt and soil dominate particulate composition on average when compared to anthropogenic particulate pollution sources.

The authors of this paper suspect the bromine source to originate from the vehicle emissions. In many countries lead is added to petrol which provides a key element for the fingerprinting of this source. New Zealand petrol has been lead free since 1996. Our future work will include sampling in locations where vehicle emissions are high in an effort to confirm that the "bromine" labeled source originates from vehicle emissions and whether other elements should be included in this fingerprint. Interestingly, the bromine particulate showed an inverse proportionality relationship to rainfall (Figure 11). While the exact significance of this relationship is unclear at this stage, either the rainfall affects the production of bromine air particulates or the humidity removes the bromine air particulates out of the atmosphere.
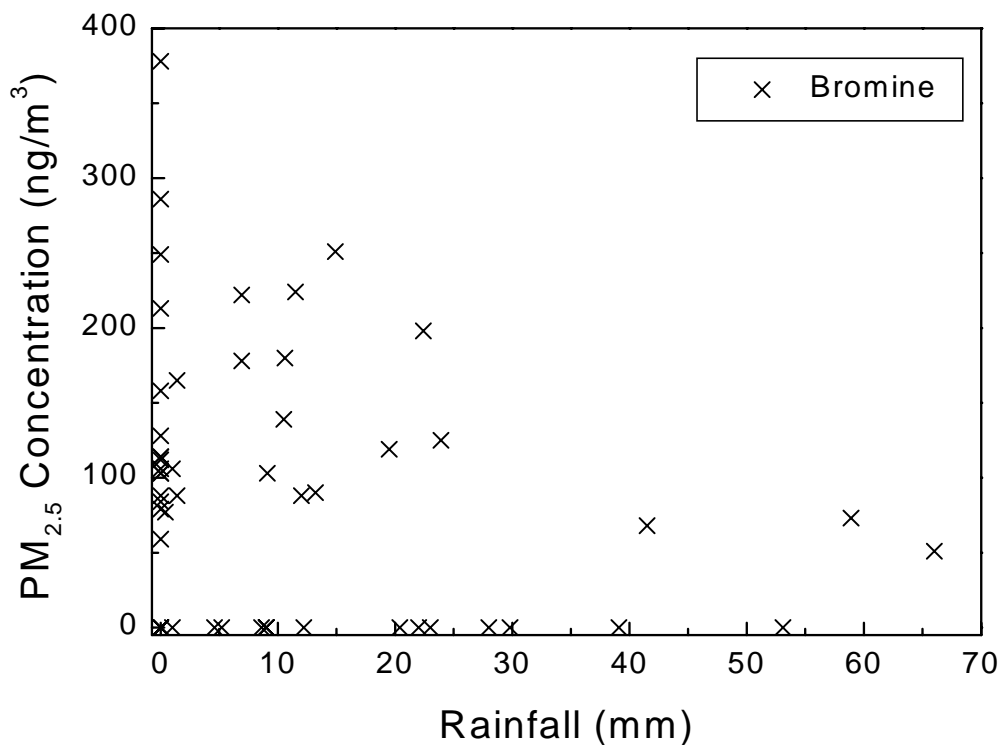
Figure 11: PM2.5 "Bromine" and rainfall

3. Conclusions

- Seasalt particulate concentrations principally depend on the wind speed, which support the understanding that these particulates are created from the mechanical action of the wind on the sea.

- There was no significant correlation between the soil particulate concentrations and wind speed for the data from the urban site (Lower Hutt). This can be explained by the high wind speeds in the Wellington region, where the air mass travels over more ocean than land and the soil particulates produced over land are diluted/dispersed into a larger volume of air.

- The Wellington region has very few large industrial type activities that discharge particulate into the atmosphere.

Acknowledgements

References

DD Cohen et al, 1996a, *Nuclear Instruments and Methods in Physics Research B 109/110* 1996 pp218-226

DD Cohen 1996b, *Proceedings of an International Symposium on Harmonization of Health Related Environmental Measurements Using Nuclear and Isotope Techniques* Organised by the IAEA Hyderabad India 4-7 November 1996, IAEA-SM-344/23.

DD Cohen et al, 2000, *Nuclear Instruments and Methods in Physics Research* B 161-163 2000 pp775-779.

PK Hopke et al, 1997, *Aerosol Science and Technology* 27:726-735.

N Motallebi, 1999, *J. Air & Waste Management Assoc.* 49: PM-25-34.

Appendix 7

Analysis of sources contributing to air particulate matter concentrations at Wairarapa College, Masterton

Elemental analysis and source apportionment of ambient particulate matter at Masterton, New Zealand

P. DAVY[1]
Wellington Regional Council, PO Box 11-646, 142-146 Wakefield Street,
Wellington, New Zealand

W.J. TROMPETTER AND A. Markwitz
The Institute of Geological and Nuclear Sciences, Rafter Laboratory, P.O. Box 31-312, Lower Hutt, New Zealand

D. C. Weatherburn
School of Chemical and Physical Sciences, Victoria University of Wellington, PO Box 600, Wellington, New Zealand

Abstract

At certain locations in the Wellington Region, pollution episodes due to air particulate matter are known to occur from time to time. Traditional gravimetric analysis of airborne particulate matter is unable to provide information on the sources contributing to air particulate concentrations. Ion Beam Analysis (IBA) is one of the few non-destructive techniques that can be used to identify the elemental composition of air particulate matter on a filter sample. In this work IBA was used to characterise air particulate matter in two size fractions, $PM_{20.}$ and $PM_{10-2.0}$, collected at a monitoring station in Masterton, New Zealand. Elements with atomic mass above neon were measured by the PIXE technique. Elemental carbon was measured with a light reflectance device. Elemental 'fingerprints' of contributing sources were determined by performing factor analysis of the elemental composition. The results indicate that 'Sea Salt' and 'Soil' sources are major contributors to the coarse ($PM_{10-2.0}$) fraction and 'Combustion' sources dominate the fine ($PM_{2.0}$) fraction of air particulate matter. Analysis of seasonal differences was a useful tool in elucidating source profiles.

Keywords: Particulate Matter; PIXE; Source Apportionment; New Zealand

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 collects two different size fractions, $PM_{2.0}$ or fine particulate matter and $PM_{10-2.0}$ or coarse particulate matter on to 47mm polycarbonate filters[1]. This paper presents the results of air particulate

---

[1] Correspondence to: P K Davy, Wellington Regional Council, PO Box 11-646, 142-146 Wakefield Street, Wellington, New Zealand, Tel. ++64-4-384-5708; Fax: ++64-4-385-6960; email: perry.davy@gw.govt.nz

sampling carried out at Masterton NZ, from April 2002 to November 2004. The purpose of the monitoring program was to characterise the elemental composition of ambient particles and then use the results for source apportionment of ambient particulate matter.

The concentrations of $PM_{2.0}$ and $PM_{10-2.0}$ collected by the GENT sampler at Masterton were determined gravimetrically and then the elemental composition of particulate matter on the filters was analysed at the New Zealand Ion Beam Analysis facility[2]. The fingerprints of the contributing sources were determined by performing factor analysis on the elemental concentrations of air particulate on the filters.

1. Monitoring location

The Wairarapa College monitoring site was approximately 1 kilometre from the central business district of Masterton. Masterton is a town with a population of around 20,000 and lies in the Wairarapa Valley 80 km to the northeast of Wellington City. Predominate land uses around the town are rural agricultural activities. 10 km to the west of the town are the Tararua Ranges, which rise to approximately 1500m. 10 km to the east are a range of hills 300m high and 30 km beyond that is the eastern coast. Co-located at the site were the GENT sampler used for this study, continuous CO, NOx and PM_{10} (TEOM) analysers and a PM_{10} high-volume sampler as a reference, various meteorological parameters were also monitored at the site. The predominant wind directions are from the northerly and southerly quarters.

2. Particulate matter concentrations at Masterton

The monitoring program at Masterton ran from April 2002 to November 2004 and total of 200 each of $PM_{2.0}$ and $PM_{10-2.0}$ filters were collected. The samples were initially collected over a 3-5 day sampling period in order to collect sufficient mass for elemental analysis, but then moved to a 1-day-in-3 sampling regime to provide better temporal resolution of sources contributing to ambient air particulate concentrations. A consequence of the shorter sampling periods is that on occasions throughout the sampling period, little or no gravimetric mass change was detected due to low ambient air particulate matter concentrations. Figure 1 shows the gravimetric results for GENT $PM_{2.0}$ and $PM_{10-2.0}$.

Fine particle concentrations at Masterton 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 results in the stagnation of local air masses which, coupled with emissions from combustion sources from such as solid fuel fires for domestic heating, can lead to elevated fine particle concentrations[3]. Monitoring results from both the TEOM and high volume sampler show that PM_{10} concentrations in Masterton exceed the New Zealand National Environmental Standard for PM_{10} (50 μg/m^3) on 5-6 occasions each winter[4].
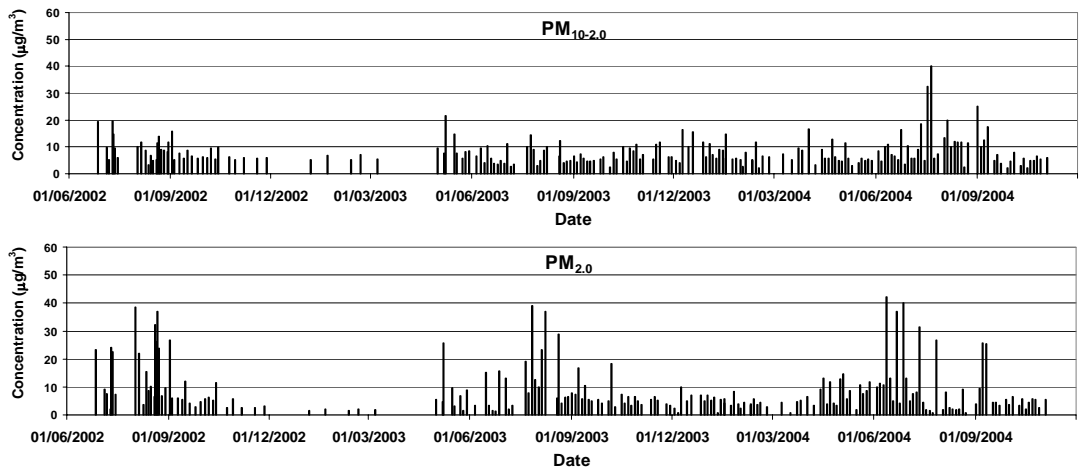
Fig. 1: PM2.0 and PM10-2.0 concentrations at Masterton

3. Elemental composition of air particulate matter at Masterton

Elemental analysis of the particulate collected on the filters was carried out using Ion Beam Analysis (IBA) at the New Zealand Ion Beam Analysis facility, Lower Hutt, Wellington. Sodium was measured using proton induced gamma-ray emission (PIGE) and elements with atomic numbers greater than 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 are presented elsewhere[2]. Figure 2 displays the range of elements and their respective concentrations (maximum, average, minimum) for $PM_{2.0}$ and $PM_{2.0-10}$ detected on the filters. The elements included in Figure 2 are those that were present in concentrations above the limit of detection in each size fraction for the IBA techniques.
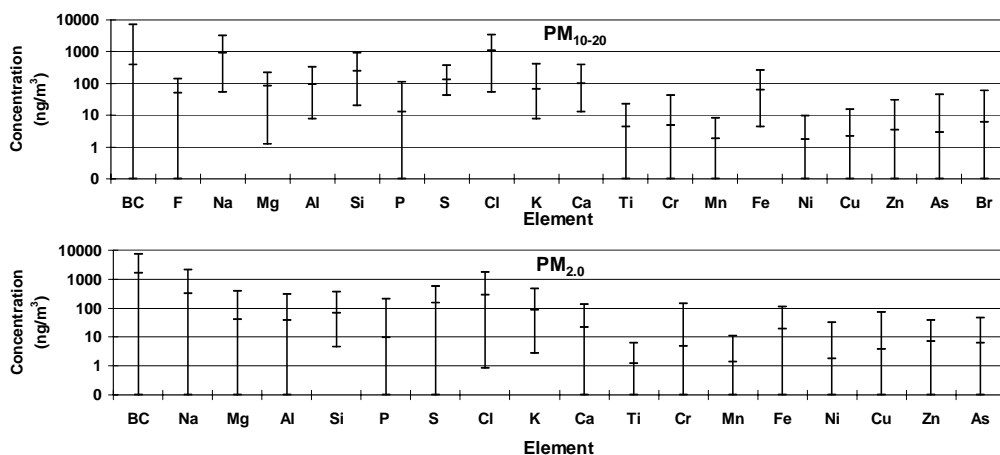

Fig. 2: PM2.0 , PM10-2.0 elemental concentrations (max, average, min) at Masterton

4. Factor analysis of air particulate matter at Masterton

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 Principal Components Analysis (PCA) to determine the grouping of elements that vary together and therefore determine the components of a factor or 'fingerprint' for each different source. In practice 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. In general, factor loadings extracted from the PCA correlation matrix were rotated (Varimax) to facilitate factor identification. Table 1 lists the fingerprints or factors identified for the $PM_{10-2.0}$ and $PM_{2.0}$ fractions at Masterton.

Table 1: Sources of ambient $PM_{10-2.0}$ and $PM_{2.0}$ identified by factor analysis

	Coarse Particle Fraction ($PM_{10-2.0}$)					Fine Particle Fraction ($PM_{2.0}$)			
	Soil	Seasalt	Burning	Cr/Ni		Burning	Ni/Cr	Seasalt	Soil
Si	**0.95**	0.02	0.10	-0.07	BC	**0.91**	-0.01	-0.04	0.11
Al	**0.94**	-0.07	0.17	0.02	K	**0.86**	-0.03	0.11	0.24
Fe	**0.90**	0.01	0.19	0.24	Zn	**0.72**	0.05	0.07	0.20
Ca	**0.85**	0.23	0.15	0.10	Fe	**0.64**	0.13	0.41	0.04
Ti	**0.83**	0.03	-0.11	0.26	As	**0.56**	-0.00	0.22	-0.04
Mn	**0.58**	-0.05	0.07	0.25	Ni	0.03	**0.95**	0.02	0.05
Cl	-0.16	**0.96**	-0.01	-0.11	Cr	0.01	**0.95**	0.07	0.07
Na	0.02	**0.92**	-0.11	0.15	Ca	0.36	0.07	**0.78**	0.24
S	0.01	**0.81**	0.46	-0.09	Cl	-0.06	0.00	**0.78**	-0.11
Mg	0.43	**0.65**	0.07	0.16	S	0.21	0.03	**0.75**	0.36
BC	0.03	-0.05	**0.94**	0.21	Si	0.36	0.05	0.57	**0.63**
K	0.24	0.29	**0.89**	0.12	Al	0.25	0.09	0.16	**0.92**
Zn	0.20	-0.05	**0.59**	0.44	Mg	0.16	0.12	0.10	**0.89**
Cr	0.25	0.06	0.16	**0.84**	Na	0.15	0.10	0.29	-0.33
Ni	0.11	0.04	0.23	**0.80**					

Four significant factors or sources were determined for both the coarse particle fraction and fine particle fractions at Masterton. These have been labelled 'Soil', 'Seasalt' 'Burning' and 'Ni/Cr' respectively as shown in Table 1. The name 'Soil' was 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 sea salt. Both the 'Soil' and 'Seasalt' factors are most likely from natural sources of air particulate matter. The 'Burning' factor has been named by virtue of presence of elemental or black carbon (BC) and potassium which are a typical fingerprint for biomass burning such as the particulate matter (smoke) produced by solid fuel fires[6,7].

The 'Ni/Cr' source is a minor contributor (<1%) to particle loadings in Masterton and can be attributed to motor vehicle emissions, either from the re-suspension of roadside dust or exhaust emissions[8,9]. However, further analysis is required before this can be confirmed. Previous work[9-11] on the characterisation of source elemental profiles at other sites in the Wellington

region has shown similar groupings of elements for the sources identified in Table 1.

5. Relative source contributions to particulate matter in Masterton

Using the source profiles elucidated from PCA of the dataset, the relative contributions of the different sources to ambient particle concentrations were reconstructed from the dataset. Note that these are relative contributions based on elemental composition rather than being based on full mass closure, however, we consider this to be a reasonable approximation of the situation at Masterton, particularly for high pollution days when combustion sources dominate. Figures 3a and 3b show the relative contributions to particle mass size fraction of the different sources. In these figures the Cr/Ni fraction is not obvious due to the low contribution from this fraction.

The relative contributions depicted in Figures 3a and 3b show that 'Seasalt' particles dominate the coarse fraction but that there is also a seasonal variation with the contribution from biomass combustion becoming more predominant in the winter and strongly dominating the fine particle fraction during the winter months. On reconstructing source contributions to individual samples taken during pollution events (i.e. $PM_{10} > 50$ g/m^3) at Masterton (all pollution events during winter months) it was found that the relative contribution of combustion sources was ~92%, Seasalt 6%, Soil 2% and Cr/Ni > 0.1%. The contribution of the Ni/Cr factor cannot be seen in the charts due to the low relative contribution of that factor to particle mass loadings.
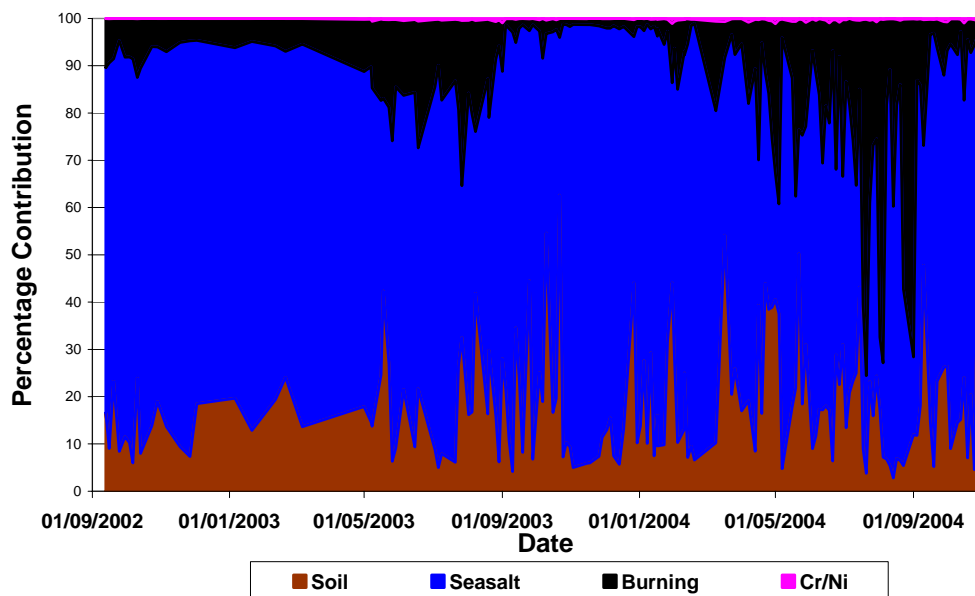

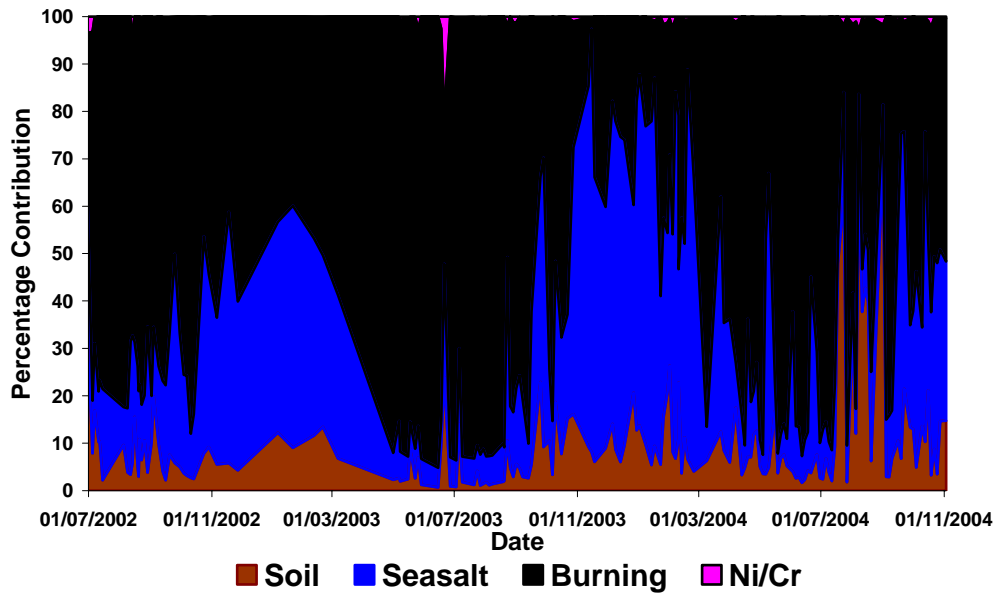Fig. 3a: Relative source contributions to PM10-2.0 at Masterton

Fig. 3b: Relative source contributions to PM2.0 at Masterton

6. Conclusions

Ion Beam Analysis (IBA) provides highly sensitive multi-elemental and cost effective analysis of air particulates for identifying source elemental fingerprints and determining the relative contribution of biogenic and anthropogenic sources of air particulate pollution. IBA analysis of air particulate matter and subsequent principal components analysis of two particle size fractions ($PM_{2.0}$ and $PM_{10-2.0}$) collected at Masterton, New Zealand have shown that there were four significant sources, Seasalt, Soil, Burning and Ni/Cr. Seasalt derived particulate matter along with soil dominates the coarse particle fraction. Particles resulting from the combustion of biomass, principally from the use of solid fuel fires for domestic heating, were found to dominate the fine particle fraction, particularly during winter months. The source labelled Ni/Cr was found to be a relatively minor contributor and is thought to be associated with motor vehicle emissions.

Relative contributions by the various sources to air particulate matter during air pollution events ($PM_{10} > 50\mu g/m^3$) was found to be in the order: Burning 92%, Seasalt 6%, Soil 2% and Ni/Cr < 0.1%.

Acknowledgements

References

1. P.K. Hopke, Y. Xie, T. Raunemaa, S. Biegalski, S. Landsberger, W. Maenhaut, P. Artaxo and D. Cohen, 'Characterisation of the Gent Stacked Filter Unit PM_{10} Sampler', *Aerosol Sci. Technol.* **27** (1997) 726-735.

2. A. Markwitz and W. J. Trompetter , 'The GNS Ion Beam Analysis Facility Plays a Key Role in the Analysis of Ambient Particulate Matter in New Zealand', *Proc. 16th Int. Clean Air Environ. Conf., Christchurch*, 2002, Clean Air Society of Australia and New Zealand, Eastwood, NSW, Australia.

3. New Zealand Ministry for the Environment, 'Health Effects of PM_{10} in New Zealand', *Air Quality Technical Report No. 39*, (2003), New Zealand Ministry for the Environment.

4. P. K. Davy, **Annual Air Quality Monitoring Report** (2003) *Wellington Regional Council Technical Report WRC/RINV-T-03/58.*

5. W. J. Trompetter, A. Markwitz and P. Davy, 'Air Particulate Research Capability at the New Zealand Ion Beam Analysis Facility Using PIXE and IBA Techniques', *Int. J. PIXE.* **XX** (2005) xxx-xxx.

6. D. D. Cohen, 'Characterisation of atmospheric fine particles using IBA techniques', *Nucl. Inst. Meth. Phys. Res.* **B136** (1998) 14-22.

7. W. C. Malm, J. F. Sisler, D. Huffman, R. A. Eldred, T. A. Cahill, 'Spatial and Seasonal Trends in Particle Concentration and Optical Extinction in the United States', *J. Geophys. Res.,* **99**, No.D1, (1994) 1347-1370.

8. J. M. Ondov, W. H. Zoller, and G. E. Gordon, 'Trace element emissions on aerosols from motor vehicles' *Environ. Sci. Technol.* **16** (6) (1982) 318-328.

9. P. Davy, A. Markwitz and W. J. Trompetter., 'Source Characterisation of Air Particulate Emissions from a Road Tunnel in Wellington, New Zealand', *Proc. 16th Int. Clean Air Environ. Conf., Christchurch,* (2002), Clean Air Society of Australia and New Zealand, Eastwood, NSW, Australia.

10. W. J. Trompetter, A. Markwitz and P. Davy, 'Using Ion Beam Analysis to characterise sources of air particulates in the Wellington region of New Zealand*, Proc. 15th Int. Clean Air Environ. Conf., Sydney*, (2000)*,* Clean Air Society of Australia and New Zealand, Eastwood, NSW, Australia, pp. 382-386.

11. P. Davy, A. Markwitz and W. J. Trompetter, 'Elemental Analysis and Source Apportionment of Ambient Particulate Matter in the Wellington Region of New

Zealand', *Proc. 16th Int. Clean Air Environ. Conf., Christchurch,* (2002), Clean Air Society of Australia and New Zealand, Eastwood, NSW, Australia.

Appendix 8

Analysis of sources contributing to air particulate matter concentrations at Otaki

Scanning electron microscopy and semi-quantitative source apportionment of ambient PM$_{10}$ in the Wellington region of New Zealand

P.K. Davy[1,3] A. Markwitz[2] and D.C .Weatherburn[3]

[1]Greater Wellington Regional Council, PO Box 11-646, 142-146 Wakefield Street, Wellington, New Zealand, [2]Institute of Geological and Nuclear Sciences, PO Box 31-312, 30 Gracefield Road, Lower Hutt, New Zealand and [3]School of Chemical and Physical Sciences, Victoria University of Wellington, PO Box 600, Wellington, New Zealand.

Abstract

Traditional gravimetric analysis of airborne particulate matter is unable to provide information on the sources contributing to air particulate concentrations. Source apportionment is a key tool for identifying the sources and determining the relative contribution of biogenic and anthropogenic sources to air particulate matter pollution and can provide a basis for innovative air quality management. Scanning electron microscopy has been used to identify the size distribution and elemental composition of air particulate matter collected onto high-volume sampler glass fibre filters. PM$_{10}$ was collected in a rural location at Otaki in the Wellington Region from October 1998 to February 2000. PM$_{10}$ concentrations were determined gravimetrically. The filters were examined and photographed by scanning electron microscopy (SEM). The elemental composition of the particles was then determined by Energy Dispersive Spectroscopy (EDS). The relative contributions of various sources to ambient particulate concentrations were assessed using Na/Cl and Al as markers for seasalt and soil contributions respectively, and C as a marker for biogenic and combustion sources. Significant sources of airborne particulate matter at Otaki were determined to be: soil, pollen, seasalt and a minor contribution from combustion sources. The implications for airshed management have been evaluated.

Keywords: Air Particulate Matter, Scanning Electron Microscopy, Elemental Analysis, Source Apportionment

1. Introduction

The Greater Wellington Regional Council (GW) has been monitoring air particulate matter at various locations in the Wellington Region since 1997. Initially, monitoring focussed on gravimetric measurement of PM_{10} (TEOM, high-volume sampler (HVS)), however, the monitoring has shown that there were elevated concentrations of PM_{10} at certain locations and that this may have implications for human health. The recently promulgated New Zealand National Environmental Standard (NES) for PM_{10} of $50\mu g/m^3$ requires airsheds to have no more than one exceedence per year by 2013. Traditional gravimetric analyses of airborne particulate matter such as the HVS method (USEPA 40 CFR Appendix J) is unable to provide information on the sources contributing to air particulate concentrations. There are analytical methods such as ICP-MS or AAS that would provide a limited range of elemental speciation, the main drawback of these methods is that they involve labour intensive wet chemistry that is not particularly sensitive to low concentrations of collected particulate matter.

GW has a programme for determining air particulate matter composition using a GENT SFU system (Hopke et al, 1997). The purpose of the GENT sampler programme was to characterise the elemental composition of aerosols by Proton Induced X-ray Emission (PIXE) and the analytical results are subsequently used for source characterisation and source apportionment studies. Unfortunately, the HVS glass fibre filter matrix interferes with determination of elements by PIXE and cannot be used. This presents a problem in areas where high volume sampling shows elevated concentrations of PM_{10} and there are no samples suitable for elemental speciation. The glass fibre filters were therefore examined by SEM for particle size distribution, particle morphology and provide an indication of particle composition by using the energy dispersive spectroscopy facility of the electron microscope. The method is, at best, only semi-quantitative due to the small area of focus ($<100\mu m$) by the SEM and the depth of the glass fibre filter matrix ($\sim 500\mu m$). However, we believe that the information gained is sufficient to provide a positive identification of some particle sources relevant for air quality management purposes and to add value to the large collection of glass fibre filters that the Regional Council has collected over the years.

2. Otaki sampling location and results

2.1 Sampling site location and description

The high volume sampler was located at the Regional Council's Otaki depot (NZMS Grid Reference E2691005; N6046390, elevation 17m) on the Kapiti Coast from October 1998 until February 2000. The instrument was operated on a one-day-in-six sampling regime. Figures 1 and 2 show the site location and surrounds.
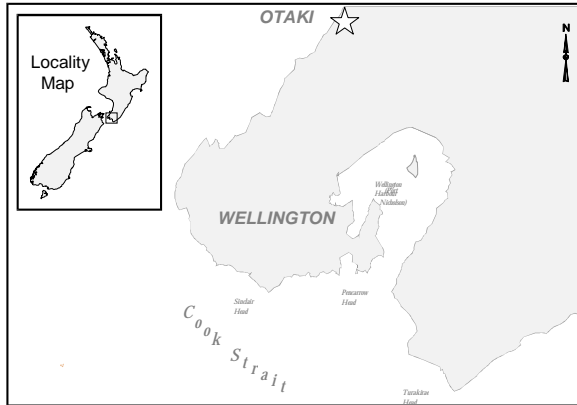
Figure 1: Map showing the Otaki sampling location (★)

Figure 2: Otaki site and sampling location ( )

The Otaki River is approximately 200 m to the south of the depot, on which there is a gravel road. This road is used periodically by trucks transporting gravel from the Otaki river to a shingle plant situated 150m upstream of State Highway 1 overbridge. A small industrial area is located 300m to the north there was and 4km to the west of the site is Otaki Beach and beyond that, the Tasman Sea.

2.2 PM$_{10}$ sampling results at Otaki

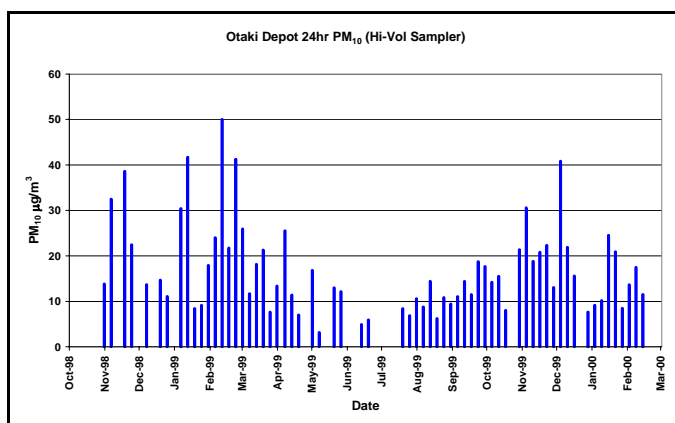A total of 70 PM$_{10}$ glass fibre filters were collected. Figure 3 shows the gravimetric results for these filters.

Figure 3: HVS PM10 sampling results for Otaki Oct 98 – Feb 2000

PM_{10} concentrations (average 17 $\mu g/m^3$) at Otaki were generally higher during the summer than winter. A peak concentration of 50 $\mu g/m^3$ was recorded on 11 February 1999. The pattern of peak concentrations of particulate matter at Otaki during summer is opposite to that at other locations in the Wellington Region where peak concentrations occur during winter and are associated with the use of solid fuel fires for domestic heating. With peak concentrations at Otaki approaching the NES, we needed to answer the questions of what was the cause and what could we do about it in terms of air quality management.

3. Scanning electron microscopy

Selected samples of glass fibre filters were prepared for SEM by punching out a 11mm disc, attaching these to 12.5 mm aluminium stubs with carbon tape and coating the targets with a 4 nm layer of gold. SEM was performed using a JEOL JSM 6500F at Victoria University of Wellington. Elemental analysis of the particulate collected on the filters was carried out using the EDS function of the electron microscope.

3.1 Analysis of SEM images

A number of images were taken of each glass fibre filter. It was found that the most useful magnification was around 1100X as this provided good particle resolution while giving as wide a field view as possible (~ 100 m). Figures 4 and 5 show representative SEM images of the filter with the highest particulate matter concentration (50 g/m^3) collected on 11 February 1999.
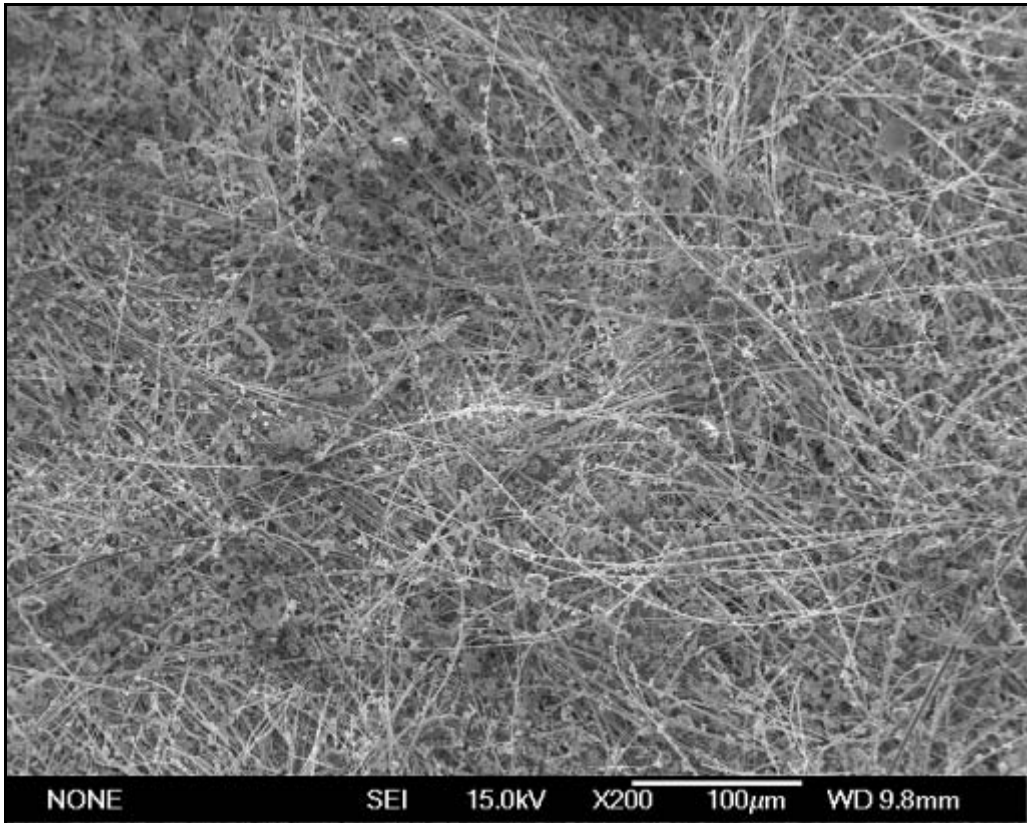
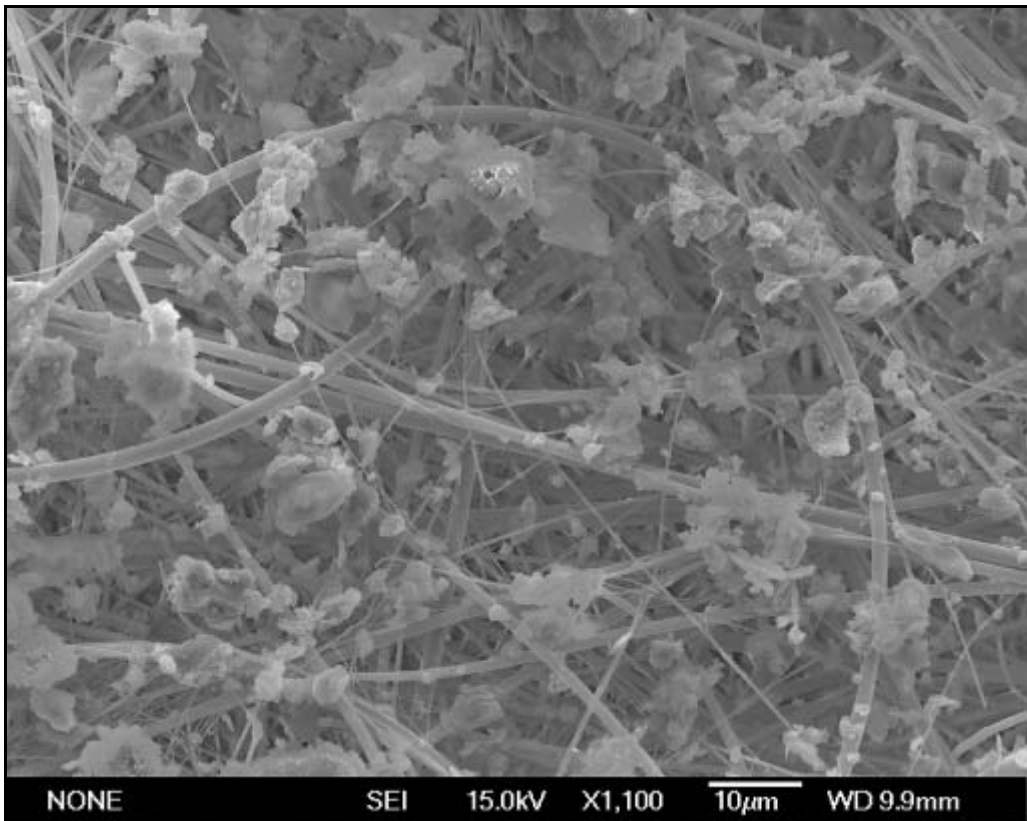**Figure 4: SEM of Otaki filter #6545546 (200X)**

Figure 5: SEM of Otaki filter #6545546 (1100X)

As can be seen from Figures 4 and 5 the filter is loaded with particles, most of which are in the 'coarse' particle size fraction between 2.5 and 10µm ($PM_{10-2.5}$). $PM_{10-2.5}$ air particulate matter are formed typically by mechanical grinding or wind action and weathering processes and generally do not contain particulate matter derived from combustion processes. Mechanical processes are involved in the production of seasalt (wind and waves), soil (wind blown soil) and some industry air particulate matter (quarrying, vehicle movements on unsealed roads). Previous work in the Wellington region determining particle composition and source apportionment has shown that the significant sources of particulate matter are: seasalt and soil in the coarse fraction and combustion sources in the fine ($<PM_{2.5}$) fraction (Trompetter et al 2000, Davy et al 2002, 2004).

The elements that make up a fingerprint for each source of air particulate matter are determined by statistically analysing the elemental composition of the particulate matter over a large number of filter samples. A statistical analysis such as Factor Analysis or Principal Components Analysis can be used to determine the grouping of elements that vary together and therefore determine the components of a fingerprint. As expected from previous studies in the Wellington Region we know that Na and Cl are strongly associated with seasalt particles; Al and Si with soil particles; and C with combustion particles (soot). In the case of emissions from solid fuel fires for domestic heating; C was found to be correlated with K.

3.1.1 Energy dispersive spectroscopy

Energy Dispersive Spectroscopy (EDS) is a commonly used technique for identifying and quantifying elemental composition of targets and sample areas as small as a few cubic micrometers. EDS analysis was used to determine the elemental content of the particles shown in Figure 5 (the same filter area was scanned). Then, using those marker elements discussed above, the particulate matter was apportioned to different sources. Figures 6 through to 8 show the results of the EDS scans for the filter image in Figure 5.
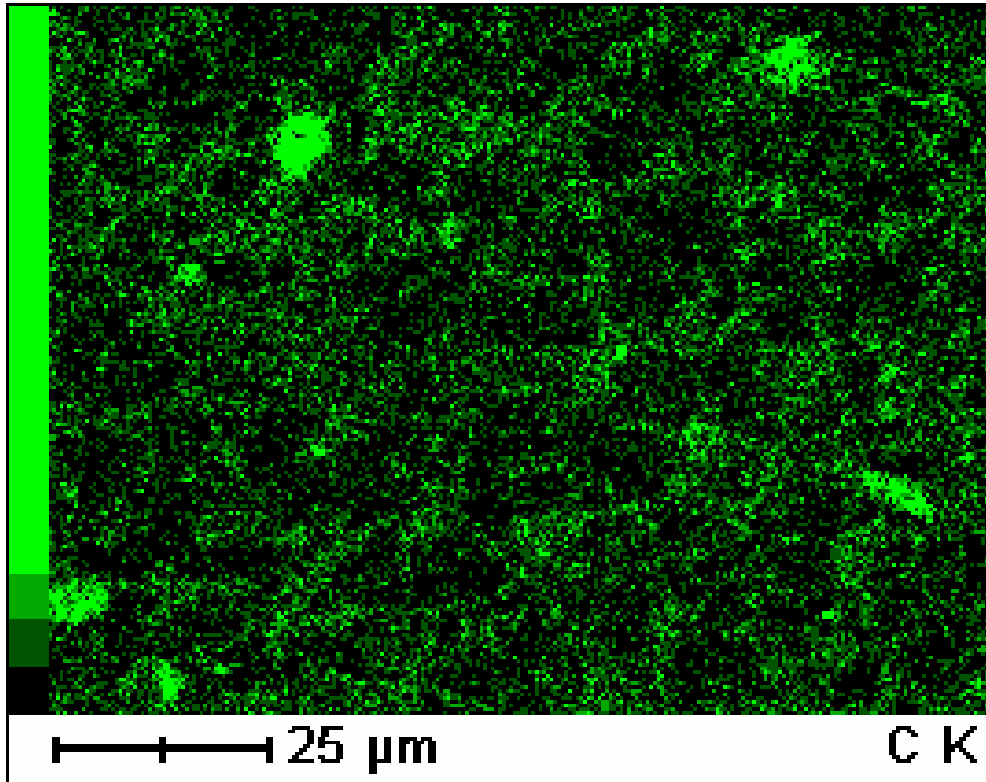
Figure 6: Carbon containing particles (bright areas)

The analysis software associated with the EDS allows one to overlay individual spectra for different elements and so provides a composite image of particle composition. For clarity only the 'marker' elements are shown in Figures 6-8.
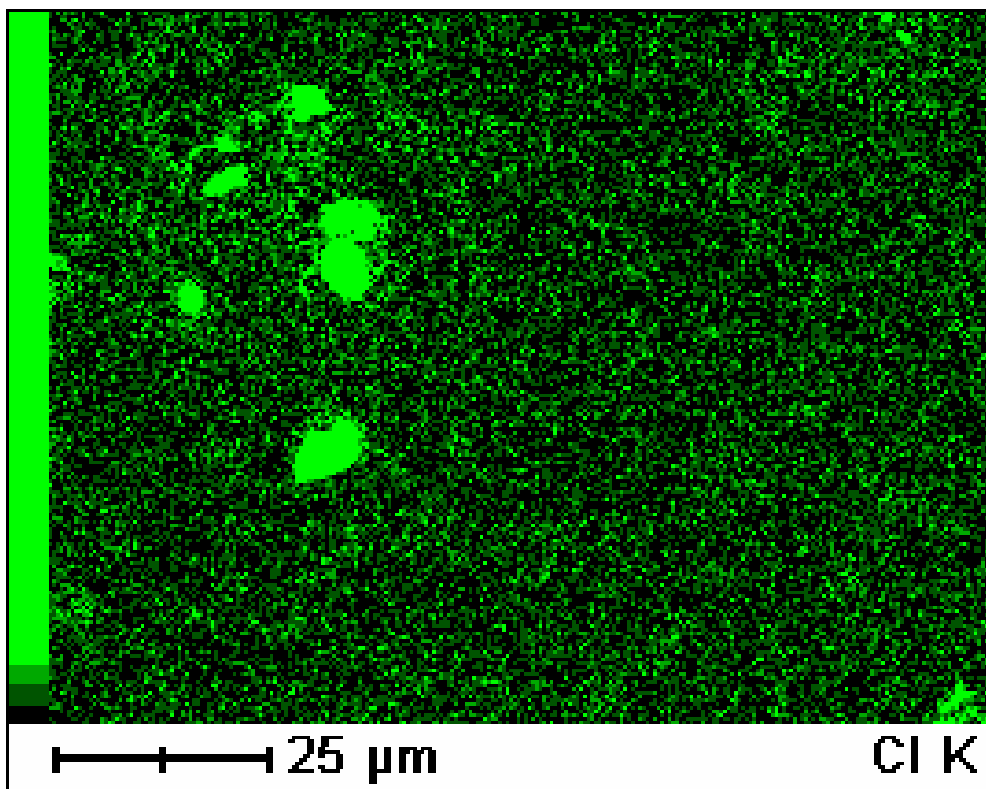

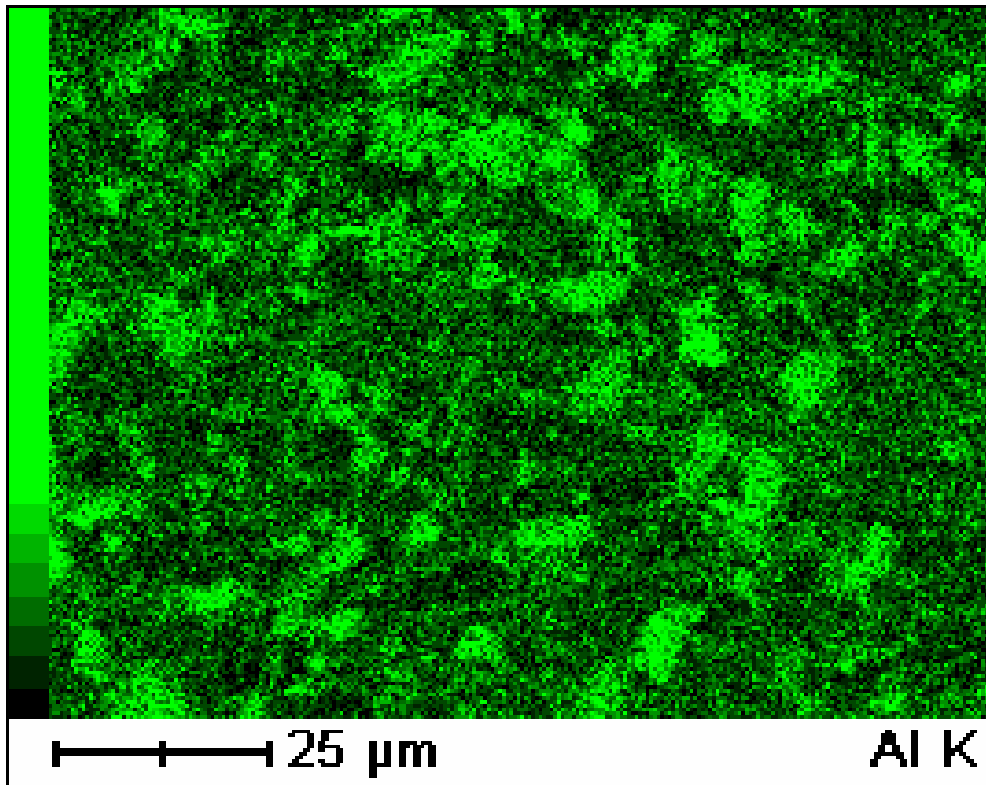Figure 7: Chlorine containing particles - seasalt

Figure 8: Aluminium containing particles - soil

From these images it was deduced that soil (Al) particles dominate on the filter with a few seasalt (Cl) and combustion/organic (C) particles scattered about. Higher magnification SEM images for individual particles was found to be sufficient to distinguish between carbon containing particles of combustion or biogenic origin. Combustion particles are agglomerations of smaller particles and have a filamentous appearance (Grassi *et al* 2004). Figure 9 shows an SEM image of a combustion type particle. Particles of biogenic origin either appear fibrous (such as bark or leaf parts) or more frequently, as individual pollen particles such as that shown Figure 10.
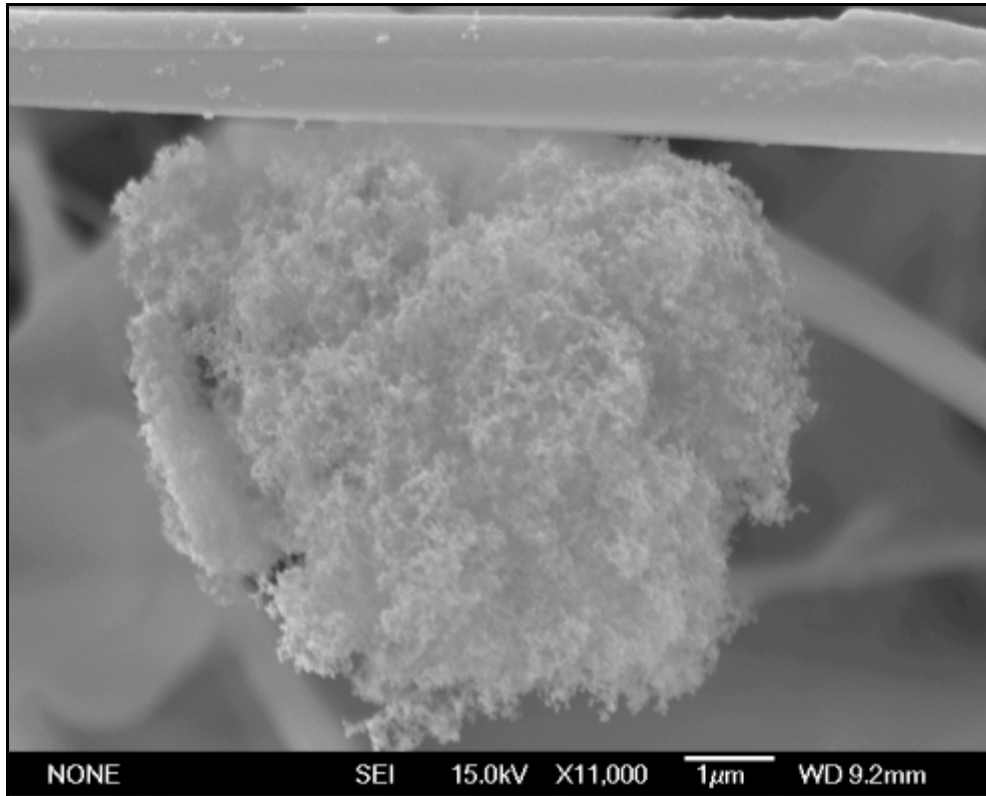
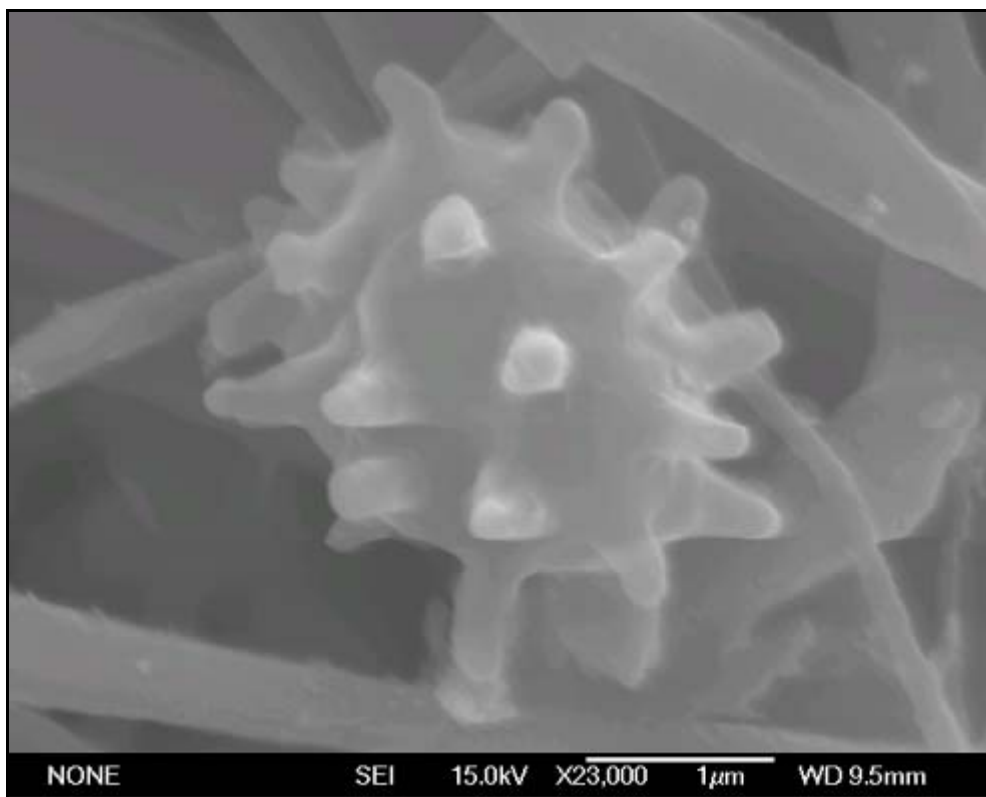Figure 9: Filamentous combustion particle (filter #6545517)

Figure 10: Pollen particle (filter #6545527)

Similar analysis methodology was applied to multiple SEM images of the same filter and of a range of filters (10 plus one blank) selected from throughout the

sampling period at Otaki. Filters were chosen to reflect both high and low loadings during summer and winter.

3.1.2   Results

Each SEM image and accompanying EDS scan image was analysed for particle composition to provide source identification. The relative percentage contribution of particles from each source was estimated and recorded. Table 1 presents the results.

Table 1: SEM image analysis of Otaki filters

				SEM 1			SEM 2		
Filter No.	Date On	Date Off	PM10	% Soil	%seasalt	%carbon	% Soil	%seasalt	%carbon
6545554	17/11/1998	18/11/1998	38.1	95	0	5	95	0	5
6545551	11/01/1999	12/01/1999	41.1	93	2	5	93	2	5
6545543	23/01/1999	24/01/1999	9.1	20	60	20	20	60	20
6545546	10/02/1999	11/02/1999	50	90	5	5	93	5	2
6545527	19/05/1999	20/05/1999	12.8	30	10	60	40	10	50
6545517	18/07/1999	19/07/1999	8.5	20	5	75	5	5	90
6545515	30/07/1999	31/07/1999	10.6	70	10	20	80	10	10
6545506	11/08/1999	12/08/1999	14.4	70	5	25			
6869620	03/12/1999	04/12/1999	40.8	85	0	15	80	5	15
Average				64	11	26	63	12	25
Std Dev				30	18	24	34	18	29
				% Soil	%seasalt	%carbon	% Soil	%seasalt	%carbon
6946895-1	14/01/2000	15/01/2000	24.5	30	5	65	35	0	65
6946895-2	14/01/2000	15/01/2000	24.5	30	0	70			
6946895-3	14/01/2000	15/01/2000	24.5	35	0	65	20	2	78
6946895-4	14/01/2000	15/01/2000	24.5	40	0	60	45	0	55
6946895-5	14/01/2000	15/01/2000	24.5	30	0	70	35	0	65
6946895-6	14/01/2000	15/01/2000	24.5	45	0	55	50	0	50
6946895-7	14/01/2000	15/01/2000	24.5	50	0	50	35	0	65
6946895-8	14/01/2000	15/01/2000	24.5	50	0	50	45	0	55
6946895-9	14/01/2000	15/01/2000	24.5	40	5	55	55	0	45
Average				39	1	60	40	0	60
Std Dev				8	2	8	11	1	11

Table 1 shows that there is reasonable consistency within samples from the same filter. (SEM 1 and SEM 2 refer to SEM scans of different areas of the same filter). The percentages given in Table 1 were arrived at by estimating the relative percentage contribution of each identified source to overall particle loadings on a filter sample. Variations between filters are dependent on meteorology and season. A correlation matrix of the results is shown in Table 2.

Table 2: Correlation matrix for the results in Table 1

Correlations	PM$_{10}$	% Soil	%seasalt	%carbon	% Soil	%seasalt	%carbon
PM10	1.00						
% Soil	0.83	1.00					
%seasalt	-0.47	-0.61	1.00				
%carbon	-0.69	-0.80	0.01	1.00			
% Soil	0.81	0.98	-0.54	-0.82	1.00		
%seasalt	-0.50	-0.59	1.00	0.00	-0.53	1.00	
%carbon	-0.64	-0.78	0.00	0.97	-0.84	-0.01	1

Table 2 indicates that an increase in soil particles on the filters is associated with an increase in PM$_{10}$. Higher PM$_{10}$ values recorded during the drier summer months are due to increases in suspended soil particles.

4. Discussion

The analyses of glass fibre filters from a high volume sampler monitoring programme in rural Otaki by SEM shows that the major sources of air particulate matter at that location are:

- soil (crustal matter);
- seasalt; and
- biogenic carbon (predominantly pollen) particles.

The presence of some combustion-type carbon containing particles was also observed but in low numbers, which indicates that combustion sources such as motor vehicles and domestic solid fuel fires are not significant contributors to PM$_{10}$ levels at the rural Otaki site. The SEM analyses also shows that most of the PM$_{10}$ particles collected were in the coarse or PM$_{10-2.5}$ size range.

Motor vehicle movements on unsealed roads in the area may have been a mechanism for re-suspension of soil particles; however, considering that a major gravel-bed river (the Otaki River) is nearby, re-suspension of alluvial fines by wind action is most likely to be the dominant source of soil particles at that location. Meteorological records indicate that the higher levels of soil particles were associated with moderate to strong winds during the 24-hour sampling period.

5. Conclusions/Summary

Ambient air quality monitoring for PM$_{10}$ by HVS at a rural site near Otaki in the Wellington region has shown that on occasion during the summer months the area can experience elevated (maximum 50 g/m^3) concentrations of air particulate matter. Examination of filter samples by SEM and EDS showed that, for sampling periods with higher concentrations of PM$_{10}$, most particles were in the 'coarse' fraction (2.5 m<PM<10 m) and were of crustal origin (soil).

It was found that the combination of SEM and EDS was a useful method for identifying and determining the relative contributions of air particulate matter

sources to ambient loadings. This is particularly with regard to HVS glass-fibre filters that do not lend themselves easily to more quantitative methods of analysis such as PIXE.

The most likely source of the suspended soil particles is through the action of wind on alluvial fines from the nearby Otaki River and environs. Little can be done from a practical air quality management perspective in order reduce local levels of PM_{10}, even if there are the occasional exceedences of the New Zealand National Environmental Standard for PM_{10} (50 g/m^3).

Acknowledgments

References

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_{10} Sampler', *Aerosol Science and Technology* **27**:726-735. Elsevier Science Inc.

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.

Davy P.K., 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.

Davy P.K., Markwitz A., Trompetter W.J., Weatherburn D.C. 2004, 'Elemental Analysis and Source Apportionment of Airborne Particles at an Industrial Area in Wellington, New Zealand', *Proceedings of the 13th World Clean Air and Environment Protection Conference, London, 2004.*

Grassi C., Narducci P., Tognotti L., 2004, 'Atmospheric Particulate Matter by SEM-EDX', *Proceedings of the 13th World Clean Air and Environment Protection Conference, London, 2004.*