Atmospheric Monitoring of $PM_{2.5}$, $PM_{10-2.5}$, PM_{10}, Arsenic and Carbonaceous Aerosol at Wainuiomata.

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ABSTRACT

Air pollution is harming our health and that of our children and parents. Air pollution causes many harmful effects, ranging from premature death, to headaches, coughing and asthma attacks. Previous studies (2008-2009) of particulate matter at Wainuiomata, Lower Hutt showed that biomass burning was primarily responsible for peak $PM_{2.5}$ and PM_{10} concentrations and exceedances of the National Environmental Standard (NES) and the New Zealand Ambient Air Quality Guidelines (NZAAQG). Arsenic was also found to be associated with biomass burning sources during winter at Wainuiomata. The source of arsenic was considered to be due to the use of copper chromium arsenate (CCA) treated timber as solid fuel for fires for domestic heating. While particulate matter pollution from domestic fires itself presents a health risk for the exposed population, the addition of arsenic to the mix enhances the potential risk. The use of CCA treated timber was unlikely to be used on a regular basis hence the peak arsenic concentrations did not always coincide with peak contributions from domestic fires and that the use of CCA – treated timber is more intermittent and opportunistic.

This work compared several different analytical methodologies for the determination of arsenic in air particulate matter. The primary purpose was to use a standard analytical method as recommended by the NZAAQ guidelines and compare those results with the Ion Beam Analysis (IBA) and X-ray Fluorescence Spectroscopy (XRF) methods used to determine arsenic concentrations in previous studies.

Through this collaborative research with GNS Science and GWRC, it was found that annual PM_{10} and $PM_{2.5}$ averages were well within the NZAAQG values of; 20 µg m^{-3} and 10 µg m^{-3} respectively. There was a much correlated seasonal and temporal variations observed for black carbon (BC), $PM_{2.5}$ and arsenic concentrations. The overall concentrations of BC, $PM_{2.5}$ and PM_{10} have decreased significantly in the Wainuiomata airshed compared to previous studies as reported in 2009 with fewer exceedances of the NES and NZAAQG on a 24 hour daily average.

The overall weighted mean arsenic concentration as measured by GF-AAS was 6.3 ± 0.8 ng m^{-3} and that measured by XRF and IBA was 3.8 ± 2.0 ng m^{-3} and 3.1 ± 5.9 ng m^{-3} respectively. The XRF and IBA arsenic concentrations were consistently lower than that of GF-AAS. The two annual arsenic averages (GF-AAS) were 6.5 ± 0.9 ng m^{-3} and 5.9 ± 0.7 ng m^{-3} respectively, for

the entire sampling period. In both the cases the NZAAQG value of 5.5 ng m^{-3} were exceeded. The exceedance in the second year of sampling was not statistically significant as the guideline value 5.5 ngm^{-3} falls within the given uncertainty of the measured annual averages for arsenic.

However, it is definitely an area of concern as the overall arsenic concentrations during winter periods was 12.2 ± 1.0 ng m^{-3}. Moreover, burning CCA treated timber is effectively banned through regional plan rules and the problem presents itself as one of enforcement and/or public education.

The inter-method comparison showed that IBA technique can be used for "screening" purposes due to high limit of detection (LOD) and analytical noise. While XRF can still be used interchangeably with GF-AAS but with Teflon or thinner filter membrane, for long term environmental monitoring of arsenic and other elemental compositions. Given the excellent recoveries of 99.2 ± 0.8% for duplicate spiked analysis and 102.7 ± 0.9% for lab blank filters spiked analysis, at 95% confidence intervals, GF-AAS method is highly reproducible and should be used in the determination of arsenic in ambient air for the purpose of comparing with the NZAAQG values.

Keywords

Arsenic, air particulate matter (APM), PM$_{10}$, PM$_{2.5}$, copper chromium arsenate (CCA), carbonaceous aerosols, black carbon (BC), biomass burning, Graphite Furnace Atomic Absorption Spectrometry(GF-AAS), Ion Beam Analysis (IBA), and X-Ray Fluorescence Spectroscopy (XRF) .

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AIMS AND OBJECTIVES

GENERAL:

The aim of this study was to collect filter samples of $PM_{2.5}$, $PM_{10-2.5}$ and PM_{10} in an air shed affected by particulate matter air pollution and determine gravimetric mass, arsenic concentrations, along with black carbon (BC), and Ion Beam Analysis (IBA) elemental concentrations.

SPECIFIC OBJECTIVES:

➢ To measure the black carbon (BC) concentrations in quartz filters collected by High Volume sampler (High-Vol) and polycarbonate fine and coarse filters collected by GENT sampler, using the M43D Digital Smoke Stain Reflectometer.

➢ To measure gravimetrically PM_{10} and $PM_{2.5}$ mass concentrations in ambient air.

➢ To develop a methodology for accurate determination of arsenic in ambient air by Graphite Furnace Atomic Absorption Spectrometry (GF-AAS).

➢ To validate the GF-AAS method using quality control (QC), quality assurance (QA) protocols and quantification of uncertainties used in each of the method development processes.

➢ To statistically analyse results at 95% confidence intervals for accurate and precise interpretation of arsenic, PM_{10}, $PM_{2.5}$, and BC data obtained by different instruments.

➢ To statistically analyse GF-AAS method (VUW), XRF method (GNS), and IBA method (GNS) using Bland-Altman method comparison.

➢ To compare the XRF and IBA data against the standard method, GF-AAS. These had been used in the determination of arsenic in ambient air in previous studies. This process will have a statistical as well as analytical importance for the XRF and IBA methods used in the determination of arsenic in ambient air in future.

1.0   INTRODUCTION

1.1   OVERVIEW OF AIR PARTICULATE MATTER RESEARCH

Air is the receiving environment for emissions arising from many day-to-day activities, such as driving, heating homes with wood or coal, lawn mowing and outdoor burning, as well as industrial and commercial activities (Mitchell, T., 2012).

These emissions contain contaminants such as particulate matter (PM), carbon monoxide, nitrogen oxides, polyaromatic hydrocarbons (PAH's) and heavy metals such as arsenic, lead, copper, chromium, etc. If these contaminants exceed their permissible levels, it will adversely affect the health of exposed populations (Mitchell, T., 2012).

Particulate matter is one of the key indicators of air quality in an air shed. The PM is a complex mixture of organic and inorganic aerosols that are dispersed in air. PM occurs in a range of sizes with diverse chemical and physical properties depending on the emission source and atmospheric transformations.

PM_{10} is that portion of particulate matter with an equivalent aerodynamic cross-section less than 10 micrometres. This size fraction is small enough to be inhaled into the respiratory system (Figure 1.1).
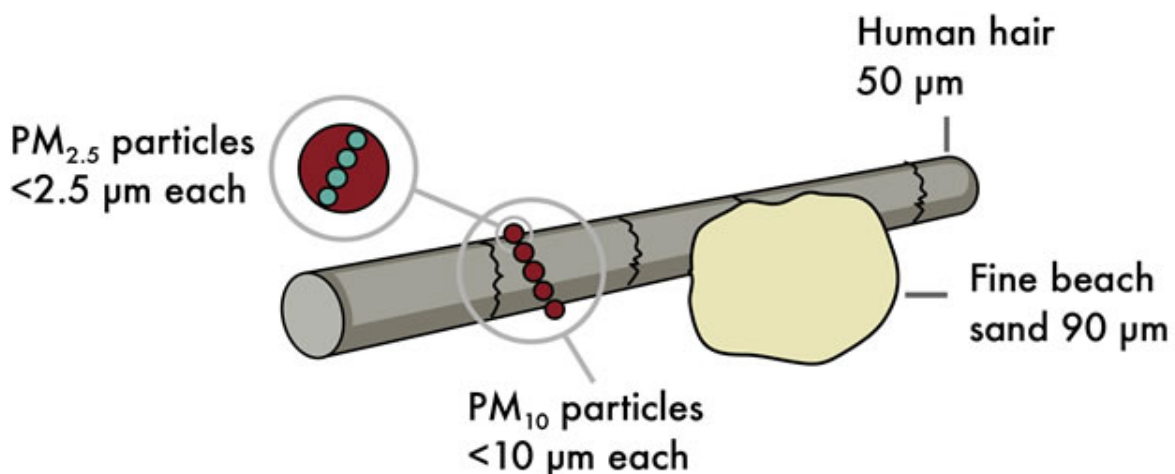
Source: Ministry for the Environment

Figure 1.1   The relative size of particulate matter

Figure 1.1 illustrates the relative size of particulate matter. It compares the size of PM_{10} and $PM_{2.5}$ to a strand of hair and a grain of beach sand.

The airborne particles commonly occur in two distinct sizes- 'fine' (aerodynamic cross section less than 2.5 micrometres) denoted as $PM_{2.5}$ and 'coarse' (2.5 -10 micrometres), $PM_{2.5-10}$. The PM_{10} consists of both fine and the coarse fractions. The fine and coarse PM typically differ in their origin, dispersal properties and site of deposition within the human respiratory track (Mitchell, 2012).

The fine particles ($PM_{2.5}$) mainly arise from combustion processes, such as vehicle exhaust and wood and coal burning. Fine PM includes inorganic species, organic aerosols, metals and black carbon (BC) or soot. Fine particles can remain suspended in air for long periods and may be transported across large distances (hundreds to thousands of kilometres).

In contrast, coarse particles are largely produced by mechanical processes, such as crushing, abrasion and wind action. Anthropogenic sources include suspended dust from roads and industrial activities. Natural sources, such as marine aerosol and wind- blown soils, are often a major component of the coarse fraction (Mitchell, 2012). The coarse PM tends to settle out more quickly after being formed or emitted than the finer $PM_{2.5}$.

In response to growing evidence of significant health effects associated with airborne particle pollution, the New Zealand government introduced in 2005 a National Environmental Standard (NES) of 50 µg m^{-3} for particles less than 10 µm in aerodynamic cross-section (denoted as PM_{10}). The NES places an onus on Regional Councils to monitor PM_{10} and publicly report if the air quality in their region exceeds the standard. Regional councils are required to comply with the standard by 2016. In areas where the PM_{10} standard is exceeded, information on the sources contributing to those air pollution episodes is required in order to effectively manage air quality and formulate appropriate mitigation strategies (Davy et al., 2009).

Short-term meteorological events are largely responsible for air pollution episodes. For example under still conditions, fine particles ($PM_{2.5}$) and other contaminants are trapped near to the ground because low wind speeds restrict horizontal mixing and temperature inversions restrict vertical mixing (Figure 1.2). Climatology examines weather conditions averaged over longer periods of time and this assists our understanding of why some areas

are more susceptible to poor air quality than others. In the Wellington region, topography strongly influences airshed climatology as reported by Mitchell, 2012.
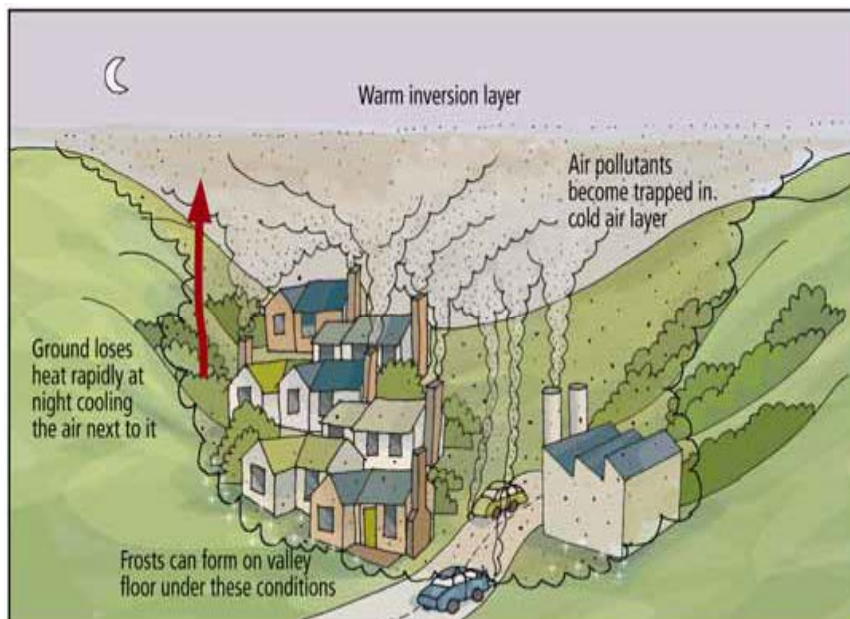
(Source: Greater Wellington publication GW/RP-G-03/57)

Figure 1.2   Night time temperature inversion trapping pollutants near the surface

In addition to the PM_{10} NES, the Ministry for the Environment issued ambient air quality guidelines for air pollutants in 2002 that included a guideline value of 25 µg m^{-3} for $PM_{2.5}$ (24- hour average). More recently, the World Health Organisation (WHO) has confirmed a $PM_{2.5}$ ambient air quality guideline value of 25 µg m^{-3} (24-hour average) based on the relationship between 24-hour and annual PM levels (WHO, 2006). The WHO annual average guideline for $PM_{2.5}$ is 10 µg m^{-3}. These are the lowest levels at which total, cardiopulmonary and lung cancer mortality have been shown to increase with more than 95% confidence in response to exposure to $PM_{2.5}$. WHO recommends the use of $PM_{2.5}$ guidelines over PM_{10} as epidemiological studies have shown that most of the adverse health effects associated with PM_{10} is due to $PM_{2.5}$.

1.2   AIR PARTICULATE MATTER RESEARCH FINDINGS IN NEW ZEALAND

Many urban areas in New Zealand experience poor air quality during the winter as a result of particulate matter (PM_{10}) pollution (Ancelet et al., 2012). Studies have shown that domestic heating emissions from biomass burning are the dominant source of PM during the winter throughout the country (Ancelet et al., 2012; Cavanagh et al., 2012; Wilton et al., 2009).

During the summer, PM_{10} concentrations throughout New Zealand tend to be low and are largely influenced by natural sources like marine aerosols and soils (Ancelet, 2012). However this is not the case during winter when the PM_{10} concentrations frequently exceed the NES guidelines in a number of regions (Trompetter, 2010).

A nationwide study on PM_{10} further shows that residents of low income communities or neighbourhoods, along with other features associated with socio-economic status, tend to have higher exposure to elevated PM_{10} concentrations (Pearce & Kingham, 2008). The report further suggested that the uneven exposure plays an important role in the desperate health status amongst the low income communities in New Zealand. The report provided useful information about PM_{10} concentrations in New Zealand.

The national indicator graph shows that the annual averages of PM_{10} concentrations are decreasing according to the Ministry for Environment 2014 report.

The report states that from 2006 to 2012, New Zealand's annual average PM_{10} concentration declined (Figure 1.3). Since a peak of 17.0 µg m^{-3} in 2006 and 2007, overall concentrations have fallen 8 percent to 15.6 µg m^{-3}.

The increase in 2011 (up 0.3 µg m^{-3} from 2010) was influenced by higher concentrations in Christchurch. This was due to increased dust dispersion from liquefaction and damaged roads resulting from the Canterbury earthquakes.

The report is based on annual averages as they give the best indication of general air quality conditions and long-term exposure. Most PM_{10} health impacts are associated with long-term exposure to PM_{10}.

Annual average PM$_{10}$ concentration in air – New Zealand
2006–12

Note: PM$_{10}$ concentrations are given in micrograms per cubic metre of air, or µg/m³.

Source: Regional councils of Northland, Bay of Plenty, Waikato, Hawke's Bay, Manawatu-Wanganui, Wellington, Canterbury, West Coast, Otago, Southland; District councils of Marlborough and Tasman; City Council of Nelson; Auckland Council; Genesis Energy Limited.

Figure 1.3   New Zealand's annual average PM$_{10}$ concentration (Source: Ministry for the Environment)

(http://www.mfe.govt.nz/more/environmental-reporti ng/air/air-domain-report-2014/state-new-zealands-air/pm$_{10}$).

1.2.1   AUCKLAND

Ancelet 2012, has done a complete review of the air particulate research in New Zealand focussing more on Auckland and Christchurch. Auckland being the largest city in New Zealand with a population of, 1.3 million, has been the centre of a significant amount of wide-ranging PM research.

While it enjoys a well-ventilated open space, there are areas that are subject to the formation of localised micro-climates that can significantly elevate PM$_{10}$ concentrations for a number of days (Longley & Harper, 2010).

Wang et al., 2005, determined the concentrations of different carbonaceous and ionic components in PM$_{10}$ during the winter in Auckland using Principal Component Analysis (PCA). It was found that the marine aerosol was the most significant contributor to PM$_{10}$ followed by vehicular emissions. The important finding was that PM$_{10}$ due to the domestic heating was not significant, based on low concentration of non-sea salt (NSS) potassium.

Source apportionment studies provide further useful information on the sources of PM and the contribution of the identified sources to PM mass (Ancelet 2012). The 'brown haze' investigation in Auckland using enrichment factors and PCA concluded that emissions from diesel-fuelled vehicles, and to a lesser extent, coal combustion, were responsible for these events (Senaratne & Shooter, 2004). However their study was limited to fewer samples and hence further study was required.

A long-term, multi-site source apportionment study had been commissioned by Auckland Council since 2006 (Davy et al., 2010). The study involved the analysis of 5000 samples of filters, $PM_{2.5}$ and PM_{10}, for elemental content using Ion Beam Analysis (IBA) techniques and black carbon (BC). Five common source contributors were identified for $PM_{2.5}$ and PM_{10}, samples from each site, including biomass burning, motor vehicles, sulphate, marine aerosol and soil or crustal matter. Site specific sources such as industrial, shipping emissions and road works were also identified.

Some important features of that study as reported by Davy et al., 2010, were that:

➢ The $PM_{2.5}$ was largely responsible for peak PM_{10} concentrations during the winter, with motor vehicles and biomass burning being the primary contributors to $PM_{2.5.}$ Peak $PM_{2.5}$ concentrations were primarily the result of biomass burning.

➢ The motor vehicles provided consistent mass contributions to $PM_{2.5}$ and PM_{10} throughout the year, illustrating that the coarse fraction is an important metric due to motor vehicle contributions to coarse fraction heavy metal concentrations.

➢ The marine aerosol was responsible for peak PM_{10} concentrations during the spring and the summer, and at times, when coupled with contributions from other sources, may be sufficient to result in exceedances of the NES.

The study also showed elevated levels of arsenic during winter which will be discussed later in this thesis.

1.2.2 CHRISTCHURCH

Christchurch, despite having smaller population compared to Auckland (approx. 350,000) has been well documented to have degraded air quality during the winter. The poor air quality in Christchurch has been the result of the two main factors, significant biomass burning (wood and coal) and frequent meteorological conditions conducive to pollutant build-up (Ancelet et al., 2012).

These conditions are: low wind speeds, strong shallow surface based inversions and topographically influenced local wind systems occurring during anti-cyclonic periods (Sponken-Smith et al., 2001). According to Wilton 2003, the poor visibility in Christchurch was mainly due to motor vehicle emission and secondary particles. The ionic species in Christchurch has also been associated with marine aerosols in spring and summer as in Auckland.

Based on the abundance of the biomass burning tracers during the winter, Wang & Shooter, 2002, suggested that residential heating was the most significant contributor to the elevated PM_{10} concentrations measured during the winter.

The source apportionment studies using enrichment factors, PCA and absolute PCA identified five PM_{10} sources in Christchurch (Senaratne et al., 2005). The five sources identified were: domestic emissions (biomass burning) - 29%, sea spray - 20%, road dust/ crustal matter - 21 % and diesel/ petrol emissions – 30%. In a separate study on the sources of $PM_{2.5}$ in Christchurch identified five sources, including biomass burning, marine aerosol, motor vehicles, secondary aerosols and aged aerosols (Scott, 2006). The aged aerosols were the main contributor of $PM_{2.5}$ during summer while biomass burning was by far the most significant $PM_{2.5}$ source during the winter which accounted for 92% of the measured $PM_{2.5}$ mass on average.

1.2.3 Other locations

1.2.3.1 Nelson and Alexandra

Apart from the large urban centres, smaller urban and sub-urban centres have also reported high PM_{10} and hence poor air qualities (Grange et al., 2013). Populations in small townships in the cooler South Island of New Zealand like Nelson, Arrowtown and Alexandra have reported poorest air quality as well (Davy & Clarkson, 2007; Fisher et al., 2007; Trompetter et al., 2010).

Populations in these townships, often located in regions of complex terrain with low annual winds, rely heavily on wood burners for space heating (Fisher et al., 2007; Trompetter et al., 2010). Very high levels of PM_{10} were observed for Nelson South air shed during winter time especially during anti-cyclonic situations. Under these cold and calm situations, nocturnal temperature inversions limited the vertical and horizontal dispersion of pollutants (Grange, et al., 2013).

High concentrations of PM_{10} were observed during the late evenings and an unusual second peak in the mid- morning throughout the Nelson valley (Grange, et al., 2013). The late evening peaks were well associated with the period of high emissions and very stable boundary layer conditions close to the surface (Grange, et al., 2013), while, the mid-morning peaks may be accounted by the hypothesis that vertical mixing of elevated layers of pollution stored aloft down to the surface (Trompetter, et al., 2010).

According to MfE, 2014, five locations in New Zealand have been monitoring and reporting annual average PM_{10} longer than many other locations. The information provided shows the long-term trends in PM_{10} concentrations.

Figure 1.4 also shows the PM_{10} concentrations for one site in each of the five main cities over the past 15 years. For cities with more than one monitoring site, the site based on how long the site had been monitored had been selected and on advice from councils about representativeness.

For every city, the concentrations were lower in 2012 than 10 years before. Concentrations at the Christchurch site have been declining since 1997. The higher concentrations in Christchurch during 2011 were attributed to increases in dust and its dispersion due to

liquefaction and damaged roads resulting from the Canterbury earthquakes as mentioned earlier. The Auckland and Hamilton monitoring sites recorded decreasing concentrations from 2006 to 2010.

Annual average PM₁₀ concentration – selected urban centres
1997–2012

Note: PM₁₀ concentrations are given in micrograms per cubic metre of air, or µg/m³.
A 2003 PM₁₀ annual average concentration for Dunedin is not available as monitoring did not meet good practice guidance.
WHO – World Health Organization.

Source: Regional councils of Waikato, Wellington, Canterbury, Otago; Auckland Council

Figure 1.4 PM_{10} concentrations for one site in each of the five main cities over the past 15 years. (Source: Ministry for the Environment, 2014).

The WHO provides an annual health guideline of 20 µg m^{-3} for PM_{10} concentrations. However, adverse health effects can be experienced at very low concentrations (even below the guideline). WHO recommends this guideline to provide a minimum level of protection against long-term health risks (WHO, 2006). The above graph (Figure 1.4) shows that the WHO guideline of 20 µg m^{-3} had been exceeded in Christchurch and Dunedin cities despite the declining trends shown.

1.3 CARBONACEOUS AEROSOLS AND PAH'S

The carbonaceous species in the atmosphere in Auckland was also determined which included organic poly aromatic hydrocarbons (PAH's), elemental carbon (EC) and inorganic carbonates (Jacobson et al., 2000). The poly aromatic hydrocarbon (PAH's) pollutants are of

concern because of their known carcinogenic and mutagenic properties (IARC, 1998). The main one of concern is Benzo-a-pyrene (BaP), which has been classified as a priority pollutant by the Ministry for the Environment. The New Zealand ambient air quality guideline (NZAAQG), annual average for BaP is 0.3 ng m^{-3} (MfE, 1999).

Studies in Auckland have shown that the annual average concentration of BaP was found to be 0.33 ng m^{-3} (Khanal & Shooter., 2004) while Cavanagh, et al., 2009, determined that the median total concentration of quantified PAH's was 91 ng mg^{-1} of PM_{10} and the median BaP concentration was 6.24 ng mg^{-1} of PM_{10}.

1.3.1 Carbonaceous aerosols (PM, OC, EC and TC) and PAH's in Masterton

Ancelet (2013) reported the results from Masterton where the average PM_{10} concentration (gravimetric) over all days that samples were collected was: 21.0 ± 14.8 µg m^{-3}. This average was in excellent agreement with and not significantly different ($p<0.05$) than the daily average PM_{10} concentration from the co–located FH62 operated by the Greater Wellington Regional Council (GWRC) (22.1 ± 14.6 µg m^{-3}).

He further reported that over the period sampled, two exceedances of the NES of 50 µg m^{-3} occurred. The average $PM_{10-2.5}$, $PM_{2.5}$, OC, EC and TC concentrations ± associated standard deviations along with the percent contribution of each to the average PM_{10} concentration was reported as shown in Table 1.1.

Table 1.1   Concentrations with % standard deviations of various components of APM at Masterton.

	Concentration (µg m^{-3})	Percentage of PM_{10}
$PM_{10-2.5}$	7.6 ± 4.9	36.4
$PM_{2.5}$	13.4 ± 9.9	63.6
OC	6.5 ± 4.7	30.9
EC	3.4 ± 2.7	16.2
TC	9.9 ± 7.4	47.1

From the Table 1.1, it was evident that $PM_{2.5}$ concentrations during the study were the most significant contributor to PM_{10} concentrations, contributing on average, and 64% to the

measured PM_{10} concentrations. This high $PM_{2.5}$ contribution demonstrates that elevated fine particle concentrations are the main reason for the NES.

1.3.1.1 Particle–phase PAHs

Average particle–phase PAH concentrations measured in Masterton were reported. The total average concentration of the 17 PAHs quantified was 38.9 ± 25.9 ng m^{-3}, which accounted for 0.3% of the $PM_{2.5}$. Fluoranthene and pyrene were the most abundant particle–phase PAHs, with concentrations ranging from 13.5 – 0.6 ng m^{-3} and 12.6 – 0.5 ng m^{-3}, respectively. Particle–phase PAH concentrations for the 16 PAHs classified as priority pollutants by the USEPA displayed a similar trend to emissions from wood burning appliances commonly used in New Zealand for home heating purposes (Ancelet et al., 2010; Ancelet et al., 2011b).

Ancelet et al., 2013 further concluded that their study has demonstrated that in communities where residential wood combustion is common, PM_{10} standard is likely not providing a sufficient measure of the population's exposure to potentially harmful concentrations of particles. Over the duration of the study, two exceedances of the New Zealand NES for PM_{10} occurred and these exceedances were the result of highly elevated $PM_{2.5}$ concentrations.

Cavanagh et al., 2012, further outlines that Benzo-a-pyrene, (BaP), and arsenic (As), levels in ambient air in New Zealand notably exceed national and international guideline and standards. Annual average BaP concentrations in some New Zealand cities are estimated to exceed the national ambient air guideline of 0.3 ng m^{-3} by up to 20 times and the European Union target value of 1 ng m^{-3} by up to 6 times (both annual averages), whereas average concentrations of As at urban locations in New Zealand can exceed the national ambient air quality guideline of 5.5 ng m^{-3}and the EU target value of 6 ng m^{-3} by up to 2 times.

They further reiterate that New Zealand air is not as clean as we might think and that greater regulatory focus should be given to air pollutants. However their recommendations were based on very limited studies and that more consistent sampling and analytical

methodologies need to be employed to better assess the extent of elevated concentrations of BaP and As across New Zealand.

1.4 AIR PARTICULATE MATTER POLLUTION IN WAINUIOMATA - WELLINGTON SUBURB

Wainuiomata is a suburban town with a population of approximately 16,000 located 15 km to the northeast of Wellington, the capital city of New Zealand. Wainuiomata is located in a valley basin with south-end of the town narrowing to a constricted valley that runs down to the ocean. While the air quality in Wainuiomata is generally good, the local topography makes the town susceptible to strong inversion conditions in the winter that significantly increases daily average PM_{10} of 50 ug m^{-3} (24 hour average), which has important implications for local policy makers (Davy et al., 2011).

As a result there has been a receptor modelling study of air particulate matter samples from an ambient air quality monitoring site at Wainuiomata by the Institute of Geological and Nuclear Sciences Limited (GNS Science) which has provided significant results and information relevant to GWRC's air quality management responsibilities (Davy et al., 2009).

The key results of the source appointment analysis which identified primary contributors to ambient concentrations of particulate matter as measured at the site were:

1. Marine aerosol (due to New Zealand's remote oceanic location) and crustal matter were the primary source contributors to $PM_{10-2.5}$,

2. Biomass burning was the significant contributor to high $PM_{2.5}$ concentrations during winter and exceedances of the $PM_{2.5}$ ambient air quality guidelines;

3. Biomass burning was primarily responsible for peak PM_{10} concentrations and exceedances of the PM_{10} National Environmental Standard, and

4. Arsenic and toxic organic compounds have been found to be associated with the biomass burning, suggesting the use of copper chrome arsenate, CCA, treated timber for domestic heating source and, due to the potential for adverse health effects, these compounds need to be factored into air quality monitoring strategies and air quality management initiatives.

Furthermore, the study by (Davy et al., 2009) of the particulate matter composition at Wainuiomata, Lower Hutt in Wellington found the results described in the following sections.

1.4.1 Sources of $PM_{2.5}$

Peak $PM_{2.5}$ concentrations at Wainuiomata concentrations exceeded the current NZAAQG for $PM_{2.5}$ (25 μg m^{-3}) on a number of occasions each winter monitored. It was found that combustion sources (from biomass burning (48%) and motor vehicle emissions (7%) and secondary sulphate particles (20%) along with the ubiquitous presence of marine aerosol (21%) were the primary contributors to $PM_{2.5}$. Biomass burning, primarily due to emissions from solid fuel fires from domestic heating, was responsible for exceedances of both the $PM_{2.5}$ NZAAQG and PM_{10} NES during winter.

Arsenic was found to be associated with the biomass burning source and this was considered to result from the use of CCA treated timber as fuel in domestic fires. An analysis of seasonal contributions showed that the biomass burning source dominates $PM_{2.5}$ during winter and that secondary sulphate particles and marine aerosol are the primary source of $PM_{2.5}$ during summer.

1.4.2 Sources of $PM_{10-2.5}$

Marine aerosol (68%) along with crustal matter sources are the predominant contributors to $PM_{10-2.5}$. A dust source was identified as originating from local roads due to a distinct source profile. Marine aerosol concentrations tended to be higher during spring and summer.

1.4.3 Sources of PM_{10}

The source apportionment results for the fine and coarse particle fractions were combined to provide estimates for source contributions for PM_{10}. This showed that PM_{10} in Wainuiomata is dominated by biomass burning (23%) and marine aerosol (46%) sources.

An analysis of peak PM_{10} events showed that they occur during winter and that PM_{10} concentrations on these days, including exceedances of the NES were primarily due to emissions from solid fuel fires used for domestic heating.

1.4.4   Recommendations/ Implications

It was found that there were toxic compounds (arsenic and PAHs) associated with the biomass burning source at Wainuiomata, Lower Hutt in 2008 - 2009 (Davy et al., 2009) and that these compounds may exceed their respective health guidelines.

Thus there was a need for further long term monitoring and analysis of these toxic compounds in Wainuiomata by standard methodologies in order to compare their annual average concentrations with ambient air quality guidelines.

The in-depth study by Davy et al., 2009, forms the basis of current research thesis to carry out the atmospheric monitoring of $PM_{2.5}$ /$PM_{10-2.5}$ /PM_{10} and arsenic by standard methodology using Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) and carbonaceous aerosol at Wainuiomata for the 2011 – 2013, period.

The findings will be of specific use to the Greater Wellington Regional Council (GWRC) as the council is responsible for air quality management in the Wellington region. Rules prescribed in the Regional Air Plan ban the burning of CCA treated timber in any appliance; therefore the problem is one of enforcement and/or public education to remove treated timber from the fuel stream. There may be further implications to provide government assistance to residents in this area to resort to other heating methods during winter in order to reduce particulate matter loadings and associated toxic contaminants (Davy et al., 2009).

1.5 ARSENIC – BACKGROUND LITERATURE

1.5.1 Physical and Chemical Nature of Arsenic and Arsenic Compounds

Elemental arsenic (As, Chemical Abstract Service [CAS] No. 7440-38-2) is a silver-grey crystalline metallic solid that exhibits low thermal conductivity. Although arsenic is often referred to as a metal, it is classified chemically as a non-metal or metalloid belonging to Group 15 (VA) of the periodic table. The principal valances of arsenic are +3, +5 and -3. Only one stable isotope of arsenic having mass 75 (100 percent natural abundance) has been observed. Arsenic typically exists in the (alpha)-crystalline metallic form which is steel-grey in appearance and brittle in nature, and in the beta-form, a dark grey amorphous solid. "Metallic" arsenic remains stable in dry air, but its surface will oxidize when exposed to humid air, creating a superficial golden bronze tarnish that turns black upon prolonged exposure (EPA, 1998). The physical properties of arsenic are presented in Table 1.2.

Table 1.2   Physical properties of arsenic

Property	Value
Atomic weight	74.92
Melting point (at 39.1 MPa)a	816°C
Boiling point	615°C[b]
Specific gravity (26°C)	5,778 kg/m^3
Specific heat	24.6 J/(mol K)[c]
Latent heat of fusion	27,740 J/(mol K)[c]
Latent heat of sublimation	31,974 J/(mol K)[c]
Linear coefficient of thermal expansion (20°C)	5.6 μm/(m ^{o}C)
Electrical resistivity (0°C)	26 μΩ/cm
Crystal system	hexagonal (rhombohedra)
Lattice constants (26°C, mm)	a = 0.376 e = 1.0548

Source: Kirk-Othmer Encyclopaedia of Chemical Technology. 4th Edition, Volume 3

Note:
a To convert MPa to psi multiply by 145.
b Sublimes.
c To convert to cal/(mol K) divide by 4.184.

1.5.2 Common Arsenic Inorganic Compounds and Uses

Pure arsenic is rarely found in the environment. More commonly, it bonds with various elements such as oxygen, sulphur, and chlorine to form inorganic arsenic compounds and with carbon and hydrogen to form organic arsenic compounds. The water-soluble trivalent and pentavalent oxidation states of inorganic arsenic are the most toxic arsenic compounds (World Bank Group, 1998).

1.5.2.1 Arsenic Hydrides

The primary binary compound of arsenic and hydrogen is arsine ("arsenic hydride"). It is the only known hydrogen compound of arsenic. Arsine is a colourless, very poisonous gas that exhibits unpleasant garlic like odour. It is formed when any inorganic arsenic-bearing material is brought in contact with zinc and sulphuric acid. Arsine is used as a dopant in the semiconductor industry, and is used to produce gallium arsenide, (GaAs), which is used in the field of optoelectronic and microwave devices (Kirk-Othmer: *Encyclopaedia of Chemical Technology*. 4th Edition 1992).

1.5.2.2 Arsenic Halides

While arsenic forms a complete series of tri-halides, only arsenic pentafluoride is a well-known pentahalide. All of the arsenic halides are covalent compounds that hydrolyse in water and can be formed by direct combination of the elements. Arsenic tri-chloride is the most common and commercially significant of all arsenic halides. With a low boiling point, it is easily separated from tin tri-chloride and the chlorides of other metals. It can also be formed by spontaneous combustion of the elements. Arsenic tri-chloride has been used as a starting material for the production of numerous organoarsenic compounds and for the preparation of chlorine derivatives of the arsines. In addition, it is used as a dopant in the semiconductor industry and in the production of high-purity arsenic metal (Kirk-Othmer: *Encyclopaedia of Chemical Technology*. 4th Edition 1992).

1.5.2.3 Arsenic Oxides – Arsenic Trioxide

The only arsenic oxides that are commercially significant are the trioxide and pentoxide. Arsenic trioxide is also known as white arsenic. It is the most commercially important arsenic compound. It can occur in two different crystalline forms and one amorphous variety. The octahedral or cubic modification, arsenolite, is the most common form and is stable at room temperature. It changes into a monoclinic modification, claudetite (consisting of sheets of As_2O_3 pyramids sharing oxygen), at temperatures above 221 °C. This modification is formed when condensation occurs at temperatures above 221 °C. Condensation above 250 °C will generally form the amorphous, glassy phase which devitrifies into the octahedral modification at room temperature. This octahedral variety is a white solid that sublimes above 135 °C and melts at 275 °C under its own vapour pressure (Kirk-Othmer: *Encyclopaedia of Chemical Technology*. 4th Edition 1992).

Arsenic trioxide slightly dissolves in water to form a weakly acidic solution. It is soluble in acids and bases (amphoteric). It can be made by burning arsenic in air, or by the hydrolysis of an arsenic tri-halide. Commercially, it is prepared by roasting arsenopyrites. It is often used as a primary analytical standard in oxidimetry since it is readily attainable in a high state of purity and is quantitatively oxidized by many reagents commonly used in volumetric analysis (Kirk-Othmer: *Encyclopaedia of Chemical Technology*. 4th Edition 1992).

1.5.2.3.1   Arsenic Pentoxide

Arsenic pentoxide is a "white glassy mass," made up of equal numbers of octahedral and tetrahedral sharing corner oxygen to give cross-linked strands (Hanusch et al., 1985). It is an oxidizing agent capable of liberating chlorine from hydrogen chloride. The compound deliquesces in air to form arsenic acid. It dissolves in water slowly, is thermally unstable, and begins to decompose near the melting point, around 300 °C. The vapour is made up of arsenic trioxide and oxygen. The pentoxide can be made by reacting arsenic trioxide with oxygen under pressure, or by dehydration of crystalline arsenic acid at temperatures above 200 °C (Kirk-Othmer: *Encyclopaedia of Chemical Technology*. 4th Edition 1992).

1.5.2.4 Arsenic Sulphides

Arsenic di-sulphide ("red glass") exists in ruby-red crystals or as an amorphous reddish mass. It occurs naturally as the mineral realger. At 267 °C it changes into a black allotropic modification and at 307 °C the compound melts. Its purity and fineness rather than its chemical composition determine its commercial value. Industrially manufactured red arsenic glass varies in its composition. Today, red glasses typically contain around 61 - 64% arsenic and 36 - 39% sulphur. Commercially, the compound is produced by heating a mixture of iron pyrites and arsenopyrites or by heating arsenic trioxide with sulphur.

Arsenic (III) sulphide is known as orpiment and occurs as a yellow mineral. It is made by precipitation of trivalent arsenic compounds with hydrogen sulphide. The colloidal solution of the arsenic trisulphide can be flocculated with hydrochloric acid, in which it is insoluble. It readily dissolves in basic reagents. Orpiment contains unchanged arsenic trioxide and is poisonous. It was used in the past for cosmetic purposes, but currently it is used in the semiconductor industry, in the production of infrared-permeable windows, and as a pigment.

Arsenic (V) sulphide (also referred to as arsenic pentasulphide) is made by fusing stoichiometric quantities of arsenic and sulphur powder or by precipitation from highly acidic arsenate (V) solution with H_2S. Arsenic (V) sulphide will decompose into arsenic (III) sulphide and sulphur. The compound is stable in air up to temperatures of 95°C, but begins to dissociate into arsenous sulphide and sulphur at higher temperatures. It can be hydrolysed by boiling with water resulting in arsenous acid and sulphur (Kirk-Othmer: *Encyclopaedia of Chemical Technology*. 4th Edition 1992).

TABLE 1.3   Common arsenic compounds

Compound	Chemical Formula/ Description	Uses
Arsenic acid	$H_3AsO_4 \cdot \frac{1}{2}H2O$	*Manufacture of arsenates, glass making, wood treating process, defoliant (regulated), desiccant for cotton, soil sterilant.*
Arsenic di-sulphide	As_2S_2	*Leather industry, depilatory agent, paint pigment, shot manufacture, pyrotechnics, rodenticide, taxidermy.*
Arsenic penta-fluoride	AsF_5	*Doping agent in electro-conductive polymers.*
Arsenic penta-sulphide	As_2S_5	*Paint pigments, light filters, other arsenic compounds.*
Arsenic pentoxide	As_2O_5	*Arsenates, insecticides, dyeing and printing, weed killer, coloured glass, metal adhesives.*
Arsenic thioarsenate	$As(AsS_4)$	*Scavenger for certain oxidation catalysts and thermal protectant for metal-bonded adhesives and coating resins.*
Arsenic tri-bromide	$AsBr_3$	*Analytical chemistry, medicine.*
Arsenic tri-chloride	$AsCl_3$	*Intermediate for organic arsenicals (pharmaceuticals, insecticides), ceramics.*
Arsenic tri-fluoride	AsF_3	*Fluorinating reagent, catalyst, ion implantation source, and dopant.*
Arsenic trioxide	As_2O_3	*Pigments, ceramic enamels, aniline colours, decolorizing agent in glass, insecticide, rodenticide, herbicide, sheep and cattle dip, hide preservative, preparation of other arsenic compounds.*
Arsenic tri-sulphide	As_2S_3	*Pigment, reducing agent, pyrotechnics, glass used for infrared lenses, semiconductors, hair removal from hides.*
Arsenic hydride (arsine)	AsH_3	*Organic synthesis, military poison, doping agent for solid-state electronic compounds.*

Source: *Hawley's Condensed Chemical Dictionary*, 12th Ed.

1.5.2.5 Organic Arsenic Compounds

Arsenic combines easily with carbon to form a wide variety of organic compounds with one or more As-C bonds. There are many known organoarsenic compounds. Organic arsenic compounds can be grouped into aliphatic organoarsenic compounds and aromatic organoarsenic compounds.

1.5.2.5.1   Aliphatic Organoarsenic Compounds

This class of compounds is still used as herbicides and fungicides in rice, cotton, fruit, and coffee plantations, particularly in Eastern Asia. The three main aliphatic organoarsenic compounds are described below.

i)   Methanearsonic Acid

Salts of methanearsonic acid, particularly the iron ammonium salt, Neoasozin, are used as a fungicide in rice growing. The sodium, ammonium, and diethanolammonium salts are used as herbicides in cotton growing (Hanusch et al., 1985).

ii) Dimethylarsinic Acid

Dimethylarsinic acid, also called Ansar 160, is used as a total herbicide and desiccant. Generally, it is produced by reaction of methyl halide with a salt of arsenous acid (Hanusch et al., 1985).

iii) Arsonic Acids

Arsonic acids are used in various industrial applications. For example, they have been used as corrosion inhibitors for iron and steel, and as additives for motor fuel, agricultural bactericides, herbicides, and fungicides. The primary use of the arsonic acids was in their supplementary processing to arsenobenzenes and "arsenic oxides" by reduction with SO_2, phosphorus tri-chloride, sodium dithionite, phosphorous acid, or tin (II) chloride. Reduction with zinc dust and hydrochloric acid yields the arsines, which are re-oxidized in air (e.g., phenylarsine, rapidly oxidized in air to form the arseno-compound, $C_6H_5As_n$). Additional

uptake of oxygen is considerably slower unless catalysed (e.g., by iron) (Hanusch et al., 1985).

1.5.2.5.2   Aromatic Arsenobenzenes

Aromatic arseno compounds have amino or hydroxyl groups and are soluble in acids and alkalis. Aromatic arseno compounds will become soluble in water with the addition of a formaldehyde sulphoxylate or formaldehyde hydrogen sulphite into the amino group.

i)   Organic Oxoarsenic Compounds ("Arsenic Oxides")

The reduction of organoarsenic compounds can be controlled by using an appropriate reducing agent so that reaction terminates at the preferred intermediate stage. However, this does not occur with oxidation. In the most commonly used method for the production of organic oxoarsenic compounds from arsonic acids, the acid is directly reduced to the anhydride of the arsonous acid with SO_2.

Organic oxoarsenic compounds are the anhydrides of the arsonous acids. They are extremely poisonous, amphoteric substances barely soluble in water. When dissolved in acids and alkalis, they form salts and can be precipitated from those solutions by carbon dioxide or ammonium chloride (Hanusch et al., 1985).

1.5.3   Sources and Fate of Arsenic in the New Zealand Environments

Arsenic is ubiquitous, and is emitted naturally from many sources (e.g., volcanoes, forest wild fires, erosion from mineral deposits). However, the releases originating from human activities (e.g., metal smelting, chemical production and use, coal combustion, waste disposal, pesticide application) are the emissions that can cause substantial environmental contamination. The greatest environmental concentrations of arsenic have been observed in air and soil around mining and smelter operations, whereas coal combustion distributes arsenic to the air in much lower concentrations over a wider area. A brief discussion of the fate of arsenic upon being released to the air, water, and soil is provided below.

1.5.3.1 Sources and Fate of arsenic in Soils

Arsenic is distributed widely in the earth's crust. Arsenic occurs naturally in many soils and parent rock in New Zealand, with concentrations typically in the 2 to 6 ppm range although this can be considerably more (50 ppm) in geothermal zones (Craw et al., 2000).

Robinson et al., 2004, reported that in New Zealand, elevated levels of arsenic in soils and waters occur as a result of geothermal activity, exacerbated by geothermal power exploitation, and the past and present use of arsenic-based pesticides and certain industrial wastes can increase concentrations. Approximately 80 percent of the total amount of arsenic that is released to the environment from anthropogenic activities is released to soil (USEPA, 1982). The major anthropogenic sources contributing to arsenic in soils include the application of pesticides and disposal of solid wastes from fossil fuel combustion and industrial processes. Organoarsenical pesticides (e.g., monosodium methanearsonate, disodium methanearsonate) applied to soils are metabolized by soil bacteria to form alkyl arsines and arsenate (Hood, 1985).

Land application of sewage sludge has proven to be another source of arsenic in soil. While arsenic has been observed in soil at various hazardous waste sites, it is not always obvious that it was a result of the waste site or from natural causes. Regardless of the source or form of arsenical, arsenic will react with soil components (USEPA, 1982).

The predominant reaction is adsorption onto and reaction with hydrous iron and aluminium oxides which coat soil particles. Heavier soils with higher clay content and hydrous oxide content adsorb more arsenic than do lighter sandier soils with low clay content (US EPA, 1982). In addition, arsenicals react with ions in solution, such as iron, aluminium, calcium, and magnesium, but may also include manganese and lead. The pH of the soil will affect the solubility of these compounds; therefore, changing the soil pH may affect each arsenical's solubility (USEPA, 1982).

There are two known types of oxidation that are responsible for transforming arsenicals environmentally. One type destroys the carbon/arsenic bond and is associated with microbial activity, while the other type causes a change in oxidation state which may or may not be affected by microbial activity. Transformations of arsenic in soil are similar to those

seen in aquatic systems, with As (V) predominant in aerobic soils; As (III) in slightly reduced soils (e.g., temporarily flooded); and arsine, methylated arsenic, and elemental arsenic in highly reduced conditions (e.g., swamps and bogs) (US Department of Health and Human Resources, 1992). Some arsenate may be reduced to arsenite under certain environmental conditions. Arsenic in sediments or in flooded anaerobic soil may be reduced as a function of reduction/oxidation potential USEPA, 1998).

Soils associated with the production and use of Copper Chromium Arsenate (CCA) treated timber also exhibit elevated arsenic concentrations. Wood-waste and timber-treatment sites often contain arsenic hot spots that present a risk to groundwater. The extensive use of CCA-treated posts in agricultural and horticultural systems might lead to the long-term arsenic contamination of New Zealand's productive soils (Robinson et al., 2004).

They further reported that, the arsenic concentration in the soil samples collected from several sites was greater than the threshold level (100 mg kg^{-1} arsenic) set by the Australian National Environmental Protection Council (ANEPC), for agricultural soils. Across all sites, 25% of the samples were above the ANPEC guidelines for arsenic and 10% of the samples were above ANPEC guidelines for chromium (100 mg kg^{-1}). None of the copper values exceeded ANPEC guidelines (1000 mg kg^{-1}).

Therefore, the results from general survey indicate that CCA does leach from treated posts over time. As the average post life is expected to be 25 years, and around 4% of the posts are replaced annually, the use of treated posts will lead to a gradual accumulation of CCA in the soil and possible movement of arsenic away from the posts. CCA levels might eventually accumulate locally around the post to the point where they could have negative impacts although the rate of accumulation is likely to be low (Robinson et al., 2004).

They have further reported that, regarding the use of CCA timber treatment, there has been a great deal of emotive discussion both for and against its continued use. However, since no viable alternative for CCA treatment currently exists, future research should focus on innovative technologies that prevent arsenic from entering soils and surface or groundwater. There could be several low-cost means of reducing / eliminating CCA from new or replacement posts.

As a remedial option in the report Robinson et al., 2004, mentioned that according to Lebow & Evans, 1999, lacquering CCA-treated posts has been demonstrated as an inexpensive way of reducing CCA leaching from treated timber. However, it is unclear how much of the lacquer will be removed when the post is rammed into the ground. Alternatively, soil amendments may be used to immobilise any CCA leachate.

The historical use of arsenic based pesticides in sheep-dips has resulted in an estimated 50,000 sites contaminated with arsenic and persistent organic pollutants (POP's) such as dieldrin. Urbanisation of agricultural land has resulted in the belated discovery of arsenic-contaminated residential soils. As well, past pesticide practices in agriculture and horticulture employed arsenic - based compounds. Recently sampling of previously productive soils has uncovered high levels of arsenic in some soils (Robinson et al., 2004).

Lesser sources of arsenic contamination in New Zealand originate from coal ash disposal, and the mining industry (Nriagu & Pacyna 1988; Eisler 2004). Arsenic trioxide (As_2O_3) is extensively used in the manufacturing of ceramic and glass, electronics, pigments and antifouling agents, cosmetics, fireworks and copper (Cu) based alloys (Leonard 1991). Coal combustion not only releases gaseous arsenic into the atmosphere but also generates fly and bottom ash containing varied amounts of arsenic. Disposal of these materials often leads to arsenic- contamination of soil and water (Beretka & Nelson 1994).

Continuous application of fertilisers that contain trace levels of arsenic also results in arsenic contamination of soil, thereby reaching the food chain through plant uptake (McLaughlin et al., 1996).

1.5.3.2 Sources of arsenic and Fate in Water/ Plants/ Food

Arsenic can be found in surface water, groundwater, and finished drinking water. The majority of arsenic in natural water is a mixture of arsenate and arsenite, with arsenate usually predominating (US Department of Health and Human Resources, 1992).

Arsenic is released to water in several ways, including natural weathering processes, discharge from industrial facilities, and leaching from landfills, soil or urban runoff. Once in water, arsenic can go through a complex series of transformations, including oxidation reduction reactions, ligand exchange, and bio-transformations (USEPA, 1998).

The factors that most strongly influence the transformations that arsenic will undergo are the oxidation-reduction potential (Eh), pH, metal sulphide and sulphide ion concentrations, iron concentrations, temperature, salinity, and distribution and composition of the biota (US Department of Health and Human Resources, 1992). Arsenate is usually the predominant form of arsenic in water; however, aquatic microorganisms may reduce the arsenate to arsenite and a variety of methylated arsenicals.

Once in water, the transport and partitioning of arsenic will depend upon its chemical form as well as interactions with other materials present. Any soluble forms will move with the water, and can be carried long distances through rivers. However, arsenic can also be adsorbed from water onto sediments and soils, particularly clays, iron oxides, aluminium hydroxides, manganese compounds, and organic material (US Department of Health and Human Resources, 1992). Once in sediments, arsenic can be released back into the water through chemical and biological inter-conversions of arsenic species (USEPA, 1998).

In New Zealand, Robinson et al., 2004, reported that some lakes and rivers in the Taupo Volcanic Zone (TVZ), North Island, (Figure 1.4) have arsenic concentrations above the World Health Organisation's (WHO) limit for arsenic in drinking water (0.01 mg L^{-1}). The aquatic plants from this region accumulate inordinate amounts of arsenic, in some cases to more than 1000 mg kg^{-1} on a dry weight basis, the threshold for arsenic hyper-accumulation. At least one of these species, watercress (*Rorippa nasturtium-aquaticum*), is consumed by humans and that ground and surface water used for irrigation may lead to accumulation of arsenic in agricultural soils.
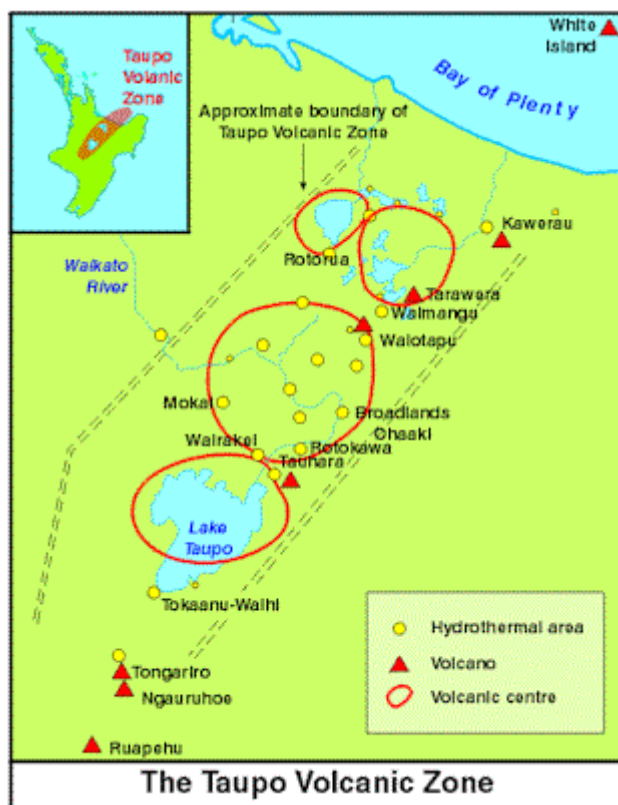
Figure 1.4   Taupo Volcanic Zone (Image: GNS Science)

Other sources of arsenic in the New Zealand water environment are primarily anthropogenic in origin, for example timber treatment and use of treated timber, pesticides, herbicides, fertilisers and mining operations (gold, coal) (Robinson et al., 2004). Leaching usually occurs after rain and arsenic finds its way into the waterways.

Once arsenic enters the environment, it enters the food chain. Bio-concentration of arsenic occurs in aquatic organisms, mainly in algae and lower invertebrates. Low levels of arsenic have been measured in freshwater invertebrates and fish, while higher levels have been observed in marine oysters. Apparently, bio-magnification in aquatic food chains is not significant, although some fish and invertebrates have high levels of arsenic compounds (USEPA, 1998).

1.5.3.3 Sources, Fate and Occurrence of Arsenic in Air

Arsenic can be released to air from natural sources (e.g., volcanoes and forest fires) and from various industrial sources (e.g., coal combustion, smelter and mining activities) and pesticide application. Arsenic in air primarily exists in the form of particulate matter (mostly

in particles less than 10 µm (PM_{10}) in diameter) and is usually a mixture of arsenite and arsenate (inorganic form). These particles can be transported by wind and air currents until they are brought back to earth by wet or dry deposition. The residence time of arsenic bound to particulate depends on particle size and meteorological conditions; however, a typical value is approximately 9 days (U.S. Department of Health and Human Resources, 1992).

As it may be expected, levels of arsenic in air vary with distance from the source, height of the stack, and wind speed. In general, large cities have higher levels of arsenic air concentrations than smaller ones. This is probably due to emissions from coal powered plants. In addition, areas that are near nonferrous metal smelters have reported extremely high arsenic air concentrations (USEPA, 1998).

Mean levels in ambient air in the United States range from <1 to 3 ng m^{-3} in remote areas and from 20 – 30ng m^{-3} in urban areas. Mean airborne concentrations of arsenic in 11 Canadian cities and one rural site amounted to 1 ng m^{-3} while in England; the mean concentration was 5.4 ng m^{-3}. There was a declining trend observed in England, over the period, 1957-1974 (WHO, 2000).

Particulate arsenic compounds may be inhaled, deposited in the respiratory tract and absorbed into the blood. Inhalation of arsenic from ambient air is usually a minor exposure route for the general population (WHO, 2000). Atmospheric arsenic deposits to the soil, and is then absorbed by plants, leached to groundwater and surface water, and taken up by plants and animals. Airborne concentrations of arsenic range from a few nanograms per cubic meter (ng m^{-3}) to a few tenths of a microgram per cubic meter (µg m^{-3}), but concentrations may exceed 1 µg m^{-3} near stationary sources of emissions (Bencko, 1987).

There has only been a limited monitoring campaign undertaken with the objective of determining arsenic in air in New Zealand. Short-term measurements of arsenic and lead were made within the vicinity of a lead-acid battery recycling plant in Lower Hutt in 2008 and in 2009 to evaluate appropriateness of environmental controls on fugitive emissions (Mitchell, 2008; Mitchell, 2009). This study determined average concentrations of arsenic in TSP (determined by ICP-MS) of 4.4 and 3.9 ng m^{-3} respectively for two community monitoring sites close to the plant (Mitchell, 2009).

Monitoring of arsenic deposition rates, required as a condition of the battery-recycling plant's discharge to air permit issued by GWRC, found the median deposition rate for arsenic was 135 µg m^{-2}/month between 2006 and 2011 the at the two community monitoring sites. Contamination of a local stream that received storm water containing lead and arsenic arising from deposition of airborne emissions from the recycling plant onto paved surfaces has also been documented (Markland et al., 2005). The battery recycling plant closed in 2012 and there are now no other known significant industrial emitters of arsenic in particulate matter in New Zealand (Mitchell, 2015).

As part of a wider study evaluating the *in vitro* toxicity of particulate matter, a winter average of 13.0 ng m^{-3} for water-soluble fraction of arsenic was found in PM_{10} collected on glass fibre filters in Timaru (Cavanagh et al., 2010). However, these monitoring campaigns were not designed to follow the standard sampling frequency and/or arsenic analysis techniques to assess compliance with the national ambient air quality guideline.

1.5.4 Arsenic Pollution and CCA Treated Timber

WHO (2001) observes that arsenic (and other arsenicals) is produced from arsenic trioxide, a by-product of metal smelting operations, and that it has been estimated that 70% of world arsenic production is used in timber treatment as CCA, 22% in agricultural chemicals, and the remainder in glass, pharmaceuticals and non-ferrous alloys. Thus there may be significant implications for world demand for arsenic from falling agricultural and timber treatment use.

Arsenic associated with air particulate matter pollution is primarily due the combustion of arsenic containing fuels such as coal and copper chromium arsenate (CCA) treated timber. CCA is extensively used as a preservative in timber treatment in New Zealand.

Figure 1.5   CCA treated (greenish coloured) pine ready to be used as posts

CCA has been used to pressure treat lumber since 1940's. Since the 1970's, the majority of the wood used in outdoor residential settings has been CCA-treated wood. CCA has been used to preserve wood from insects, fungi and water damage for many years, and is still used today (Helsen & Van den Bulck, 2003). Pressure treated wood containing CCA is being widely used in most residential settings, including decks, play sets, fences, building posts etc. (ToersBijns, 2012).

The New Zealand pine (*pinus radiate*), has been described as the wonder timber in New Zealand as it is the mainstay of the expansive forestry industry, which is widely used for building houses, for posts and poles as well as outdoor furniture, decks and handrails. However this wonder timber is vulnerable to insects and fungi hence impregnated with cocktail of CCA. New Zealand has been a pioneer of CCA timber treatment since the 1930's and today we are reputedly the highest per capita users of it in the world (http://www.elementmagazine.co.nz/people/healthy-homes/is -our-wood-making-us-sick/).

Most of this treated timber, when disposed or thrown into the waste pile; it can become an accident waiting for anyone who misuses this type of wood in an open fire.

Figure 1.6   Typical wood burner open fires in New Zealand homes during winter seasons

Burning CCA treated timber releases 90% of the arsenic in the smoke and about 10% remains concentrated in the ash according to Graham, technical advisor to New Zealand government and United Nations agencies. He further pointed out that "In New Zealand the building industry is based around CCA and alternatives are more expensive. To suddenly say

you can't use CCA anymore would be another political whipping post" as reported in (http://www.elementmagazine.co.nz/people/healthy-homes/is-our-wood-making-us-sick/).

Soft wood is injected with an aqueous solution of copper, chromate, and arsenic under pressure. The arsenic is chemically bound in the wood by the chromate, and the copper gives it that slight greenish tint. The solution is water based, which is why the wood often feels damp in the lumber yard.

Then CCA treated timber can release the poison from the wood in several ways that include, burning the wood, mechanical abrasion, direct contact or when acid (acid rain) contacts the treated lumber.

The most important being combustion as burning of CCA treated timber does not destroy arsenic. The burning of CCA treated timber is of environmental concern as the smoke contains high levels of arsenic while the ash retains high levels of copper and chromium, all of which can be toxic to the environment (ToersBijns, 2012).

An analysis by Helsen and co-workers suggests both +3 and +4 oxide states of arsenic are released and that low temperature pyrolysis (< 327 °C) may retain arsenic in the ash (Helsen & Van Den Bulck, 2003). It has also been shown that the copper and chromium components are preferentially retained in the ash during combustion of CCA treated timber. They have further concluded that zero arsenic release during pyrolysis of CCA treated timber seems to be impossible due to the reduction reaction as shown below:

$$(As_2O_5 \longrightarrow As_2O_3 + O_2) \tag{1.1}$$
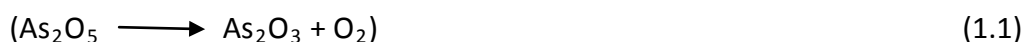
The above reaction cannot be avoided in the reducing environment, created by the presence of wood, char and pyrolysis vapours. Once the trivalent oxide is formed it is released (Helsen & Van Den Bulck, 2003).

A major potential means of disposal of treated timber and treated wood waste is combustion. Studies show that, depending on the combustion conditions, 10-90% of the arsenic present in CCA-treated timber may be lost to air, either as volatilised arsenic oxide, As_2O_3, or particulate matter.

With the growing concern regarding the use of CCA treated timber, Helsen and the team have done significant research to find the best and the most appropriate thermochemical disposal process to dispose of any waste timber treated with CCA. They concluded that:

- On the short term: co-incineration as long as CCA treated timber has not to be treated separately and dilution is allowed.

- On the long term a sustainable solution has to be found: with preference to recycle as much material as possible in a cost -effective way. Further work is required on the following methods:

  i)   Low temperature(380 °C) pyrolysis in a moving bed;

  ii)   High temperature gasification (1100-1500 °C) in a metallurgical furnace.

In another research, Niyobuhungiro & Blottnitz, 2013, reported that occurrence of waste timber previously treated by copper chromium arsenate (CCA) insecticide in the fuel supplies of informally operating caterers in the Cape Town region. The report showed evidence that the burning of CCA-treated timber by informal caterers does lead to arsenic enrichment of the smoke.

It was further reported that under controlled conditions, the concentrations of arsenic volatilised from (H2 and H5) were 19 and 52 $\mu g\ m^{-3}$, and the As : Cu and As : Cr ratios strongly increased compared the ratios found in the timber. The lowest concentration of PM_{10} was found around the Nyanga taxi rank at a distance of ± 100 m from caterers, at 33 $\mu g\ m^{-3}$, while the highest concentration was 8139 $\mu g\ m^{-3}$ for a 1-hour sample representing occupational exposure close to wood burning fires. Arsenic was detected in 15 smoke samples. The average arsenic level of positive samples was 1.3 $\mu g\ m^{-3}$. The arsenic levels measured exceed normal background levels, which have been reported by the WHO to be 0.02–4 $ng\ m^{-3}$ in rural air and up to 30 $ng\ m^{-3}$ in urban air.

As a result it was confirmed by the researchers that where CCA-treated timber is burnt by informally operating caterers, significantly elevated arsenic levels have been found. Moreover, even where this is not directly the case, arsenic was measured at elevated levels,

possibly indicative of burning of CCA-treated timber elsewhere or recently in the studied areas.

1.5.5 Arsenic in Particulate Matter Research in New Zealand

In an extensive research, a multi-year receptor modelling study of air particulate matter (APM) conducted by Auckland Council (AC). Samples have been collected at six air quality monitoring sites across greater Auckland with more than 7000 $PM_{2.5}$ and PM_{10} filters analysed since 2004 and elemental concentrations determined by ion beam analysis (IBA) to provide the basis for apportioning airborne particle mass concentrations to various sources by positive matrix factorisation (Davy et al., 2011).

IBA is a mature and well developed technology used by many research groups around the world to study a variety of routine analytical applications including analysis of atmospheric aerosol (Maenhaut & Malmqvist, 2001).

The limit of detection for the determination of arsenic by IBA on Teflon filters used by the Auckland Council was 20-30 ng m^{-3}. (Note that the LOD for As can be considerably lower for very thin Teflon or polycarbonate filters (As LOD $\approx$ 3 ng m^{-3}) since the LOD is a function of filter material and sample matrix, (Davy et al., 2011).

Furthermore arsenic has been found to be associated with biomass burning sources during winter. The source of arsenic was considered to be due to the use of copper chromium arsenate (CCA) treated timber as a fuel in solid fuel fires for domestic heating. While particulate matter pollution from domestic fires itself presents a health risk for the exposed populace, the addition of arsenic to the mix exacerbates the potential risk. The use of CCA treated timber as fuel appears to be intermittent and most likely opportunistic as peak arsenic concentrations did not always coincide with peak contributions from domestic fire sources (Davy et al., 2011).

Table 1.4   Average arsenic concentrations at Auckland and other locations (monitoring period indicated)

	Auckland Sites	Wainuiomata	Tahunanui	Hastings
Average (ng m^{-3})	3.6 ± 2.3	6.3 ± 3.2	4.4 ± 2.4	6.3 ± 1.6
Total samples	3610	221	185	120
NO. of samples As > LOD	458	44	30	67
% of total samples	13	20	16	56

In terms of inhalation health risk, the NZAAQG stipulate a mean annual concentration of, 5.5 ng m^{-3}, for inorganic arsenic, in order to protect public health. Therefore it can be seen from the data that the New Zealand Ambient air guidelines may have exceeded at some locations (Davy et al., 2011).

The potential for combustion of CCA treated timber as a source of arsenic emissions was signalled in by a technical review of the 1994 ambient air quality guidelines published in 2000 (Chido & Rolfe, 2000). However, national level interest/concern about arsenic in ambient air that might arise from domestic burning of CCA treated timber has only relatively recently been raised following the emergence of a common pattern of winter elevated arsenic concentrations largely from studies involving elemental speciation of particulate matter (Cavanagh et al., 2012; Davy et al., 2014). In addition, hourly elemental speciation measurements in four urban areas of New Zealand found arsenic concentrations displayed the same diurnal pattern as particulate matter concentrations in wood smoke environments with a large peak in the evening and a smaller peak in the morning (Ancelet et al., 2014). The results were from IBA data which as discussed was not a standard methodology and has LOD much higher than the NZAAQ guidelines.

It was in fact these alarming figures that triggered this research in November, 2011 by GNS Sciences and GWRC, using standard methodologies, more consistent sampling, at least two

winters to derive an annual average, and compare them with IBA data and the NZAAQ guidelines.

Two other studies have specifically looked at arsenic levels in the urban environment. In the first study, Waikato Regional Council also found an average arsenic concentration of 6.1 ng m^{-3} in PM_{10} (determined by ICP-MS) using filters exposed for a consecutive four day period in urban Hamilton from November 2010 to November 2012. The second study involved a retrospective determination of multi-element concentrations by XRF in particulate matter collected on PM_{10} glass fibre filters in urban Whangarei from 2004 to 2012. In this study the average concentration of arsenic determined by XRF was 3 ng m^{-3} (Davy & Ancelet, 2014).

To compare the results of the XRF in the above study, a filter punch of 47mm of each glass fibre filter analysed (about 450 samples) was acid digested in the GNS laboratory according to the method developed as part of this research, and simultaneously analysed by ICP-MS at Hill Laboratories in Hamilton.

Moreover, burning CCA treated timber is effectively banned through regional plan rules and the problem presents itself as one of enforcement and/or public education. From the results of their analysis and discussions, the implications for air quality management in Auckland and, more broadly, New Zealand, as the practice of using CCA treated timber for fuel is not isolated to Auckland alone (Davy et al., 2011). Further research from Dunedin, Timaru, Nelson and Wellington showed similar trends whereby the elevated concentrations of arsenic occur every winter in many urban areas (Nelson and Timaru recording highest levels) as a result of the use of CCA treated timber as fuel for domestic space-heating appliances. The results have implications for both chronic health effects associated with exposure to elevated winter concentrations of particulate arsenic (Davy et al., 2013).

Hence, from an environmental point of view deliberate burning of CCA-treated timber or wood waste should be avoided because there is a risk of contamination of the atmosphere with arsenic during combustion and of soil and water by contaminated ash.

The presence of arsenic in airborne particulate matter (PM) represents a risk for human health where smaller the diameter of the particles, the greater the ability to enter the organism through the respiratory system. In this sense, particles with aerodynamic

diameters equal or smaller than 10 μm and 2.5 μm (referred as PM_{10} and $PM_{2.5}$) are considered in most atmospheric pollution studies, as $PM_{2.5}$ particles can get into the lungs (Harrison et al., 1997). Also, it has been described that the most toxic trace elements, arsenic amongst them, tend to accumulate in the smallest respirable particles (Natusch & Wallace, 1976).

1.5.6 Health Effects of Arsenic Exposure

Ingestion is the main route of exposure to arsenic for the general population. Arsenic can have both acute and chronic toxic effects on humans (World Bank group, 1998).

Acute inhalation exposure to inorganic arsenic may result in gastrointestinal effects, haemolysis, and central and peripheral nervous system disorders in humans. Effects of acute exposure to arsine (a gaseous compound of arsenic) include haemolytic anaemia, haemoglobinuria and jaundice, and can lead to kidney failure. Acute inhalation exposure to arsine can lead to death: it has been reported that exposure to 87–170 mg m^{-3} arsine for half an hour can be lethal (MfE, 2002).

Chronic inhalation exposure to, and contact with, inorganic arsenic is associated with irritation of the skin and mucous membranes, including dermatitis, conjunctivitis, pharyngitis and rhinitis. Several studies of women working or living near metal smelters, and in the electronics industry, have associated exposure to arsenic and arsine gas with an increased incidence of spontaneous abortions and lower birth weights. However, the studies have limitations due to simultaneous exposure to other pollutants, and small numbers in some studies. Human inhalation studies have reported that inorganic arsenic exposure is strongly associated with lung cancer. Human exposure by ingestion has also been associated with an increased risk of skin, bladder, liver and lung cancer (MfE, 2002).

Short-term acute poisoning cases involving the daily ingestion of 1.3-3.6 mg arsenic by children in Japan resulted in acute renal damage, disturbed heart function and death (WHO, 1981).

The USEPA has classified inorganic arsenic as a Group A carcinogen of high potency, but it has not classified arsine (MfE, 2002). Similarly the International agency for Research on Cancer (IARC) evaluated arsenic in 1980 and classified, "Arsenic and Arsenic compounds"

into its Group 1, which includes the chemicals and groups of chemicals which are "causally associated with cancer in humans" (California Air Resources Board (CARB), 1990).

The board also declared arsenic as genotoxic: it induces chromosomal aberrations and sister chromatic exchange and it may inhibit DNA repair (CARB, 1990).

Furthermore, evidence for carcinogenicity in humans due to inhaled arsenic is strong. Studies of smelter workers exposed to arsenic and workers in the pesticide manufacturing industry have found strong, consistent, statistically significant associations between respiratory cancer mortality and arsenic exposure (CARB, 1990).

The toxicity of arsenic depends on the oxidation state and molecular form in which this element is included. Inorganic As(III) is more toxic than As(V), and both are more toxic than the penta-valent methylated arsenic molecules (Jomova et al., 2011). The toxicity and carcinogenesis of trivalent arsenic is due to binding to macromolecules by (-SH) and (-OH) groups. (The –SH functional group itself is referred to as either a *thiol* group or a *sulfhydryl* group (https://en.wikipedia.org/wiki/Thiol), while –OH are the hyroxyl radicals). Penta-valent inorganic arsenic can be reduced in vivo to As(III) to exert toxic effect, although As(V) also mimics inorganic phosphate (Kitchin et al., 2008).

Trivalent inorganic arsenic interferes with enzymes, resulting in an inactivation of pyruvate dehydrogenase by complexation with As(III), preventing the generation of adenosine-5-triphosphate (ATP) and thus affecting the cellular energy cycle (Mandal & Suzuki, 2002). Arsenic exposure may also generate free radicals and change the methylation state of cellular DNA being related to several types of cancer such as skin, lung and urinary bladder (Englyst et al., 2001) and (Cantor & Lubin, 2007).

Table1.5   Showing typical findings of Chronic Arsenic Poisoning and organs affected

Affected Organ	Features of Chronic Arsenic poisoning
Skin	• *Excessive darkening of skin (hyperpigmentation) in areas that are not exposed to sunlight.* • *Excessive formation of scaly skin on the palms and soles (arsenical keratosis).* • *Exfoliative dermatitis.* • *Arsenic- induced skin cancers (especially Bowen disease)*

Nails and Hair	➢ *Transverse white bands of arsenic deposits across the bed of the fingernails (Mee's lines)* ➢ *Arsenic deposits in hair.*
Nervous System	❖ *Sensory changes, numbness and tingling in a "shocking-glove" distribution (sensory peripheral neuropathy)* ❖ *Headache, drowsiness, confusion* ❖ *Distal weakness of small muscles e.g. Hands and feet*
Blood and Urine	✓ *Haemolytic anaemia (moderate)* ✓ *Leukopenia (Low white cell count)* ✓ *Proteinuria (protein in Urine)*
Other	▪ *Inflammation of respiratory mucosa* ▪ *Peripheral vascular insufficiency* ▪ *Increased risk of cancer of lung, liver, bladder, kidney and colon*

Source: http://dermnetnz.org/reactions/arsenic.html

1.5.7   WHO Air Quality Guidelines on Arsenic exposure

Arsenic is a human carcinogen. Present risk estimates have been derived from studies in exposed human populations in the United States and Sweden, when assuming a linear dose-response relation, a safe level for inhalation exposure cannot be recommended.

At an air concentration of 1 ug m^{-3} an estimate of lifetime risk is 1.5 x 10^{-3}. This means that the excess lifetime risk level **is 1:10,000, 1:100,000 or 1:1000, 000** at an air concentration of about **66 ng m^{-3}, 6.6 ng m^{-3} or 0.66 ngm^{-3}** (WHO, 2000).

1.5.8   Air quality guidelines for Arsenic in New Zealand

The New Zealand ambient air quality guidelines (NZAAQG) contains inhalation based health risk guidelines for arsenic species (MfE, 2002). The guideline value for inorganic arsenic is 0.0055 μg m^{-3} which is equivalent to 5.5 ng.m^{-3} (annual average), and for arsine (AsH$_3$) the guideline value is 0.055 μg m$^{-3`}$ (annual average). At temperatures above 230 °C arsine decomposes to arsenic oxides (Lide, 1992), therefore arsine is unlikely to be present in combustion emissions. For the purposes of this discussion we assume that arsenic emitted from combustion processes is present as inorganic oxides.

2.0 METHODOLOGY

2.1 WAINUIOMATA SITE AND SAMPLING METHODOLOGY

2.1.1 Site description

Samples of airborne particles were collected at an ambient air quality monitoring station located within the grounds of the Wainuiomata Bowling Club, off Moohan Road, Wainuiomata (Latitude: -41.2681°, Longitude: 174.9534°). This is the same location used by the Greater Wellington Regional Council (GWRC) for monitoring ambient PM_{10} and $PM_{2.5}$ using a non-gravimetric method and co-located meteorological parameters. Collection of PM_{10} by gravimetric method (high-vol sampler) was undertaken at the same location so that concentrations of arsenic and other elements could be determined as well as providing comparison of PM_{10} data from two co-located instruments.
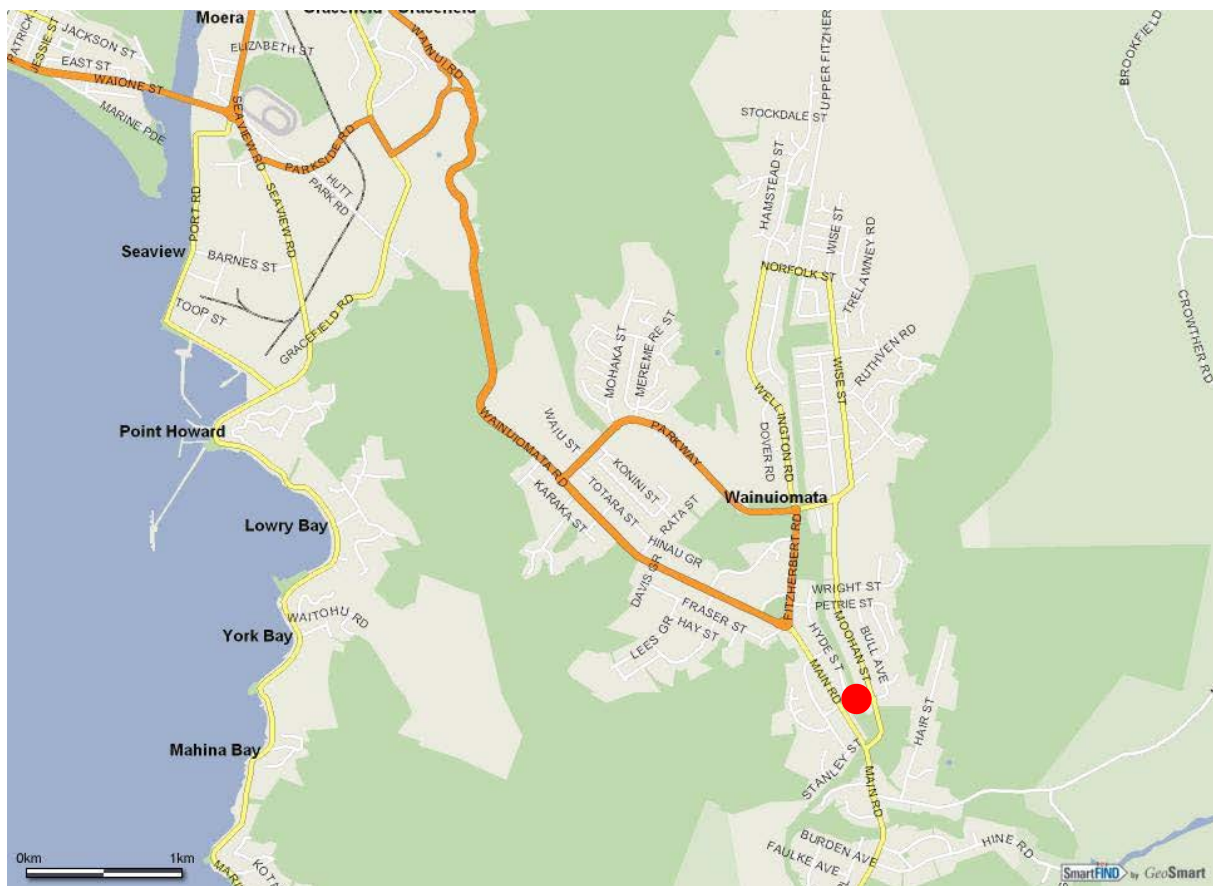
Figure 2.1   Map showing location of Wainuiomata monitoring site (●) (Source: Wises Maps www.wises.co.nz).

Wainuiomata is located in a valley basin surrounded by hills approximately 200 m high to the north and west; to the east the hills rise into the Rimutaka range up to ~800 m high. The

south end of Wainuiomata narrows to a constricted valley which runs 20 km down to the ocean. Wellington City is approximately 15 km to the southwest across the hills and harbour. Figure 2.2 provides an aerial photo of Wainuiomata and its immediate environments (Davy et al., 2009).

Figure 2.2   Aerial view of Wainuiomata and monitoring site (●) (Source: Google Maps 2007).

2.2 APM OVERVIEW, MONITORING PERIOD AND SAMPLING FREQUENCY

The preferred reference method for measurement of arsenic in air, outlined further below, involves chemical analysis of filters collected using the high volume method for gravimetric determination of PM_{10}, following United States Environmental Protection Agency (USEPA) protocols (MfE, 2002). Applied to arsenic, this method assumes that:

a) Almost all arsenic in air is likely to be in particulate (rather than vapour) form, and

b) This arsenic will be present in the PM_{10} fraction (Maggs, 2000). As the fraction retained by the lungs, PM_{10} should also represent the best estimate of inhalation exposure to arsenic in air.

2.3 PM_{10} GRAVIMETRIC SAMPLING

PM_{10} was sampled using a high volume sampler (Lear Siegler, serial no. A107) fitted with a PM_{10} size selective inlet (Graseby Andersen, serial no. 4491). This instrument was operated in accordance with AS/NZS 3580.9.6:2003 *Method 9.6: Determination of suspended particulate matter – PM_{10} high volume sampler with size selective method – gravimetric method.* This standard is based on (USEPA, Title 40 CFR Part 50, Appendix J) – "Reference Method for the Determination of Particulate Matter as PM_{10} in the Atmosphere", which is the monitoring method recommended by the ambient air quality guidelines (MfE, 2002). The instrument was calibrated monthly using a critical orifice calibrator (Lear Siegler, serial no. 026) to ensure flow rate was maintained between 65 and 75 m^3 per hour as required by AS/NZS 3580.9.6:2003 (Mitchell, 2015).

PM_{10} sampling was undertaken by GWRC from the period 22 October, 2011 –29 October 2013 for the period of two years (including 2 winters) using the High- Vol sampler on quartz fibre filters.

Sequentially numbered 8 x 10 inch Whatman grade QM-A quartz filters were conditioned and weighed at constant humidity by GNS Science in accordance with AS/NZS 3580.9.6:2003. The preconditioned (pre-weighed) filters were then kept in zip-locked plastic bags to avoid any moisture and contamination.

The filters were picked and taken to the sampling site as described above and were then exposed for 24-hours (midnight to midnight) on a one-in-three (1:3) day sampling regime which was increased to a one-in-two (1:2) day frequency between May and August. After exposure, filters were re-conditioned and re-weighed and then stored at -18°C to minimise loss of the volatile fraction of particulate matter prior to further analysis (Mitchell, 2015).

As the new filters were put in the sampler, previously sampled filters were again put in the zip-locked plastic bags and brought back to the GNS facility for further treatment.

During the monitoring campaign, 14 field blanks were deployed for quality assurance purposes to ensure that filter handling and transport did not bias results. Field blanks are filters that were subject to the same handling procedures as sample filters except that the high volume sampler was not turned on and the filter was mounted in the sampler and then removed immediately. Likewise, laboratory blanks are filters that were prepared for use but were not removed from the laboratory environment to ensure that laboratory conditions were not biasing results. In total, 10 laboratory blanks, were processed. According to AS/NZS 3580.9.:2003, field and laboratory blanks should be used at a frequency of not less than 1 in 20 (5%), which in this case would equal 14 filters (Mitchell, 2015).

Mass concentrations of PM$_{10}$ analysed were previously determined gravimetrically, where a filter of known weight was used to collect the particulate matter from a known volume of sampled air followed by re-weighing of the filter. The average concentration of particulate matter, PM$_{10}$ in the sampled air was then calculated (Davy, 2009).

PM$_{10}$ concentrations per filter were calculated using Equation 2.1 corrected to standard temperature and pressure (STP), i.e., 273.15 K (0°C) and 101.3 KPa, using barometric pressure (KPa) and temperature (°C) measurements from 2 m above ground level at the GWRC weather station at Wainuiomata Bowling Club. Volumetric flow rate was maintained at 70 m^{3} per hour based on the instrument's flow rate set point (Mitchell, 2015).

$$C_{PM10} = \frac{(m_f - m_i) \times 10^3}{V}$$

(2.1)

Where:

C_{PM10} = concentration of PM_{10} ($\mu g\ m^{-3}$)

m_f = final mass of filter (mg)

m_i = initial mass of filter (mg)

V = volume corrected to STP, calculated as:

$$V = Q \times t \times \frac{273}{T_1} \times \frac{P_1}{101.3}$$

(2.2)

Where:

V = volume of air sampled (m^3) corrected to reference conditions of 0°C and 101.3 KPa

Q = volumetric flow rate ($m^3\ minute^{-1}$)

t = sampling time (minutes)

T_1 = mean ambient temperature over sampling period (K)

P_1 = mean ambient barometric pressure over sampling period (KPa)

Figure 2.3   Wainuiomata sampling site with High Volume and Gent samplers

2.4 THE GENT SAMPLER

Previous and current study also used a GENT sampler that was designed by the University of Ghent, Belgium under contract to the International Atomic Energy Agency (IAEA), Vienna, Austria. The sampler design and performance is described by the designers (Maenhaut & Francois et al. 1993).

The GENT sampler was totally installed and monitored and calibrated by the GNS Sciences as part of their long term monitoring of the air particulate matter in Wainuiomata. This also meets one of the objectives of this project to validate the IBA data as the high volume ampler and the GENT sampler were sampling simultaneously i.e. the two instruments would start and stop at the same time on the sampling days.

The GENT sampler consists of a PM_{10} size selective inlet and stacked filter unit assembly connected to a pump and gas meter by 3/8 inch PVC tubing. The stacked filter unit (SFU) is made up of two filters in series, the top filter collects the particulate size fraction between 10 microns and 2.5 microns in aerodynamic diameter ($PM_{10-2.5}$, designated the '**coarse' fraction**), the bottom filter collects particulate matter 2.5 microns and less in aerodynamic diameter ($PM_{2.5}$, designated the **'fine' fraction**) (Davy et al., 2009).

The performance of the SFU and the size selective inlet has been assessed against other particle monitoring systems (Hopke, Xie et al., 1997). Hopke et al. concluded "the sampler will provide aerodynamically well-defined samples that will serve as a basis for comparative analysis of the airborne particulate mass and composition data from the various sampling locations around the world." Figure 2.4 presents a schematic diagram of the GENT SFU and sampler assembly.

Hopke and co-workers earlier found that the GENT sampler inlet has a slight excess collection around 20 μm when compared to the theoretical PM_{10} sampler efficiency as defined in the USEPA regulations for PM_{10} inlets (US Code of Federal Regulations, 1996), but otherwise provides a reasonable match to the requirements of a PM_{10} sampler. The sampler inlet has not been tested in a wind tunnel therefore cannot be considered a reference PM_{10} inlet under USEPA regulations (Hopke, Xie et al., 1997).

Two size fractions or airborne particles, $PM_{10\text{-}2.5}$ and $PM_{2.5}$ designated the coarse and fine fractions respectively, were collected for analysis by GNS Sciences. A total of 247 filters of $PM_{2.5}$ and $PM_{10\text{-}2.5}$ samples using a GENT sampler were collected from 9 December, 2011 – 31 October, 2013, for the current study. However, the monitoring of the air particulate matter using the GENT sampler still continues for a long term APM database by GNS Sciences.
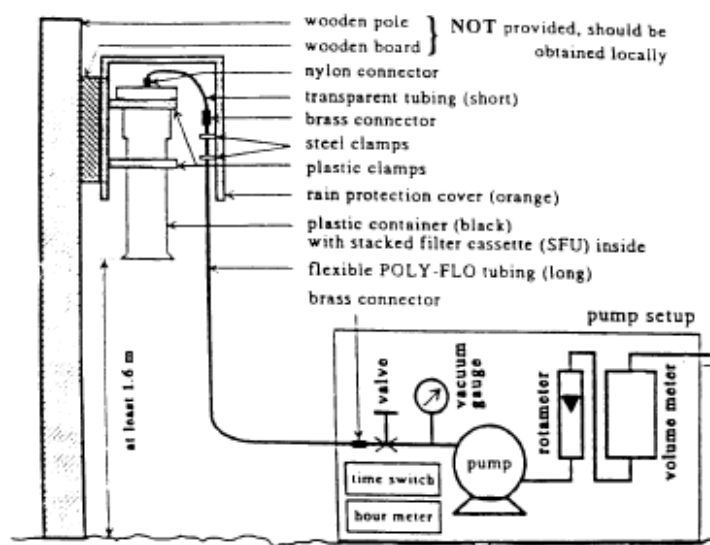
Figure 2.4   Schematic of GENT sampler system (source: GENT Operation Manual)

2.5 CONCEPTUAL RECEPTOR MODEL FOR PARTICULATE MATTER AT WAINUIOMATA

An important part of the receptor modelling process is to formulate a conceptual model of the receptor site. This means understanding and identifying the major sources that may influence ambient particulate matter concentrations at the site. For the Wainuiomata site the initial conceptual model includes local emission sources:

➢ Motor vehicles – all roads in the area act as line sources and roads with higher density traffic will dominate;

➢ Domestic activities – likely to be dominated by biomass burning such as emissions from solid fuel fires used for domestic heating during the winter;

➢ Local wind-blown soil or road dust sources as there are many unpaved vehicle access ways and yards in the locality.

Sources that originate from longer distances may also contribute to ambient particle loadings and these include:

➢ Marine aerosol;

➢ Secondary particulate matter resulting from atmospheric gas-to-particle conversion processes (sulphate and nitrate species, organic particle species);

➢ Potential for long range transport of industrial emissions.

Another category of emission sources that may contribute are those considered as 'one-off' emission sources:

➢ Fireworks displays and other special events (e.g. Guy Fawkes day);

➢ Short-term road works and demolition/construction activities.

The variety of sources described above can be recognised and accounted for by appropriate data analysis methods, such as examination of seasonal differences, temporal variations and receptor modelling itself (Davy et al., 2009).

2.6 LOCAL METEOROLOGY AT THE WAINUIOMATA SITE

A meteorological station is located at the monitoring site and is owned and operated by GWRC. One-hour meteorological measurements were obtained from the 10 m meteorological mast from the Wainuiomata air quality monitoring station.

Wind roses for the monitoring period by season show the year-round dominance of winds from the northerly quarter and the lower wind speeds during autumn and winter (Figure 2.5). The relative lack of westerly and easterly winds is a consequence of the valley topography being orientated north to south. The distribution of 1-hour temperature averages and minima for each month shows the expected seasonal effects, i.e., lower temperatures and wind speeds during the winter months compared to the rest of the year (Figure 2.6). Note that June and August in 2013 were warmer and windier than the corresponding months in 2012 as shown in Figure 2.5.
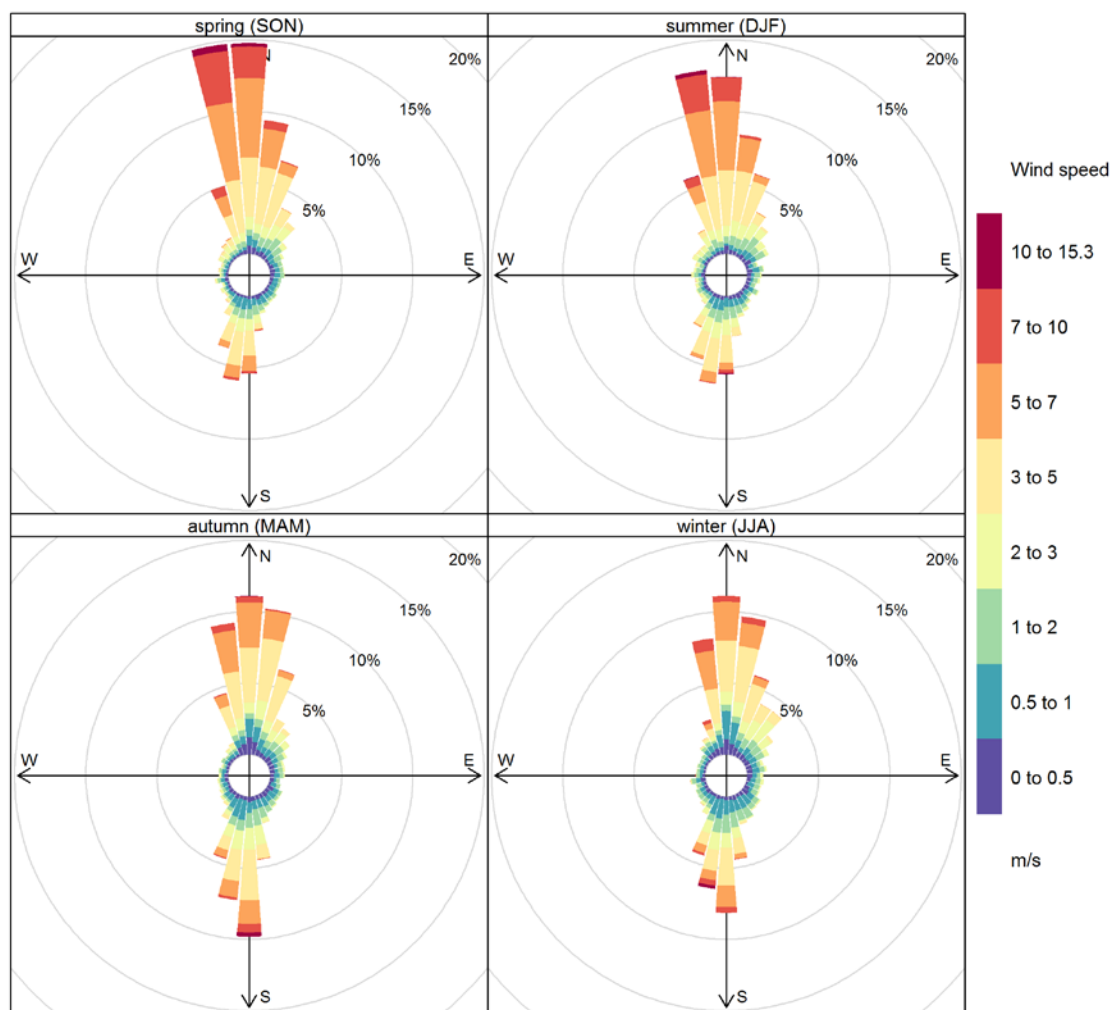
Figure 2.5   Wind roses showing frequencies of hours by wind direction for the monitoring period by season
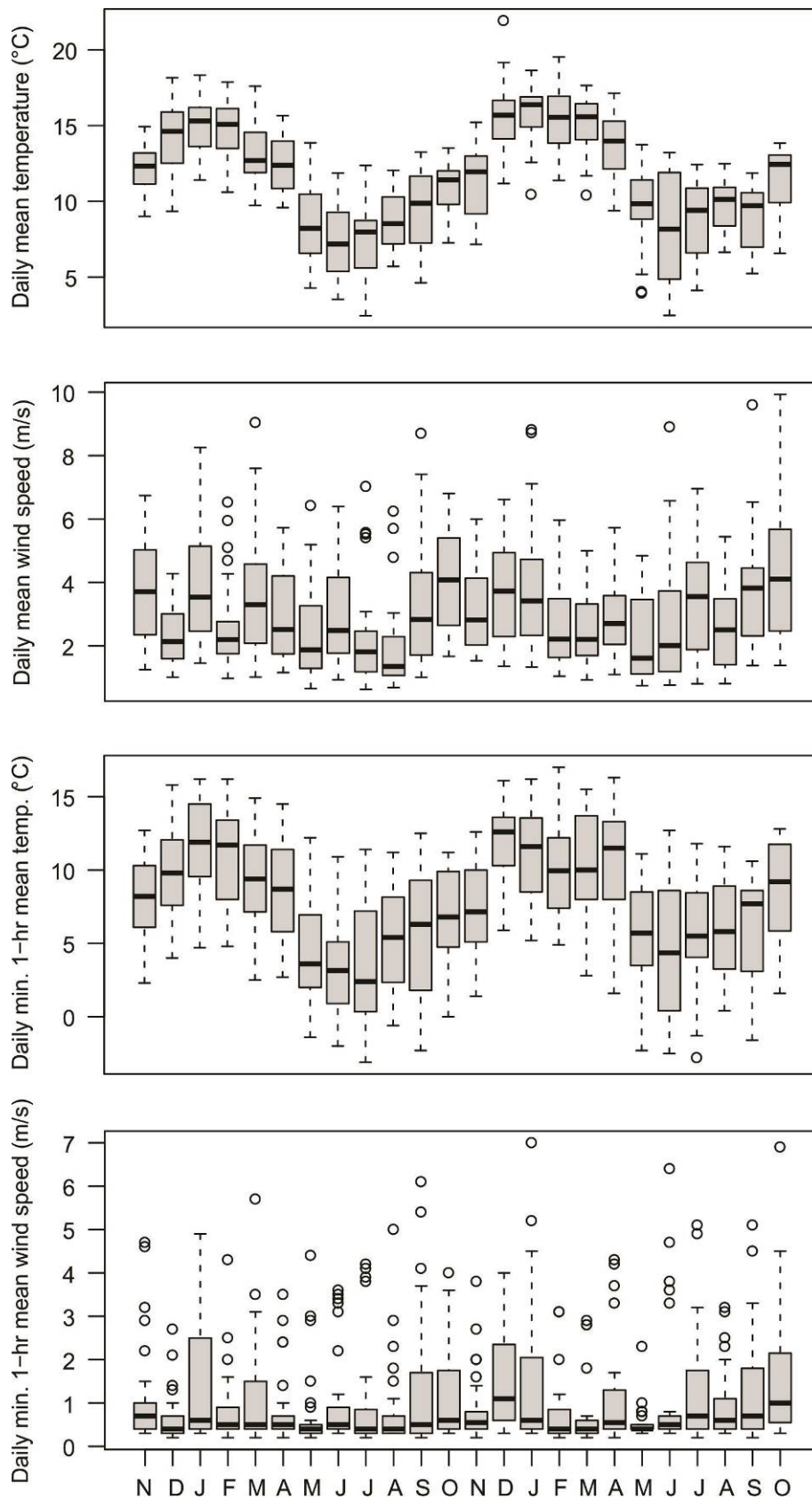
Figure 2.6   Box plots of temperature and wind speed variables by month (Source: GWRC: Mitchell, 2015)

2.7 BLACK CARBON MEASUREMENTS

Black carbon (BC) has been studied extensively but it is still not clear to what degree it is elemental carbon (EC (or graphitic) C (0)) or high molecular weight refractory weight organic species or a combination of both (Jacobson & Hansson, 2000). Current literature suggests that BC is likely a combination of both, and that for combustion sources such as petrol and diesel fuelled vehicles and biomass combustion (wood burning, coal burning), EC and organic carbon compounds (OC) are the principal aerosol components emitted (Jacobson & Hansson, 2000; Fine & Cass, 2001; Watson & Zhu, 2002; Salma & Chi, 2004).

Determination of carbon (soot) on filters was performed by light reflection to provide the BC concentration. The absorption and reflection of visible light on particles in the atmosphere or collected on filters is dependent on the particle concentration, density, refractive index and size. For atmospheric particles, BC is the most highly absorbing component in the visible light spectrum with very much smaller components coming from soils, sulphates and nitrate (Horvath 1993; Horvath 1997). Hence, to the first order it can be assumed that all the absorption on atmospheric filters is due to BC. The main sources of atmospheric BC are anthropogenic combustion sources and include biomass burning, motor vehicles and industrial emissions (Cohen & Taha, 2000). Cohen and co-workers found that BC is typically 10 – 40% of the fine mass ($PM_{2.5}$) fraction in many urban areas of Australia.

When measuring BC by light reflection/transmission, light from a light source is transmitted through a filter onto a photocell. The amount of light absorption is proportional to the amount of black carbon present and provides a value that is a measure of the black carbon on the filter. Conversion of the absorbance value to an atmospheric concentration value of BC requires the use of an empirically derived equation (Cohen & Taha, 2000):

$$BC\ (\mu g\ cm^{-2}) = (100/2(F\epsilon))\ ln[R_0/R] \qquad\qquad (2.3)$$

Where: ϵ is the mass absorbent coefficient for BC ($m^2\ g^{-1}$) at a given wavelength;

        F   is a correction factor to account for other absorbing factors such as sulphates, nitrates, shadowing and filter loading. These effects are generally assumed to be negligible and F is set at 1.00;

      R_0, R   is the pre- and post- reflection intensity measurements respectively.

Black carbon was measured at GNS using the M43D Digital Smoke Stain Reflectometer. The following equation (from Willy Maenhaut, Institute for Nuclear Sciences, University of Gent Proeftuinstraat 86, B-9000 GENT, Belgium), is used for obtaining BC from reflectance measurements on nucleopore polycarbonate filters or Pall Life Sciences Teflon filters:

$$BC\ (\mu g\ cm^{-2}) = [1000 \times LOG\ (R_{blank}/R_{sample}) + 2.39]\ /\ 45.8 \qquad (2.4)$$

Where:

R_{blank}: the average reflectance for a series of blank filters; R_{blank} is close (but not identical) to 100; (GNS Science always used the same blank filter for adjusting to 100).

R_{sample}: the reflectance for a filter sample (normally lower than 100).

With: 2.39 and 45.8 constants derived using a series of 100 nucleopore polycarbonate filter samples which served as secondary standards, relative to standards, which was prepared by collecting burning acetylene soot on filters and determining the mass concentration gravimetrically (the BC loading (in $\mu g\ cm^{-2}$) for these samples had been determined by Prof. Dr. M.O. Andreae (Max Planck Institute of Chemistry, Mainz, Germany), (Trompetter, 2004).

2.8 METHOD DEVELOPMENT FOR ARSENIC ANALYSIS BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY (GF-AAS)

2.8.1 SCOPE AND APPLICATION

This method is applicable to the determination of arsenic in PM_{10} collected from ambient air by means of a Hi-Vol sampler, on quartz fiber filters.

The detection limit is dependent on the volume of air used in the collection of the particulates and the sensitivity of the instrument used for the determination. The concentration of an element due to the filter (filter lab blank) must be determined for each lot of filters. If this is higher than the normal detection limit the higher value must be used.

This method assumed that PM_{10} has been measured in the same survey. Filters were pre-weighed by GNS Science, and one field blank filter was taken after every 10 - 15 filters were

sampled. Total of 14 field blanks had been deployed as mentioned earlier. A total of 10 lab blank filters were also provided with the survey as described earlier. The winter sampling dates were from 04/05/2012 -31/08/2012 for the first year and 02/05/2012 – 30/08/2012 for the second year. All the rest would be called non-winter sampling period.

It is assumed that the distribution of the analyte (particulate matter) on the filter is expected to be uniform, so one of the four 47 mm punches is to be analyzed from each filter for arsenic. Simultaneously one punch was analyzed by Hill Laboratories as part of GWRC's independent enquiry, while another was analyzed by GNS Sciences using XRF instrument. The GF-AAS methodology would then be used to validate the XRF and IBA data.

2.8.2   SAFETY AND WASTE HANDLING

Arsenic compounds are toxic and should be handled with care. All unused solutions were disposed of as per the Victoria University of Wellington (VUW) safety disposal requirements.

Nitric acid is a strong oxidizer so skin contact was avoided by wearing gloves. All waste nitric acid solutions were disposed in waste acid gallons provided by GNS Sciences. Nitric acid fumes can be toxic, and are a strong irritant to eyes and nasal membranes even in small doses. All operations with nitric acid were performed in a fume hood at GNS Science Laboratory facilities.

2.8.3   SUMMARY OF METHOD

Particulate matter less than 10 micrometers in effective aerodynamic cross-section (PM_{10}), suspended in ambient air were collected for 24 hours on a quartz filter using a size-selective high volume air sampler on a one-in-three day basis and one-in-two day basis during winter. After the filter was weighed for PM_{10} determination, a portion (47 mm punches) of the filter was extracted with nitric acid, and the extract was analyzed by graphite furnace atomic absorption spectrophotometry (GF-AAS), using the EPA 200.9 method and the Thermo-Fisher SOLAAR software program.

The concentration of arsenic in the air sample is calculated from the concentration determined in the extract, the fraction of the filter taken, and the volume of air passed through the Hi-Vol sampler.

2.8.4 SAMPLE HANDLING

Quartz filters to be analyzed for metals were first weighed for PM_{10} using analytical balance under standard conditions at GNS Science facility.

Filters and 47 mm punches were always handled with forceps to avoid contamination. Absolute care was taken to prevent loss of particulate matter from the filter. The filters were kept in plastic bags after weighing and the 47 mm punches were kept in petri dishes. All filters were refrigerated and kept at temperature of -18 °C as described earlier to avoid loss of any analyte.

2.8.5 INTERFERENCES

Chemical interferences are not known to be a problem with the extraction, although arsenic species can be volatile.

Spectral interferences due to line overlap are well known and characterized. Aluminium **(Al)** interferes with arsenic (**As)** at 193.7 nm (Castro & Aller, 2003), (Flajnik & Delles, 2010). Zeeman background correction is recommended for all arsenic analyses using graphite furnace atomic absorption. However, the instrument at Victoria University (VUW) does not have the Zeeman hardware provisions; hence the background correction was done with deuterium component as per the SOLAAR program. Deuterium has shown to eliminate aluminium interference with Al concentration below 20 mg L^{-1} (Flajnik & Delles, 2010).

2.8.5.1 Matrix Matched Standards

Aqueous standards and simple calculation procedures are used when matrix components in the sample do not interfere with the analytical signal. However, in many cases interference does exist. In order to overcome interference, matrix matched standards are used to

calibrate the analyses. Nickel nitrate modifier was used throughout the arsenic graphite furnace analyses.

2.8.6   INSTRUMENTATION

Model: Thermo Fisher Scientific (iCE 3000 series) - Atomic Absorption Spectrophotometer with Graphite Furnace **(**Graphite Sample Tubes and Contact Rings)

Automatic Sampler with sample cups

SOLAAR software program: - (installed on the PC provided).

Lamps and lamp accessories - Arsenic Hollow-Cathode Lamp (HCL)

Glassware and Accessories

Pipettes (1 ml, 5 ml, 10 ml, 20 ml, 50 ml)

100 mL and 50 ml ± 0.06 ml volumetric flasks Class A, GLASSCO brand.

Beakers (50 ml, 100 ml, 250 ml, 500 ml)

Volumetric Flasks (50 ml, 100 ml, 250 ml, 1 L and 2 L (for 10% HNO_3))

Volumetric flasks for graphite furnace atomic absorption were kept separate from flasks used elsewhere in the laboratory. These flasks are not washed with the rest of the glassware, but rather are rinsed thoroughly with both tap and RO water (ultra-pure) and stored with approximately 5% HNO_3 until ready for use. The acid should touch the bottom of the cap, and the flask should so stand for at least 2 or 3 days before reuse. The acid is discarded as per GNS regulations and the flask again rinsed with tap and RO water before use. All the digestion vessels used were also treated the same way as the volumetric flasks. The RO water was provided at GNS Science facility.

Pressure Cooker Digestion Apparatus

Savillex pressure digestion vessels- (50ml)-(Green circled)

Nine place circular Teflon sample holder for the digestion vessels

Electric pressure cooker.
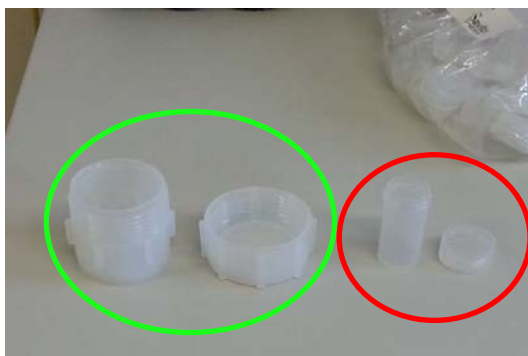
Figure 2.7   Savillex Digestion vessels

General apparatus/ Equipments

Centrifuge tubes, about 28 mm x 114 mm, *sarstedt*

Style (polyethylene screw caps), 50 ml size - 350

47 mm stainless steel punches for filter cuttings.

50ml graduated, conical bottom with support skirt sample tubes- 400 pieces

Forceps and protective disposable gloves for handling the filters and pieces

Disposable particle mask to be worn while cutting filters

Quartz filters treated as specified.

Centrifuge

2.8.7   REAGENTS

RO Water: The laboratory at GNS Science has water is passed through an ultrapure mixed-bed resin, which is collected in 20L containers provided.

Nitric Acid: Analytical grade which was diluted to 10% (Vol), for digestions.

Atomic Absorption Arsenic Standard: 999 ± 2 mg AsL^{-1}. This is the certified reference material (CRM)

2.8.7.1 Matrix Modifiers

Nickel Nitrate: Dissolved 24.77 g of Ni (NO$_3$)$_2$.6 H$_2$0 in water and dilute to l00 mL (approx. 5% Ni solution)

Hydrogen Peroxide: Commercial 30% hydrogen peroxide (H$_2$O$_2$) was used as received. It was kept refrigerated.

2.8.7.2 Stock Standard

Pipetted 1 mL aliquot of the 999 ± 2 mg L^{-1} As solution in a 100 mL volumetric flask, to which had been added 2 mL concentrated nitric acid and about 50 mL of RO water. It was then diluted to volume with RO water.

2.8.7.3 Working Standards: 100 µg L^{-1} Arsenic Standard

100 mL volumetric flask was filled about halfway with water. 1mL of concentrated nitric acid was added to the flask, and washed down the inside of the neck with RO water. 1 ml aliquot of the stock arsenic standard was then added to the volumetric flask and then made up to the mark.

2.8.8   INSTRUMENT CALIBRATION

The calibration of the Thermo-Fisher Scientific Graphite Furnace Atomic Absorption Spectrophotometer (GF-AAS) was done as per the Instrument Operating Manual, available at the VUW (Thermo-Fisher Scientific Corporation, 2008), Instrument Laboratory. The instrument was calibrated by trained technicians at the university

2.8.9   ANALYTICAL PROCEDURE

2.8.9.1 Sample preparation/ Digestion

1. A 47 mm filter was punched from the exposed filter using the 47 mm punch. Four punches were taken from the exposed area for different analysis.
2. The punched filter was folded in half twice and placed at the bottom of the digestion vessel.
3. 20 mL of 10% (Vol), nitric acid was added to the digestion vessel to completely cover the filter paper.
4. The digestion vessel was then tightly screwed using the tool provided and placed in the circular holder (this was done to make it air tight and to ensure that there is no loss of analyte). The circular holder was then placed in the pressure cooker half filled with water to completely immerse the digestion vessels and heated under pressure for 10 minutes as programmed on the pressure cooker. (10 minute digestion gave optimum results when blank filters were spiked with known concentrations of arsenic solution and boiled in pressure cooker for 5, 10 and 20 minutes respectively).

5. A total of nine vessels containing filter and acid solution were digested each time. The digestion vessels were cooled for 30 minutes before opening. The digested contents were then added to a 50ml centrifuge tube and rinsed with 10ml of RO water to get a volume of 30ml. The cap was tightened and shaken well.

6. The digested filter was centrifuged for 10 minutes. The supernatant liquid was poured into a 50 mL volumetric flask. The remaining filter was rinsed carefully into the volumetric flask with the help of a funnel and then made up to the mark.

7. The solution was poured into a labeled sampled storage bottle and tightly capped. The samples were put in racks in batches of 20 and kept in fridge before analyses.

8. For each batch of 20 filters, the following quality control samples were prepared: 1 reagent blank; 1 filter blank; 1 duplicate filter and one duplicate spiked filter (USEPA - Compendium of Methods- IO-3.1, 1999).

2.8.9.2 Sample analysis

1. Each solution was analyzed for arsenic, using the procedures described in EPA method 200.9; **"Determination of trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption"** (USEPA, 1994) and USEPA - Compendium Method IO-3.2, 1999).
   a. The instrument quality control protocols used were as stipulated in USEPA methods described above.
2. The background, theory and principles of Atomic Absorption Spectrometry are well documented in the GFAAS methods manual (Appendix 1, A3.0). Further instructions on the operation of the Thermo-Fisher GF-AAS were also contained in the Operating Manual and the Manufacturer's Manuals (Thermo-Fisher Scientific Corporation, 2008).

2.8.10 SET UP AND OPTIMIZATION

2.8.10.1 Spectrometer

The default spectrometer parameters provided by the SOLAAR Series Software Manual, 2011, for Graphite Furnace arsenic measurements were used, except that the Transient Area signal measurement was selected, as recommended in the method. Each measurement was performed in duplicate, and so the number of resamples parameter was set to 3. The final set of spectrometer parameters were as shown in Figure 2.8.
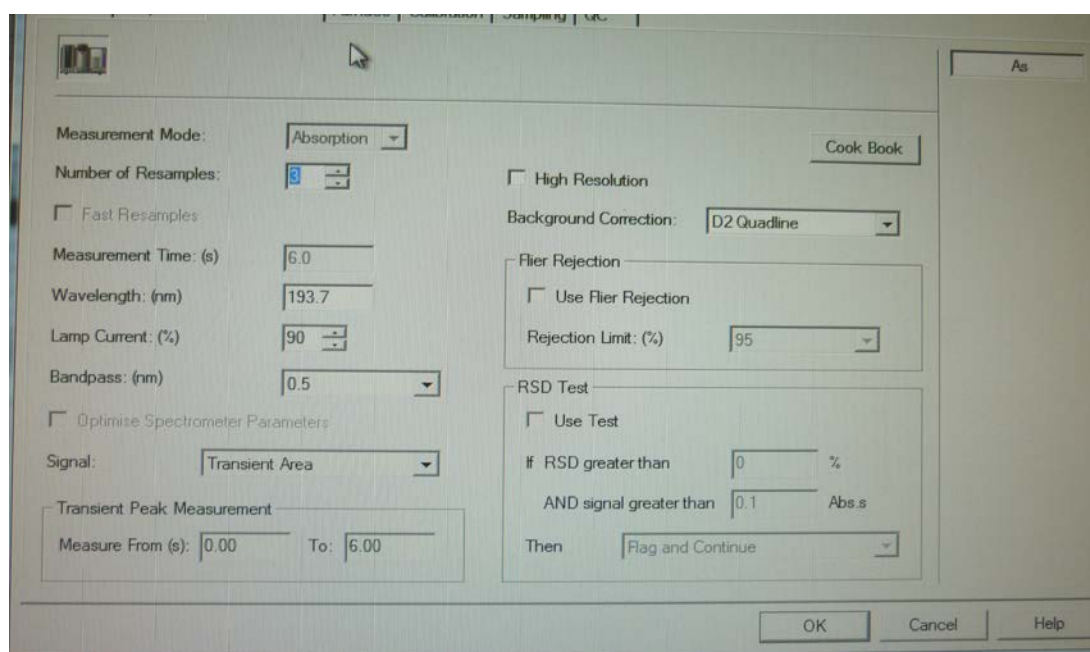
Figure 2.8   Spectrometer parameters

2.8.10.2 Graphite Furnace Auto Sampler

❖ *Injection*

The height of the Furnace Auto Sampler capillary tip in the cuvette was adjusted while observing the injection using the Graphite Furnace Television (GFTV) accessory fitted to the spectrometer, as described in reference manual. The final capillary tip position and resulting sample injection were shown in Figure 2.9.
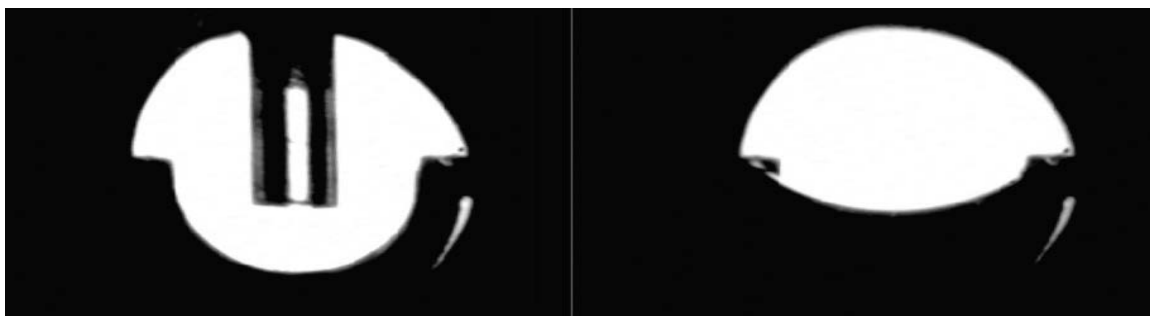
Figure 2.9:   Optimized Capillary Tip position and Sample Injection

❖ *Sampling*

The Furnace Auto-Sampler sampling parameters were set up as described in Summary.

Although the Furnace Auto-sampler automatically included a wash cycle after every injection, it had an additional facility that would cause a second wash cycle to be performed if the previous signal exceeded a specified value. This was found to be useful to improve the on-going Calibration Blank (QC) measurements as described below. A trigger value of 0.3 absorbance, was used, equivalent to a concentration of approximately, 60 µg L^{-1}. The final set of sampling parameters that were used is shown in Figure 2.10.

Figure 2.10   Sampling parameters

The master arsenic standard was 50 µg L^{-1}, and the auto sampler diluted the standards as per the set up in the SOLAAR Program. The diluted standards were 10, 20, 30, and 40 µg L^{-1}, respectively. The range of the arsenic standards were 0 - 50 µg L^{-1}.

2.8.10.3 Graphite Furnace Program

- *Dry phase*

    Optimization of the dry phase of the Furnace Program using the GFTV image was set up as described in reference manual.

- *Ash and Atomize phases*

    The method recommends ash (Char) and atomisation temperatures of 1300 °C and 2200 °C respectively for arsenic, but also suggests that these should be optimized for individual instruments. The automatic "Ash Atomize Function" provided in the SOLAAR software was therefore used to optimize these parameters.

The final set of Graphite Furnace parameters used as shown in Figure 2.11.
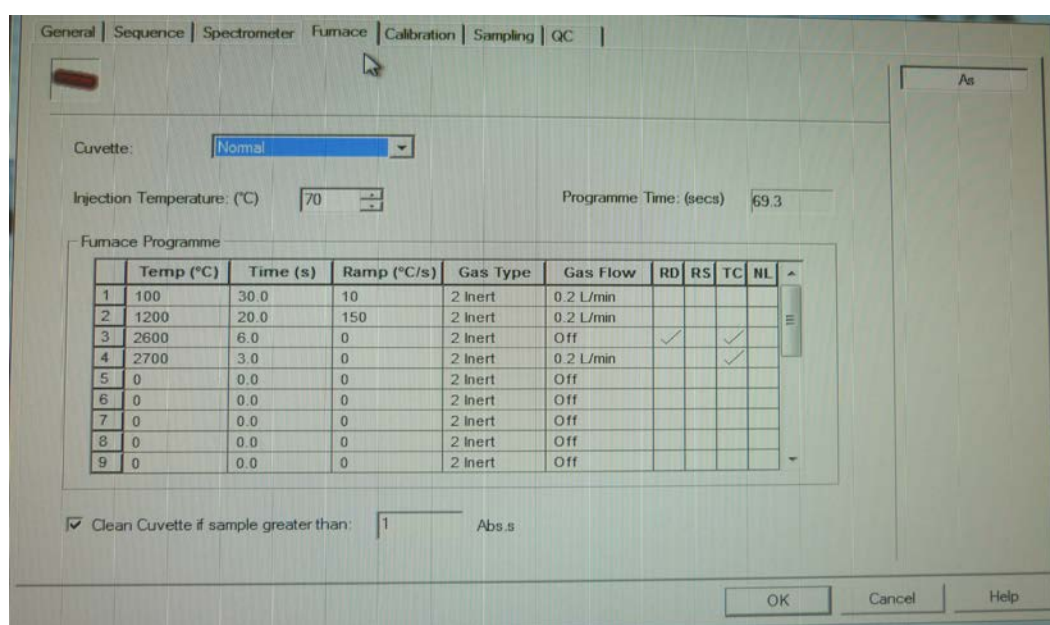
Figure: 2.11   Optimized Furnace Program

2.8.11 INSTRUMENT PARAMETERS AND METHOD SUMMARY

➢ **REAGENT DETAILS**

Matrix Modifier 1   Ni- 5 g L^{-1}

Matrix Modifier 2 H_2O_2 -30% (Vol)

➢ **SPECTROMETER PARAMETERS**

Element: As

Measurement Mode: Absorbance

Wavelength: 193.7 nm

Bandpass: 0.5nm

Lamp Current: 90%

➢ **BACKGROUND CORRECTION:**   Deuterium (D2)

High Resolution: Off

Optimise Spectrometer Parameters: No

Signal Type: Transient

Transient Type: Area

Number of Resamples: 3 (triplicates)

Measurement Time: 6.0 sec

Flier Mode: No

Measure Peak From: 0.00   To: 6.00 sec

Use RSD Test: No

➢ **FURNACE PARAMETERS**

Cuvette Type: Normal

Injection Temperature: 70°C

Clean Cuvette if sample greater than: 1.000

Furnace Programme (sec):   69.3

Table 2. 1:   Furnace Ashing parameters

Phase	Temp (°C)	Time (sec)	Ramp (°C/sec)	Gas Type	Gas Flow	Commands
1	100	30	10	2	0.2L min^{-1}	
2	1200	20	150	2	0.2L min^{-1}	
3	2600	6	0	2	Off	RD TC
4	2700	3	0	2	0.2L min^{-1}	TC

➢ **SAMPLING PARAMETERS**

Sampling: Furnace

Automatic Spike Prep: No

Working Volume: 20.0 µL

Sample Volume: 20.0 µL

Table 2.2:   Sampling parameters

Modifier	Method	Volume	Order
1 Ni 5 g L^{-1}	Wet-mixed	4	1
2 H$_2$O$_2$ (30%)	Wet-mixed	1	2
3	None	20	3
4	None	20	4
5	None	20	5
6	None	20	6

➢ **Sample Preparation:** None

Standard Preparation: Fixed

Standard Additions: None

Slow Solution Uptake: No

Slow Injection: No

Sampling Delay: No

Number of Washes: 1

Wash Auto sampler if sample greater than: 0.100

> **CALIBRATION PARAMETERS**

Calibration Mode: Normal

Line Fit: Linear

Use Stored Calibration: No

Concentration Units: $\mu g\ L^{-1}$

Scaled Units: $\mu g\ L^{-1}$

Scaling Factor: 1.0000

Acceptable Fit: 0.995

Rescale Limit: %   10.0

Failure Action: Flag and Continue

Standards: As per table 2.3

Table 2.3   Calibration Standards

Master Standard	50ug/L
Standard 1	10ug/L
Standard 2	20ug/L
Standard 3	30ug/L
Standard 4	40ug/L
Standard 5	50ug/L

> **Instrument Detection Limit**

The method requires that the Method Detection Limit (MDL) must be established for all analytes, and the procedure for doing this is described in detail in EPA method 200.9. The "Check Instrument Performance Wizard" provided in the SOLAAR software can be first used to estimate the Instrumental Detection Limit (IDL).

Previous sample results of three separate runs of the wizard, performed at various times throughout the investigation were as shown in Table 2.4. (USEPA –Methods 200.9)

Table 2.4   IDL Results

Run	Characteristic Concentration (μg L^{-1})	IDL (μg L^{-1})	Drift factor	Warnings
1	0.7	1.5	0.1	None
2	0.6	1.4	0.6	None
3	0.7	1.2	0.2	None
Mean	0.67	1.4		

- The drift factor estimates the contribution that any time dependent variations of the results make to the calculated detection limit - values less than 1 indicate that time dependent variations are not significant. The wizard did not generate any warnings, indicating that its internal statistical tests were satisfied. The IDL for arsenic measured under the conditions described has therefore been shown to be **1.4 μg L^{-1}.**

- The procedure for estimating the MDL requires that the laboratory blank (1% nitric acid) should be fortified with the analyte at a level of 2-3 times the estimated IDL. For initial estimates of the MDL, the laboratory blank was therefore fortified with 2.5 μg L^{-1} of arsenic. The method requires that the relative standard deviation of the seven replicate results used to calculate the MDL should be greater than 10%, to confirm that the analyte concentration in the fortified blank is not inappropriately high. Thermo-Fisher, 2010, calculated the method detection limit as part of arsenic determination on natural waters by GF-AAS using EPA Method 200.9. The mean MDL value of all estimates was **0.6 μg L^{-1}** with a relative standard deviation of MDL to be 12%. The results obtained confirmed that the Thermo Scientific GF-AAS instrument met or exceeded the requirements set out for the initial demonstration of performance in the EPA 200.9 Method for the determination of arsenic.

The detection limits for As determination by different methods range between:

- 1 μg L^{-1} L to 1000 μg L^{-1} for FAAS,

- 0.05 **μg L^{-1}**to 100 **μg L^{-1}** for ICP-OES Emission – radial,

- 0.1 **μg L^{-1}**to 10 **μg L^{-1}**for ICP-OES Emission-axial,

- 0.005 **μg L^{-1}** to 0.1 **μg L^{-1}**for AAS-HG,

- 0.01 **μg L^{-1}**to 0.1 **μg L^{-1}**for GF-AAS and

- 0.001 **μg L^{-1}**to 0.01 **μg L^{-1}**for ICP-MS.

Atomic Absorption Spectrometry is a superior technique in comparison to other techniques like XRF and ICP-OES (Singh et al., 2010)

2.8.12 CALCULATIONS

The calculations to calculate the concentrations of arsenic in the extracts were performed off-line with a PC (Windows 2010/13 - Excel program). All calculations were performed as in the method referenced above (USEPA CRL Method 206.2 DNS, 1987). The blank filter correction was made with each batch of extraction. The As concentrations obtained from GF-AAS were relative to the blank and the standards of each batch of analyses.

The concentration of arsenic in the ambient air was calculated as follows:

$$C_{As} = \frac{C_s \times 1000}{V \times p}$$

(2.5)

Where:

C_{As} = arsenic concentration in air (ng.m^{-3}) at STP
C_s = arsenic concentration in test solution (μg/sample)
V = volume of air sampled (m^3) corrected to reference conditions of 0°C and 101.3 KPa
p = proportion of filter used (unit less), calculated as:

$$p = \frac{Area\ filter\ punch}{Total\ area\ exposed\ filter}$$

(2.6)

Where:

Filter punch = 17.33 cm^2
Exposed filter = 419 cm^2

The instrument detection limit (IDL) for GF-AAS analysis of arsenic is 1.4 µg L^{-1}, or 0.07 µg sample^{-1}. Therefore the LOD for arsenic in ambient air (ng m^{-3}) may differ slightly for each exposed filter depending on the volume of air sampled in that 24-hour period. The mean volume of air was calibrated to 69.7 m^3. In this case the IDL for arsenic concentrations will be 1.0 ng m^{-3}.

Results at or near the detection limit were reported with one significant figure. Higher results were reported with two significant figures. For the purpose of this research, the values obtained below the detection limit will be treated as actual values when calculating the annual arsenic averages, but would be reported as <LOD for analytical reporting.

2.8.13 QUALITY CONTROL

The instrument quality control consists of a blank and a quality assurance check sample. The instrument quality control is run as specified in the referenced method (USEPA, CRL Method 206.2 DNS, 1987).

Extraction quality control includes reagent blanks, filter blanks, and duplicate filter punches. These audits were included at a frequency of one set for each 20 samples or fraction thereof. Corrective action for failure of any of these audits was re-preparation of the extracts and re-analysis. If triplicate extractions have been performed it should be certain that sufficient filter remains for all other analysis before attempting re-preparation.

A reagent blank was the extraction conducted only with the reagents but without a filter punch. Any contamination from the extraction process should be seen in this audit. The acceptable variation was the detection limit.

Filter blank (lab blank) is a filter punch from an unexposed filter of the same lot as the exposed filters. This was in addition to the blanks which were checked in the original determination before the lot was weighed and exposed. This audit shall not exceed the average plus two standard deviation of the previous lot analysis.

A duplicate filter punch was extracted for each group of 20 or less samples. If variation in the coating of the filter was suspected and triplicate samples were taken hence no duplicates were run. The limit for the duplicate pair is the detection limit as a difference, or 10% relative percent difference. Relative percent difference calculation was performed as shown by the Equation 2.7:

|(Duplicate Filter – Original Filter)| / [(Duplicate Filter+ Original Filter)/2] x 100%

$$(2.7)$$

Analysis of a sample from the National Bureau of Standards or a reference standard from RTP should be run when the method is verified. However all efforts to obtain standard reference material proved futile as the SRM was not present on a quartz filter membrane for arsenic in ambient air.

For each batch of 20 samples, the duplicate filter was also spiked with known concentrations of arsenic standards and the % recoveries were calculated.

The final quality control procedure was performed by spiking a lab blank filter with CRM arsenic concentrations: 2, 4, 6, 8, and 10 μg L^{-1} respectively and % recoveries were calculated. This would validate the entire digestion and GF-AAS analysis methodology by eliminating the biasness.

According to EURACHEM/CITAC Guide CG4, 2000, the bias of an analytical method is usually determined by study of relevant reference materials or by spiking studies. The determination of overall bias with respect to appropriate reference values is important in establishing traceability to recognized standards. Bias may be expressed as analytical recovery (value observed/ value expected). The bias should be shown to be negligible for method validation process.

Furthermore, EURACHEM/CITAC Guide CG4, 2000, Method Validation studies rely on the determination of overall method performance parameters. These were to be obtained

during method development and inter-laboratory study or following in-house validation protocols. These are:

- ➢ Precision of an analytical procedure which is an essential component of overall uncertainty determined by combination or individual variances in the method in operation (Inter Laboratory/ Intra laboratory variances).

- ➢ Bias of an analytical method determined by study of reference materials or spike recoveries.

- ➢ Linearity is an important property of methods used to make measurements by a range of concentrations.

- ➢ Detection Limit is only determined to establish the lower end of the practical operating range of a method during method validation.

- ➢ Robustness/Ruggedness is an investigation to the sensitivity of particular parameters.

- ➢ Selectivity/Specificity relates to the degree to which a method responds uniquely to the required analyte or the effects of likely interferents.

2.8.14 INSTRUMENT MAINTENANCE

The Instrument Operating Manual showed the detailed specifications for instrument maintenance (Thermo-Fisher Scientific Corporation, 2008), and which had to be performed only by trained technicians

3.0 RESULTS AND DATA ANALYSIS

3.1 PM$_{10}$, PM$_{2.5}$ AND BLACK CARBON (BC) DATA ANALYSIS AND REPORTING

The receptor modelling have been used previously to report on the relative contributions of sources to particulate matter concentrations so that it may be used for monitoring strategies, air quality management and policy development (Davy et al., 2009). For the purpose of this study, the source apportionment was not carried out as it has been extensively reported in previous studies (Davy et al., 2009; Davy et al., 2012). The data have been analysed to provide the following outputs:

- mass concentrations of PM$_{10}$, PM$_{2.5}$ and BC

- temporal variation of PM$_{10}$, PM$_{2.5}$ and BC (time-series plots);

- Seasonal variations in PM$_{10}$, PM$_{2.5}$ and BC. For the purposes of this study, only winter (May – August) and non-winter (November – April and September – October) variations were considered. As mentioned earlier, the monitoring was from 25 October, 2011 – 30 October, 2013, hence the calendar months starting January was not followed. However the sampling period covered two winters and 24 months in total.

- The peak PM values would be related to sources identified in previous studies.

- The effect of wind direction as per wind rose frequency plots produced by GWRC from the meteorological station co-located at the sampling site.

Shown below are the relevant standards, guidelines and targets for APM pollution.

Table 3.1   Standards, guidelines and targets for APM pollution

Particle size	Averaging Time	Ambient Air Quality Guideline	MfE 'Acceptable' air quality category	National Environmental Standard	NES (Allowable Exceedances per annum)
PM$_{10}$	24 Hour	50 µg m^{-3}	33 µg m^{-3}	50 µg m^{-3}	1
PM$_{10}$	Annual	20 µg m^{-3}	13 µg m^{-3}		
PM$_{2.5}$	24 Hour	25 µg m^{-3}	17 µg m^{-3}		
PM$_{2.5}$	Annual	10 µg m^{-3}			

(Source: Ministry for the Environment air quality categories (MfE), 1997)

3.2 CALCULATION FOR THE METHOD DETECTION LIMIT (MDL)

The two terms that widely appears in literature as figures of merit for instruments and instrumental methods are sensitivity and detection limit. The simplest quantitative definition of sensitivity and one which is accepted by International Union of Pure and Applied Chemists (IUPAC) is calibration sensitivity, *m*, which is the slope of the calibration curve at concentration of interests. For linear calibration curves, *m* is independent of the concentration and can be derived from the relationship:

$$S = mC + S_{bl} \qquad\qquad (3.1)$$

Where:

S and **S_{bl}** are the instrument signals for the analyte and the blank respectively.

And the analytical sensitivity, Y, is defined as:

$$Y = m/s_s \qquad\qquad (3.2)$$

Where:

m is the slope and **s_s**, is the standard deviation of the signals.

The detection limit is the minimum concentration or weight of an analyte that can be detected at known confidence level. As the LOD is approached, the analytical signal and its standard deviation approach the blank signal, **S_{bl}**, and its standard deviation **s_{bl}**. The minimum analyte signal, **S_m** is taken as a multiple, ƙ, of the standard deviation of the blank, and is given by the equation:

$$S_m = S_{bl} + ƙs_{bl} \qquad\qquad (3.3)$$

Finally the equation 3.1 can be used to convert **S_m** to **C_m** which is defined as the detection limit, and is given by:

$$C_m = (S_m - S_{bl})/m \qquad\qquad (3.4)$$

(Skoog, 1985).

The average values of all the 8 batch analysis of the blanks and the standards with GF-AAS was taken and plotted as a graph shown in Figure 3.1.
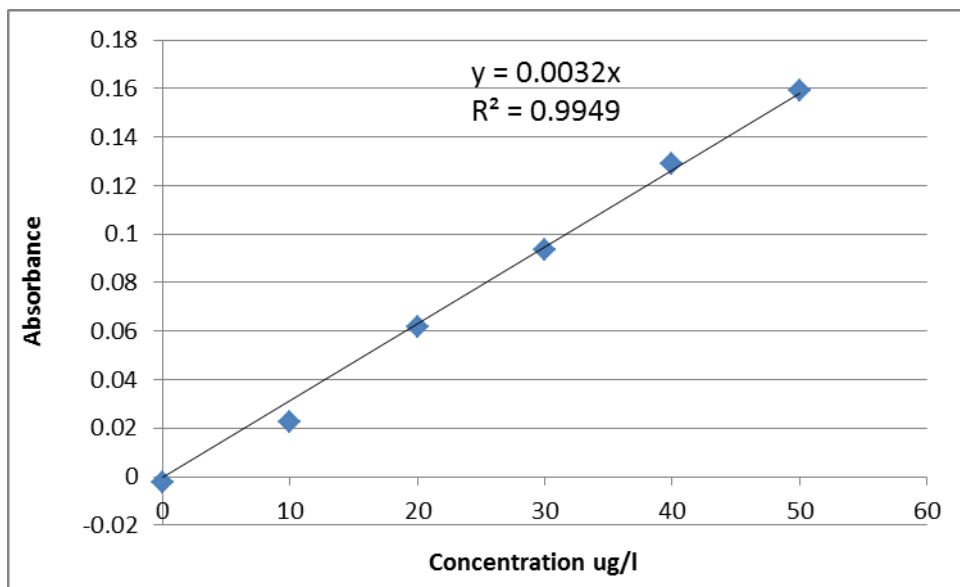
Figure 3.1   Calibration curve with As Standards

The slope of the graph and the equations 3.1 – 3.4, were used to calculate the detection limit as shown below:

The Limits of Detection (LOD) was calculated as shown below:

Equation: $y = 0.0032x$

Calibration sensitivity (slope): =   0.0032

Analytical sensitivity: =   **Y= m/ s_s**

At 50 µg L^{-1} As: 17.3

At 10 µg L^{-1} As: 7.4

Therefore: **$S_m = S_{bl} + ks_{bl}$ k= 3**

$S_{m=}$ -0.00525

Hence: $C_m = (S_m − S_{bl})/m$

LOD (µg L^{-1})   = 0.69 µg L^{-1}

LOD/sample   =   0.04 µg/sample

LOD in air   =   0.5 ng m^{-3}

Therefore it can be seen that the LOD is almost the same as that determined by Thermo-Fisher Corporation (0.6 µgL^{-1}), which validates our analytical procedure and calibration using the arsenic standards.

3.3 TREATMENT OF CONCENTRATION OF ARSENIC VALUES <LOD

Table 3.3   Statistics to show the difference between different values of LOD

	Actual Values	Half LOD	LOD=0
Average (ng m^{-3})	**7.1**	**7.1**	**7.1**
SD (ng m^{-3})	9	9	9
Number	279	279	279
Maximum (ng m^{-3})	53.2	53.2	53.2
Variance (ng m^{-3})^2	81.5	81.5	81.5
Median (ng m^{-3})	3	3	3
Minimum (ng m^{-3}	-0.2	0.3	0

There was no significant difference between the actual values, values at half LOD and values when LOD = 0 were and analysed at 95% confidence levels. Apart from the blanks, only two samples were recorded below the LOD, which accounts for the fact that there was no significant difference in the mean values of arsenic obtained above.

In environmental chemistry a variety of approaches can be used for incorporating values reported at below the LOD into statistical analyses. Typically substitution methods are used, for example, all values reported below LOD can be set to zero, set at half the LOD or at the LOD threshold. Alternatively, the actual non-reported laboratory values (if available) can be used (Mitchell, 2013).

In this thesis, the raw values would be used for the purpose of calculating the Annual average. However for analytical reporting <0.5 ng m^{-3} (LOD) would be used.

3.4 MEAN BLANK ANALYSIS- QUALITY CONTROL

Table 3.4   Blank analysis

Sample ID	Concentration (μg L^{-1})
Average Blank (RO water)	1.6 ± 1.2
Average Reagent Blanks	1.6 ± 1.1
Average Lab Blanks	1.6 ± 0.9
Average Field Blanks	1.6 ± 1.1

All the average blanks ± uncertainty, were within the acceptable range of the instrument detection limit of 1.4 μg L^{-1}. These concentrations may include acids and other background from acid digestions. The quartz fibre filters may also contain some background arsenic. However all blanks were within the analytical guidelines. This further validates the analytical methodology carried out in the determination of the arsenic in the air particulate matter.

3.5 DUPLICATE FILTER ANALYSIS

For the duplicate set of filters, the % difference was calculated using the equation shown below, as each filter had different set of values. Only difference of 5% would be accepted (at least the values should be within 95% of each other as shown below).

Filter Difference = |Duplicate Filter – Original filter| (3.5)

The absolute value was taken as sometimes the duplicate filter gave smaller values compared to the original filter values. The absolute value eliminates the negative values.

% Difference = Filter Difference/mean value of both filters X 100   (3.6)

The mean difference of the duplicate filters was 0.6 ± 0.1ug L^{-1} and the mean percentage difference was 3.1%.

The duplicate filter analysis showed that the two filters were within 96% of each other and therefore, within the analytical acceptable 10% difference range and the difference within the IDL. This further demonstrates that there is less variation in the analytical method.

3.6 PERCENTAGE RECOVERIES OF THE SPIKED SAMPLES

A duplicate filter was spiked with known concentration of arsenic standard at a regular interval of 20 samples. The mean percentage recovery of 15 duplicate filter samples was 99.2 ± 0.8%. A total of 5 blank filters were spiked with known concentrations and the mean % recovery was 102.7 ± 0.9%. Both the recoveries were consistent and above the 95% confidence level. The designated laboratory fortified matrix (LFM) recovery should be in the range of 70 - 130% with high recoveries best to be within 85 - 115% range (USEPA - Method 200.9, 1994).

This further validates the analytical methodology used for determination of As by GF-AAS. It also makes the method highly reproducible for accurate determination of arsenic in air particulate matter (APM) in ambient air.

3.7 QUANTIFYING UNCERTAINTIES IN THE DETERMINATION OF ARSENIC BY GF-AAS

In chemical metrology most of the important decisions are based on the quality and the reliability of results of quantitative analysis. In this context it is also important to have reliability of the results in the international trade and analytical results should be acceptable to all users within the country or outside the country. This can be achieved by the estimation of uncertainty in the measurements as per ISO/EURACHEM guidelines (Singh et al., 2011).

In this regard ISO has published "Guide to the expression of uncertainty in measurement (GUM)" in 1995 in collaboration with BIPM, IEC, IFCC, IUPAC, and OIML. The Second edition has been printed by EURACHEM/CITAC Guide CG4: "Quantifying Uncertainty in Analytical Measurement" (QUAM, 2000). The guide defines uncertainty as a parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand.

So the accurate and precise measurement of arsenic in the air particulate matter is of prime importance as it gives information about the level of toxicity in the environment, and preventive measures could be taken in the affected areas. Quality assurance is equally important in the measurement of arsenic in APM samples before making any decision. The quality and reliability of the data of such volatile elements depends upon the measurement

of uncertainty of each step involved from sampling to analysis. The analytical results quantifying uncertainty gives a measure of the confidence level of the concerned analytical methodology (Singh et al., 2011).

The main sources of uncertainties in the determination of arsenic by Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) were:

- Uncertainties in High-Vol sampler which was calibrated to sample at $69.7 \pm 1.1 m^3 \, hr^{-1}$ at 95% confidence level of air through the quartz filter.

- Uncertainties due to measurements involved in the calculation of the exposed area of the filter and subsequent 47 mm punches of the exposed area. The exposed area was calculated to be $419 \pm 3 \, cm^2$ while the 47 mm punch area was calculated to be $17.4 \pm 0.5 \, cm^2$. Therefore the volume of air through the 47 mm punch was calculated to be $69.7 \pm 2.4 \, m^3$.

- Uncertainties due to volumetric was also calculated using the uncertainty of each of the glassware (pipettes and volumetric flasks) that was used in the preparation of the standard arsenic solution. The final solution in 50ml volumetric flask was calculated to be $49.95 \pm 0.7 \, \mu g \, L^{-1}$ or $49.95 \, \mu g \, L^{-1} \pm 1.44 \, \%$.

- The uncertainty associated with the GF-AAS instrument was computed from the relative standard deviation of each of the replicates (triplicate analysis was done automatically by the auto-sampler of the GF-AAS as per the data entered in the SOLAAR Programme). Therefore each sample had a different set of uncertainty associated with it.

All the uncertainties were first converted to standard uncertainties and then combined using the rules associated with combining the standard uncertainty as per EURACHEM/ CITAC Guide CG4, 2000.

Rule 1:

For models, involving only a sum or difference of quantities, e g. Y= (p + q + r +…), the combined standard uncertainty u_c (y) is given by:

$$u_c \, (y \, (p,q,r,..)) = \sqrt{(u \, (p)^2) + (u \, (q)^2 + ...)} \qquad\qquad (3.7)$$

Rule 2:

For models, involving only a product or quotient of quantities, e g. Y = (p x q x r x...) or y = p/ (q x r x...), the combined standard uncertainty u_c (y) is given by

$$u_c \text{ (y)} = y \times \sqrt{\{(u\text{ (p)}^2/p)\} + \{(u\text{ (q)}^2/q)\} + ...)} \qquad (3.8)$$

Where: (u (p)/p) etc. are the uncertainties in the parameters, expressed as relative standard deviations.

Note: *Subtraction is treated in the same manner as addition, and division in the same way as multiplication*.

The uncertainty formula was used to calculate the arsenic concentrations first into $\mu g\ L^{-1}$, then $\mu g\ sample^{-1}$, and $ng\ m^{-3}$. The final result was expressed as: **X ± Y** $ng\ m^{-3}$

Where X = concentration of arsenic in ambient air and

Y = combined uncertainty.

3.8 NUMERICAL SUMMARY OF ARSENIC, PM_{10}, AND BLACK CARBON RESULTS

In total 279 PM_{10} filters were collected between 25 October 2011 and 30 October 2013. All field and laboratory blanks for gravimetric PM_{10} measurements were well within the tolerances for variations in mass in quartz filters of ± 5 mg and ± 8 mg respectively, in accordance with AS/NZ 3580.9.6:2003 (Mitchell, 2015). The field and laboratory blanks all yielded arsenic concentrations within ± 1.4 µg L^{-1}, which is the Instrument Detection Limit (IDL) of GF-AAS. Statistical summaries for observations during the monitoring period are shown in Tables 3.5 – 3.14.

Daily arsenic concentrations ranged from <0.5 to 53.2 ng m^{-3}, with an overall mean (un-weighted for sampling frequency) of 7.1 ng m^{-3}. Over the same period, particulate matter ranged from 0.9 - 33.3 µg m^{-3} for High - Vol PM_{10} (gravimetric). The overall mean values of PM_{10} were 10.8 µg m^{-3}, (gravimetric) and black carbon ranged from 0.1 - 5.7 µg m^{-3} with an overall mean value of 1.2 µg m^{-3}. The GENT $PM_{2.5}$ values ranged from 0.1 – 26.4 µg m^{-3}. The overall mean value of $PM_{2.5}$ was 4.1 µg m^{-3}.

The monitoring by GENT sampler began slightly late compared to monitoring by High - Vol sampler. GENT sampling began on 9 December, 2011. The missing data in PM_{10}, $PM_{2.5}$, BC, and arsenic analysis from GENT filters are due to the due to attrition and void samples. For the purpose of this study, only data taken from GENT sampler were the ones which exactly coincided with the sampling dates, using the High - Vol sampler. Subsequently, only 247 samples of GENT filters were considered for this study.

For the purpose of determining the annual average, only samples collected by High – Vol sampler from 01 November, 2011 to 31 October, 2012 (12 months) and 01 November, 2012 to 31 October, 2013 was considered, which totalled to 276 filter samples and were weighted to account for non-uniform sampling frequency during the winter months.

The non-winter was 243/366 days and winter was 123/366 days in first year (2012 was a leap year) while the non-winter was 242/365 and winter 123/365 days in the second year. The annual average values for each year is summarised in Table 3.5. The XRF and IBA consistently measured below GF-AAS method as shown in the annual averages for both years.

Table 3.5   Annual/ Overall weighted Average of Arsenic in Air Particulate Matter in Wainuiomata

Annual Average	GF-AAS (ng m^{-3})	XRF (ng m^{-3})	IBA (ng m^{-3})
01/11/2011- 31/10/2012	6.6 ± 0.9	4.5 ± 2.3	3.3 ± 6.1
01/11/2012- 31/10/2013	5.9 ± 0.7	3.1 ± 1.7	2.8 ± 5.7
Overall Average 01/11/2011- 30/10/2013	6.3 ± 0.8	3.8 ± 2.0	3.1 ± 5.9

3.8.1   Regulatory guideline comparison

The New Zealand ambient air quality guideline for inorganic arsenic is expressed as an annual average of arsenic in PM$_{10}$ of **5.5 ng m^{-3}** (MfE, 2002). Although not stated in the MfE guidelines, it is the norm to express annual average based on a calendar year (Mitchell, 2015). In this study the timing and duration of the monitoring campaign did not match calendar years.

It can be seen from the Table 3.5 that NZAAQG value of 5.5 ng m^{-3} had been exceeded for both the years during the sampling period as analysed by GF-AAS. However, this is not reflected by the annual averages obtained by XRF and IBA data. This will be discussed later in the thesis. The exceedances will have serious implications on the policy makers and enforcement.

Table 3.6   Summary statistics for Overall/ Year 1/Year 2 GF-AASS Arsenic (24-hour averages)

Variable	Units	All the data (un-weighted for sampling frequency)	Winter (1:2-day sampling) average	Non-winter (1:3-day sampling) average
Arsenic GF-AAS	Overall			
Min	ng m^{-3}	<0.5	<0.5	<0.5
Mean	ng m^{-3}	7.1	12.2	3.2
Median	ng m^{-3}	3.0	8.7	2.1
Maximum	ng m^{-3}	53.2	53.2	34.9
SD	ng m^{-3}	9.0	11.0	4.1
Variance	(ng m^{-3})^2	81.5	121.8	16.4
n		279	120	159
Arsenic GF-AAS	Year 1			
Min	ng m^{-3}	0.6	1.8	0.6
Mean	ng m^{-3}	**7.5 ± 0.9**	**13.2 ± 1.4**	**3.2 ± 0.7**
Median	ng m^{-3}	3.4	9.0	2.1
Maximum	ng m^{-3}	48.6	48.6	34.9
SD	ng m^{-3}	9.0	10.4	4.2
Variance	(ng m^{-3})^2	81.2	107.6	18.0
n		139	60	79
Arsenic GF-AAS	Year 2			
Min	ng m^{-3}	<0.5	<0.5	<0.5
Mean	ng m^{-3}	**6.7 ± 0.7**	**11.1 ± 0.6**	**3.2 ± 0.7**
Median	ng m^{-3}	2.8	6.0	2.2
Maximum	ng m^{-3}	53.2	53.2	29.3
SD	ng m^{-3}	9.1	11.6	3.9
Variance	(ng m^{-3})^2	82.5	133.8	15.3
n		137	60	77

Table 3.7   Summary Statistics: IBA Overall / Year 1/ Year 2 Arsenic (24 Hr Averages).

Variable	Units	All the data (un-weighted for sampling frequency)	Winter (1:2-day sampling) average	Non-winter (1:3-day sampling) average
Arsenic IBA Data	**Overall**			
Min	ng m^{-3}	0	0	0
Mean	ng m^{-3}	3.7	6.5	1.3
Median	ng m^{-3}	1.6	3.2	0
Maximum	ng m^{-3}	48.5	48.5	11.1
SD	ng m^{-3}	6.9	9.1	2.1
Variance	(ng m^{-3})^2	47.7	83.3	4.2
n		247	114	133
Arsenic IBA	**Year 1**			
Min	ng m^{-3}	0	0	0
Mean	ng m^{-3}	**4.3 ± 6.3**	**7.3 ± 6.9**	**1.3 ± 5.7**
Median	ng m^{-3}	1.8	3.7	0
Maximum	ng m^{-3}	48.5	48.5	11.1
SD	ng m^{-3}	8.1	10.5	2.3
Variance	(ng m^{-3})^2	66.3	109.3	5.4
n		112	56	56
Arsenic IBA	**Year 2**			
Min	ng m^{-3}	0	0	0
Mean	ng m^{-3}	**3.2 ± 5.7**	**5.8 ± 5.8**	**1.2 ± 5.7**
Median	ng m^{-3}	1.5	2.8	0
Maximum	ng m^{-3}	36.5	36.5	9.7
SD	ng m^{-3}	5.6	7.6	1.8
Variance	(ng m^{-3})^2	31.5	57	3.3
n		135	58	77

Table 3.8   Summary Statistics: XRF Arsenic, XRF Chromium and XRF Copper (24 Hr Averages).

Variable	Units	All the data (un-weighted for sampling frequency)	Winter (1:2-day sampling) average	Non-winter (1:3-day sampling) average
Arsenic XRF Data	**Overall**			
Min	ng m^{-3}	0	0	0
Mean	ng m^{-3}	**4.6**	**9.5**	**1.0**
Median	ng m^{-3}	0.5	5.2	0
Maximum	ng m^{-3}	59.8	59.8	40.1
SD	ng m^{-3}	9.0	11.4	3.6
Variance	(ng m^{-3})^2	80.7	130.1	12.6
n		279	120	159
Arsenic XRF	**Year 1**			
Min	ng m^{-3}	0	0	0
Mean	ng m^{-3}	**5.5 ± 2.8**	**11.2 ± 5.4**	**1.1 ± 0.8**
Median	ng m^{-3}	0.7	6.4	0
Maximum	ng m^{-3}	59.8	59.8	40.1
SD	ng m^{-3}	10.2	12.4	4.7
Variance	(ng m^{-3})^2	103.6	153.5	22.0
n		139	60	79
Arsenic XRF	**Year 2**			
Min	ng m^{-3}	0	0	0
Mean	ng m^{-3}	**3.8 ± 2.0**	**7.7 ± 3.8**	**0.8 ± 0.6**
Median	ng m^{-3}	0.5	3.2	0
Maximum	ng m^{-3}	44.1	44.1	13.2
SD	ng m^{-3}	7.6	10.0	1.8
Variance	(ng m^{-3})^2	57.4	100.4	3.3
n		137	60	77

Table 3.9   Summary Statistics: XRF Chromium, Copper and Lead Concentrations (24 Hr Averages)

Variable	Units	All the data (un-weighted for sampling frequency)	Winter (1:2-day sampling) average	Non-winter (1:3-day sampling) average
XRF -Cr	**Overall**			
Min	ng m^{-3}	0	0	0
Mean	ng m^{-3}	**0.8**	**0.7**	**0.9**
Median	ng m^{-3}	0.5	0.5	0.5
Maximum	ng m^{-3}	5.5	2.0	5.5
SD	ng m^{-3}	1.0	0.6	1.2
Variance	(ng m^{-3})^2	1.0	0.4	1.4
n		279	120	159
XRF-Cu	**Overall**			
Min	ng m^{-3}	0	0	0
Mean	ng m^{-3}	**1.5**	**1.8**	**1.3**
Median	ng m^{-3}	1.0	1.3	1.0
Maximum	ng m^{-3}	40.4	32.9	40.4
SD	ng m^{-3}	3.3	3.2	3.3
Variance	(ng m^{-3})^2	10.7	10.4	10.8
n		279	120	159
XRF-Pb	**Overall**			
Min	ng m^{-3}	0	0	0
Mean	ng m^{-3}	**18.1 ± 15.0**	**34.0 ± 26.1**	**6.1 ± 6.7**
Median	ng m^{-3}	6.5	25.3	3.2
Maximum	ng m^{-3}	124.3	124.3	83.5
SD	ng m^{-3}	25.6	30.7	10.2
Variance	(ng m^{-3})^2	656.2	944.4	105.0
n		279	120	159

Table 3.10   Summary Statistics: GENT PM_{10} / GENT BC in PM_{10} / GENT BC in $PM_{2.5}$ Concentrations (24 Hr Averages)

Variable	Units	All the data (un-weighted for sampling frequency)	Winter (1:2-day sampling) average	Non-winter (1:3-day sampling) average
PM_{10} GENT	**Overall**			
Min	$\mu g\ m^{-3}$	0.9	1.1	0.9
Mean	$\mu g\ m^{-3}$	9.3	9.5	9.1
Median	$\mu g\ m^{-3}$	8.7	8.9	8.2
Maximum	$\mu g\ m^{-3}$	31.2	31.2	27.5
SD	$\mu g\ m^{-3}$	5.3	5.3	5.3
Variance	$(\mu g\ m^{-3})^2$	28.4	28.5	28.5
n		247	114	133

Variable	Units	All the data (un-weighted for sampling frequency)	Winter (1:2-day sampling) average	Non-winter (1:3-day sampling) average
BC GENT PM_{10}	Overall			
Min	$\mu g\ m^{-3}$	0.1	0.1	0.1
Mean	$\mu g\ m^{-3}$	1.0	1.6	0.4
Median	$\mu g\ m^{-3}$	0.5	1.3	0.3
Maximum	$\mu g\ m^{-3}$	6.2	6.2	1.8
SD	$\mu g\ m^{-3}$	1.1	1.3	0.3
Variance	$(\mu g\ m^{-3})^2$	1.2	1.8	0.1
n		247	114	133

Variable	Units	All the data	Winter	Non-winter
BC GENT $PM_{2.5}$	**Overall**			
Min	$\mu g\ m^{-3}$	0	0	0
Mean	$\mu g\ m^{-3}$	0.8	1.5	0.3
Median	$\mu g\ m^{-3}$	0.4	1.1	0.2
Maximum	$\mu g\ m^{-3}$	5.6	5.6	1.6
SD	$\mu g\ m^{-3}$	1.0	1.2	0.3
Variance	$(\mu g\ m^{-3})^2$	1.0	1.5	0.1
n		247	114	133

Table 3.11   Summary Statistics: Overall/ Year 1/ Year 2 GENT PM$_{2.5}$ (24 Hr Averages)

Variable	Units	All the data (un-weighted for sampling frequency)	Winter (1:2-day sampling) average	Non-winter (1:3-day sampling) average
GENT PM$_{2.5}$	Overall			
Min	µg m^{-3}	0.1	0.1	0.1
Mean	µg m^{-3}	4.1	5.1	3.2
Median	µg m^{-3}	3.3	4.0	2.9
Maximum	µg m^{-3}	26.4	26.4	9.7
SD	µg m^{-3}	3.4	4.4	1.9
Variance	(µg m^{-3})^2	11.6	19.0	3.5
n		247	114	133
GENT PM$_{2.5}$	Year 1			
Min	µg m^{-3}	0.3	0.4	0.3
Mean	µg m^{-3}	4.2	5.4	3.0
Median	µg m^{-3}	3.3	3.7	2.4
Maximum	µg m^{-3}	26.4	26.4	8.9
SD	µg m^{-3}	4.0	5.0	2.0
Variance	(µg m^{-3})^2	16.4	25.5	4.2
n		112	56	56
GENT PM$_{2.5}$	Year 2			
Min	µg m^{-3}	0.1	0.1	0.1
Mean	µg m^{-3}	4.0	4.8	3.3
Median	µg m^{-3}	3.4	4.0	3.0
Maximum	µg m^{-3}	15.8	15.8	9.7
SD	µg m^{-3}	2.8	3.5	1.7
Variance	(µg m^{-3})^2	7.6	12.5	2.9
n		135	58	77

Table 3.12   Summary Statistics: Overall/ Year 1/ Year 2 High-Vol PM$_{10}$ (24 Hr Averages)

Variable	Units	All the data (un-weighted for sampling frequency)	Winter (1:2-day sampling) average	Non-winter (1:3-day sampling) average
High-Vol PM$_{10}$	Overall			
Min	µg m^{-3}	0.9	0.9	1.3
Mean	µg m^{-3}	10.8	12.6	9.5
Median	µg m^{-3}	9.9	10.7	9
Maximum	µg m^{-3}	33.3	33.3	24.2
SD	µg m^{-3}	5.8	6.7	4.5
Variance	(µg m^{-3})^2	33.2	45.1	20.1
n		279	120	159
High-Vol PM$_{10}$	**Year 1**			
Min	µg m^{-3}	0.9	0.9	1.3
Mean	µg m^{-3}	10.9	13.0	9.3
Median	µg m^{-3}	9.9	11.6	8.9
Maximum	µg m^{-3}	33.3	33.3	24.2
SD	µg m^{-3}	6.1	7.0	4.7
Variance	(µg m^{-3})^2	37.1	49.0	21.9
n		139	60	79
High-Vol PM$_{10}$	**Year 2**			
Min	µg m^{-3}	2.4	3.3	2.4
Mean	µg m^{-3}	10.7	12.2	9.6
Median	µg m^{-3}	9.8	10.4	9.5
Maximum	µg m^{-3}	32.1	32.1	22.3
SD	µg m^{-3}	5.5	6.4	4.3
Variance	(µg m^{-3})^2	29.7	40.4	18.6
n		137	60	77

Table 3.13   Summary Statistics: Overall/ Year 1/ Year 2 High-Vol BC in PM$_{10}$ (24 Hr Averages)

Variable	Units	All the data (un-weighted for sampling frequency)	Winter (1:2-day sampling) average	Non-winter (1:3-day sampling) average
High-Vol BC in PM$_{10}$	Overall			
Min	µg m^{-3}	0.1	0.2	0.1
Mean	µg m^{-3}	1.2	2.0	0.6
Median	µg m^{-3}	0.7	1.8	0.5
Maximum	µg m^{-3}	5.7	5.7	2.7
SD	µg m^{-3}	1.2	1.4	0.4
Variance	(µg m^{-3})^2	1.5	2.0	0.2
n		279	120	159
High-Vol BC in PM$_{10}$	**Year 1**			
Min	µg m^{-3}	0.1	0.2	0.1
Mean	µg m^{-3}	1.3	2.2	0.7
Median	µg m^{-3}	0.7	2.2	0.5
Maximum	µg m^{-3}	5.0	5.0	2.7
SD	µg m^{-3}	1.2	1.4	0.5
Variance	(µg m^{-3})^2	1.5	1.9	0.2
n		139	60	79
High-Vol BC in PM$_{10}$	**Year 2**			
Min	µg m^{-3}	0.1	0.3	0.1
Mean	µg m^{-3}	1.2	1.9	0.6
Median	µg m^{-3}	0.6	1.7	0.5
Maximum	µg m^{-3}	5.7	5.7	2.4
SD	µg m^{-3}	1.2	1.4	0.4
Variance	(µg m^{-3})^2	1.4	2.0	0.2
n		137	60	77

Table 3.14   Summary Statistics: Arsenic Weighted and Non-Weighted by all Methods (24 Hr Averages)

Method	GF-AAS- As		XRF- As		IBA- As	
	Weighted Average	Non-Weighted Average	Weighted Average	Non-Weighted Average	Weighted Average	Non-Weighted Average
Units	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}
Overall	**6.3 ± 0.8**	**7.1 ± 0.8**	**3.8 ± 2.0**	**4.6 ± 2.4**	**3.1 ± 5.9**	**3.7 ± 6.0**
Winter	4.1 ± 0.5	12.2 ± 1.0	3.2 ± 1.6	9.5 ± 4.6	2.2 ± 2.1	6.5 ± 6.4
Non- Winter	2.2 ± 0.3	3.2 ± 0.7	0.6 ± 0.4	1.0 ± 0.7	0.8 ± 3.8	1.3 ± 5.7
Year 1 Annual Average	**6.5 ± 0.9**	**7.5 ± 0.9**	**4.5 ± 2.3**	**5.5 ± 2.8**	**3.3 ± 6.1**	**4.3 ± 6.3**
Winter	4.4 ± 0.5	13.2 ± 1.4	3.8 ± 1.8	11.2 ± 5.4	2.5 ± 2.3	7.3 ± 6.9
Non- Winter	2.1 ± 0.5	3.2 ± 0.7	0.7 ± 0.5	1.1 ± 0.8	0.9 ± 3.8	1.3 ± 5.7
Year 2 Annual Average	**5.9 ± 0.7**	**6.7 ± 0.7**	**3.1 ± 1.7**	**3.8 ± 2.0**	**2.7 ± 5.7**	**3.2 ± 5.7**
Winter	3.7 ± 0.2	11.1 ± 0.6	2.6 ± 1.3	7.7 ± 3.8	2.0 ± 2.0	5.8 ± 5.8
Non-Winter	2.1 ± 0.5	3.2 ± 0.7	0.5 ± 0.4	0.8 ± 0.6	0.8 ± 3.8	1.2 ± 5.7

4.0   STATISTICAL DATA ANALYSIS AND DISCUSSION

The Time-Series graphs and the scatter plots were plotted using simple line graphs and scatter from the Microsoft Excel 2010 program.

The **CORREL** and **PEARSON** worksheet functions both calculate the correlation coefficient between two measurement variables when measurements on each variable are observed for each of N subjects. The correlation analysis tool in the excel 2010 programme is particularly useful when there are more than two measurement variables for each of N subjects. It provides an output table, a correlation matrix that shows the value of **CORREL** (or **PEARSON**) applied to each possible pair of measurement variables.

The correlation coefficient, like the covariance, is a measure of the extent to which two measurement variables "vary together." Unlike the covariance, the correlation coefficient is scaled so that its value is independent of the units in which the two measurement variables are expressed. The value of any correlation coefficient must be between -1 and +1 inclusive.

The correlation analysis tool to examine each pair of measurement variables to determine whether the two measurement variables tend to move together — that is, whether large values of one variable tend to be associated with large values of the other (positive correlation), whether small values of one variable tend to be associated with large values of the other (negative correlation), or whether values of both variables tend to be unrelated (correlation near 0 (zero)).

The statistical analysis was performed using ANOVA analysis tools in the Microsoft Excel 2010 program; provide different types of variance analysis. The analyses were reported using Single Factor and Two-Factor with replication to test the hypothesis.

ANOVA: Single Factor tool performs a simple analysis of variance on data for two or more samples. The analysis provides a test of the hypothesis that each sample is drawn from the same underlying probability distribution against the alternative hypothesis that underlying probability distributions are not the same for all samples.

ANOVA: Two-Factor with replication tool is useful when data can be classified along two different dimensions. For example in this analysis, the data can be grouped in methods against years/ seasons, the analysis had been carried out.

4.1 PM$_{10}$ IN AMBIENT AIR BY HIGH- VOL SAMPLER AND GENT SAMPLER

The PM$_{2.5}$ and PM$_{10-2.5}$ datasets were combined to provide mass concentration values for GENT PM$_{10}$ as source contributions to PM$_{10}$ on peak days are of interest with regard to the NES and air quality management. Figure 4.2 presents the temporal variation in GENT PM$_{10}$ gravimetric concentrations that shows winter peaks in PM$_{10}$, as identified from the temporal variations in High-Vol PM$_{10}$ shown in Figure 4.3.

The measured gravimetric High-Vol PM$_{10}$ ranged from $0.9 - 33.3$ µg m^{-3} during the entire sampling period while GENT PM$_{10}$ ranged from $0.9 - 31.2$ µg m^{-3} for the same period.

The mean values obtained for gravimetric High-Vol PM$_{10}$ in ambient air for the entire sampling period was; 10.8 µg m^{-3}. The mean values for winter (1:2 day sampling) and non-winter (1:3 day sampling) were 12.6 µg m^{-3} and 9.5 µg m^{-3} respectively. While the mean values obtained for GENT PM$_{10}$ was:- 9.3 µg m^{-3}. 9.5 µg m^{-3} and 9.1 µg m^{-3} mean values were obtained for winter and non-winter periods respectively for the same sampling period. The values obtained by GENT PM$_{10}$ were consistently lower than that obtained by High-Vol PM$_{10}$.

In general the elevated particulate matter concentrations observed throughout New Zealand during the winter period are due to the presence of meteorological conditions that promote "environmental confinement" of biomass burning emissions (Trompetter et al., 2010). This leads to the formation of an "Inversion Layer" which leads to the environmental confinement of the air particulate matter. The photograph in Figure 4.1 was taken on 13 August 2013 at 9.39am shows the formation of the inversion layer in Wainuiomata from the previous night.

Figure 4.1   Photograph taken on 13 August 2013 at 9.39am shows the formation of the inversion layer in Wainuiomata from the previous night

The graphs of GENT PM_{10} and High-Vol PM_{10} presented in Figures 4.2 and 4.3 respectively, show strong seasonal attributions, with high peaks mostly around winter seasons (May – August) for both years. The biomass burning has been previously reported to contribute to high PM_{10} during winter seasons (Ancelet et al., 2012; Trompetter et al., 2010; Davy et al., 2012).   However, there were occasionally high peaks observed during the non-winter periods as well, which accounts for the other sources apart from biomass burning as identified in previous studies. These sources were motor vehicles, sulphates, marine aerosols, road dust and soil (Davy et al., 2009)

The coarse fraction source contributions from marine aerosol dominated the average PM_{10} mass concentrations, yet during winter biomass burning sources were responsible for peak PM_{10} concentrations (Davy et al., 2009).
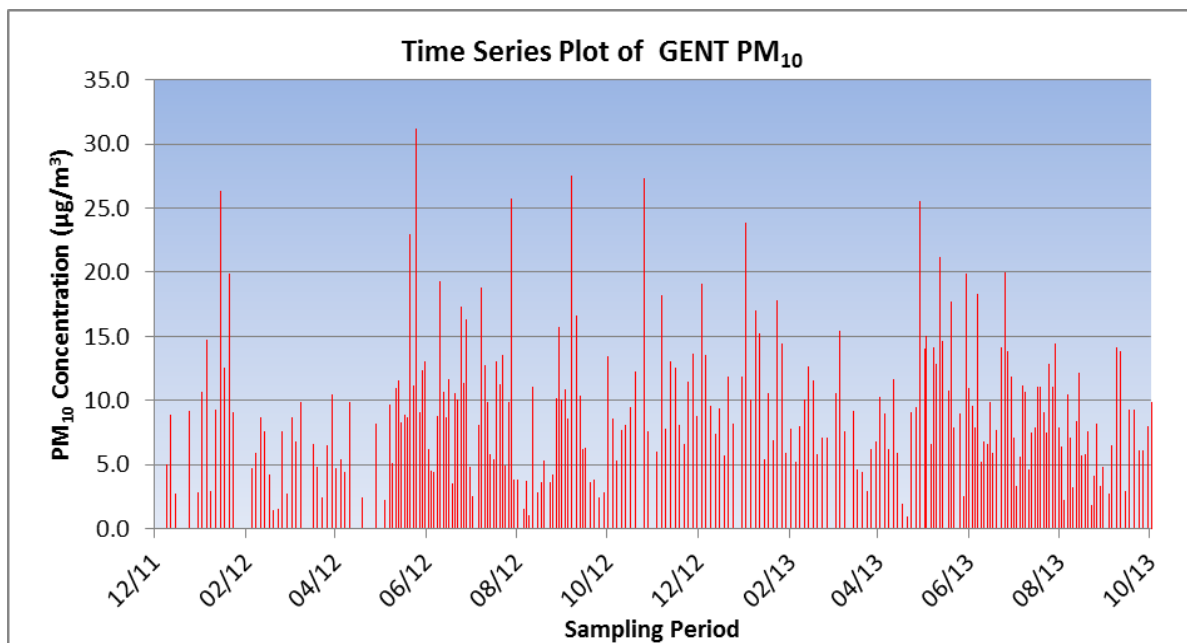
Figure 4.2   Time Series plots of GENT PM$_{10}$ showing higher peaks around winter seasons.
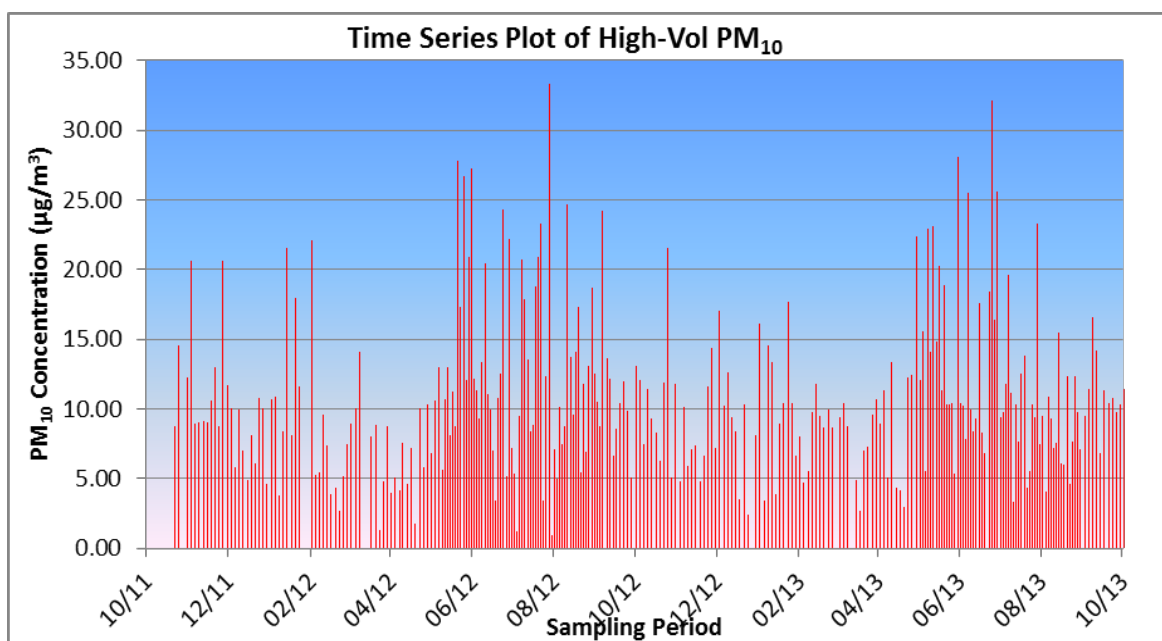
Figure 4.3   Time Series plots of PM$_{10}$ by High-Vol Sampler showing higher peaks around winter seasons

For air quality management purposes the contribution of the various sources to peak PM$_{10}$ events is of most interest. Therefore the mass contributions of sources to all PM$_{10}$ concentrations over 33 µg m^{-3}(the Ministry for the Environment 'Alert' level as discussed in Section 3.1) had been recorded. For the entire sampling period, only exceedance of 33.3 µg m^{-3} was recorded on 28 July, 2012 on High-Vol quartz filter.

None of the measured PM_{10} exceeded the 24 hour guideline of $50\mu gm^{-3}$ during the entire sampling period for this study. The annual average of $20\mu gm^{-3}$ was also not exceeded during the entire sampling period.

Previous studies show that there were 5 exceedances of 33 $\mu g\ m^{-3}$ (MfE allowable exceedance) and one of 50 $\mu g\ m^{-3}$ (24 hour average) from 2007 – 2008 whereby the peak PM_{10} events at Wainuiomata primarily occurred during autumn and winter and that biomass burning was responsible for approximately 70-80% of PM_{10} mass during those air pollution events (Davy et al., 2009).

This shows that there has been significant decrease in the PM_{10} concentrations for the period 25 October 2011 - 31 October 2013 as measured in the Wainuiomata air shed compared to what was reported in 2009.
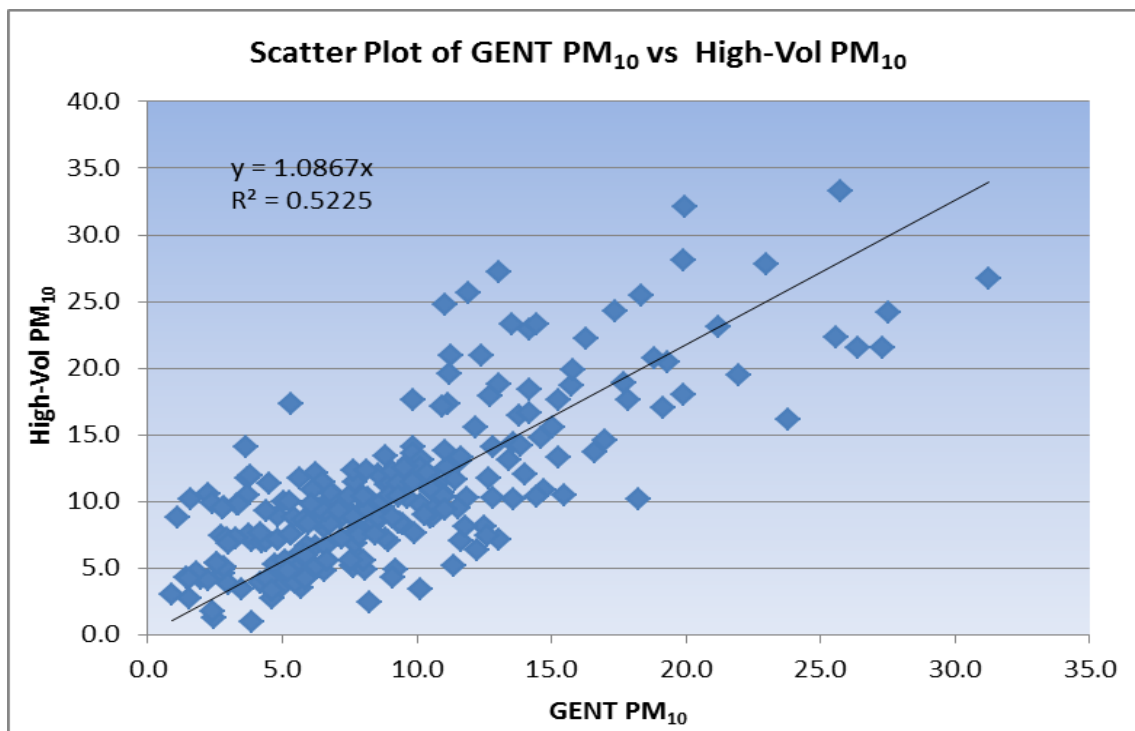
Figure 4.4: Scatter plot of PM_{10} measured by Gent filters compared to PM_{10} by High-Vol filters

The scatter plot Figure 4.4 shows a positive correlation between the PM_{10} measured by both methods. There appeared to be a tendency for seasonal effect on the magnitude and sign of the difference between the co-located PM_{10} measurements, with less variation in the difference between the methods and the gravimetric method to produce higher concentrations than those obtained by GENT sampler during the monitoring period. This is also reflected from the available data where the PM_{10} collected by High- Vol quartz filters

consistently measures above the PM_{10} observed from polycarbonate Gent filters. This could be because the polycarbonate filters are plastic in nature and gets affected by static charges easily, hence there were problems encountered during the weighing process, which could account for the observed differences.

The quartz filters are known to be more absorbing than polycarbonate filters, so there is a possibility of absorption of organic components in the air samples onto the quartz filters which could also account for the observed difference in the PM_{10} by the two methods (Chow et al., 2010).

4.2 BLACK CARBON (BC) IN AMBIENT AIR BY HIGH-VOL AND GENT SAMPLERS

The PM_{10} High-Vol quartz filter set was analysed for black carbon (BC) concentrations. Black carbon (BC) has been studied extensively, but it is still not clear to what degree it is elemental carbon (EC) (or graphitic), C (0) or high molecular weight refractory weight organic species or a combination of both, and that for combustion sources such as petrol and diesel fuelled vehicles, biomass combustion (wood burning) and fossil fuels (coal burning), EC and organic carbon compounds (OC) are the principal aerosol components emitted (Fine et al., 2001; Jacobson et al., 2000; Salma et al., 2004; Watson et al., 2002).

Determination of carbon (soot) on the filters was performed by light reflection to provide the BC concentration. The absorption and reflection of visible light on particles in the atmosphere or collection filters is dependent on the particle concentration, density, refractive index and size as explained in Chapter 2, Section 2.7 of this thesis.

For atmospheric particles, BC is the most highly absorbing component in the visible light spectrum with very much smaller components coming from soils, sulphates and nitrates (Horvath, 1993; Horvath 1997). Hence, to the first order it can be assumed that all the absorption on atmospheric filters is from BC. The main sources of atmospheric BC are industrial emissions (Cohen et al., 2000). Cohen and co-workers found that BC is typically 10-40% of the fine mass ($PM_{2.5}$) fraction in many urban areas of Australia.

The interesting point about BC is that is closely associated with the $PM_{2.5}$ component of the PM_{10} and therefore provides an indication of $PM_{2.5}$ concentration pattern and time series (Davy et al., 2014).

The light reflectance (Reflectometer) measured High-Vol BC in PM_{10} ranged from $0.1 - 5.7$ µg m^{-3} during the entire sampling period while GENT BC in PM_{10} ranged from $0.1 - 6.2$ µg m^{-3} for the same period.

The mean value obtained for High-Vol BC in PM_{10} in ambient for the entire sampling period was 1.2 µg m^{-3}. The mean values for winter (1:2 day sampling) and non-winter (1:3 day sampling) were: 2.0 µg m^{-3} and 0.6 µg m^{-3} respectively. While the mean values obtained for GENT BC in PM_{10} was 1.0 µg m^{-3} for the entire sampling period. 1.6 µg m^{-3} and 0.4 µg m^{-3} values were obtained for winter and non-winter periods respectively. The mean values obtained for GENT BC in PM_{10} was consistently lower than that obtained by High-Vol BC in PM_{10}.

Figures 4.5 and 4.6 are the Time-Series plots of GENT BC and that by High- Vol BC in PM_{10} respectively.

Both the graphs show strong seasonal attributions in BC concentrations in the Wainuiomata airshed, indicating that peak concentrations from combustion sources (and by inference peak combustion source emissions) were likely to occur during winter (May – August) for both the years.
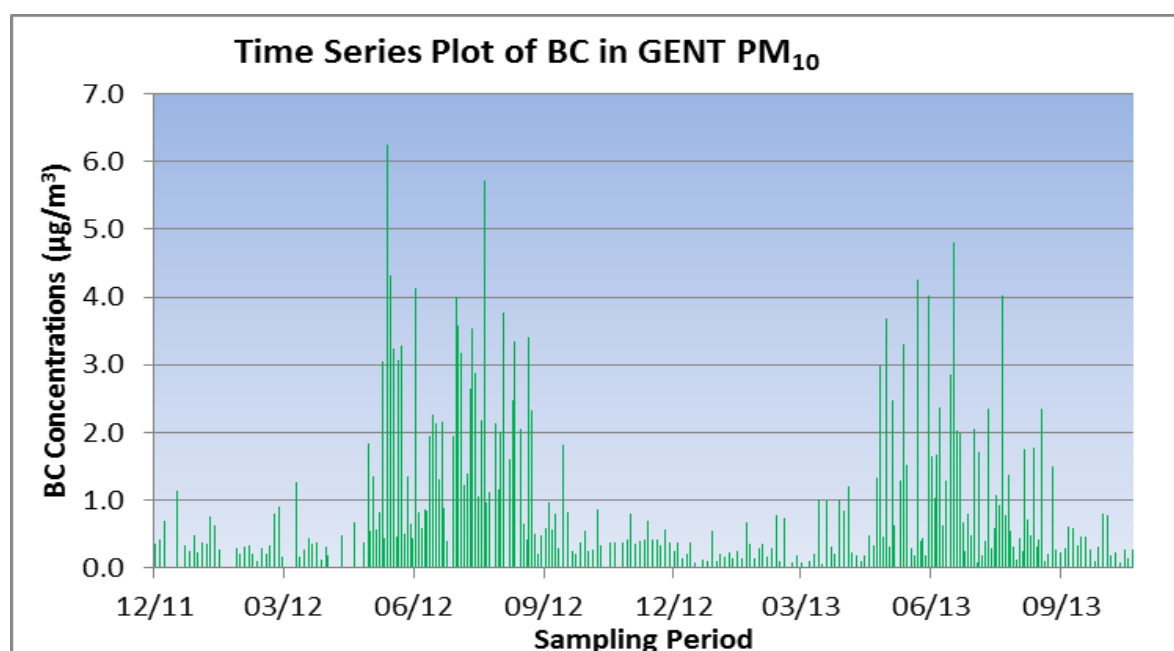
Figure: 4.5 Time Series plot of GENT BC in PM_{10} showing distinct peak heights during winter seasons.
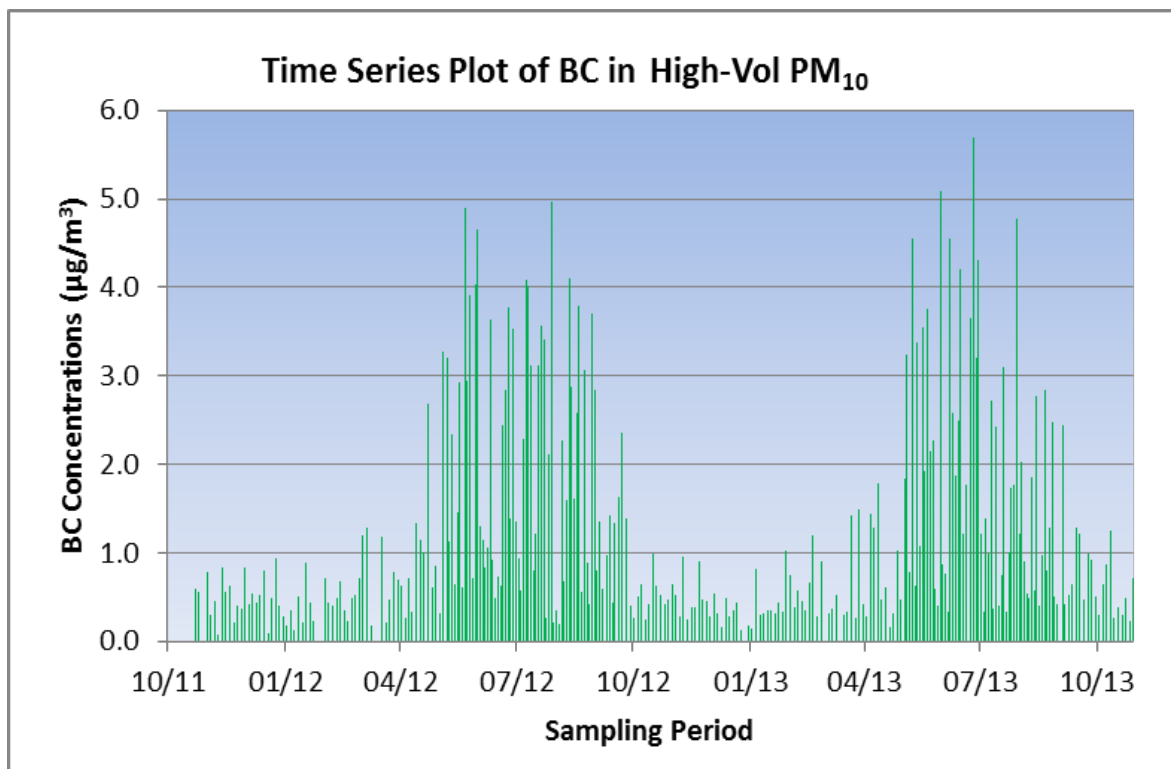
Figure: 4.6 Time Series plot of High-Vol BC in PM_{10} showing distinct peak heights during winter seasons.
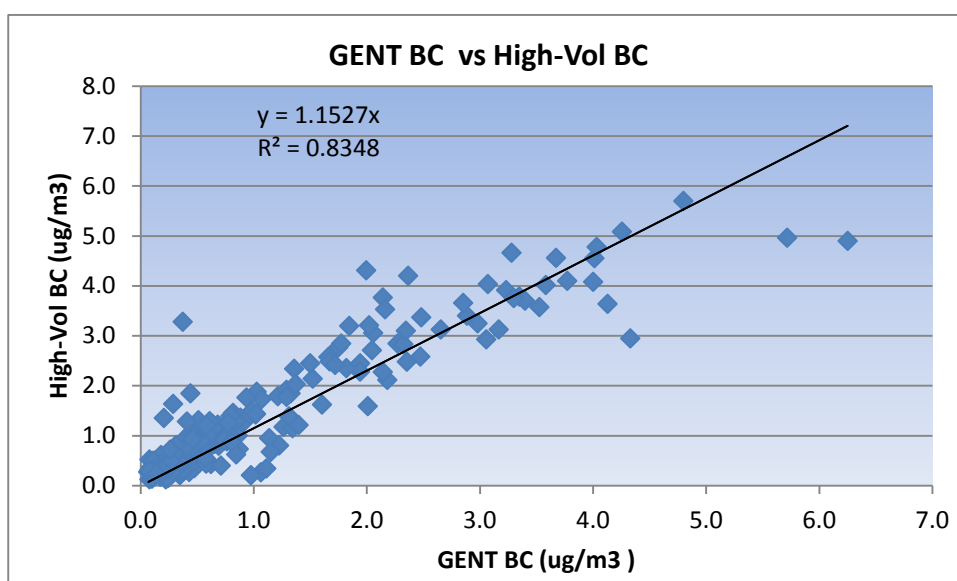
Figure: 4.7   Scatter plot of BC in PM_{10} by Gent Sampler vs BC in PM_{10} by High – Vol Sampler showing good correlation between the two sampling methods

The scatter plot shows a positive with very good correlation between the BC in PM_{10} measured by both methods. The inconsistency could be due to the missing data from the GENT measurements.
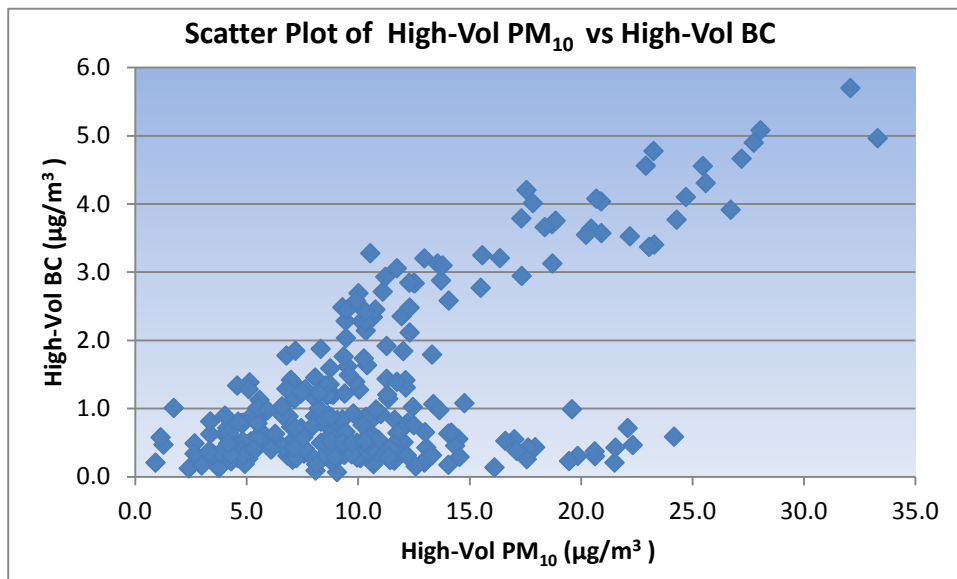
Figure: 4.8a   Scatter plot of High-Vol PM_{10} vs High-Vol BC in PM_{10} showing a positive correlation
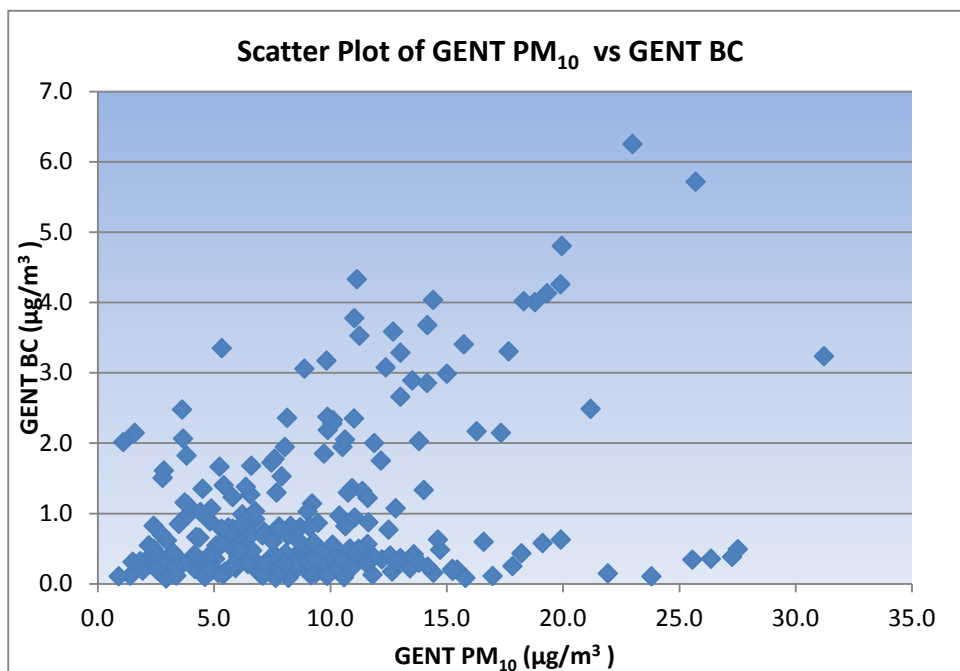
Figure: 4.8b   Scatter plot of GENT PM_{10} vs GENT BC in PM_{10} showing positive correlation

Figure 4.8a showed the scatter plot of High-Vol PM_{10} and BC in High-Vol PM_{10} while Figure 4.8b showed a scatter plot of GENT PM_{10} vs GENT BC in PM_{10}. Both plots show a positive correlation between the two. This showed us that BC is one of the main components of the entire PM_{10}. The other components of PM_{10} was known to be from other sources such as motor vehicles, sulphates marine aerosols road dust and soil as mentioned earlier (Davy et al, 2009).

4.3 PM$_{2.5}$ IN AMBIENT AIR BY GENT SAMPLER

The PM$_{2.5}$ samples from the Wainuiomata site were collected with a GENT sampler (as described in Section 2.4) from 9 December 2011 – 31 October 2013. PM$_{2.5}$ concentrations were determined gravimetrically.

The gravimetric results for GENT PM$_{2.5}$ show that the values ranged from 0.1- 26.4 µg m^{-3}and for light reflectance BC in PM$_{2.5}$ ranged from 0- 5.6 µg m^{-3}during the entire sampling period.

The mean value obtained for GENT PM$_{2.5}$ in ambient for the entire sampling period was 4.1 µg m^{-3}. The mean values for winter (1:2 day sampling) and non-winter (1:3 day sampling) were: 5.1 µg m^{-3}and 3.2 µg m^{-3}respectively. While the mean value obtained for BC in GENT PM$_{2.5}$ was 0.8 µg m^{-3}for the entire sampling period and 1.5 µg m^{-3}and 0.3 µg m^{-3} for winter and non-winter periods respectively. The values obtained for BC in GENT PM$_{10}$ (Table 3.10) was slightly higher than that obtained by BC in GENT PM$_{2.5}$ (Table 3.10). This could be because the **PM$_{10}$= PM$_{10-2.5}$ + PM$_{2.5}$** (i.e., GENT PM$_{10}$ is the sum of GENT $_{coarse}$ filter and GENT $_{fine}$ fractions).

The Time-Series plots of GENT PM$_{2.5}$ filters and BC in GENT PM$_{2.5}$ filters are shown in Figures 4.9 and 4.10 respectively.

Both the graphs showed strong seasonal attributions, with high winter peaks (May – August), at Wainuiomata was due to biomass burning, most likely from solid fuel fire emissions for domestic heating for both years. There was only one exceedance of the NZAAQG for PM$_{2.5}$ of 25 µg m^{-3}and three exceedances of MfE 'acceptable' air quality category of 17 µg m^{-3} recorded throughout the sampling period. The exceedance occurred on 25 May, 2012 with PM$_{2.5}$ concentration of 26.4 µg m^{-3} while for the MfE 'acceptable' air quality exceedance were noted on 21 and 25 May, 2012 and 28 July, 2012. The PM$_{2.5}$ concentrations were 18.3, 26.4 and 20.5 µg m^{-3}respectively.
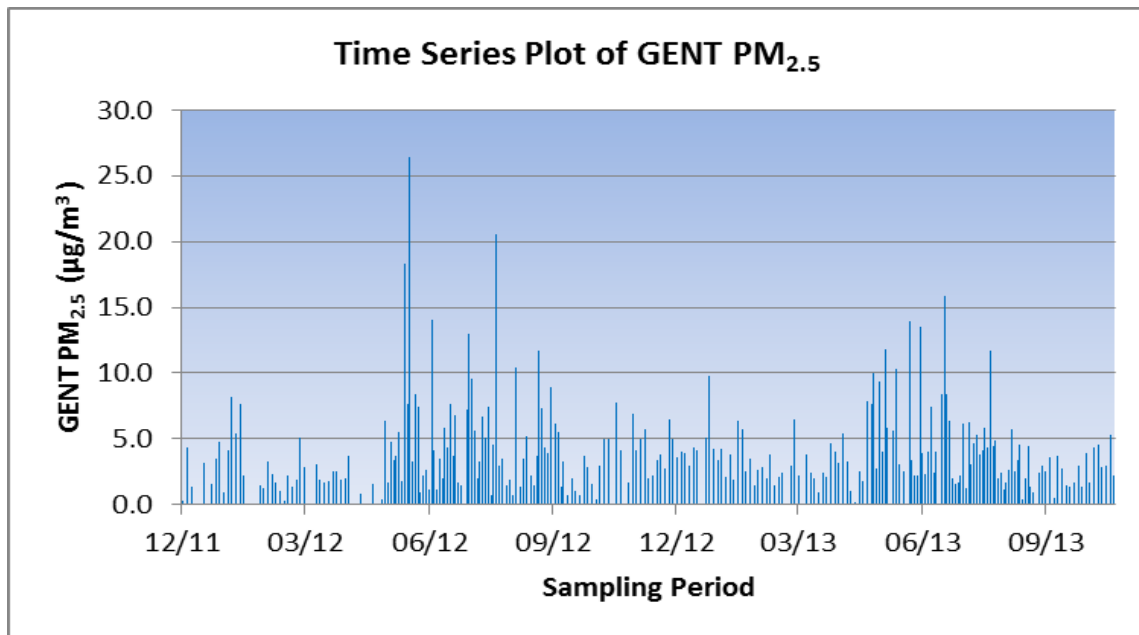
Figure: 4.9   Time Series plot of GENT $PM_{2.5}$ showing distinct peak heights during winter seasons.
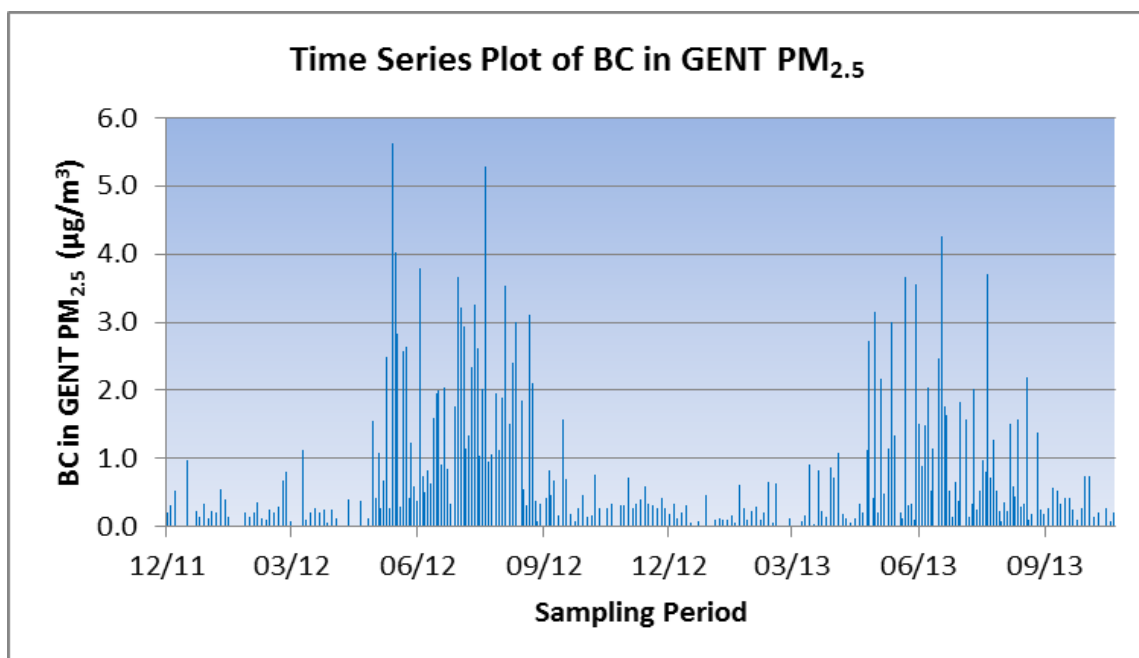
Figure: 4.10   Time Series plot of BC in GENT $PM_{2.5}$ showing distinct peak heights during winter seasons.

Previous studies have shown that the $PM_{2.5}$ sources in the Wainuiomata airshed were:

- The first source was due to biomass burning and contains H (as an indicator of organic compounds), BC and K as primary species along with some Zn, and interestingly, arsenic was also found to be associated with this source.

- The second source contribution had been identified as originating from motor vehicle emissions due to the presence of H, BC, Ca and Fe.

- The third factor had been labelled sulphate due to the dominance of sulphur in the profile and this source contribution was from secondary sulphate aerosol.

- The fourth factor had been identified as a marine aerosol source due to the presence of Na and Cl along with some Mg, S, K, and Ca.

- The fifth source was due to airborne crustal matter and contains Al, Si, S, K, Ca and Fe as primary species (Davy et al., 2009).

The temporal variation indicated that $PM_{2.5}$ mass was dominated by the biomass burning source during winter, predominantly due to emissions from solid fuel fires used for domestic heating. At other times secondary sulphate and marine aerosol were significant contributors to $PM_{2.5}$ concentrations in Wainuiomata airshed as previously reported (Davy et al., 2009; Davy et al., 2012).
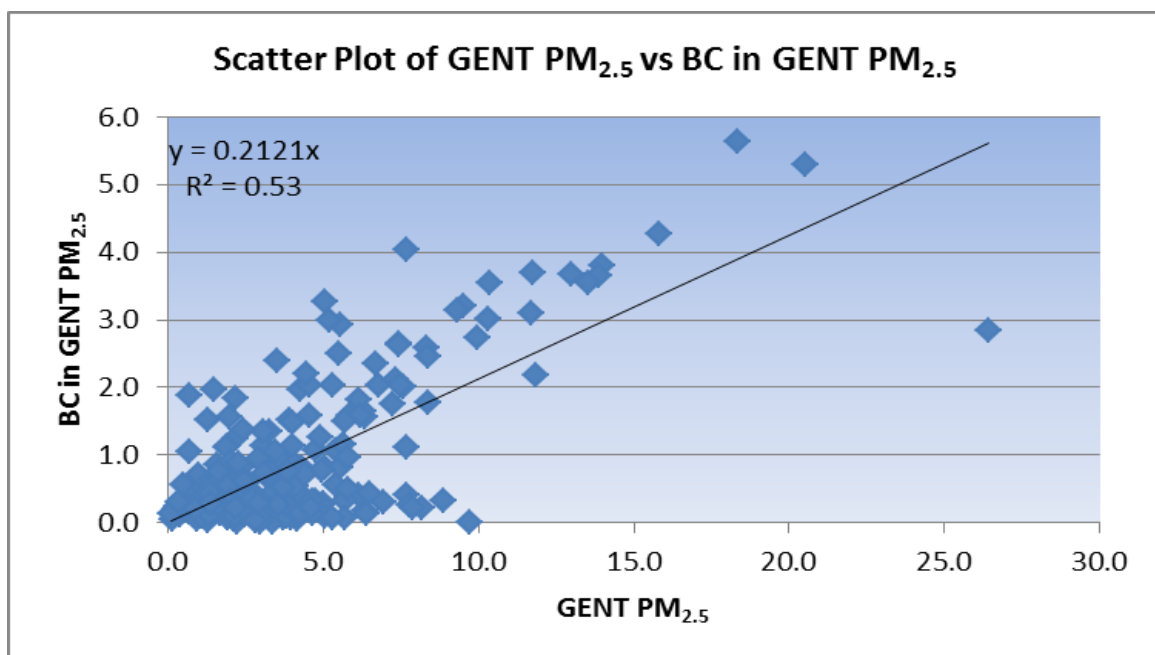
Figure: 4.11   Scatter plot of GENT $PM_{2.5}$ vs BC in GENT $PM_{2.5}$ showing positive correlation.

The above scatter plot of GENT $PM_{2.5}$ vs BC in GENT $PM_{2.5}$ shows a good and positive correlation between the two indicating BC as a major contributor to $PM_{2.5}$ in Wainuiomata air shed.
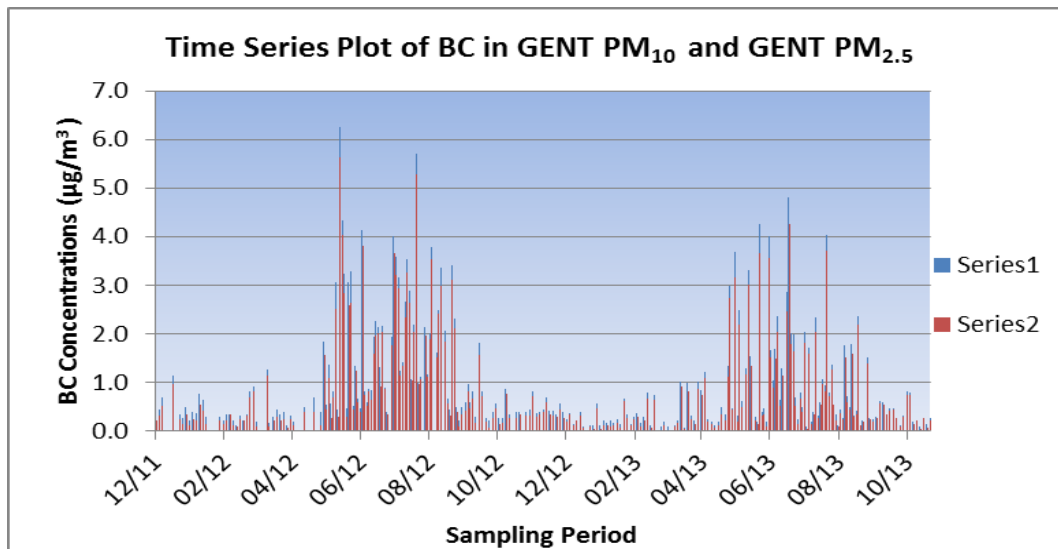
Figure 4.12   Time-Series Plot of BC in GENT PM$_{10}$ (Blue) and BC in Gent PM$_{2.5}$ (Red)

The above graphs show distinct seasonal variations and confirms that there is more BC in GENT PM$_{10}$ than there is in GENT PM$_{2.5}$. The large component of BC in PM$_{10}$ came from BC in PM$_{2.5}$ which is from biomass burning as explained earlier. The Figure 4.12 shows very small difference between GENT PM$_{10}$ (Blue) and GENT PM$_{2.5}$ (Red). This is likely to be due to the GENT sampler cutpoint such that some BC ends up in the coarse fraction. The GENT sampler fine fraction 50% cutpoint was estimated to be around 2.0 to 2.2 μm (Maenhaut & Francois et al. 1993).

The biomass burning source contributions to PM$_{2.5}$ were considered to be primarily due to emissions from domestic solid fuel fires. The peak contributions are highest on cold calm winter days under inversion conditions or with a light southerly winds, particularly during anticyclonic synnoptic conditions (Davy, 2007). Wainuiomata is known to be dominated by northerly and southerly winds with mountain barriers along the east and the western sides as explained in Section 2.6.

It was also found that arsenic was associated with the biomass burning source profile indicating that copper chromium arsenate (CCA) treated timber was being used as a component of fuel in solid fuel fires for domestic heating. It was also stated that more evidence supporting the assumption came from the temporal analysis of arsenic concentrations, which peaked during high pollution days (Davy et al., 2009; Davy et al., 2012). This result emphasises the fact that the NES for PM$_{10}$ alone is not guaranteed to protect the health of exposed populations as other toxic compounds like arsenic may be

present as a component of air pollution that can have adverse health effects in their own right (Davy et al., 2009).

4.4 ARSENIC LEVELS IN AMBIENT AIR

4.4.1 Arsenic Levels by Graphite Furnance Atomic Absorption Spectrometry (GF-AAS)

The arsenic in the ambient air in PM_{10} was measured using quartz filter on a High-Vol sampler, followed by acid digestion (wet chemistry) and analysis by Graphite Furnance Atomic Absorption Spectrometry (a standard methodology) according to EPA 200.9 methodology as described in Section 2.8 of the thesis.

The method was validated against the QC and QA protocols which was consistent throughout the sampling and analytical procedures. The recoveries obtained from certified reference material (CRM) was within the international conventions as described in EURACHEM/ CITAC Guide CG 4, 2000; ISO 5725, 1995.

The ISO 5725 – "Accuracy of Measurement Methods and Results Package", 1995, provides the general principles necessary to accurately assess measurement methods, results, application and pratical estimations.

The results obtained for arsenic (As) in ambient air measured by GF-AAS ranged from <0.5 – 53.2 ng m^{-3} for the entire sampling period.

The **weighted** mean values obtained for As in PM_{10} in ambient air for the entire sampling period was 6.3 ± 0.8 ng m^{-3}. The **weighted** mean values for winter (1:2 day sampling) and non-winter (1:3 day sampling) were: 4.1 ± 0.5 ng m^{-3} and 2.2 ± 0.3 ng m^{-3} respectively. The weighted annual average for the first year (1 Nov, 2011 – 31 Oct, 2012) was **6.5 ± 0.9** ng m^{-3} and **5.9 ± 0.7** ng m^{-3} for the second year (1 Nov, 2012 – 31 Oct, 2013).

It could be seen that the NZAAQG of 5.5 ng m^{-3} had been exceeded in both years of sampling at Wainuiomata.

The **non-weighted** mean values obtained for As in PM_{10} in ambient air for the entire sampling period was 7.1 ± 0.8 ng m^{-3}. The **non-weighted** mean values for winter (1:2 day sampling) and non-winter (1:3 day sampling) were 12.2 ± 1.0 ng m^{-3} and 3.2 ± 0.7 ng m^{-3} respectively.

The purpose of weighted means was to account for the non-uniform sampling frequency during the winter months as stated in Section 3.8.

Winter days were 123/366 and non-winter were 243/366 days in the first year (leap year in 2012) while 123/365 days winter and 242/365 days non-winter receptively in the second year.

Table 3.14 shows that the non-weighted mean concentration of As was 7.5 ± 0.9 ng m^{-3} for all the data, 13.2 ± 1.4 ng m^{-3} for winter (May - August), and 3.2 ± 0.7 ng m^{-3} for non-winter (rest of the months) in the first year (1 Nov, 2011 – 31 Oct, 2012).

For the second year (1 Nov, 2012 – 31 Oct, 2013), the concentration of As was 6.7 ± 0.7 ng m^{-3} for all the data, 11.1 ± 0.6 ng m^{-3} for winter, and 3.2 ± 0.7 ng m^{-3} for non-winter seasons. Figure 4.13 showed strong seasonal and temporal attributions, with high winter As peaks (May – August), at Wainuiomata was due to biomass burning for both years. This confirms that the As source in the Wainuiomata airshed is from copper chromium arsenate (CCA) treated timber which is being used as a component of fuel in solid fuel fires for domestic heating.
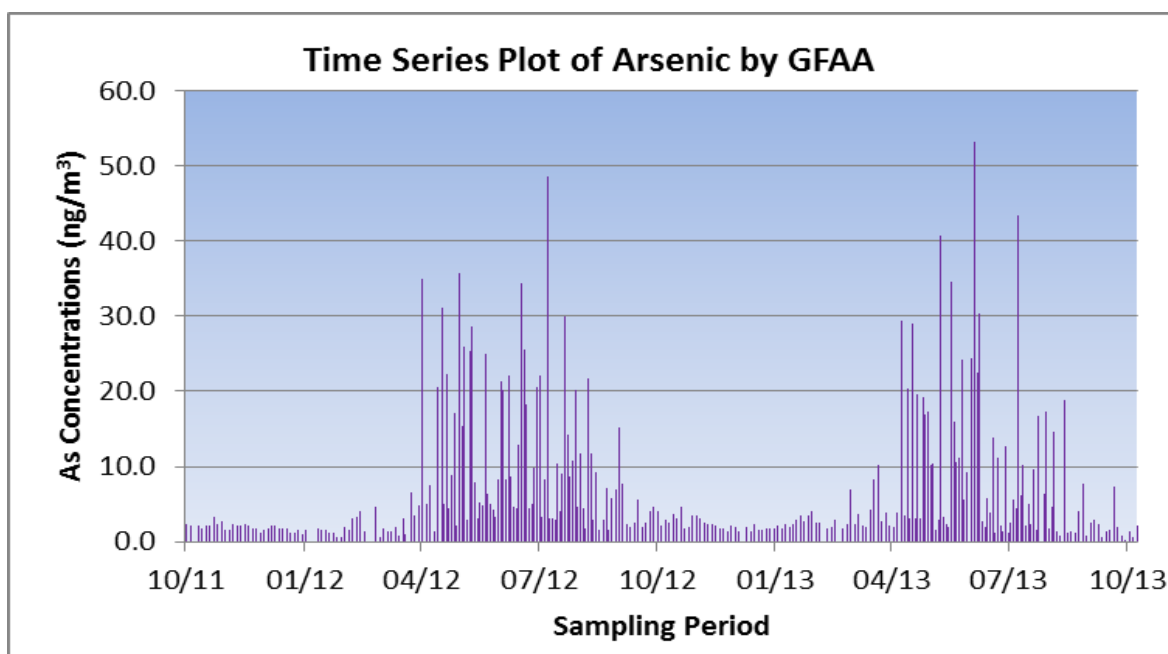
Figure 4.13   Time-Series plots showing elevated levels of Arsenic during winter seasons.

Previous studies have shown that the biomass burning source contributions to $PM_{2.5}$ are considered to be primarily due to emissions from domestic solid fuel fires (Davy et al, 2009) which is strongly correlated to the observed BC measurements.

However, the graph (Figure 4.13) further shows that the As concentrations did not necessarily peak with peak High-Vol BC in PM_{10} measurements (Figure 4.6). This demonstrated that elevated As concentrations were observed only when CCA treated timber had been used as solid fuels in domestic heating.

It had been previously reported by Niyobuhungiro & Blottnitz, 2013 that where CCA-treated timber was burnt by informally operating caterers in Cape Town region, significantly elevated arsenic levels has been found. Moreover, even where this was not directly the case, arsenic was measured at elevated levels, possibly indicative of burning of CCA-treated timber elsewhere or recently in the studied areas.
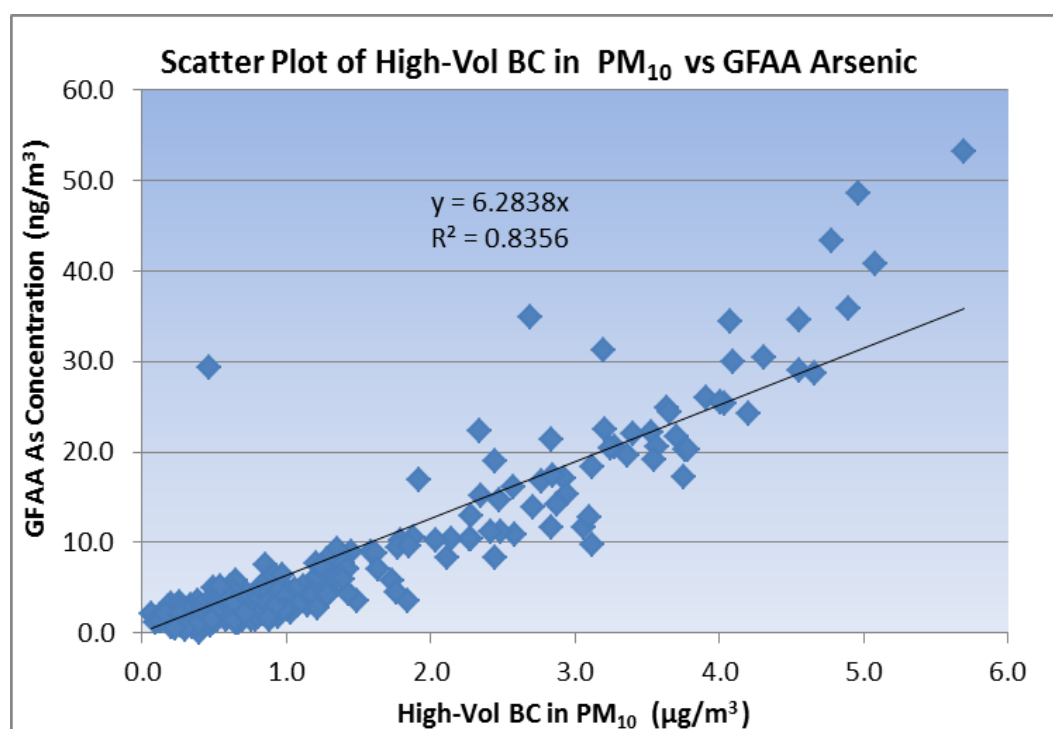
Figure 4.14   Scatter plot of High-Vol BC in PM_{10} against GF-AAS As levels

There is a strong correlation (R^2 = 0.84) between High-Vol BC in PM_{10} with that of the measured As levels by GF-AAS. The scatter (Figure 4.14) supports the observation that elevated As have not always coincided with peak BC levels.

Therefore burning of CCA treated timber has been intermittent and most probably opportunistic. That is, CCA treated timber was only used as and when it was available, for example, offcuts from building activities - it would be too expensive to use treated timber as a primary fuel source. However, sufficient quantities were burnt on a regular basis for arsenic concentrations to be elevated during most of the winter seasons.

New sub-divisions and continual upgrade of decks and fences in Wainuiomata may have produced enough CCA - treated timber in the fuel stream in the recent past and during the monitoring period to account for the elevated arsenic concentrations in the Wainuiomata airshed.

4.4.2   Arsenic levels by X-ray Fluorescence Spectroscopy (XRF)

X-ray fluorescence spectroscopy (XRF) was used to measure elemental concentrations in PM_{10} samples collected on quartz filters obtained from Wainuiomata air shed. The filters were collected for the same period as in this study. 279 filters were collected between 25 October, 2011 – 31 October, 2013. Each filter had 4 by 47 mm punches taken. One punch was for GWRC (to analyse for As levels by ICP-MS- Hills Laboratory). The second punch was for Victoria University of Wellington (VUW- to analyse for As levels by GF-AAS; this research) and the third filter punch was for GNS Sciences (to analyse for elemental concentrations by XRF). The fourth filter was kept as spare filter samples at GNS Science facility.

The XRF measurements were carried out at GNS Science XRF facility and the spectrometer used was a PANalytical Epsilon 5 (PANalytical, Netherlands). The XRF is a non - destructive and rapid method for the elemental analysis of particulate matter samples.

XRF is based on the measurements of characteristic X-rays produced by the ejection of an inner shell electron from an atom in the sample, creating a vacancy in the inner atomic shell. A higher energy electron then drops into the lower energy orbital and releases a fluorescent X-ray to remove excess energy (Watson et al., 1999 and references therein). The energy of the released X-ray is characteristic of the emitting element and the area of the fluorescent X-ray peak (intensity of the peak) is proportional to the number of emitting atoms in the sample. From the intensity it is possible to calculate a specific element's concentration by direct comparison with standards.

To eject inner shell electrons from atoms in asample, XRF spectrometer at GNS Science used a 100kV Sc/W X-ray tube. The 100kV X-rays produced by this tube are able to provide elemental information for elements from sodium – uranium (Na - U). Unlike ion beam analysis (IBA) techniques, which are similar to XRF, PANalytical Epsilon 5 is able to use characteristic "K-lines" produced by each element for quantification. This is crucial for optimising limits of detection because "K – lines" have higher intensities and are located in less crowded regions of the X-ray spectrum.

The X-rays emitted by the sample are detected using a high performance Ge detector, which further improves the detection limits.

At the GNS Science X-ray fluorescence facility, the calibration standards for each of the elements of interest were analysed prior to the samples being run. Once the calibration standards were analysed, spectral deconvolutions were performed using PANalytical software to correct for the line overlaps and ensure that the spectra was accurately fit. Calibration curves for each element of interest were produced and used to determine the elemental concentrations from the Wainuiomata air samples. A NIST reference sample was also analysed to ensure that the results obtained were robust and accurate.

The XRF theory was not stated under methodology section as it was entirely carried out by scientists at GNS Science facility, Gracefield. However the XRF and IBA instrument As data were to be validated against the Standard Method (GF-AAS), as specified under the Aim/ Objective section of this thesis.

The XRF As concentration values ranged from 0 - 59.8 ng m^{-3} for the entire sampling period. The **weighted** mean values for the first year was 4.5 ± 2.3 ng m^{-3} and 3.1 ± 1.7 ng m^{-3} for the second year. The overall **weighted** mean value for the entire sampling period was 3.8 ± 2.0 ng m^{-3}. The overall **weighted** winter As levels were 3.2 ± 1.6 ng m^{-3} while that of the non-winter was 0.6 ± 0.4 ng m^{-3}.

The overall **non-weighted** As concentrations were 4.6 ± 2.4 ng m^{-3} while for winter and non-winter were 9.5 ± 4.6 ng m^{-3} and 1.0 ± 0.7 ng m^{-3} respectively. Table 3.4 gives more details of each year of non-weighted measurements.
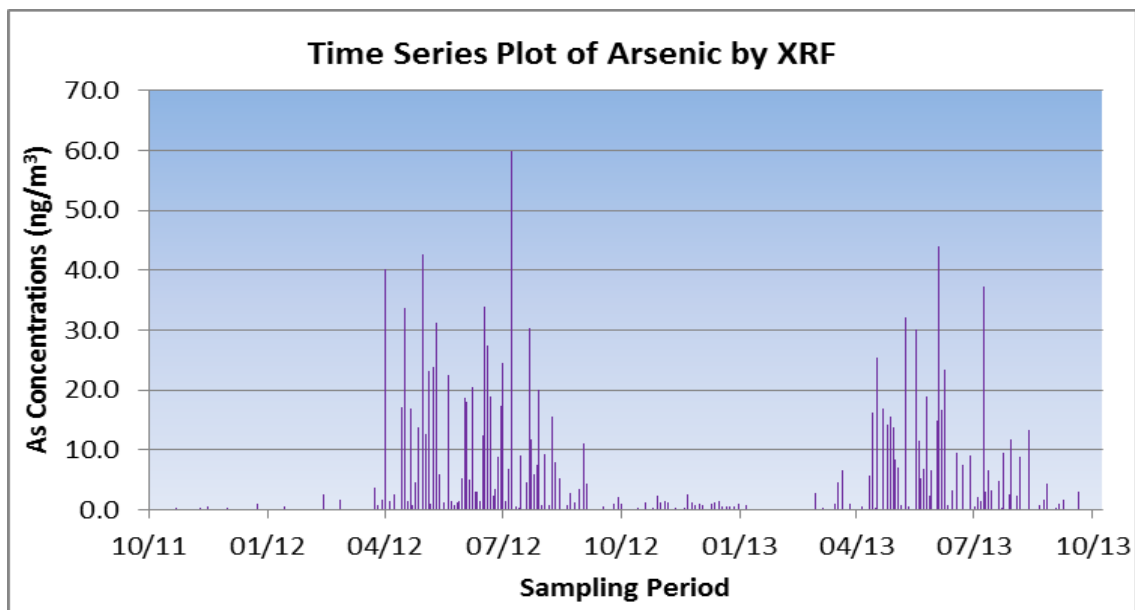
Figure 4.15   Time-Series plot of Arsenic concentrations by XRF

The Time-Series plot of arsenic concentrations by XRF shows distinct seasonal and temporal variations with elevated As levels during the winter seasons (May - August). The trend is similar to the As trends show by the standard method (GF-AAS) as seen in Figure 4.13. However careful assessment of the data and statistical analysis shows that the overall arsenic unweighted concentrations by XRF are consistently lower than those of the standard method (GF-AAS) for both years as well as for the entire sampling period.

This could be due to the penetration ability of the analytical beams into the filter material. The particulate matter has been found to be around 150-200 microns on the quartz fibre filter (Fung et al., 2002), and the analytical beam penetration is approximately 100-150 microns with the filter thickness to be approximately 500 microns.
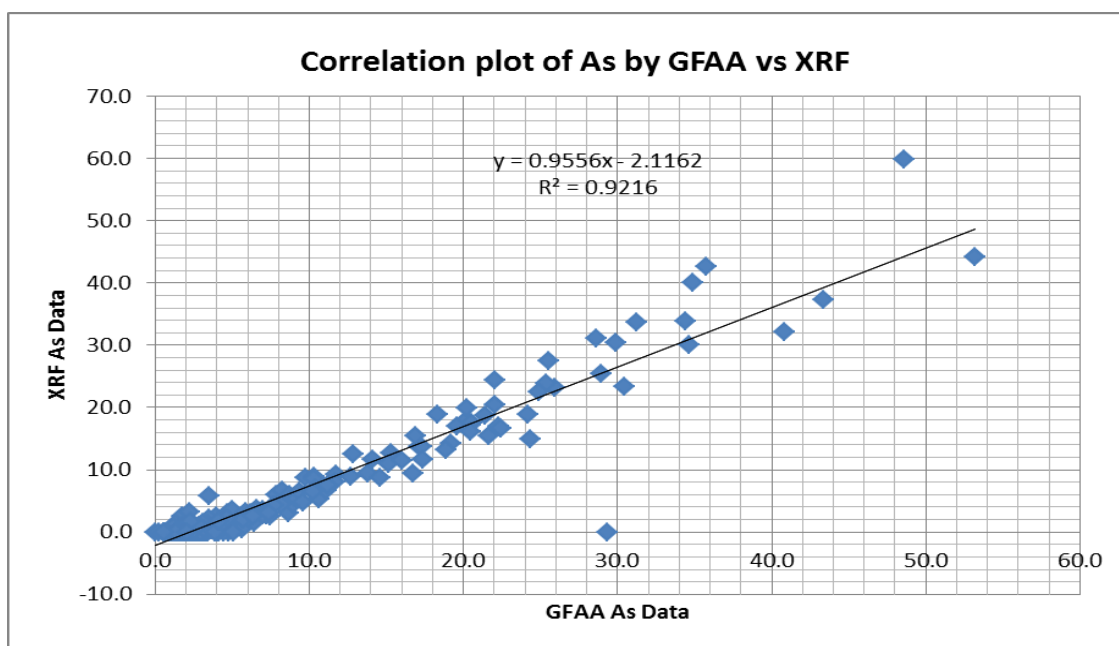
Figure 4.16   Correlation between the GF-AAS and the XRF arsenic data

Apart from few outliers in the graph, the overall arseinc data showed very good correlation between the two methods, GF-AAS and the XRF respectively.

The analysis of copper (Cu) and chromium (Cr) by XRF showed that overall non-weighted Cu concentration was 1.5 ng m^{-3} while that of Cr was 0.5 ng m^{-3}.

An analysis by Helsen and co-workers suggests both +3 and +4 oxide states of As were released and that low temperature pyrolysis (<327 °C) may retain arsenic in the ash (Helsen and van den Bulck, 2003). It has also been shown that the copper and chromium components are preferentially retained in the ash during combustion of CCA - treated timber (Davy et al., 2010a). The disposal of ash in vegetable gardens or disposed in the grounds can therefore add more problems as these heavy metals may find its way through the food chain or leach into nearby creeks or drains after heavy rain, posing risk to marine aquatic life.

Residual ash from the burning of CCA-treated timber, if not appropriately disposed of, presents a risk if inadvertently ingested due to its potentially elevated arsenic levels. It is not an uncommon practice to put wood burner ash on the garden as a soil conditioner or

fertilizer for lawns, vegetables and flowers (http://www.nzwomansweekly.co.nz/health-home/gardeni ng/ways-for-using-wood-ash-in-the-garden/).

Furthermore the ash, containing As can be accidently ingested by children under the age of 6 playing outdoors if not properly disposed or left in buckets or containers to cool off before they can be emptied into rubbish bins as reported by Mitchell, 2015.

4.4.3   Arsenic levels by Ion-Beam Analysis (IBA)

The Ion Beam Analysis (IBA) was used to measure the concentrations of elements with atomic number above neon (Ne) in the particulate matter collected. IBA measurements taken for the samples from Wainuiomata airshed for this study were carried out by the Institute of Geological and Nuclear Sciences (GNS) in Gracefield, Lower Hutt (Trompetter et al., 2005). The full suite of analysis included Particle-Induced X-Ray Emission (PIXE), Particle-Induced Gamma-Ray Emission (PIGE), Rutherford Backscattering (RBC) and Particle Elastic Scattering Analysis (PESA) (Davy et al., 2012).

The IBA has been widely used for receptor modelling and source apportionment of PM mass by PMF using the PMF2 program (Paatero, 1997). The elemental composition of the source profile and average contributions from each source to overall $PM_{2.5}$ concentrations in the Wainuiomata air shed has been extensively reported in earlier studies (Davy et al., 2009; Davy et al., 2012).

It was during this study that Davy and co-authors, 2009, concluded out that, surprisingly arsenic in the samples was found to be associated with biomass burning, suggesting that residents were using CCA - treated timber for domestic heating. This was based on the evidence that temporal analysis of arsenic concentrations, which peaked during high pollution days.

However, the IBA results had certain limitations since the limit of detection (LOD) for IBA arsenic is about 10 -20 ng m^{-3} which is about 3-4 folds more than the NZAAQG value of 5.5 ng m^{-3}. Hence there was a need of arsenic analysis in Wainuiomata air shed by a standard methodology or equivalent giving rise to the current research.

The IBA As, concentration values ranged from 0 – 48.5 ng m^{-3} for the entire sampling period. The **weighted** mean value for the first year was 3.3 ± 6.1 ng m^{-3} and 2.7 ± 5.7 ng m^{-3} for the

second year. The overall **weighted** mean value for the entire sampling period was 3.1 ± 5.9 ng/m^3. The overall **weighted** winter As levels were 2.2 ± 2.1 ng/m^3 while that of the non-winter was 0.8 ± 3.8 ng/m^3.

The overall **non-weighted** IBA As concentration was 3.7 ± 6.0 ng m^{-3} while for winter and non-winter were 6.5 ± 6.4 ng m^{-3} and 1.3 ± 5.7 ng m^{-3} respectively. Table 3.14, gives the details of each year of weighted and non-weighted arsenic measurements during the sampling period.
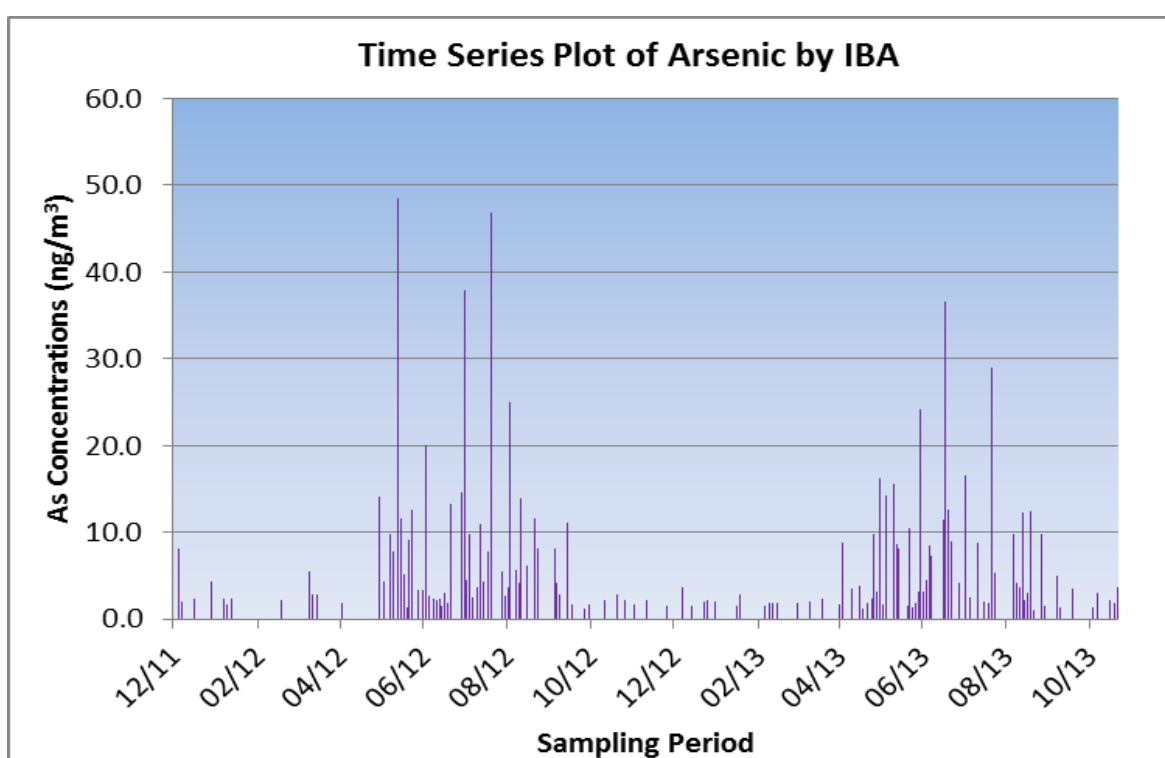
Figure 4.17   Time-Series plot of arsenic concentrations by IBA

The IBA As data shows fewer peak arsenic concentrations than GF-AAS and XRF, however there is a distinct seasonal and temporal variations observed with the peak As during the winter seasons from May-August. The gaps were due to the missing values as explained earlier.

4.5 METHOD COMPARISON AND VALIDATION

One of the main objectives of the entire research was method development and method validation. The GF-AAS method was validated against the certified reference material (CRM), blank analysis and spiked recoveries of the CRM and duplicate samples, all of which were within the given international guidelines.

The GF-AA data was then used to validate the results of IBA (current and previous data), and also to validate the As results of the new instrument, XRF.
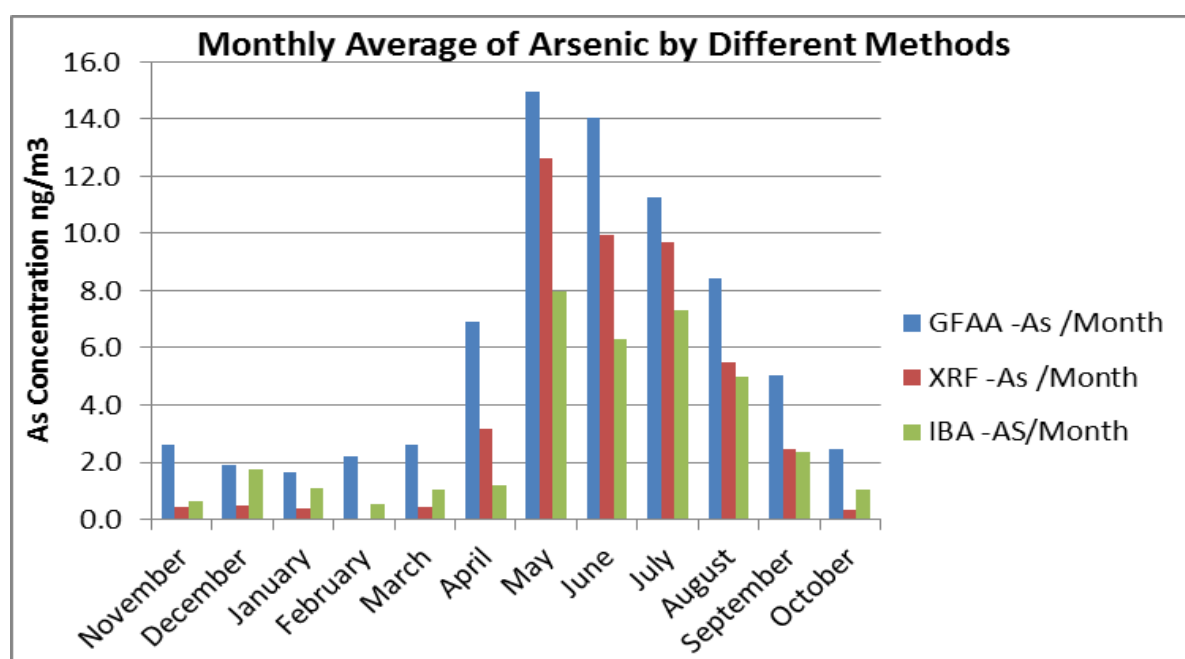
Figure 4.18   Mean arsenic variations during each month by the three methods, GF-AAS,XRF and IBA

The graphical representation in Figure 4.18 gave clear indication that the GF-AAS had consistently been measuring greater As concentrations in ambient air compared to the XRF and IBA. The XRF As data is also consistently higher than that measured by IBA.

However, all the methods showed the same seasonal and temporal variations which was consistent with the Time-Series plots of the individual methods, i.e. the elevated As levels are observed during the winter seasons (May-August) for this sampling period suggesting its source from CCA-treated timber being used as solid fuels in domestic heating.

4.5.1 Statistical analysis –Analysis of Variance (ANOVA)

A comprehensive ANOVA test was performed using one-way ANOVA and two-way ANOVA with replication, for each of the methods and then the combined methods to study the

variations between each source. The nulls hypotheses was that all the methods are sampling the As in ambient air from the same population and the alternate hypotheses was that they are not sampling As in ambient air from the same population. The results of one-way ANOVA is shown below.

The results show that in all the cases, the $F < F_{critical}$ which confirms the null hypotheses that all the methods are sampling As from the same population. The p value is also small therefore the probability of the alternate hypotheses to be true is less.

For the purpose of the two-way ANOVA equal number of sampling days were considered for each method (eg. 120 days for both winters). The two-way ANOVA for both winters against all the methods shows good correlation between samples with P-value = 0.04. However, the $F > F_{critical}$ showing that the columns (methods) are not significantly correlated, or there is a large variation between them. The single factor ANOVA between all data (247) and all methods showed clear variation between the methods as the $F > F_{critical}$.

However, ANOVA statistical package on its own was not sufficient as it did not provide any information on the "Limits of Agreement" and the biasness of the three methods as all the three methods showed good correlation between them.
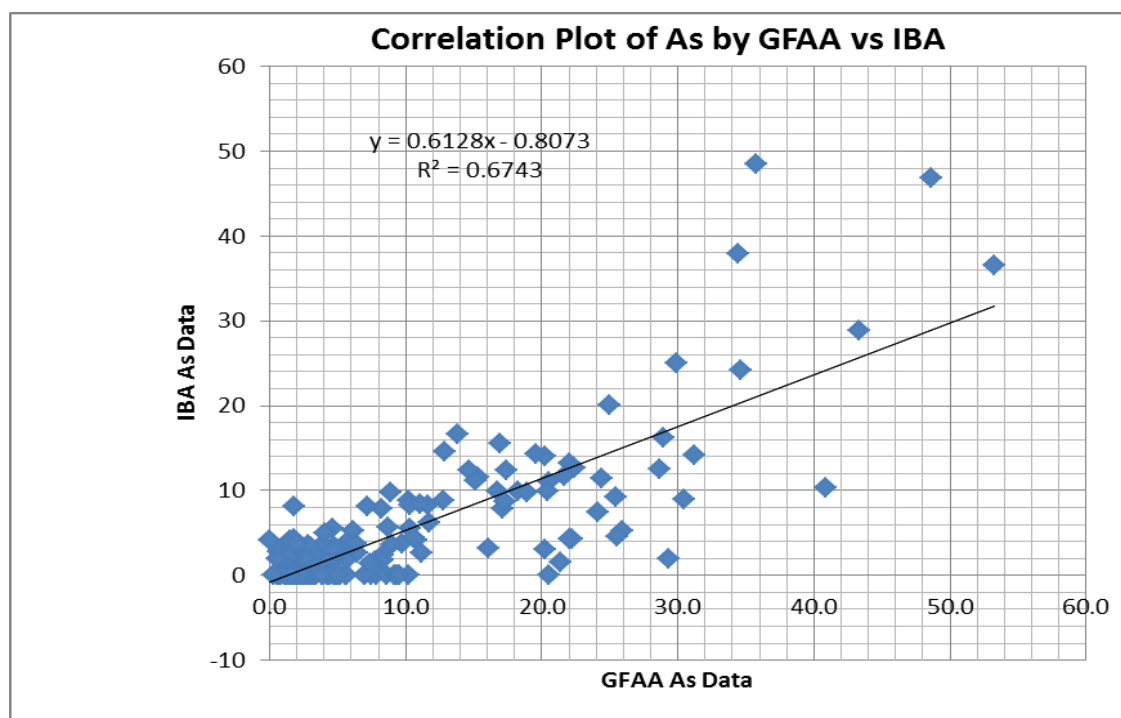
Figure 4.19   Correlation between the GF-AAS and the IBA arsenic data

IBA vs Both Years

Anova: Single Factor
SUMMARY

Groups	Count	Sum	Average	Variance
2011-2012	110	482.7	4.4	68.0
2012-2013	137	429.3	3.1	31.4

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	96.0	1	96.0	2.0	0.2	3.9
Within Groups	11675.8	245	47.7			
Total	11771.8	246				

XRF vs Both Years

Anova: Single Factor
SUMMARY

Groups	Count	Sum	Average	Variance
2011-2012	139	763.5	5.5	104.4
2012-2013	137	525.3	3.8	57.8

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	189.8	1	189.8	2.3	0.1	3.9
Within Groups	22266.7	274	81.3			
Total	22456.4	275				

GF-AAS vs Both Years

Anova: Single Factor
SUMMARY

Groups	Count	Sum	Average	Variance
2011- 2012	139	1048.2	7.5	81.8
2012 - 2013	137	911.9	6.7	83.1

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	54.0	1	54.0	0.7	0.4	3.9
Within Groups	22600.21	274	82.5			
Total	22654.2	275				

Table 4.1   Single factor ANOVA results

4.5.2   Bland- Altman Method Comparision

The correlation coefficient (*r*) has been widely used in statistical analysis to see if the two methods are linearly related. The correlation coefficient measures the strength of a relation between two variables, not the agreement between them. Data which seem to be poor in agreement can produce quite high correlations (Bland & Altman, 1999).

The Bland-Altman plot (Bland & Altman, 1986, 1999), or difference plot, is a graphical method to compare two measurements technique. In this graphical method the differences (or alternatively the ratios) between the two techniques are plotted against the averages of the two techniques. Alternatively, the differences can be plotted against one of the two methods, if this method is a reference or "gold standard" method.

Horizontal lines are drawn at the mean difference, and at the limits of agreement, which are defined as the mean difference plus and minus 1.96 times the standard deviation of the differences. If the differences within mean ± 1.96 SD are not analytically important, the two methods may be used interchangeably or the new method may replace the old method.

The plot is useful to reveal a relationship between the differences and the averages, to look for any systematic biases and to identify possible outliers.

The terminology accuracy and precision are often inconsistently used in literature, and are often used when "bias" and "repeatability" are the properties being assessed (Hanneman, 2008).

Accuracy is the degree to which an instrument measures the real value of a variable and is assessed by comparing the measurement method with a gold standard that has been calibrated to be highly accurate. However in method comparision study, the investigator is comparing a less established method with an established one. The difference in values obtained with the two methods represents the "bias" of the less established method relative to the more established method (Hanneman, 2008).

Precision is defined in two ways:

- The degree to which the same method produces the same results on repeated measurements and,

- The degree to which the values cluster around the mean of the distribution of values.

The first definition equates with "repeatability" while second defines the range within which a value from the population is likely to fall. The repeatabilty in a method-comparison is necessary, but insufficient, condition for agreement between the methods. If one or both methods do not give repeatable results, assessment of agreement between the methods is meaningless.

4.5.2.1 Measuring Agreement, Precision and Repeatability

It is most unlikely that the different methods will agree exactly, by giving identical result for all individuals. The important factor is by how much, the new method is likely to differ from the standard method. A difference plot between the methods against their mean would be more informative and allows the investigator to investigate any possible relationship between the measurement error and true value. The true value is not known in atmospheric measurements, therefore the mean of the two measurement is the best estimate that is available. For this reason, the difference plot is not plotted against either values as the difference will be related to each, a well known statistical artefact (Bland & Altman, 1999).

The biasness is calculated by the mean difference, d, and the standard deviation of the difference(s). Provided the differences are within d ± 1.96 s (95% confidence intervals), and analytically not important, the two methods can be used interchangably. These are known as "limits of agreement".

The limits of agreement are only estimates of the values which may apply to the whole population. A second sample would give different limits, therefore standard errors and confidence intervals are used to see how precise our estimates were. For the purpose of this study, the standard errors were calculated using the **Analyse-it** software instead of using mathematical tables.

The repeatability is relevant to the study of method comparison, because the repeatabilities of the two methods of measurement limit the amount of agreement which is possible. If there is considerable variation in repeated measurements on the same subject, the agreement between the two methods is bound to be poor too.

It is therefore seen that in the analysis of measurement method comparison data, neither the correlation coefficient nor techniques such as regression analysis are appropriate (Bland & Altman, 1983), hence the Bland-Altman (difference) plots replaced the above misleading analyses and are easy to plot and interpret.

The Analyse-it software which is compatable with excel, 2010 and 2013, had been used to create the Bland-Altamn plots, limits of agreements, standard error and other statistical analyses associated with it as shown in Figures 4.20 and 4.21.
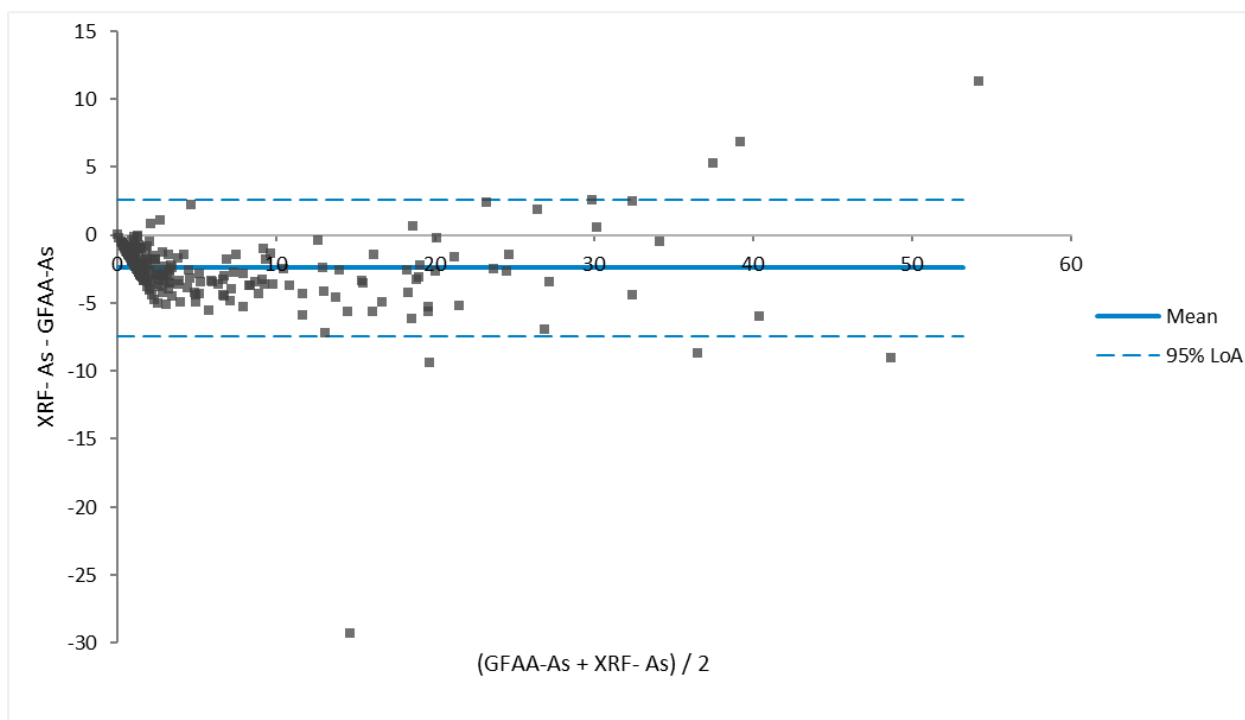
n	279	
Method	Measuring interval	
GF-AAS-As	0.0	53.2
XRF- As	0.0	59.8
Correlation - r	0.96	

Parameter	Estimate	95% CI		SE
Mean difference	-2.4	-2.7	-2.1	0.15
95% Lower LoA	-7.4	-7.9	-6.9	0.26
95% Upper LoA	2.6	2.1	3.1	0.26
SD	2.6			

Figure 4.20   Bland-Altman Plots of GF-AAS (As) vs XRF (As)
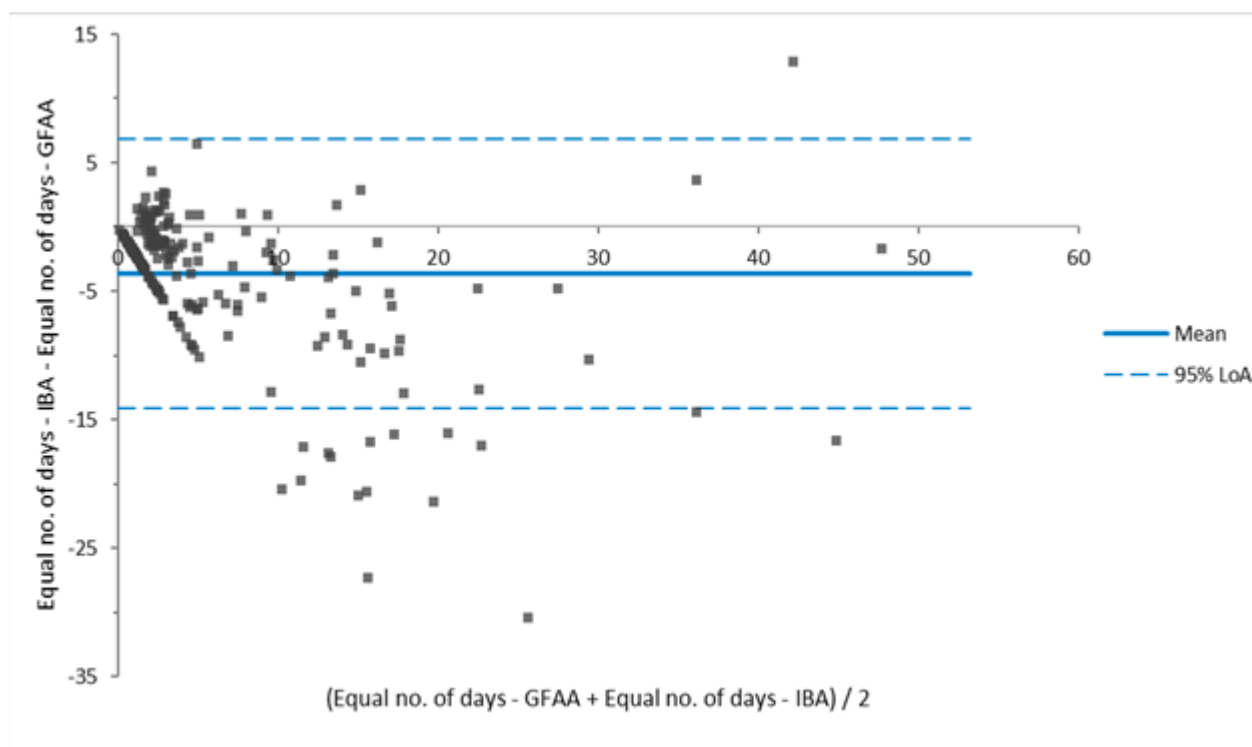
n	247	
Method	Measuring interval	
Equal no. of days - GFAA	0.0	53.2
Equal no. of days - IBA	0.0	48.5
Correlation - r	0.82	

Fit Differences:				
Parameter	Estimate	95% CI		SE
Mean difference	-3.7	-4.3	-3.0	0.34
95% Lower LoA	-14.1	-15.3	-13.0	0.58
95% Upper LoA	6.8	5.7	8.0	0.58
SD	5.3			

Figure 4.21   Bland-Altman Plots of GF-AAS (As) vs IBA ((As)

Scatter plot in Figure 4.16 shows an excellent correlation between arsenic measured by GF-AAS and that of the XRF methods (correlation coefficient of 0.92). However as mentioned earlier, the correlation coefficient itself is not sufficient to measure the agreements or the bias between the methods.

The difference plot in Figure 4.20 shows that the arsenic determined by XRF method actually is measuring 2.4 ng m^{-3} of As below the mean As value obtained by GF-AAS for the entire sampling period (279 filter samples). This is termed as the bias between the two methods.

The 95% confidence intervals are -7.4 ng m^{-3} to 2.6 ng m^{-3} (Confidence limit = 10.0 ng m^{-3}). This means that XRF method measured 2.4 ± 5.0 ng m^{-3} (95% confidence level), below the GF-AAS method. For analytical chemistry and determination of arsenic in the ambient air to check for the compliance with NZAAQG, this difference is not acceptable as the NZAAQG itself is 5.5 ng m^{-3}.

Scatter plot in Figure 4.19 showed good correlation between arsenic measured by GF-AAS and that of the IBA methods (correlation coefficient of 0.67).

The difference plot in Figure 4.21 showed that the arsenic determined by IBA method actually was measuring 3.7 ng m^{-3} of As below the mean As value obtained by GF-AAS for the entire sampling period (247 filter samples).

The 95% confidence intervals are -14.1 ng m^{-3} to 6.8 ng m^{-3} (Confidence limit = 20.9 ng m^{-3}). This meant that IBA method measured 3.7 ± 10.5 ng m^{-3} (95% confidence level), below the GF-AAS method. Again the IBA method is not acceptable given the large mean difference and the associated confidence limit between the methods. The IBA data has detection limit of about 10 - 20 ng m^{-3} as explained earlier, of As in ambient air which is almost three folds of the NZAAQ guidelines, hence not acceptable method to determine levels of arsenic in ambient air.

However, given the clear and distinct seasonal and temporal variation in As levels in ambient air by IBA techniques, it is recommended by this research, that the IBA data can be used as a "screening" process in the determination of As in air particulate matter. If As is detected on a regular basis in any analysis by IBA, then further analysis by a standard method is required to determine if the NZAAQ guidelines are met.

The XRF data has shown little statistical difference with the standard method (GF-AAS) compared to the IBA data. This may be due to the fact that APM has been around 150-200 microns on the quartz fibre filter (Fung et al., 2002), and the analytical beam penetration is approximately 100-150 microns with the filter thickness to be approximately 500 microns. This means that the analytical beams may have not reached to all the APM on the quartz filter.

The standard senstive wet chemistry based methodologies, GF-AAS and ICP-MS even though have showed very small detection limits, and arsenic levels detected with absolute accuracy and precision, these methods are labour intensive and requires extensive time to go through the digestion processes. The methods also employ expensive sample pre-treatment/ analysis, and well qualified operators. Besides sample pre-treatment may also cause contamination of the samples, even when maximum attention is taken (Yatkin et al., 2011).

As a result many researchers explore alternative analytical techniques that shows equivalence to reference methods (GF-AAS and ICP-MS) and can be demonstrated following the "Guide to the Demonstration of Equivalence of Ambient Air Monitoring Method".

XRF is one of those instruments which is faster and cheaper than ICP-MS and GF-AAS because it does not need any sample pre-treatment. Conversely to GF-AAS and ICP-MS, X-ray based techniques does not involve destruction of the samples being analysed. This is a major advantage that makes further determination of ions, organics and carbon still possible, which is essential for receptor modelling (Yatkin et al., 2011). At GNS Science XRF facility in Lower Hutt, the XRF is used extensively as there are large quantities of samples being analysed for PM_{10} and multi-elemental analysis.

The standard methods can not be replaced totally but XRF can be used as an alternative for long term monitoring and arsenic trends in air particulate matter.

The current study shows that the two methods (XRF and GF-AAS) can not be used interchangeably given that quartz filters had been used and standard methods (GF-AAS or ICP-MS) are required to check for the NZAAQ guidelines as mentioned above.

However research shows that XRF can produce almost equivalent detection limits to reference methods with the use of teflon filters, and the coefficient of determination were

higher with teflon filters than with quartz filters due to its high penetration ability of the analytical beams (Yatkin et al., 2011).

The minimum x-ray penetration depth for 4KV was estimated to be 0.77 μm. This figure exceeds the maximum PM thickness on Teflon filter of 0.22 μm calculated assuming 2 gcm^{-3} of density. Thus, the x-rays could reach and excite all particles deposited on filters (Yatkin et al., 2011).

Surprisingly the XRF data for elemental analysis for the Wainuiomata air shed has shown elevated levels of lead (Pb) in the APM. Following the phasing out of leaded petrol in 1996, ambient lead concentrations in urban areas have dropped away to background levels though there can be localised effects from the removal of old leaded paint from structures (MfE, 2002). Lead associated with particulate matter will occur in locations where wood that has been painted with leaded paint is used as fuel in fires.

The NZAAQG for lead in PM_{10} is 0.2 μg m^{-3} (200 ng m^{-3}) (3 month moving average, calculated monthly) with the recommended determination of lead by PM_{10} sampling in accordance with 40 CFR Part 50, Appendix J (i.e High-Volume sampling), followed by analysis using atomic absorption spectroscopy or an equivalent method.

The overall sampling period shows an average value of 18.1 ± 15 ng m^{-3}, while for winter and non-winter to be 34 ± 26.1 ng m^{-3} and 6.1 ± 6.7 ng m^{-3} respectively. The NZAAQ guidelines for Pb is not exceeded in this case.
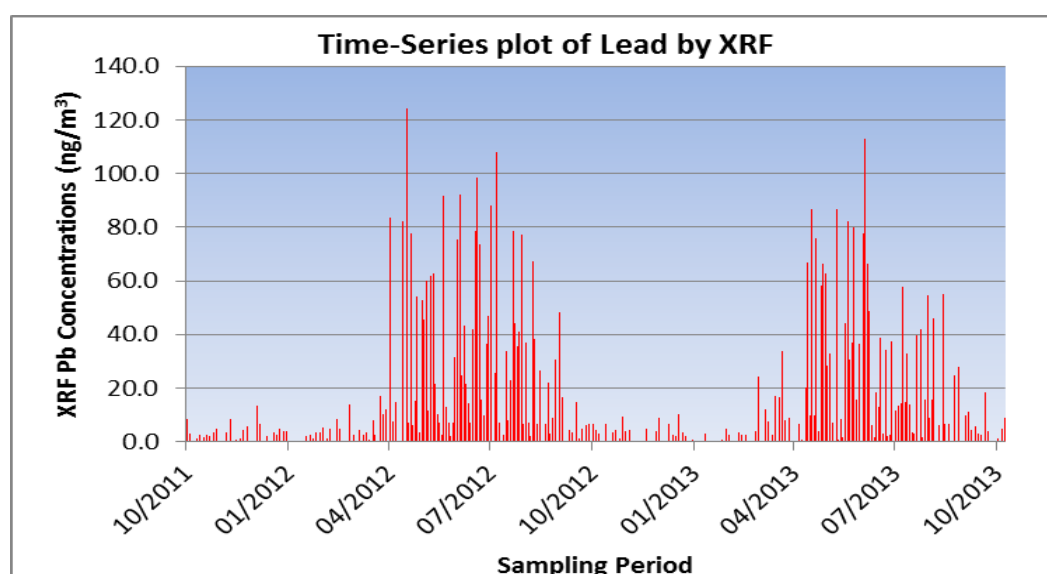
Figure 4.22   Time series for lead concentrations at Wainuiomata

However, given the distinct winter seasonal and temporal variations, it is quite evident that the lead is also originating from combustion sources related to domestic heating using painted timber.

This forms the basis for further investigation of lead in PM_{10} in ambient air by standard method to check against the compliance with NZAAQG values.

Lead remains an important environmental health issue because exposure to high levels has been associated with serious health effects, including neurological impairments such as seizures, mental retardation, and behavioural disorders (CDC, 2009; USEPA, 2006). Even at low doses, lead exposure can have adverse effects on the nervous systems of foetuses and young children (USEPA, 2006).

People can be exposed to lead by inhaling airborne particles that contain lead, drinking contaminated water, eating contaminated food items, or ingesting non-food items that contain lead, such as dust and paint chips.

It is quite evident that people may be burning any wood or timber available to them for domestic heating purposes, whether treated or untreated, painted or unpainted, natural or processed. The problem is therefore one of education and enforcement by the relevant authorities. Immediate action is required to reduce the levels of arsenic and lead in ambient air to meet the requirements set according to the NZAAQ guidelines.

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The monitoring results were split into two 12-month periods, November to October inclusive, so that two consecutive annual averages could be calculated for comparison with the New Zealand ambient air quality guideline (NZAAQG) value of 5.5 ng m^{-3} (MfE, 2002).

Annual averages used to assess compliance with the guideline were calculated using excel, 2010 program and simple statistical tools, to take into account non-uniform monitoring frequency. Shown in Table 3.14, the details of weighted and non-weighted As averages for the overall sampling period, first year (November 2011- October 2012) and second year (November, 2012- October 2013), by all the methods; GF-AAS, IBA, and XRF.

It also shows the weighted and non-weighted winter and non-winter values. The number of sampling days for winter in first year was 123/366 and non-winter was 243/366 days with 2012 being a leap year. For the second year, winter was again 123/365 and non-winter was 242/365 days. The weighted values were calculated based on the ratio of the number of days for winter and non-winter respectively.

The weighted annual As averages for the consecutive 12-month monitoring periods for each year using GF-AAS were 6.5 ± 0.8 ng m^{-3} and 5.9 ± 0.7 ng m^{-3} respectively. For XRF, the weighted annual As averages were 4.5 ± 2.3 ng m^{-3} and 3.1 ± 1.7 ng m^{-3} and that by IBA was 3.3 ± 6.1 ng m^{-3} and 2.7 ± 5.7 ng m^{-3}.

According to the GF-AAS (standard method) NZAAQ annual average guideline were not met in both the years. The XRF and IBA data did not show the same trend as it consistently measured below the standard method, hence they cannot be used to compare with the NZAAQ guidelines.

Input values for the health risk assessment can be taken as 6.3 ± 0.8 ng m^{-3} to represent the long term average outdoor concentration, and 12.2 ng m^{-3} to represent the shorter term winter outdoor concentration for the entire sampling period. For this study, the health risk assessment was not conducted.

The ANOVA results show that there were no statistical difference between the sampling years and that all the methods were sampling from the same population as the $F < F_{critical}$ in all the cases. However, there was significant difference observed with the different methods.

Tables 3.6 - 3.14 shows the inter-annual, inter-seasonal and overall variations in arsenic, PM_{10}, $PM_{2.5}$ and BC concentrations for the two monitoring years by different instruments. Shown in Table 3.9 is the overall, seasonal lead (Pb), chromium (Cr) and copper (Cu) variations in the ambient air during the sampling period as measured by XRF instrument.

Annual non-weighted mean PM_{10} concentrations (High-Vol PM_{10}) for the two monitoring years were **10.9 µg m^{-3}** for the first year and **10.7 µg m^{-3}** for the second year. Hence the PM_{10} concentrations were almost the same for both the years with no significant difference between them. This is well within the national ambient air quality guideline PM_{10} annual average value of 20 µg m^{-3} (MfE, 2002).

For air quality management purposes the contribution of the various sources to peak PM_{10} events is of most interest. Therefore all PM_{10} concentrations over 33 µg m^{-3} (the Ministry for the Environment 'Alert' level as discussed in Table 3.1) had been noted. For the entire sampling period, only exceedance (33.3 µg m^{-3}) was recorded on 28 July, 2012 on High-Vol quartz filter.

When compared to previous study of air particulate matter in the Wainuiomata airshed (Davy et al., 2009), the PM_{10} levels have decreased significantly over the years, with very few exceedances (24 hr averages) noted against the NZAAQG values compared to what was reported by Davy et al., 2009.

$PM_{2.5}$ data were only available for GENT filters (fine) so an annual average was calculated based on that (only 247 samples were obtained for GENT filters as the sampling started on 9 December, 2011 and there were missing data due to attrition and void samples).

The $PM_{2.5}$ annual average for the first year was at 4.2 µg m^{-3} and 4.0 µg m^{-3} for the second year, which was well within the World Health Organization (WHO) annual guideline value of 10 µg m^{-3} for $PM_{2.5}$ (WHO, 2006). Daily $PM_{2.5}$ concentrations were higher than the WHO guideline threshold of 25 µg m^{-3} on one day in the first year and none for the second year as measured by GENT fine polycarbonate filters.

Compliance with the WHO 24-hour average guideline for $PM_{2.5}$ is based on no more than three exceedance days per year. In this case the guidelines were met. However, it is still an area of concern for relevant authorities, as BAM $PM_{2.5}$ data shows that there had been several exceedances of the guidelines in the two monitoring years (Mitchell, 2015).

The annual average values for High-Vol BC in PM_{10} were 1.3 μg m^{-3}, for the first year and 1.2 μg m^{-3} in the second year of monitoring. There are no regulatory guidelines for black carbon, but there a distinct seasonal trend which is associated with biomass burning.

Mitchell, 2015 has reported that the point estimates of annual average arsenic concentration quantifies the potential random sampling error associated with not capturing measurements for all the 24-hour periods over the monitoring period. If the different days for sampling were taken, then the resulting mean might have been different. The 95% confidence interval represents the range of possible means that could be obtained 95 times out of 100 times based on that particular sample size.

She has further reported the two other main areas of uncertainty in the estimation of the mean that have not been taken into account: heterogeneity in arsenic concentrations across the airshed and instrument (ICP-MS) measurement error.

For the analysis by GF-AAS, in this study, the instrument uncertainty was calculated based on the percentage relative standard deviation (% RSD) of the replicates of each of the samples.

The mean arsenic and its associated confidence interval represent only outdoor air at the monitoring site. There is no information on spatial variability of arsenic in other parts of the airshed. The estimation of the bulk property from a small sample gives rise to the heterogeneity in the sampling (EURACHEM/CITAC Guide CG4 (QUAM) 2000). However, the monitoring station is thought to be broadly representative of the wider airshed and as the station is located at the valley exit it is likely to be influenced by drainage of polluted air from other parts of the valley (Mitchell, 2015).

Measurement error refers to the ability of the monitoring instrument to accurately and precisely measure the contaminant of interest. Accuracy, in terms of whether the instrument is measuring the 'true' quantity of particulate, as defined by the standard reference method, was achieved through appropriate instrument operation and calibration.

Instrument precision, that is, how repeatable the measurements were, was not assessed in this work as this would have required co-location of duplicate instruments which were not available.

There is no suitable standard reference material (SRM) available for determining the concentration of arsenic in ambient air on quartz filter matrix to check for the method bias. The SRM available were not on quartz filter membrane matrix. Attempts to obtain the closest SRM for arsenic in ambient air from NIST proved futile.

Analytical validation of the GF-AAS methodology was dependent on all the quality control, quality assurance (QC/QA) protocols and quantitative treatment of the combined uncertainties in the sampling and the analytical procedures.

The standard uncertainties associated with the individual input parameters, such as measurements of the filters, sampling volumes, volumetric apparatus & equipment, and instrumentation, was all combined using the law of propagation of uncertainties (EURACHEM/CITAC Guide CG4 (QUAM), 2000).

Analysis of reagent blank audit showed if there was any contamination from the extraction process with variations accepted to be within instrument detection limit (IDL) of 1.4 µg L^{-1}. The value obtained was 1.6 ± 1.1 µg L^{-1}.

Analysis of lab blank filter (unexposed), was not to exceed the average ± 2SD of the previous lot of blank analysis and within the difference of the IDL. The average lab blank was calculated to be 1.6 ± 0.9 µg L^{-1}. All the blank audits had produced consistent results.

Analysis of duplicate filter audit was to be within the difference of the IDL or 10% relative percent difference. The relative % difference was calculated by the absolute difference of the two values divided by the average of the two values times 100%. The relative percentage difference of the duplicate analysis was obtained as 3.1%. Therefore 96.9% data obtained was almost equivalent between the analyses of duplicate samples.

The data included estimates of reproducibility standard deviation to estimate the bias based on certified reference material (CRM - arsenic standard) studies by method of standard additions. The analyses of the standard addition recoveries of the CRM (spiked As standards) were to be within 95% confidence limits.

The use of Teflon based air tight pressurised digestion vessels proved worthwhile as the loss of analytes were minimised during the digestion process in electric pressure cooker system. It also enabled us to carry out 9 sample digestions at once enabling faster acid digestion process (as compared to open beaker, hot plate digestion processes). The cross contamination was also minimised by acid rinsing the Teflon digestion vessels after each digestion, followed by rinsing with RO water as provided and oven drying. All the glassware used was treated in similar manner.

All the QC/QA protocols were as per the "Standard Operating Procedure for the determination of arsenic in suspended particulate matter collected from ambient air as measured by Graphite Furnace Atomic Absorption" (USEPA, 1988).

For the purpose of method validation, all the QC/QA protocols employed were met within the stipulated guidelines of (AOAC/ IUPAC protocol [H.9], 1995) or (ISO 5725 standard [H.10], 1994).

The CRM standard additions technique gave excellent recoveries of 99.2 ± 0.8% for duplicate spiked analysis and 102.7 ± 0.9% for lab blank filter spiked analysis. This makes the analytical method highly reproducible and for accurate and precise determination of arsenic in ambient air by GF-AAS.

Time-Series plots of 24-hour averages for arsenic, PM_{10}, $PM_{2.5}$, black carbon was presented in Figures 4.2 to 4.18, which shows clear and distinct winter peaks between the months of May- August, where sampling frequency was increased to 1:2 days. Analysis of lead by XRF showed similar trends as shown in Figure 4.22.

Arsenic measurements were strongly seasonal, with elevated concentrations observed almost exclusively during the winter monitoring period as defined from May to August inclusive. There was not an abrupt seasonal demarcation as arsenic was also present in the 'shoulder' months of April and September when home fires was still used, albeit by a lesser proportion of households (Wilton, 2006).

Both, PM_{10} gravimetric High-Vol and GENT PM_{10} showed less seasonal variation than arsenic, $PM_{2.5}$ and black carbon, although the number of 24-hour PM_{10} averages above 20 μg m^{-3} was greater during the winter compared to non-winter period (Figure 4.2 and Figure 4.3).

The less pronounced seasonality for PM_{10} was due to the influence of non-combustion sources, e.g., "crustal matter", "marine aerosol" and "road dust" that were present all year round, as identified by past receptor modelling (Davy et al., 2009).

$PM_{2.5}$ and black carbon were strongly seasonal, indicating the inferred impact of domestic fires on concentrations during the winter period (as shown in Figures 4.5, 4.6, 4.9 and 4.10). Other receptor modelled sources of $PM_{2.5}$ that have been found to be present throughout the year are "motor vehicles" and "secondary sulphate" (Davy et al., 2009).

In the non-home heating season (January, February, March, October, November, December) average arsenic levels were very low, approximately 2 ng m^{-3} by GF-AAS (Figure 4.18) and few values at levels below the analytical limit of detection (<0.5 ng m^{-3}). These non-winter levels most likely represent the background levels of arsenic as a naturally occurring trace element in crustal matter (Mitchell, 2015).

The arsenic, $PM_{2.5}$ and black carbon measurements show most enhanced levels during the months of May, June and July. However, arsenic shows a much higher variation (variance) compared to the other parameters (BC, $PM_{2.5}$ and PM_{10}), indicating a much larger variability compared with the mean (Tables 3.6 - 3.13).

For PM_{10} and $PM_{2.5}$, these results are as expected and similar patterns were observed elsewhere in New Zealand, with the majority of days (particularly in summer) showing good air quality, a subset of winter days showing degraded air quality, and relatively few days exhibiting the worst air quality. In general the elevated particulate matter concentrations observed throughout New Zealand during the winter period were due to the presence of meteorological conditions that promote "environmental confinement" of biomass burning emissions (Trompetter et al., 2010). This leads to the formation of an "Inversion Layer" which leads to the environmental confinement of the air particulate matter.

The finding of higher day-to-day variability in winter arsenic levels compared to $PM_{2.5}$ and black carbon is most likely due to greater spatial and temporal variability in the emission sources of arsenic. The number of households using CCA-timber instead of untreated wood would have varied from night to night and from place to place within the Wainuiomata airshed (Mitchell, 2015).

Arsenic concentrations (24-hour averages) in Wainuiomata air shed were strongly seasonal, with elevated levels observed during the main home heating period from May to August in 2012 and in 2013. Arsenic was also present, although at much lower concentrations, during the shoulder months of April and September when home fires are used by a smaller proportion of households. These patterns broadly match appliance use reported by Wainuiomata residents in a home heating survey in 2006 (Wilton, 2006). Arsenic was at very low levels or non-detectable for the rest of the year when home heating is not being used and is most likely from a natural component of soils and crustal matter (Mitchell, 2015).

The weighted annual average with given uncertainties for arsenic was 6.5 ± 0.8 ng m^{-3} in the first year of monitoring and 5.9 ± 0.7 ng m^{-3} in the second. Therefore, based on the absolute value of the mean (an approach often used for regulatory purposes) arsenic failed to meet the New Zealand ambient air quality guideline of 5.5 ng m^{-3} in the two monitoring years.

However, when the analytical uncertainties are taken into account, the arsenic average for the second year has no significant difference to the NZAAQG value of 5.5 ng/m^3 as it also falls within the given uncertainty.

Both researchers used the same samples to analyse for arsenic but by different analytical methods. Mitchell, 2015 used the results of ICP-MS performed by Hill Laboratories (independent analysis) and looked more at the social, health aspects and mitigation factors surrounding the arsenic pollution in Wainuiomata air shed with the Massey University while this research was more involved with analytical method development, method validation and to determine arsenic by a standard method (GF-AAS) at Victoria University of Wellington. It was a joint collaborative research by the GWRC and GNS Sciences, National Isotope Centre (NIC).

Arsenic has been found in high levels in fine particulate matter evolved when CCA-treated timber is burnt in domestic wood burners (Abbott & Rogers, 1989; Cavanagh et al., unpublished manuscript) and therefore was originally suspected to be the principal source of arsenic due to temporal coincidence with home heating throughout New Zealand (Cavanagh et al., 2012; Davy et al., 2011). Strong correlations of arsenic with other products of combustion (e.g., black carbon) and trace elements typically emitted from burning of

untreated wood adds to the weight of evidence linking domestic fires as the source of winter arsenic.

The highest levels of PM_{10}, $PM_{2.5}$, black carbon and arsenic were measured on cold calm days. These weather conditions restrict the dispersal of domestic heating emissions and are therefore an important factor leading to PM_{10} exceedances throughout New Zealand (MfE, 2014). It is also possible that on cooler days there is an increased level of wood burning due to the inverse relationship between energy use and external temperature during the home heating season (Isaacs et al., 2010).

Other factors, such as lifestyle and home occupancy patterns, play a role in timing of fire lighting, duration of burn and quantity of fuel used, independent of temperature (Wilton & Bluett, 2012b). Therefore it can be difficult to disentangle the joint effects of human behaviour, emissions and meteorology on ambient air contaminant concentrations.

Day-to-day variability in arsenic was greater than that observed for $PM_{2.5}$ and black carbon. This indicates that the general level of "biomass burning" and short term meteorological conditions did not fully explain the very high arsenic concentrations found on one day and not on another despite similar environmental conditions. A plausible explanation is the temporal and spatial variation in households burning CCA-treated timber on any given night. It appears likely that the number of residences burning treated timber is approximately proportional to the overall number of households using wood for heating. However, on any given night the number of residents using treated timber (and the proximity of their house to the monitoring site) randomly fluctuates within the airshed. Therefore, high arsenic concentration may occur during the peak burning months of May, June and July (when appliance use is greatest), and when conditions are unfavourable for dispersion, and if one, two or more houses are burning CCA-treated timber instead of untreated wood, close to the monitoring site (Mitchell, 2015).

Linear modelling of arsenic using $PM_{2.5}$, wind speed and temperature as predictor variables showed utility for predicting the winter average for arsenic. The 1:2 day sampling frequency captured enough of the variability in arsenic to build a model that is useful for calculating a winter arsenic average for Wainuiomata assuming that burning behaviour relating to use of CCA-treated timber does not change significantly. However, arsenic concentrations for a

particular day, based on ambient $PM_{2.5}$ and meteorology could not be accurately estimated by linear modelling. This may be better approached using a non-linear modelling technique or a model based on an underlying 'extreme value' probability distribution for arsenic (Mitchell, 2015).

Winter and annual averages across the airshed are likely to be similar. However, the day to day variability means that short term exposures (i.e., 24-hours) may differ markedly across the airshed depending on proximity to a household burning CCA-treated timber as burning of CCA-treated timber is more intermittent and opportunistic as reported (Davy et al., 2009; Davy et al., 2012).

As it was initially proposed by GNS Sciences to measure arsenic levels by GF-AAS or equivalent with comparisons made on the concentrations, limit of detection and analytical uncertainty as measured against the IBA method as the previous reports on elevated arsenic levels were based on IBA data.

The XRF instrument was purchased by GNS Sciences during the period of study, hence it was further proposed to include the XRF data sets into the current research so that both the methods (IBA and XRF) used to determine As in the ambient air can be compared and validated against the standard method.

To meet the requirements of this objective, the GF-AAS data was validated against the QC/QA protocols with much emphasis on the quantification of uncertainties, as explained earlier.

There was excellent correlation of measured arsenic observed between the GF-AAS and the XRF (Correlation coefficient = 0.92) while that with IBA data was 0.67. With such high correlation coefficient, it could be predicted with reasonable confidence that arsenic measurement with XRF is almost equivalent to GF-AAS method and that IBA method is close enough.

However, the correlation coefficient only measures the strength of a relation between two variables, and not the agreement between them thus, Bland-Altman method comparison was used to compare the arsenic concentration obtained by each of the methods.

Bland-Altman method comparison was performed using "**Analyse-it"** statistical software program compatible with Windows Excel, 2010/2013. Data which seem to be poor in agreement can produce quite high correlations (Bland & Altman, 1999).

The Bland-Altman plot (Bland & Altman; 1986, 1999), or difference plot, is a graphical method to compare two measurements techniques. In this graphical method the differences (or alternatively the ratios) between the two techniques are plotted against the averages of the two techniques. Alternatively, the differences can be plotted against one of the two methods, if this method is a reference or "gold standard" method.

The difference plot in Figure 4.20 showed that the arsenic determined by XRF method actually is measuring 2.4 ng m^{-3} of arsenic below the mean As value obtained by GF-AAS for the entire sampling period (279 filter samples). This was termed as the bias between the two methods.

The 95% confidence intervals were -7.4 ng m^{-3} to 2.6 ng m^{-3} (Confidence limit = 10.0 ng m^{-3}). This means that XRF method measured 2.4 ± 5.0 ng m^{-3} (95% confidence level), below the GF-AAS method. For analytical chemistry and determination of arsenic in the ambient air to check for the compliance with NZAAQG, this difference is not acceptable as the NZAAQG itself is 5.5 ng m^{-3}.

The difference plot in Figure 4.21 shows that the arsenic determined by IBA method actually is measuring 3.7 ng m^{-3} of As below the mean As value obtained by GF-AAS for the entire sampling period (247 filter samples).

The 95% confidence intervals are -14.1 ng m^{-3} to 6.8 ng m^{-3} (Confidence limit = 20.9 ng m^{-3}). This means that IBA method measured 3.7 ± 10.5 ng m^{-3} (95% confidence level), below the GF-AAS method. Again the IBA method is not acceptable given the large mean difference and the associated confidence limit between the methods. The IBA data has detection limit of about 10 - 20 ng m^{-3} of As in ambient air which is almost three folds of the NZAAQ guidelines.

However, given the clear and distinct seasonal and temporal variation in As levels in ambient air by IBA techniques, it is recommended by this research, that the IBA data can be used as a

"screening" process in the determination of As in air particulate matter. If As is detected in any analysis by IBA, then further analysis by a standard method is required to determine if the NZAAQ guidelines are met or have been exceeded.

The XRF data has shown little difference compared to the IBA data with the standard method (GF-AAs). This may be due to the fact that APM has been around 150-200 microns on the quartz fibre filter (Fung et al., 2002), and the analytical beam penetration is approximately 100-150 microns with the filter thickness to be approximately 500 microns. This means that the analytical beams may have not reached to all the APM on the quartz filter. Hence, this study shows that the two methods (XRF and GF-AAS) can not be used interchangeably given that quartz filters had been used.

However research shows that XRF can produce almost equivalent detection limits to reference methods with the use of Teflon filters, and the coefficient of determination were higher with teflon filters than with quartz filters due to its high penetration ability of the analytical beams. Thus, the x-rays could reach and excite all particles deposited on filters (Yatkin et al., 2011).

XRF is one of those instruments which is faster and cheaper than ICP-MS and GF-AAS because it does not need any sample pre-treatment. Conversely to GF-AAS and ICP-MS, X-ray based techniques does not involve destruction of the samples being analysed. This is a major advantage that makes further determination of ions, organics and carbon still possible, which is essential for receptor modelling (Yatkin et al., 2011).

At GNS Science XRF facility in Lower Hutt, the XRF is used extensively as there are large quantities of samples being analysed for PM_{10} and multi-elemental analysis in the air particulate matter.

With this regard, the XRF can be used as an alternative for long term monitoring of arsenic trends in air particulate matter but with Teflon filters (or equivalent) instead of quartz. However the standard methods can not be replaced totally and should be used to check for compliance with NZAAQG as per MfE and WHO rules and regulations.

Furthermore, the XRF data for elemental analysis in the Wainuiomata air shed has shown elevated levels of lead (Pb) in the APM. Following the phasing out of leaded petrol in 1996,

ambient lead concentrations in urban areas have dropped away to background levels though there can be localised effects from the removal of old leaded paint from structures (MfE, 2002). Lead associated with particulate matter will occur in locations where wood that has been painted with leaded paints when lead based paints were in use, and now is used as solid fuel in domestic fires.

The NZAAQG for lead in PM_{10} is 0.2 µg m^{-3} (200 ng m^{-3}) (3 month moving average, calculated monthly). The overall sampling period showed an average value of 18.1 ± 15 ng m^{-3}, while for winter and non-winter to be 34 ± 26.1 ng m^{-3} and 6.1 ± 6.7 ng m^{-3} respectively. The NZAAQ guidelines for Pb has not exceeded in this case.

However, given the distinct winter seasonal and temporal variations, it was quite evident that the lead was also originating from combustion sources related to domestic heating using painted timber. This forms the basis for further investigation of lead in PM_{10} in ambient air by a standard method to check against the compliance with NZAAQ guidelines.

5.2 RECOMMENDATIONS

From the findings of the entire research, the following recommendations are made:

➢ That there are elevated levels of arsenic in the Wainuiomata air shed observed during the winter months of May - August as detailed in this research. Hence there is an urgent need for greater education and awareness program to be implemented by relevant authorities to reduce the arsenic levels in ambient air not only in Wainuiomata but on a national level as the arsenic pollution is not confined to Wainuiomata or Wellington region. This needs to be integrated in environmental education programmes in the school curriculum at various levels.

➢ That the issue of arsenic pollution in ambient air is related to the combustion of CCA treated timber used as fuel for domestic heating. The levels of arsenic exposure in the indoor air are not known. Further research needs to be undertaken to completely understand the extent of arsenic exposure with its relation to the health risk.

➢ That lead has been found associated with air particulate matter, and given the distinct winter seasonal and temporal variations, it is quite evident that the lead is also originating from combustion sources related to domestic heating using painted timber. Further investigation of lead in PM_{10} in ambient air by a standard method is required immediately to check against the compliance with NZAAQ guidelines.

➢ That the IBA datasets can be used as a "screening" process to identify the elemental pollutants in ambient air.

➢ That XRF datasets can be used for long term monitoring of elemental pollutants in ambient air, and can be used interchangeably with standard methods but with a thinner filter membranes like Teflon or polycarbonate filters which has greater analytical beam penetration.

➢ That for accurate and precise determination of elemental (As/Pb) pollutant concentration in ambient air with respect to the New Zealand Ambient Air Guidelines (NZAAQG), standard method like GF-AAS or equivalent has to be used.

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APPENDICES

APPENDIX 1: ANALYSIS TECHNIQUES

A1.1 ION BEAM ANALYSIS

Ion beam analysis (IBA) was used to measure the elemental concentrations of particulate matter on the size-resolved filter samples from the Coles Place monitoring site shown in Figure 2.1. IBA is based on the measurement of characteristic X-rays and γ-rays of an element produced by ion-atom interactions using high-energy protons in the 2–5 million electron-volt (MeV) range. IBA is a mature and well developed science, with many research groups around the world using IBA in a variety of routine analytical applications, including the analysis of atmospheric aerosols (Maenhaut and Malmqvist 2001; Trompetter, Markwitz et al. 2005). IBA techniques do not require sample preparation and are fast, non-destructive and sensitive (Cohen 1999; Maenhaut & Malmqvist, 2001; Trompetter, Markwitz et al. 2005).

IBA measurements for this study were carried out at the New Zealand IBA facility operated by GNS Science. Figure A1.1 shows the PM analysis chamber with its associated X-ray, γ-ray and particle detectors for Proton-Induced X-ray Emission (PIXE), Proton-Induced Gamma-ray Emission (PIGE), Proton Elastic Scattering Analysis (PESA) and Rutherford Backscattering (RBS) measurements.
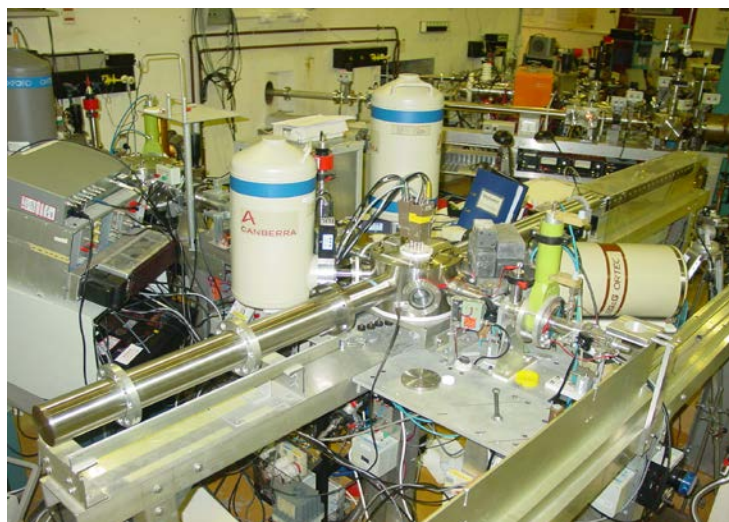
Figure A1.1   Particulate matter analysis chamber with its associated detectors.

The following sections provide a generalised overview of the IBA techniques used for elemental analysis and the analytical setup at GNS Science (Cohen, Bailey et al. 1996; Cohen, 1998; Trompetter, 2004; Trompetter and Davy 2005). Figure A2.2 presents a schematic diagram of the typical experimental setup for IBA of air particulate filters at GNS Science.
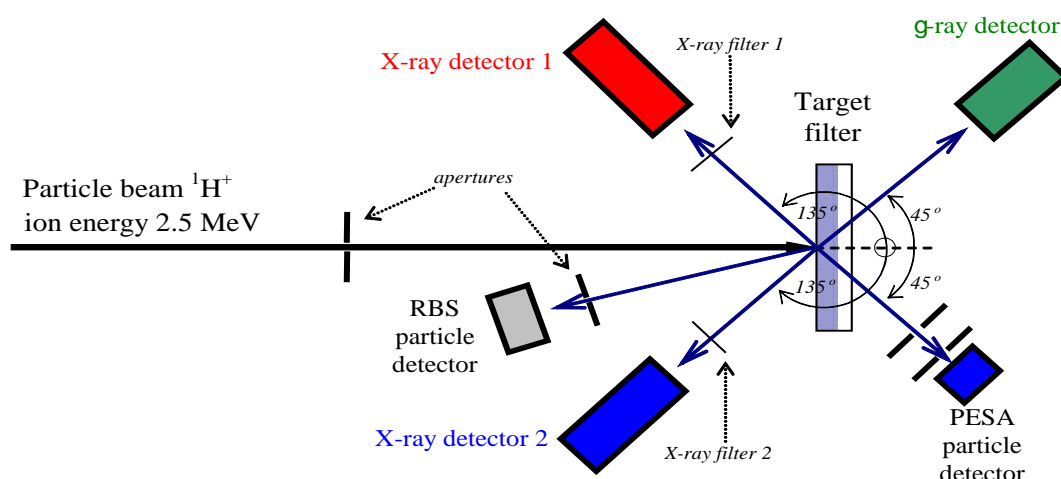
Figure A1.2   Schematic of the typical IBA experimental setup at GNS Science.

A1.2   PARTICLE-INDUCED X-RAY EMISSION

Particle induced X-ray emission (PIXE), is used to determine elemental concentrations heavier than neon by exposing the filter samples to a proton beam accelerated to 2.5 million volts (MeV) by the GNS 3 MeV van-de-Graaff accelerator. When high energy protons interact with atoms in the sample, characteristic X-rays (from each element) are emitted by ion-electron processes. These X-rays are recorded in an energy spectrum. While all elements heavier than boron emit K X-rays, their production become too few to satisfactorily measure elements heavier than strontium. Elements heavier than strontium are detected via their lower energy L X-rays. The X-rays are detected using a Si (Li) detector and the pulses from the detector are amplified and recorded in a pulse height analyser. In practice, sensitivities are further improved for the lighter elements by using two X-ray detectors, one for light element X-rays and the other for heavier element X-rays, each with different filtering and collimation. Figure A1.3

shows an example of a PIXE spectrum for airborne particles collected on a filter and analysed at the GNS IBA facility.
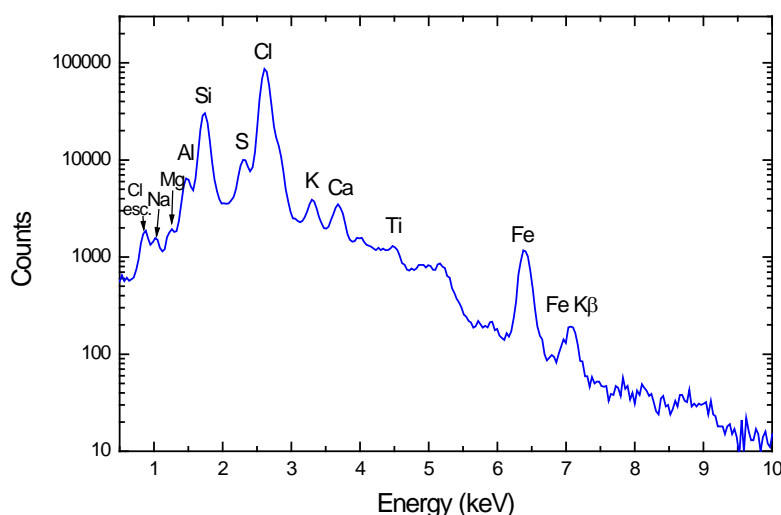
Figure A1.3   Typical PIXE spectrum for an aerosol sample analysed by PIXE.

As the PIXE spectrum consists of many peaks from different elements (and a Bremsstrahlung background), some of them overlapping, the spectrum is analysed with quantitative X-ray analysis software. In the case of this study, Gupix Software was used to perform the deconvolution with high accuracy.The number of pulses (counts) in each peak for a given element is used by the Gupix software to calculate the concentration of that element. The background and neighbouring elements determine the statistical error and the limit of detection. Note, that Gupix provides a specific statistical error and limit of detection (LOD) for each element in any filter, which is essential for source apportionment studies.

Typically 20–25 elements from Mg–Pb are routinely determined above their respective LODs. Sodium (and fluorine) was determined using both PIXE and PIGE.

A1.3   PARTICLE-INDUCED GAMMA-RAY EMISSION

Particle Induced Gamma-Ray Emission (PIGE) refers to Y-rays produced when an incident beam of protons interacts with the nuclei of an element in the sample (filter). During the de-

excitation process, nuclei emit Y-ray photons of characteristic energies specific to each element. Typical elements measured with Y-ray are:

Element	nuclear reaction	gamma ray energy (keV)
Sodium	$^{23}Na(p,\alpha\gamma)^{20}Ne$	440, 1634
Fluorine	$^{19}F(p,\alpha\gamma)^{16}O$	197, 6129

Gamma rays are higher in energy than X-rays and are detected with a germanium detector. Measurements of a light element such as sodium can be measured more accurately using PIGE because the Y-rays are not attenuated to the same extent in the filter matrix or the detector material, a problem in the measurement of low energy X-rays of sodium. Figure A.1.4 shows a typical PIGE spectrum.
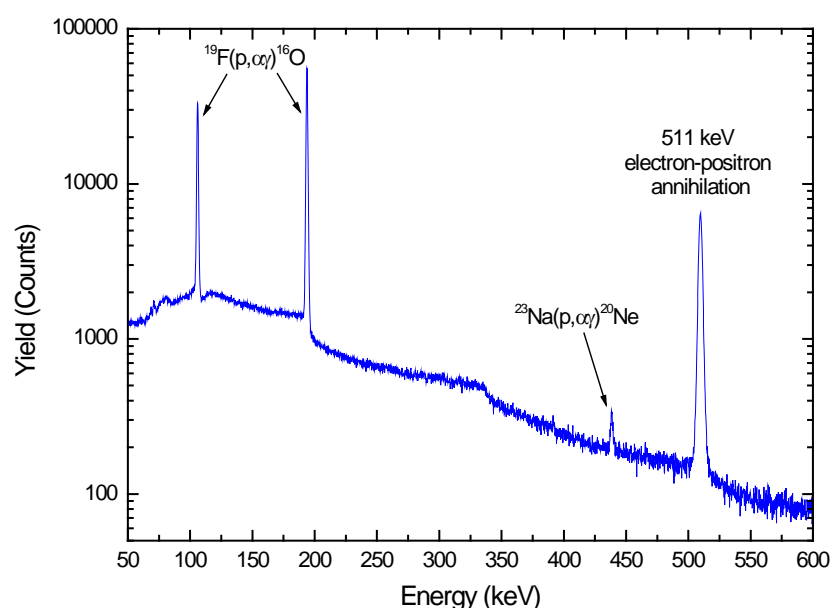
Figure A1.4   Typical PIGE spectrum for an aerosol sample.

A1.4   PARTICLE ELASTIC SCATTERING ANALYSIS

Particle Elastic Scattering Analysis (PESA) allows hydrogen to be measured quantitatively in air particulate matter collected on a filter providing the filter material contains no or little

hydrogen atoms, e.g. Teflon filters. Note that Teflon contains fluorine that introduces a significant background in the X-ray spectra which increases the limits of detection (LODs) of PIXE. Hydrogen can be detected by measuring the elastically scattered protons in a forward direction for a proton beam passing through the air particulate matter filter. At a forward scattering angle of 45º, the protons are elastically scattered from hydrogen with 50 % of the initial proton energy (i.e. for an incident beam of 2.50 MeV the energy of protons scattered off hydrogen is 1.25 MeV) which is much less energy than the energy of the protons scattered from the other heavier elements in the filter. Thus, in the PESA spectrum of a sample filter, a peak corresponding to protons elastically scattered from hydrogen occurs separated from the protons elastically scattered from the other atoms in the air particulate matter filter. The air particulate matter filter is thin enough for this measurement when the hydrogen PESA peak is separated from the noise at the low end of the spectrum and from protons elastically scattered from heavier atoms at the high energy end of the spectrum. For Teflon filters analysed with a 2.5 MeV proton beam, proton scattering energies for PESA are shown in Table A1.1 and Figure A1.5 presents a typical PESA spectrum.

Table A1.1   Proton scattering energies of various elements for a 2.5MeV proton beam

Element	Energy detected at 45° forward (MeV)
H	1.250
C	2.380
O	2.410
F	2.424
Fe	2.474
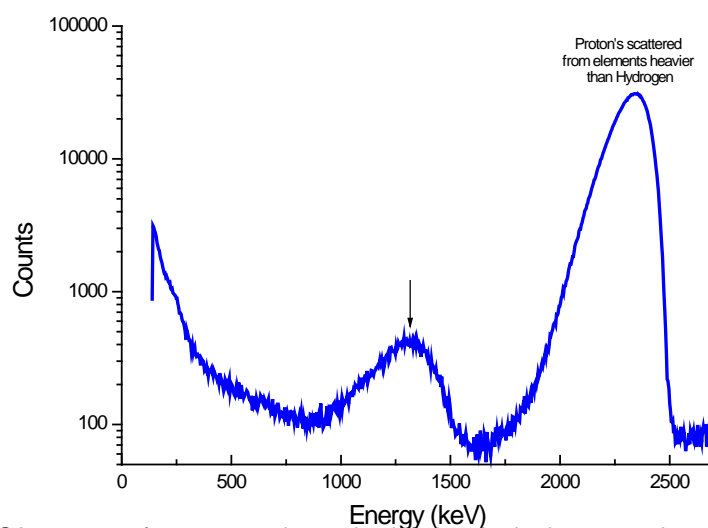
Figure A1.5   PESA spectrum for an aerosol sample showing the hydrogen peak at 1.250 MeV.

Because PESA, and IBA measurements in general, are conducted in high vacuum (residual gas pressure better than 10^{-6} mbar), free water vapour and VOCs are volatilised before analysis and only bound hydrogen is detected (e.g. SVOCs and ammonium ions) (Cohen 1999). PESA was used to determine hydrogen concentrations in all samples from Coles Place.

A1.5   IBA DATA REPORTING

Most filters used to collect particulate matter samples for IBA analysis are sufficiently thin that the ion beam penetrates the entire depth producing a quantitative analysis of elements present. Because of the thin nature of the air particulate matter filters, the concentrations reported from the IBA analyses are therefore in aerial density units (ng cm^{-2}) and the total concentration of each element on the filters is calculated by multiplying with the exposed area of the filter. Typically the exposed area is 11.95 cm^2 for filters collected with the Partisol sampler used in this study. For example, to convert from Cl (ng cm^{-2}) into Cl (ng m^{-3}) for filter samples, the equation is:

$$\text{Cl (ng m}^{-3}) = 11.95(\text{cm}^2) \times \text{Cl (ng cm}^{-2}) / \text{Vol(m}^3) \tag{A1.1}$$

A1.6   LIMITS OF DETECTION FOR ELEMENTS DETERMINED BY IBA

The exact limits of detection for reporting the concentration of each element depends on a number of factors such as:

- the method of detection;

- filter composition;

- sample composition;

- the detector resolution;

- spectral interference from other elements.

To determine the concentration of each element the background is subtracted and peak areas fitted and calculated. The background occurs through energy loss, scattering and interactions of the ion beam as it passes through the filter material or from Y-rays produced in the target and scattered in the detector system (Cohen 1999). The peaks of elements in spectra that have interferences or backgrounds from other elements present in the air particulate matter, or filter matrix itself, will have higher limits of detection. Choice of filter material is an important consideration with respect to elements of interest as is avoiding sources of contamination. The GNS IBA laboratory routinely runs filter blanks to correct for filter derived analytical artefacts as part of their QA/QC procedures. Figure A1.6 shows the LODs typically achieved by PIXE for each element at the GNS IBA facility. All IBA elemental concentrations determined in this work were accompanied by their respective LODs. The use of elemental LODs is important in receptor modelling applications.

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Environmental, Industrial and Process control Technologies, Vol 1, Gordon and Breach Science Publishers, The Netherlands; Pp 139-196
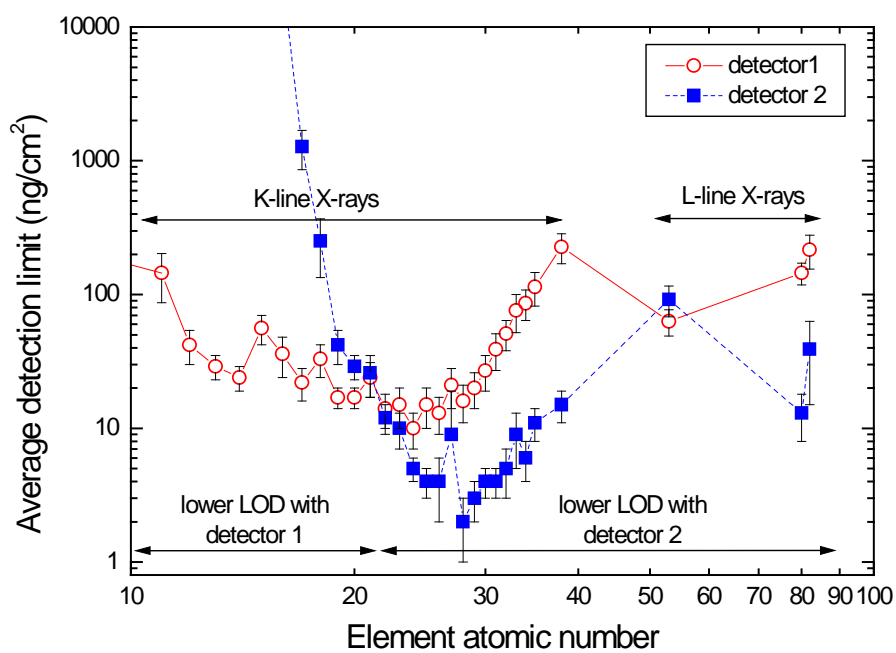
Figure A1.6   Elemental limits of detection for PIXE routinely achieved as the GNS IBA facility for air filters.

APPENDIX 2: X-RAY FLUORESCENCE SPECTROSCOPY

X-ray fluorescence spectroscopy (XRF) was used to measure elemental concentrations in PM_{10} samples collected on glass fibre filters at the Water Street monitoring site in Whangarei. XRF measurements in this study were carried out at the GNS Science XRF facility and the spectrometer used was a PANalytical Epsilon 5 (PANalytical, the Netherlands). The Epsilon 5 is shown in Figure A1.1. XRF is a non-destructive and relatively rapid method for the elemental analysis of particulate matter samples.

Figure A2.1   The PANalytical Epsilon 5 spectrometer.

XRF is based on the measurement of characteristic X-rays produced by the ejection of an inner shell electron from an atom in the sample, creating a vacancy in the inner atomic shell. A higher energy electron then drops into the lower energy orbital and releases a fluorescent X-ray to remove excess energy (Watson et al., 1999 and references therein). The energy of the released X-ray is characteristic of the emitting element and the area of the fluorescent X-ray peak (intensity of the peak) is proportional to the number of emitting atoms in the sample. From the intensity it is possible to calculate a specific element's concentration by direct comparison with standards.

To eject inner shell electrons from atoms in a sample, XRF spectrometer at GNS Science uses a 100 kV Sc/W X-ray tube. The 100 kV X-rays produced by this tube are able to provide elemental information for elements from Na–U. Unlike ion beam analysis techniques, which are similar to XRF, the PANalytical Epsilon 5 is able to use characteristic K-lines produced by each element for quantification. This is crucial for optimising limits of detection because K-lines have higher intensities and are located in less crowded regions of the X-ray spectrum. The X-rays emitted by the sample are detected using a high performance Ge detector, which further improves the detection limits. Figure A2.1 presents a sample X-ray spectrum of the PM_{10} samples.
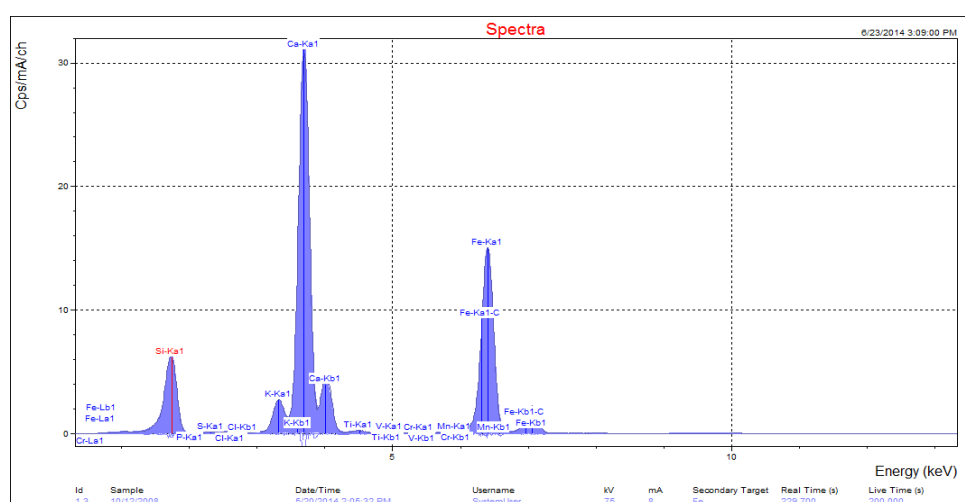
Figure A2.2   Example X-ray spectrum from a PM10 sample

In this study, calibration standards for each of the elements of interest were analysed prior to the samples being run. Once the calibration standards were analysed, spectral deconvolutions were performed using PANalytical software to correct for line overlaps and ensure that the spectra were accurately fit. Calibration curves for each element of interest were produced and used to determine the elemental concentrations from the samples. A NIST reference sample was also analysed to ensure that the results obtained were robust and accurate. The measurements with XRF were exclusively done by scientists at GNS Sciences.

Watson, J. G., Chow, J. C., Frazier, C. A., 1999. X-ray Fluorescence Analysis of Ambient Air Samples, in *Advances in Environmental, industrial and Process Control Technologies* 1, 139-196.

APPENDIX 3: ATOMIC ABSORPTION SPECTROMETRY

A3.1 HISTORICAL BACKGROUND

The technique of AAS can be thought of as having its origin in 1666 with Isaac Newton who used a prism to separate the colours of the solar spectrum. Wollaston in 1802 recorded his observation that the spectrum of sunlight which was at the time thought to be continuous, was in fact interrupted by dark lines. Later in 1814 Fraunhofer found a series of lines in the visible region of the solar spectrum and labelled the principal lines alphabetically without identifying their chemical origin.

In 1832, Brewster, who is associated with the invention of the kaleidoscope investigated the absorption of light by various vapours and suggested that Fraunhofer lines were due to certain vapours in the sun's atmosphere. Kirchhoff in 1860 deduced from Fraunhofer's results the presence of certain elements in the solar atmosphere and with Bunsen in 1861 laid the foundations of a new method of chemical analysis using flames. Fraunhofer and Kirchhoff had been observing atomic absorption and atomic emission respectively. Foucault demonstrated the reversal of spectral lines, for example when the spectral source is surrounded by atomic vapours from the substance emitting the spectrum and the atomic vapours absorb the radiation that they themselves are emitting.

In 1902 Wood illustrated the emission-absorption relationship by heating sodium in a partially evacuated glass bulb and irradiated the bulb with light from a sodium flame. He demonstrated an increase in absorption effect by heating the bulb more strongly. Wood named the lines emitted and absorbed by sodium atoms as resonance lines and carried out experiments to show the possibility of using the resonance effect to detect traces of mercury. This may have been the first analysis carried out by atomic absorption spectrometry. Wood does not seem to have been able to impress either chemists or spectroscopists who were more interested in emission spectroscopy and few followed in the field of atomic absorption and its applications.

The advances made by Kirchhoff, Bunsen, Foucault and Wood did interest astronomers who used atomic absorption to study the composition of the solar and stellar atmospheres.

In 1924 Angerer and Joos studied the atomic absorption spectra of metals in the iron group and Frayne and Smith in 1926 of indium, gallium, aluminium and thallium. Hughes and Thomas in 1927 studied the absorption and resonance effects of mercury. Lunegardh in 1928 demonstrated atomic emission spectroscopy (AES) in an air-acetylene flame using a pneumatic nebulizer. In 1930 Mueller and Pringsheim published an atomic absorption method of measuring mercury content of air thereby carrying on Woods original project of 1913 and 1919.

The first real applications of atomic absorption to chemical analysis were made by Walsh in 1955, and Alkemade in the same year. Walsh made significant contributions to the development of AAS as an analytical tool. He used the hollow cathode lamps as a line source, greatly reducing the resolution required for successful analysis. As photomultipliers had become available, the problems associated with measuring absorption with a photographic plate were eliminated.

His introduction of modulation into the system permitted the detector to distinguish between absorption and emission by atoms at the same wavelength. He also utilized the flame for atomization.

A3.2 WHAT IS ATOMIC ABSORPTION SPECTROMETRY (AAS)?

Atomic absorption is a process involving the absorption by free atoms of an element of light at a wavelength specific to that element, or put more simply, it is a means by which the concentration of metals can be measured. In Atomic Spectrometry, emission, absorption and fluorescence, energy is put into the atom population by thermal, electromagnetic, chemical and electrical forms of energy and is converted to light energy by various atomic and electronic processes before measurement. Atomic Absorption Spectrometry is useful not only for the identification but also the quantitative determination of many elements present in samples. The technique is specific, in that individual elements in each sample can be reliably identified

and it is sensitive, enabling small amounts of an element to be detected down to around 1μg g-1 (1ppm) i.e. one part in one million using straightforward flame procedures. Lower levels can be determined down to 0.001ppm using more sophisticated procedures.

When a sample or sample solution is burned in a flame or heated in a tube, the individual atoms of the sample are released to form a cloud inside the flame or tube. Each atom consists of a positively charged nucleus surrounded by a number of electrons in rapid motion around the nucleus. For each electron in each atom there is a discrete set of energy levels that the electron can occupy. The spacing of the energy levels is different for each electron in the atom, but for similar atoms corresponding electrons have identical spacing. The energy levels are usually labelled E0, the ground state, through E1, E2 etc. to E∞.

For an unexcited atom, each electron is in the ground state. To excite the atom, one or more electrons can be raised to the first or higher energy levels by the absorption of energy by the atom. This energy can be supplied by photons or by collisions due to heat. Those electrons furthest from the nucleus require least energy to go from the ground state E0 to the first energy level E1∞. The energy E corresponds to the energy gap between the ground state and the first energy level

$$E = E_1 - E_0 \hspace{4cm} \text{A3.1}$$

The energy required for this transition can be supplied by a photon of light with an energy given by:

$$E = h\nu \hspace{4cm} \text{A3.2}$$

where h = Planck's constant and ν the frequency.

This corresponds to a wavelength (λ) of:

$$\lambda = hc/E \hspace{4cm} \text{A3.3}$$

Where: *c* is the speed of light in vacuum.

However, for all non-conducting elements (insulators) and for most of the electrons in the atoms of conducting elements, the energy gap E1-E0, is very large and thus a very energetic photon, perhaps in the vacuum UV or X-Ray region, would be required to excite the atom. Metallic and metalloid elements, contain so-called valence electrons which are relatively loosely bound to the nucleus and which can be excited by photons of wavelengths in the optical range 190-900nm. For each atom of a metal or metalloid the energy gap E1-E0 for a particular valence electron is nearly identical. Furthermore, the energy gap is not found in any other element. If light of sufficiently narrow wavelength range, centred on

$$\lambda = \quad hc\ /\ E_1 - E_0 \qquad\qquad\qquad A3.4$$

is sent through a cloud of various atoms, only atoms of one particular element will absorb photons, hence, the selectivity of the atomic absorption technique. Atoms in the cloud move at high speed and collide with each other, and absorb over a very narrow range of wavelengths. The width of a typical absorption line is about 0.001nm. For atomic absorption instrument purposes, an emission source with an emission line of the same frequency and a width of about 0.001nm is normally used. This requirement is satisfied by an emission spectrum of the element of interest, generated by a hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL). Another requirement to obtain a high absorption signal is that most atoms should be in the ground state and a large number of electrons should be able to be excited to the first state when a photon of correct frequency is absorbed. The number of atoms in the ground state and first excited state is given by the general statement of the Maxwell-Boltzmann law.

(Thermo Scientific. (2008).Atomic Absorption Spectrometry Methods Manual, 9499 400 30011 Issue 5, Thermo Fisher Corporation, UK, 2008.)
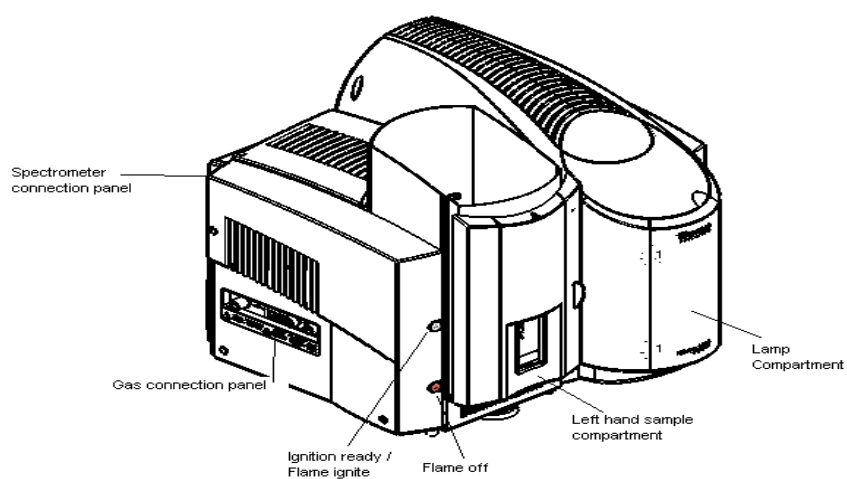
Figure A 3.1   iCE 3000 Series Spectrometer - General View

Figure A3.2   Graphite Furnace Atomic Absorption with Auto-sampler at VUW used for this study.

A3.3 SOLAAR PROGRAM- Furnace Method for Arsenic Determination

A3.3.1 Furnace Analysis

This section guides through the process of setting up and performing a simple graphite furnace analysis for Arsenic.

To carry out a simple furnace analysis, one must:

- set up a Method

- install and align a hollow cathode lamp

- install and align the Graphite Furnace

- install and align the Graphite Furnace Auto-sampler

- load the sample solution into the Auto-sampler.

You can then run the analysis, save the results and print a Report of the results.

To work through the example described below, you will need:

- Arsenic hollow cathode lamp
- 50ug/L As master standard solution in 0.1% v/v nitric acid
- sample solutions containing unknown arsenic concentrations
- a blank solution containing 0.1% v/v nitric acid
- a ridged, coated cuvette for the Graphite Furnace.

There are a range of Graphite Furnace systems available for Thermo Scientific AA Spectrometers. Although the furnaces differ in mechanical design, the principles involved in using them and the software that controls them are identical. The Hardware manual covers the details of the mechanical controls of all designs of furnace.

A3.3.2 Before Starting

Check that the AA Spectrometer system, Graphite Furnace accessory and Furnace Auto-sampler have been correctly installed, and that the necessary services are correctly connected and

adjusted to their normal operating conditions. Graphite Furnace Atomic Absorption Spectrometry is an inherently safe procedure, as no inflammable or explosive gases are used. However, one should still review the appropriate sections of the Hardware manual and ensure that they understand the hazards involved and the precautions necessary.

Start the SOLAAR application, and log in as described in the SOLAAR Installation / Starting the SOLAAR Application and SOLAAR Installation / Logging into SOLAAR sections.

A3.3.3 Setting up the Method

Set up the Method using the Method property pages provided on the Method property sheet. For this example analysis one will use the default values for most of the parameters, then save the Method in the Methods database.

To set up the furnace Method:

Click on the Methods button to open the Method property sheet.

The following subsections describe how to set the parameters on the Method property sheet pages.

A3.3.3.1 General Method Parameters
To set general analysis parameters for the method:

  1. If the General Method property page is not displayed, click on the General tab.

  2. Set the Technique to Furnace:

  3. Type in a Method Name for the analysis Method.

  4. If required, edit the name in the Operator field – it shows the name of the logged in user by default.

  5. Type a description of the analysis in the Description field.

  6. Set the remaining controls to the following values:

      Auto-sampler = Furnace

Rack Code = this is disabled when Auto-sampler is set to Furnace

Shared Standards = Checked

A3.3.3.2 Sequence Method Parameters

The next step is to specify the element for which one wants to run the analysis, the actions to be carried out during the analysis and the Sample Details. It can be done in exactly the same way as for a Flame Method.

See the instructions for setting the *Sequence Method parameters* in Section 2.1.2 of SOLAAR Series Software Manual and set up a Sequence for a arsenic analysis containing a Calibration action, and at least three Sample Actions.

Additional actions are available for one to use in a Furnace Method. In particular, it is good practise start the Action List with a Cuvette Clean action, which will cause a Cuvette Clean cycle to be run automatically before making any measurements. This will ensure that the cuvette is clean and that the components in the Graphite Furnace have reached their normal operating temperatures.

A3.3.3.3 Spectrometer Method Parameters

To view the Spectrometer parameters for manganese analysis in the method:

1. Click on the Spectrometer tab to display the Spectrometer property page:

2. Confirm that the Background Correction technique is set to D2 Quadline.

3. Confirm that the other settings are set to their default values, as in the picture above.

4. Click on Cook Book to display a Help window with the Cook Book information for arsenic.

A3.3.3.4 Furnace Method Parameters

To view the Furnace parameters for the method:

1. Click on the Furnace tab to display the Furnace property page:

2. Review the default parameters, but do not change any at this stage.

A3.3.3.5 Calibration Method Parameters

To set the Calibration parameters for the method:

1. Click on the Calibration tab to display the Calibration property page:

2. Confirm that the Calibration Method is set to Normal Segmented Curve Fit.

3. Confirm that the Concentration Units field shows µg/L.

4. Set the Number of Standards to 5 – the first five fields in the Standard Concentrations table will become enabled.

5. Set the first three fields in the Standard Concentrations table to the concentration values of the standard solutions you have prepared.

6. Set the Master Standard Concentration field to the concentration of your top standard.

7. Confirm that the other calibration parameters are set to their default values.

A3.3.3.6 Sampling Method Parameters
To set the Sampling parameters for the method:

1. Click on the Sampling tab to display the Sampling property page:

2. Set the Working Volume to 20.0µL.

3. Confirm that the other Sampling parameters are set to their default values

Note: Since any QC Test actions in the sequence were not included, the settings on the QC Method property page are not applicable. All QC protocols were included manually.

A3.3.3.7 Installing and Aligning the Lamp
This completes the definition of the Method. Save the Method in the Methods database as per the manual (see: Getting Started / A Simple Flame Analysis / Saving and Loading Methods Section)

Ensure that the optical path in the left-hand (flame) sample compartment of the dual atomiser instrument is clear. (The left hand sample compartment is used for setting the reference beam in dual atomizer instruments). If it has a tilt mounted furnace one can ensure that the optical

path in the right-hand compartment is also clear while aligning the lamp by tilting the Furnace Head forward towards the front of the instrument. If it has a furnace on the fixed mount, confirm that a cuvette is correctly fitted and that the furnace windows are clean.

If it has a single atomiser instrument, the combined Auto-sampler and Furnace System will be fitted in the sample compartment. If one is not confident that the alignment of the Furnace is correct, remove the furnace before attempting to align the lamp. Refer to the Operators Manual for instructions as to how to do this.

(See Getting Started / A Simple Flame Analysis / Installing the Lamp and Getting Started / A Simple Flame Analysis / Setting up the lamp sections for how to install and align the hollow cathode lamp.)

A3.3.3.8 Installing and Aligning the Graphite Furnace

The Furnace system will have been installed by the Thermo Scientific Service Engineer.

Some spectrometer configurations allow permanent set-up of the furnace. For these configurations, once installed, the furnace will not normally need re-aligning. For configurations where the furnace is removed, checking the alignment of the furnace upon re-installation is recommended. Alignment procedures for all types of Furnace system are provided in the Operators Manual.

A3.3.3.9 Aligning the Graphite Furnace Auto-Sampler

One must align the Graphite Furnace Auto-sampler so that the capillary tip enters the injection hole in the cuvette vertically, without touching the sides of the injection hole. This adjustment may have been set up on installation, however you should check it at regular intervals and whenever you change the auto-sampler capillary tip.

One must then set the vertical position of the tip inside the cuvette, so that the sample solution is deposited correctly on to the floor of the cuvette.

The GFTV accessory will greatly simplify this process. If this is not available one can use a small dental mirror, to view the capillary tip inside the cuvette.

One will need:

• Either:

– The GFTV accessory fitted, or

– A small dental mirror.

• A small torch or desk lamp positioned over the furnace head will also be useful if the lighting is poor.

Before starting to align the Auto-sampler, one should:

• install and align a hollow cathode lamp.

• install and align the Graphite Furnace in the Spectrometer.

• install and align a cuvette.

• check that the communications, power, cooling and gas supply services are properly connected to the Graphite Furnace.

To align the Graphite Furnace Auto-sampler:

1. Check the Status Line and confirm that the System Status is ONLINE.

2. Refer to the Hardware Manual and:

a. Fit the Auto-sampler to the Spectrometer and locate the position adjustment controls.

b. Confirm that the capillary tip is fitted correctly and is not bent.

c. Confirm that the electrical and gas connections are correct.

d. Confirm that the Auto-sampler wash reservoir is full.

3. Click on the Methods button to open the Method property sheet at its General page dialogue box and confirm that the Auto-sampler is set to Furnace (this may differ depending upon your instrument type). Close the Method property sheet.

4. Click on the Align Capillary Tip button to move the Auto-sampler arm into position over the furnace head.

5. Adjust the position of the Auto-sampler until the capillary tip enters the cuvette injection hole.

6. To adjust the height of the capillary tip until it is just above the cuvette ridges:

Either:

Position the dental mirror to view the reflected image of the capillary tip inside the cuvette, or

a. Click on the GFTV button to display the GFTV dialogue box:

b. Set the Camera Mode to Analysis.

c. Click on OK to display the GFTV image (note: the GFTV image appears in the Spectrometer Status window. One must have this window open to view the GFTV video):
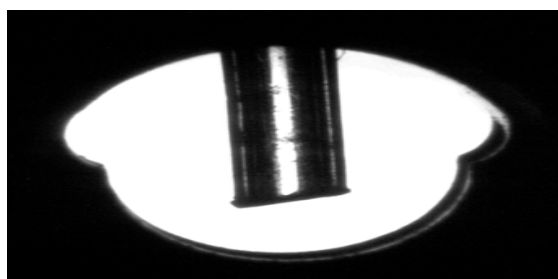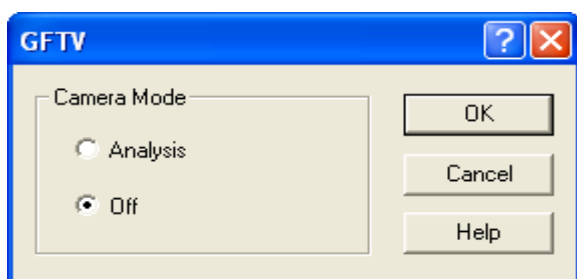
Figure A3.3   GFTV set up and screen

d. Finally, optimise the height of the capillary tip by observing a sample injection and adjusting the height to obtain a smooth, complete deposition of the sample in the bottom of the cuvette.

One has now correctly aligned the Furnace Auto-sampler.

It is good practice to purge the Auto-sampler after fitting and aligning it, to remove any contamination from the capillary tip and ensure that there are no bubbles trapped in the liquid handling system.

To purge the Auto-sampler:

Click on the Auto-sampler Purge button.

It will take approximately two minutes to purge the Auto-sampler. The System Status will be BUSY while the Auto-sampler is being purged and will return to ONLINE when the purge has finished.

A3.3.4 Loading the Sample Solution on to the Auto-Sampler

After having defined a Method, SOLAAR determines the default positions for the solutions on the Auto-sampler. You can find out what these are using the Auto-sampler Loading Guide, abbreviated to ASLG. If you need to change the positions of any samples or standards you can simply drag them from their original place on the schematic of the auto-sampler (right-hand side of the screen), and drop them in a new location. The list view on the left-hand side of the screen will automatically update as you modify the locations of samples, standards or blanks.

To look at the Auto-sampler Loading Guide:

Click SLG in the View menu:
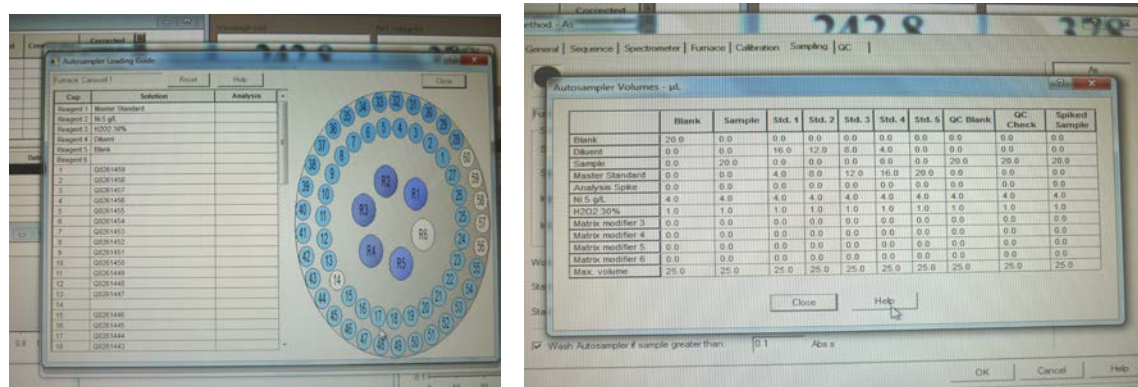
Figure A3.4   Auto-Sampler Filling Guide and auto- sampler volumes as per SOLAAR Program
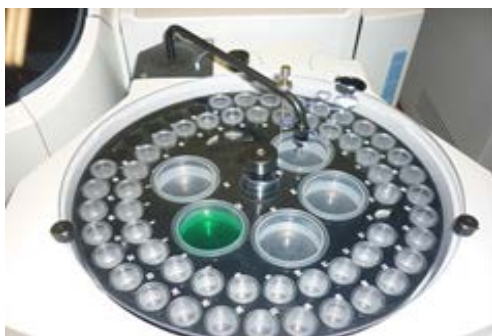
Note: One can also open the Auto-sampler Loading Guide by clicking on ASLG on the Sequence property page of the Method property sheet.

To print the Auto-sampler Loading Guide: Click on the Print command on the File menu and then click on Auto-sampler Loading Guide.

Refer to the Auto-sampler Loading Guide and place your solutions in sample cups in the correct positions on the Auto-sampler carousel, then replace the carousel on the Auto-sampler.

A3.3.5 Running the Analysis

Before running the analysis, one should install and align the lamp, the Graphite Furnace and the Graphite Furnace Auto-sampler, as described above.

The analysis uses the *Current Method* – one can see the definition of the Current Method by opening the Method property sheet. If one does not want to use this Method, use the Method property sheet to define the required Method or to load a previously saved one.

Before starting

1. Turn on the lamp and allow the instrument to stabilise for at least ten minutes.

2. Confirm that the solutions have been correctly loaded into the Auto-sampler.

3. It is good practice to carry out an Auto-sampler Wash and a Cuvette Clean cycle immediately before starting the analysis by clicking the Auto-sampler Wash button and Cuvette Clean button. If one has included these as Actions in the Sequence, it will take place automatically when the analysis starts.

To run the furnace analysis:

1. Open the Results window to see the results as they are measured.

2. Open the Signal window to monitor the absorbance signals through the furnace cycle.

3. If it has the GFTV accessory fitted:

a. Click on the GFTV button to open the GFTV dialogue box.

b. Set the Camera Mode to Analysis.

c. Click on OK to display the GFTV image so that you can monitor the sample injections.

(Note that the absorbance signal will only be displayed on the Signal window for the Atomise phase of the furnace program when the GFTV accessory is in use).

4. Click on the Analyse button to start the analysis.

The analysis will then be carried out automatically. The results will appear in the Results window and the displays on the Status windows will be updated as the results are measured.

5. When all the solutions have been measured, a prompt will be displayed confirming that the analysis has been completed. Click on **OK** to acknowledge this.

One has now carried out a simple furnace analysis to determine arsenic concentrations.

A3.3.6 Viewing and Printing the Results

The procedures for viewing and printing the results of a furnace analysis are identical to those used to view and print the results of a flame analysis – see Getting Started / A Simple Flame Analysis / Viewing the Results and Getting Started / A Simple Flame Analysis / Printing the Results sections as per the manual.

A3.3.6.1 Viewing Absorbance Signals

When one selects a resample result in the Results window, the absorbance signal peak recorded during atomise phase, will be displayed in the Signal window. Examining the shape of this peak is often a good way to identify problems with furnace analysis.

One can adjust the display in the Signal window using the commands and options available in the Signal Options dialogue box.

To adjust the signal display:

1. Right-click in the display area of the Signal window to display the Signal window context menu.

2. Click on the Options command to open the Signal Options dialogue box:

3. Set the options that one wants to use and click on OK to adjust the Signal window display.

(Thermo Scientific. (2011). SOLAAR Series Software Manual- Thermo FisherCorporation, U.K, 2011.)

APPENDIX 4:   OVERALL DATA SETS FOR ARSENIC/ PM10/ BC & PM2.5

		Arsenic Data						PM10 Data				BC Data							PM2.5	
		GF-AAS		XRF		IBA		IBA-GENT		High-Vol		High-Vol		High-Vol		GENT-BC			IBA-GENT	
DATE	SAMPLE ID	Concentration	Uncertainty	Concentration	Uncertainty	Concentration	Uncertainty	Concentration	Uncertainty	Concentration	Uncertainty	Concentration	Uncertainty	Concentration	Uncert.	Concentration	Uncertainty	Uncert.	Concentration	Uncertainty
Units		ng/m3	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3	µg/m3	µg/m3	µg/m3	µg/m3	µg/m3	µg/m3	(ng/m3)	(ng/m3)	µg/m3	µg/m3	(ng/m3)	µg/m3	µg/m3
22/10/2011	Q0261497	2.4	0.4	0.2	0.1					8.79	0.01	0.586	0.001	586.2	1.5					
25/10/2011	Q0261499	2.1	0.3	0.0	0.2					14.51	0.01	0.553	0.001	553.3	1.5					
31/10/2011	Q0261498	2.1	0.3	0.0	0.4					12.22	0.01	0.789	0.001	788.6	1.5					
03/11/2011	Q0261496	1.8	0.2	0.0	0.0					20.64	0.01	0.299	0.001	298.9	1.5					
06/11/2011	Q0261495	2.1	0.3	0.0	0.4					8.97	0.01	0.456	0.001	456.0	1.5					
09/11/2011	Q0261494	2.1	0.3	0.0	0.1					9.07	0.01	0.066	0.005	66.4	4.8					
12/11/2011	Q0261493	3.3	0.5	0.2	0.1					9.09	0.01	0.829	0.001	829.0	1.5					
15/11/2011	Q0261492	2.4	0.4	0.0	0.5					9.00	0.01	0.564	0.001	564.2	1.5					
18/11/2011	Q0261491	2.7	0.2	0.0	0.2					10.60	0.01	0.628	0.001	627.5	1.5					
21/11/2011	Q0261490	1.5	0.6	0.0	0.7					12.99	0.01	0.207	0.002	207.3	1.5					
24/11/2011	Q0261489	1.5	0.6	0.0	0.4					8.75	0.01	0.393	0.001	393.2	1.5					
27/11/2011	Q0261488	2.4	0.4	0.0	0.2					20.63	0.01	0.371	0.001	370.9	1.5					
30/11/2011	Q0261487	2.1	0.3	0.2	0.1					11.65	0.01	0.836	0.001	836.3	1.5					
03/12/2011	Q0261486	2.1	0.3	0.0	0.4					10.03	0.01	0.424	0.001	424.5	1.5					
06/12/2011	Q0261485	2.4	0.4	0.5	0.2					5.79	0.01	0.538	0.001	537.7	1.5					
09/12/2011	Q0261484	2.1	0.3	0.0	0.8	0.0	6.0	5.1	2.6	9.98	0.01	0.431	0.001	431.2	1.5	0.4	0.3	303.6	0.3	2.4
12/12/2011	Q0261483	1.8	0.2	0.0	0.6	8.2	5.0	8.9	0.7	7.04	0.01	0.520	0.001	519.6	1.5	0.4	0.3	250.4	4.3	0.1
15/12/2011	Q0261482	1.8	0.2	0.0	0.2	2.1	5.8	2.8	0.8	4.87	0.01	0.793	0.001	793.2	1.5	0.7	0.4	361.1	1.4	0.6
18/12/2011	Q0261481	1.2	0.3	0.0	0.4					8.11	0.01	0.091	0.003	90.6	2.9					
21/12/2011	Q0261480	1.5	0.6	0.2	0.1					6.06	0.01	0.480	0.001	480.4	1.5					
24/12/2011	Q0261479	1.8	0.2	0.0	0.4	2.4	5.4	9.2	0.6	10.76	0.01	0.946	0.001	946.5	1.5	1.1	0.4	409.4	3.2	0.1
27/12/2011	Q0261478	2.1	0.3	0.0	0.4					10.01	0.01	0.398	0.001	398.1	1.5					
30/12/2011	Q0261477	2.1	0.3	0.0	0.2	0.0	4.9	2.8	0.7	4.60	0.01	0.276	0.001	276.0	1.5	0.3	0.2	208.3	1.6	0.3
02/01/2012	Q0261476	1.8	0.2	0.0	0.6	0.0	4.7	10.6	0.4	10.70	0.01	0.185	0.002	185.0	1.6	0.3	0.2	227.5	3.5	0.2
05/01/2012	Q0261475	1.8	0.2	0.0	0.7	4.3	8.1	14.7	0.6	10.85	0.01	0.348	0.001	347.6	1.5	0.5	0.3	297.8	4.8	0.2
08/01/2012	Q0261473	1.8	0.2	0.0	0.2	0.0	6.0	3.0	0.9	3.76	0.01	0.124	0.002	124.5	2.0	0.2	0.2	213.9	0.9	0.4
11/01/2012	Q0261472	1.2	0.3	0.0	0.2	0.0	5.6	9.3	0.7	8.35	0.01	0.499	0.001	498.8	1.5	0.4	0.3	294.6	4.1	0.1
14/01/2012	Q0261471	1.2	0.3	1.0	0.5	2.3	6.4	26.4	0.5	21.51	0.01	0.208	0.002	208.1	1.5	0.3	0.3	271.0	8.2	0.1
17/01/2012	Q0261470	1.5	0.6	0.0	0.8	1.7	6.1	12.5	1.1	8.08	0.01	0.887	0.001	887.4	1.5	0.8	0.5	453.8	5.4	0.1
20/01/2012	Q0261469	0.9	0.2	0.0	0.2	2.3	6.9	19.9	0.6	17.96	0.01	0.433	0.001	433.2	1.5	0.6	0.4	443.5	7.7	0.1
23/01/2012	Q0261468	1.5	0.6	0.0	0.2	0.0	8.3	9.1	0.9	11.64	0.01	0.233	0.002	233.1	1.5	0.3	0.3	271.3	2.2	0.3
01/02/2012	Q0261466	1.8	0.2	0.0	0.4					22.10	0.01	0.713	0.001	712.7	1.5					
04/02/2012	Q0261465	1.5	0.6	0.5	0.2	0.0	7.6	4.7	1.2	5.22	0.02	0.432	0.001	431.8	1.5	0.3	0.2	162.3	1.4	0.5
07/02/2012	Q0261464	1.5	0.6	0.0	0.6	0.0	6.6	5.9	1.0	5.42	0.01	0.405	0.001	405.3	1.5	0.2	0.2	161.2	1.3	0.6
10/02/2012	Q0261463	1.2	0.3	0.0	0.5	0.0	8.1	8.7	0.9	9.56	0.01	0.486	0.001	486.4	1.5	0.3	0.2	224.4	3.3	0.3
13/02/2012	Q0261462	1.2	0.3	0.0	0.4	0.0	6.5	7.7	0.7	7.40	0.01	0.673	0.001	672.7	1.5	0.3	0.2	231.0	2.3	0.4
16/02/2012	Q0261461	0.6	0.2	0.0	0.0	0.0	3.1	4.2	1.1	3.86	0.01	0.351	0.001	350.6	1.5	0.2	0.2	157.0	1.7	0.6
19/02/2012	Q0261460	0.6	0.2	0.0	0.5	0.0	6.5	1.4	1.0	4.32	0.02	0.224	0.002	224.2	1.5	0.1	0.0	36.4	1.0	0.7
22/02/2012	Q0261459	1.9	0.5	0.0	0.6	0.0	4.8	1.5	3.3	2.67	0.02	0.486	0.001	486.1	1.5	0.3	0.1	128.9	0.3	3.2
25/02/2012	Q0261458	1.6	0.5	0.0	0.4	2.3	5.1	7.6	1.2	5.20	0.01	0.516	0.001	516.1	1.5	0.2	0.2	223.9	2.2	0.5
28/02/2012	Q0261457	3.0	0.1	0.0	0.5	0.0	5.3	2.8	1.1	7.45	0.01	0.714	0.001	713.6	1.5	0.3	0.1	88.6	1.4	0.9
02/03/2012	Q0261456	3.3	9.2	0.0	0.7	0.0	5.4	8.7	1.0	8.89	0.01	1.198	0.001	1198.3	1.5	0.8	0.3	277.4	1.8	0.4
05/03/2012	Q0261455	4.0	2.9	2.5	1.2	0.0	7.1	6.8	0.9	10.05	0.01	1.277	0.001	1277.0	1.5	0.9	0.3	274.3	5.1	0.2
08/03/2012	Q0261453	1.3	0.3	0.0	0.1	0.0	7.6	9.9	1.0	14.07	0.01	0.175	0.002	174.7	1.6	0.2	0.2	168.6	2.9	0.4
17/03/2012	Q0261452	4.6	2.3	1.7	0.8	5.5	5.9	6.6	1.5	7.98	0.01	1.175	0.001	1175.1	1.5	1.3	0.4	377.9	3.1	0.2
20/03/2012	Q0261451	0.6	0.1	0.0	0.7	2.8	5.3	4.9	0.4	8.88	0.01	0.207	0.002	206.8	1.5	0.2	0.1	140.5	1.9	0.2
23/03/2012	Q0261450	1.8	0.8	0.0	0.7	2.9	5.8	2.4	0.9	1.28	0.02	0.468	0.001	468.4	1.5	0.3	0.2	152.7	1.6	0.4
26/03/2012	Q0261449	1.4	0.3	0.0	0.5	0.0	4.8	6.6	1.0	4.76	0.01	0.788	0.001	787.6	1.5	0.4	0.3	322.9	1.7	0.7
29/03/2012	Q0261448	1.4	0.4	0.0	0.4	0.0	4.4	10.5	0.5	8.78	0.01	0.704	0.001	703.9	1.5	0.3	0.3	267.2	2.5	0.3
01/04/2012	Q0261447	2.0	1.9	0.0	0.4	0.0	4.6	4.7	0.9	4.01	0.02	0.624	0.001	624.5	1.5	0.4	0.3	251.7	2.5	0.2
04/04/2012	Q0261446	0.9	0.1	0.0	0.2	0.0	4.3	5.4	0.7	5.09	0.02	0.267	0.001	266.9	1.5	0.1	0.1	114.3	1.9	0.3
07/04/2012	Q0261445	3.2	0.1	0.0	0.1	0.0	7.4	4.5	0.8	4.15	0.03	0.712	0.001	712.4	1.5	0.3	0.1	146.6	2.0	0.3
09/04/2012	Q0261444	1.0	0.2	0.0	1.3	1.9	5.2	9.9	0.9	7.60	0.01	0.340	0.001	339.5	1.5	0.2	0.1	148.9	3.7	0.1
13/04/2012	Q0261443	6.6	1.1	3.7	1.8					4.59	0.02	1.334	0.001	1334.2	1.5					
16/04/2012	Q0261442	3.4	3.3	0.7	0.4					7.15	0.02	1.138	0.001	1137.9	1.5					
19/04/2012	Q0261441	4.8	1.1	1.7	0.8	0.0	6.5	2.4	1.8	1.75	0.04	1.006	0.001	1006.1	1.5	0.5	0.2	204.9	0.9	1.4
22/04/2012	Q0261440	34.9	1.2	40.1	19.1					10.03	0.01	2.690	0.001	2690.0	1.5					
25/04/2012	Q0261439	5.0	1.4	1.5	0.7					5.81	0.01	0.611	0.001	611.3	1.5					
28/04/2012	Q0261438	7.5	1.1	2.5	1.2	0.0	9.5	8.2	1.6	10.29	0.01	0.860	0.001	859.7	1.5	0.7	0.6	610.7	1.6	0.4
01/05/2012	Q0261437	1.5	0.4	0.0	0.0					6.84	0.01	0.307	0.001	307.1	1.5					

Date	Code																			
04/05/2012	Q0261436	20.5	1.2	17.2	8.2	0.0	7.6	2.2	1.4	10.56	0.01	3.276	0.001	3276.2	1.5	0.4	0.5	513.1	0.4	1.0
07/05/2012	Q0261435	31.2	1.2	33.6	16.0	14.2	9.7	9.7	0.9	12.99	0.01	3.199	0.001	3199.1	1.5	1.8	0.7	701.3	6.3	0.1
09/05/2012	Q0261434	5.1	1.8	1.5	0.7	0.0	7.2	5.1	0.9	5.59	0.01	1.124	0.001	1123.6	1.5	0.5	0.2	234.1	1.7	0.4
11/05/2012	Q0261433	22.3	0.9	16.9	8.1	4.4	6.2	11.0	1.0	10.67	0.01	2.340	0.001	2340.0	1.5	1.4	0.6	608.3	4.8	0.2
13/05/2012	Q0261432	4.5	1.0	0.7	0.4	0.0	10.5	11.6	0.7	13.01	0.01	0.651	0.001	651.0	1.5	0.6	0.6	588.6	3.4	0.3
15/05/2012	Q0261431	8.9	0.7	4.5	2.1	9.8	5.3	8.3	0.7	8.10	0.01	1.454	0.001	1454.5	1.5	0.8	0.3	304.9	3.7	0.2
17/05/2012	Q0261430	17.1	0.7	13.7	6.5	7.8	7.7	8.9	1.2	11.23	0.01	2.928	0.001	2928.0	1.5	3.1	1.4	1383.4	5.5	0.2
19/05/2012	Q0261429	2.1	0.5	0.0	0.4	0.0	6.6	8.7	0.6	8.80	0.01	0.609	0.001	609.3	1.5	0.4	0.3	331.9	1.7	0.2
21/05/2012	Q0261428	35.8	1.3	42.6	20.3	48.5	12.6	23.0	0.7	27.77	0.01	4.897	0.001	4897.2	1.5	6.2	3.2	3234.0	18.3	0.1
23/05/2012	Q0261427	15.3	0.6	12.7	6.0	11.6	10.7	11.2	1.6	17.35	0.01	2.944	0.001	2944.2	1.5	4.3	1.7	1687.6	7.7	0.0
25/05/2012	Q0261426	25.9	1.0	23.2	11.0	5.2	6.0	31.2	0.7	26.73	0.01	3.915	0.001	3915.2	1.5	3.2	1.2	1227.1	26.4	0.0
27/05/2012	Q0261425	2.9	0.1	1.0	0.5	1.3	5.0	9.1	1.3	12.04	0.01	0.719	0.001	719.3	1.5	0.5	0.3	338.6	3.3	0.2
29/05/2012	Q0261424	25.4	0.9	23.9	11.4	9.2	7.2	12.4	0.5	20.91	0.01	4.034	0.001	4034.4	1.5	3.1	1.3	1317.2	8.4	0.0
31/05/2012	Q0261423	28.7	1.1	31.1	14.8	12.5	6.3	13.0	0.8	27.21	0.01	4.664	0.001	4664.4	1.5	3.3	1.6	1599.2	7.4	0.1
02/06/2012	Q0261422	7.9	0.7	6.0	2.8	0.0	7.4	6.2	1.7	12.15	0.01	1.306	0.001	1306.0	1.5	0.5	0.2	186.5	0.9	1.4
04/06/2012	Q0261421	3.0	0.1	0.0	0.0	3.3	8.7	4.5	0.7	11.37	0.01	1.145	0.001	1145.4	1.5	1.3	0.4	359.0	2.2	0.2
06/06/2012	Q0261420	5.2	0.4	1.2	0.6	0.0	7.8	4.4	1.5	9.31	0.01	0.837	0.001	836.6	1.5	0.7	0.2	165.7	2.6	0.3
08/06/2012	Q0261419	4.8	2.5	0.0	0.1	3.4	4.6	8.8	1.4	13.39	0.01	1.064	0.001	1063.9	1.5	0.4	0.2	163.1	1.1	1.1
10/06/2012	Q0261418	24.9	1.1	22.4	10.7	20.1	7.6	19.3	1.7	20.47	0.01	3.636	0.001	3636.4	1.5	4.1	1.6	1578.5	14.0	0.1
12/06/2012	Q0261417	6.4	0.8	1.5	0.7	2.7	6.3	10.7	0.9	11.03	0.01	0.917	0.001	916.7	1.5	0.8	0.2	219.3	4.1	0.2
14/06/2012	Q0261416	5.0	0.6	0.7	0.4	0.0	4.8	8.7	1.6	9.96	0.01	0.497	0.001	496.8	1.5	0.6	0.2	176.6	1.1	1.0
16/06/2012	Q0261415	4.3	0.2	1.2	0.6	2.3	4.8	11.6	0.5	7.01	0.01	0.730	0.001	729.8	1.5	0.9	0.2	205.1	3.5	0.2
18/06/2012	Q0261414	3.3	1.6	1.5	0.7	2.3	4.5	3.5	0.5	3.38	0.03	0.624	0.001	624.2	1.5	0.8	0.5	457.2	2.0	0.3
20/06/2012	Q0261413	8.3	1.0	5.2	2.5	2.3	7.2	10.5	0.9	10.79	0.01	2.449	0.001	2449.3	1.5	1.9	0.8	841.2	5.9	0.1
22/06/2012	Q0261412	21.4	0.9	18.7	8.9	1.6	7.6	10.1	1.4	12.50	0.01	2.842	0.001	2841.8	1.5	2.3	0.8	838.3	4.3	0.2
24/06/2012	Q0261411	20.2	1.0	17.9	8.5	3.0	10.2	17.3	0.8	24.30	0.01	3.768	0.001	3768.2	1.5	2.1	0.6	619.1	7.6	0.1
26/06/2012	Q0261410	8.3	0.8	5.0	2.4	1.8	5.7	11.4	1.4	5.14	0.01	1.384	0.001	1384.3	1.5	1.3	0.9	850.2	3.7	0.4
28/06/2012	Q0261409	22.1	1.3	20.4	9.7	13.3	7.4	16.3	0.5	22.21	0.01	3.526	0.001	3526.0	1.5	2.2	0.6	631.6	6.8	0.1
30/06/2012	Q0261408	8.6	0.5	3.0	1.4	0.0	9.2	4.8	1.5	7.16	0.02	1.360	0.001	1360.1	1.5	0.9	0.2	199.7	1.6	1.1
02/07/2012	Q0261407	4.7	3.3	3.0	1.4	0.0	4.3	2.6	1.1	5.36	0.02	0.935	0.001	934.7	1.5	0.4	0.1	111.8	1.5	1.0
04/07/2012	Q0261406	4.4	0.2	1.5	0.7					1.16	0.06	0.577	0.001	577.3	1.5					
06/07/2012	Q0261405	12.9	0.7	12.5	5.9	14.5	7.3	8.1	1.3	9.45	0.01	2.281	0.001	2281.1	1.5	1.9	0.6	599.4	7.2	0.1
08/07/2012	Q0261404	34.4	1.4	33.9	16.1	38.0	7.8	18.8	1.3	20.70	0.01	4.077	0.001	4077.2	1.5	4.0	1.6	1592.8	13.0	0.0
10/07/2012	Q0261403	25.5	1.1	27.4	13.0	4.6	9.4	12.7	0.5	17.85	0.01	4.013	0.001	4012.6	1.5	3.6	1.4	1356.1	9.5	0.1
12/07/2012	Q0261297	18.3	1.5	18.9	9.0	9.9	8.0	9.8	0.9	13.57	0.01	3.124	0.001	3123.5	1.5	3.2	1.1	1082.3	5.6	0.1
14/07/2012	Q0261296	4.5	3.6	2.2	1.1	2.6	5.4	5.8	1.3	8.35	0.01	0.805	0.001	805.0	1.5	1.2	0.3	315.0	1.9	0.7
16/07/2012	Q0261295	5.0	3.0	3.5	1.7	0.0	6.8	5.4	1.3	8.80	0.02	1.210	0.001	1209.9	1.5	1.4	0.4	350.8	3.3	0.3
18/07/2012	Q0261294	9.7	0.8	8.7	4.1	3.7	6.9	13.0	1.3	18.74	0.01	3.124	0.001	3123.5	1.5	2.7	0.9	943.0	6.7	0.1
20/07/2012	Q0261293	20.6	0.9	17.4	8.3	11.0	5.9	11.3	1.0	20.93	0.01	3.571	0.001	3571.0	1.5	3.5	1.3	1280.9	5.1	0.2
22/07/2012	Q0261292	22.0	1.5	24.4	11.6	4.3	5.6	13.5	1.1	23.30	0.01	3.404	0.001	3403.7	1.5	2.9	1.0	995.7	7.4	0.1
24/07/2012	Q0261291	3.4	1.2	1.5	0.7	0.0	3.1	4.9	2.0	3.37	0.02	0.265	0.001	265.0	1.5	1.1	0.2	245.2	0.7	1.8
26/07/2012	Q0261290	8.2	1.3	6.7	3.2	7.8	5.7	9.9	0.9	12.33	0.01	2.114	0.001	2113.9	1.5	2.2	0.7	656.9	4.5	0.2
28/07/2012	Q0261289	48.6	2.4	59.8	28.4	46.8	13.4	25.7	1.7	33.32	0.01	4.961	0.001	4961.1	1.5	5.7	2.7	2675.5	20.5	0.1
30/07/2012	Q0261288	3.2	1.6	0.0	0.1	0.0	4.5	3.9	1.0	0.93	0.09	0.206	0.002	205.8	1.5	1.0	0.2	223.2	2.9	0.4
01/08/2012	Q0261287	3.1	0.5	0.5	0.2	0.0	5.7	3.9	1.6	7.05	0.01	0.342	0.001	341.7	1.5	1.1	0.3	271.3	3.5	0.6
03/08/2012	Q0261286	2.9	0.9	0.2	0.1					4.93	0.02	0.187	0.002	187.3	1.6					
05/08/2012	Q0261285	10.3	1.3	9.0	4.3	5.6	5.3	1.6	1.4	10.16	0.01	2.277	0.001	2277.5	1.5	2.1	0.7	658.7	1.5	0.7
07/08/2012	Q0261284	4.0	0.2	0.0	0.0	2.6	4.9	3.7	1.3	7.47	0.01	0.676	0.001	676.4	1.5	1.2	0.3	274.9	1.9	0.9
09/08/2012	Q0261283	9.0	1.0	4.5	2.1	3.6	4.2	1.1	2.5	8.76	0.01	1.589	0.001	1588.6	1.5	2.0	0.6	569.7	0.7	2.2
11/08/2012	Q0261282	29.9	2.0	30.4	14.5	25.0	10.8	11.1	1.6	24.72	0.01	4.100	0.001	4099.6	1.5	3.8	1.4	1434.4	10.4	0.2
13/08/2012	Q0261280	14.2	1.0	11.7	5.6					13.74	0.01	2.875	0.001	2875.5	1.5					
15/08/2012	Q0261279	8.7	1.6	6.0	2.8	5.7	5.3	2.9	1.9	9.55	0.01	1.618	0.001	1618.5	1.5	1.6	0.4	434.3	1.3	0.5
17/08/2012	Q0261278	10.8	1.2	7.5	3.6	4.2	5.1	3.6	0.8	14.08	0.01	2.581	0.001	2581.1	1.5	2.5	0.8	767.7	3.5	0.3
19/08/2012	Q0261277	20.2	1.1	19.9	9.5	14.0	5.9	5.3	1.4	17.33	0.01	3.787	0.001	3786.7	1.5	3.3	1.3	1272.9	5.2	0.2
21/08/2012	Q0261276	4.6	3.6	0.7	0.4					5.41	0.02	0.559	0.001	558.6	1.5					
23/08/2012	Q0261275	11.7	1.0	9.2	4.4	6.2	7.4	3.7	1.4	11.75	0.01	3.057	0.001	3057.1	1.5	2.1	0.7	655.4	2.2	0.3
25/08/2012	Q0261274	4.4	0.6	0.0	0.2	0.0	8.2	4.2	1.0	6.89	0.01	0.887	0.001	886.7	1.5	0.7	0.2	234.7	1.5	0.7
27/08/2012	Q0261273	1.8	0.3	0.7	0.4	0.0	4.7	10.2	1.0	13.07	0.01	0.424	0.001	424.5	1.5	0.4	0.2	225.0	3.7	0.2
29/08/2012	Q0261272	21.6	0.8	15.4	7.3	11.7	6.7	15.8	0.6	18.72	0.01	3.704	0.001	3703.6	1.5	3.4	1.3	1259.0	11.7	0.0
31/08/2012	Q0261271	11.7	0.5	8.0	3.8	8.2	5.4	10.1	1.0	12.56	0.01	2.834	0.001	2834.1	1.5	2.3	0.7	746.4	7.3	0.1
02/09/2012	Q0261270	3.0	0.1	0.0	0.0	0.0	7.3	10.8	0.9	10.52	0.01	0.800	0.001	799.7	1.5	0.5	0.2	233.1	4.4	0.2
04/09/2012	Q0261269	9.2	0.4	5.2	2.5	0.0	5.0	8.6	1.7	8.74	0.01	1.353	0.001	1353.4	1.5	0.2	0.3	256.0	4.0	0.3
06/09/2012	Q0261268	1.5	0.1	0.0	0.7	0.0	4.4	27.5	0.9	24.18	0.01	0.585	0.001	584.7	1.5	0.5	0.3	318.9	8.9	0.1
10/09/2012	Q0261266	3.0	0.2	0.7	0.4	0.0	4.1	16.6	0.6	13.66	0.01	0.976	0.001	976.3	1.5	0.6	0.4	355.0	6.1	0.3
12/09/2012	Q0261265	7.2	0.3	2.7	1.3	8.1	5.0	10.4	1.7	12.14	0.01	1.417	0.001	1416.8	1.5	1.0	0.3	343.0	5.5	0.2
14/09/2012	Q0261264	1.5	0.2	0.0	0.4	4.2	6.0	6.2	1.4	6.64	0.01	0.435	0.001	435.4	1.5	0.6	0.2	243.2	1.3	0.9
16/09/2012	Q0261263	5.7	0.2	1.2	0.6	2.9	4.2	6.4	1.5	8.55	0.01	1.337	0.001	1336.6	1.5	0.8	0.3	287.8	3.2	0.4

19/09/2012	Q0261262	7.0	0.3	3.5	1.7	0.0	5.7	3.7	2.8	10.41	0.01	1.634	0.001	1633.9	1.5	0.3	0.3	256.4	0.7	2.4	
22/09/2012	Q0261261	15.1	0.5	11.0	5.2	11.1	4.9	3.8	1.1	11.97	0.01	2.351	0.001	2351.4	1.5	1.8	0.6	642.0	2.0	0.5	
25/09/2012	Q0261260	7.7	0.3	4.2	2.0	1.6	5.8	2.4	1.5	9.89	0.01	1.394	0.001	1393.6	1.5	0.8	0.3	269.7	1.0	1.1	
28/09/2012	Q0261259	2.4	0.3	0.0	0.6	0.0	8.8	2.8	2.3	5.04	0.01	0.408	0.001	407.8	1.5	0.2	0.1	144.0	0.7	1.4	
01/10/2012	Q0261258	1.9	0.1	0.0	0.0	0.0	3.7	13.4	0.8	13.05	0.01	0.258	0.001	258.3	1.5	0.2	0.3	278.1	3.7	0.4	
04/10/2012	Q0261257	2.6	0.1	0.0	0.0	1.2	4.0	8.6	0.5	12.06	0.01	0.505	0.001	504.5	1.5	0.4	0.2	215.7	2.9	0.2	
07/10/2012	Q0261256	5.7	0.3	0.5	0.2	1.8	3.9	5.3	1.5	7.50	0.01	0.648	0.001	648.0	1.5	0.6	0.2	190.7	1.6	0.4	
10/10/2012	Q0261255	1.9	0.2	0.0	0.1	0.0	4.7	7.7	3.0	11.44	0.01	0.244	0.002	244.2	1.5	0.3	0.2	214.0	0.4	2.8	
13/10/2012	Q0261254	2.5	0.3	0.0	0.0	0.0	4.7	8.1	1.5	9.27	0.01	0.411	0.001	411.1	1.5	0.3	0.2	215.2	2.9	0.5	
16/10/2012	Q0261252	4.0	0.4	1.0	0.5	0.0	4.1	9.5	1.8	8.25	0.01	0.998	0.001	998.2	1.5	0.9	0.2	245.8	4.9	0.2	
19/10/2012	Q0261251	4.6	1.4	2.0	0.9	2.2	5.4	12.2	1.8	6.29	0.01	0.629	0.001	629.3	1.5	0.3	0.1	139.5	5.0	0.2	
22/10/2012	Q0261250	4.0	0.4	1.0	0.5					11.84	0.01	0.518	0.001	517.6	1.5						
25/10/2012	Q0261249	2.1	0.4	0.0	0.7	0.0	6.7	27.3	1.3	21.57	0.01	0.428	0.001	427.6	1.5	0.4	0.2	233.8	7.8	0.1	
28/10/2012	Q0261248	2.8	0.6	0.0	0.6	2.8	5.7	7.7	0.7	5.08	0.01	0.477	0.001	477.3	1.5	0.4	0.1	127.9	4.1	0.3	
31/10/2012	Q0261247	2.6	1.1	0.0	0.0					11.78	0.01	0.641	0.001	641.2	1.5						
03/11/2012	Q0261246	3.7	0.3	0.2	0.1	2.3	4.4	6.1	0.6	4.84	0.01	0.524	0.001	524.0	1.5	0.4	0.1	137.1	1.7	0.5	
06/11/2012	Q0261245	3.0	0.2	0.0	0.4	0.0	7.0	18.2	1.3	10.11	0.01	0.273	0.001	273.4	1.5	0.4	0.2	246.5	6.9	0.1	
09/11/2012	Q0261244	4.7	0.6	1.2	0.6	1.6	7.2	7.8	0.6	5.87	0.02	0.957	0.001	957.3	1.5	0.8	0.2	232.8	4.2	0.2	
12/11/2012	Q0261243	1.7	0.5	0.0	0.0	0.0	6.0	13.0	1.6	7.07	0.01	0.250	0.002	250.5	1.5	0.4	0.2	162.6	5.0	0.3	
15/11/2012	Q0261242	1.9	0.3	0.2	0.1	0.0	7.2	12.6	0.9	7.37	0.01	0.387	0.001	386.8	1.5	0.4	0.1	143.9	5.7	0.2	
18/11/2012	Q0261241	3.5	0.5	2.2	1.1	2.2	4.8	8.1	1.2	4.83	0.01	0.388	0.001	387.9	1.5	0.4	0.1	112.1	2.0	0.7	
21/11/2012	Q0261240	3.4	0.7	1.2	0.6	0.0	5.4	6.6	0.4	6.63	0.01	0.897	0.001	897.2	1.5	0.7	0.2	238.5	2.3	0.1	
24/11/2012	Q0261239	3.1	0.6	1.5	0.7	0.0	5.4	11.4	0.8	11.60	0.01	0.475	0.001	475.0	1.5	0.4	0.2	183.9	3.4	0.4	
27/11/2012	Q0261238	2.5	0.1	1.2	0.6	0.0	5.7	13.6	0.6	14.37	0.01	0.455	0.001	455.4	1.5	0.4	0.2	228.0	3.8	0.2	
30/11/2012	Q0261237	2.4	0.9	0.0	0.2	0.0	6.0	8.8	1.5	7.20	0.01	0.289	0.001	288.9	1.5	0.3	0.1	119.8	2.7	0.4	
03/12/2012	Q0261236	2.3	0.8	0.2	0.1	1.6	4.6	19.1	1.4	17.02	0.01	0.548	0.001	548.3	1.5	0.6	0.3	297.5	6.5	0.1	
06/12/2012	Q0261235	2.2	0.4	0.0	0.1	0.0	6.7	13.6	1.1	10.18	0.01	0.319	0.001	319.4	1.5	0.4	0.2	227.1	5.0	0.2	
09/12/2012	Q0261233	1.8	0.7	0.2	0.1	0.0	7.3	9.6	0.6	12.60	0.01	0.152	0.002	152.2	1.7	0.2	0.1	120.2	3.6	0.1	
12/12/2012	Q0261232	1.7	0.3	2.5	1.2	0.0	7.0	7.4	0.5	9.38	0.01	0.487	0.001	487.3	1.5	0.4	0.1	110.1	4.1	0.3	
15/12/2012	Q0261231	1.4	0.9	1.2	0.6	3.8	5.8	9.4	0.5	8.40	0.01	0.278	0.001	278.4	1.5	0.1	0.1	102.9	3.9	0.5	
18/12/2012	Q0261230	2.1	0.2	0.7	0.4	0.0	7.3	5.7	0.4	3.49	0.01	0.343	0.001	343.0	1.5	0.2	0.1	100.4	3.0	0.2	
21/12/2012	Q0261229	1.9	1.1	1.0	0.5	1.6	4.2	11.9	0.4	10.30	0.01	0.437	0.001	437.4	1.5	0.4	0.1	120.4	4.4	0.3	
24/12/2012	Q0261228	1.4	0.3	0.7	0.4	0.0	3.9	8.2	0.2	2.41	0.03	0.123	0.002	123.0	2.0	0.1	0.1	56.9	4.2	0.1	
30/12/2012	Q0261227	2.0	0.6	1.0	0.5	2.1	5.2	11.8	0.4	8.13	0.01	0.181	0.002	181.2	1.6	0.1	0.1	91.8	5.1	0.3	
02/01/2013	Q0261226	1.3	0.4	1.2	0.6	2.2	5.0	23.8	0.2	16.13	0.01	0.138	0.002	137.8	1.8	0.1	0.1	89.5	9.7	0.2	
05/01/2013	Q0261225	2.3	0.8	1.5	0.7	0.0	7.6	10.1	0.2	3.38	0.01	0.812	0.001	811.5	1.5	0.6	0.1	143.8	4.2	0.2	
08/01/2013	Q0261224	1.5	0.9	0.5	0.2	2.0	4.1	17.0	0.3	14.57	0.01	0.291	0.001	291.0	1.5	0.1	0.1	97.6	3.4	0.3	
11/01/2013	Q0261223	1.6	1.3	0.5	0.2	0.0	5.8	15.3	0.2	13.33	0.01	0.316	0.001	315.9	1.5	0.2	0.1	141.7	4.2	0.2	
14/01/2013	Q0261222	1.8	0.4	0.5	0.2	0.0	3.6	5.5	0.5	3.84	0.02	0.352	0.001	351.6	1.5	0.2	0.1	107.5	2.1	0.4	
17/01/2013	Q0261221	1.8	0.7	0.5	0.2	0.0	3.7	10.6	0.2	8.93	0.01	0.352	0.001	352.2	1.5	0.2	0.1	136.9	3.8	0.2	
20/01/2013	Q0261220	1.8	0.8	1.0	0.5	0.0	5.3	7.0	0.3	10.42	0.01	0.312	0.001	312.2	1.5	0.1	0.1	108.4	1.9	0.2	
23/01/2013	Q0261219	2.1	0.4	0.0	0.0	1.5	7.4	17.8	0.1	17.63	0.01	0.428	0.001	428.4	1.5	0.2	0.1	126.2	6.4	0.1	
26/01/2013	Q0261218	1.7	1.3	0.7	0.4	2.9	4.9	14.4	0.1	10.37	0.01	0.328	0.001	328.2	1.5	0.1	0.1	105.6	5.7	0.1	
29/01/2013	Q0261217	2.3	0.1	0.0	0.2	0.0	6.6	5.9	0.6	6.60	0.01	1.032	0.001	1031.9	1.5	0.7	0.1	119.5	2.6	0.5	
01/02/2013	Q0261216	2.0	0.7	0.0	0.7	0.0	6.9	7.8	0.3	7.97	0.01	0.739	0.001	739.3	1.5	0.3	0.1	132.6	3.4	0.2	
04/02/2013	Q0261214	2.4	1.3	0.0	0.5	0.0	6.5	5.2	0.5	4.72	0.01	0.382	0.001	381.9	1.5	0.1	0.1	103.0	1.4	0.5	
07/02/2013	Q0261212	2.9	0.6	0.0	0.5	0.0	6.0	8.0	0.5	5.52	0.01	0.568	0.001	567.7	1.5	0.3	0.1	118.0	2.7	0.4	
10/02/2013	Q0261211	3.4	0.2	0.0	0.4	0.0	5.7	10.1	0.3	9.74	0.01	0.460	0.001	460.5	1.5	0.4	0.1	122.1	2.8	0.3	
13/02/2013	Q0261210	2.8	0.3	0.0	0.2	1.5	5.9	12.7	0.3	11.77	0.01	0.352	0.001	351.6	1.5	0.2	0.1	120.1	2.0	0.3	
16/02/2013	Q0261209	3.4	0.7	0.0	0.1	1.9	7.3	11.5	0.3	9.45	0.01	0.654	0.001	654.1	1.5	0.3	0.1	125.2	3.8	0.2	
19/02/2013	Q0261208	4.1	0.5	0.0	0.0	1.9	4.5	5.8	0.7	8.63	0.01	1.191	0.001	1190.5	1.5	0.8	0.1	146.3	1.5	0.7	
22/02/2013	Q0261207	2.5	0.4	0.0	0.1	1.9	4.1	7.1	0.3	9.98	0.01	0.281	0.001	281.3	1.5	0.1	0.1	76.6	2.1	0.3	
25/02/2013	Q0261206	2.5	0.4	0.0	0.1	0.0	7.0	7.2	0.4	8.67	0.01	0.898	0.001	897.9	1.5	0.7	0.1	148.6	2.4	0.4	
03/03/2013	Q0261204	1.8	4.1	0.0	0.2	0.0	7.8	10.6	0.3	9.40	0.01	0.319	0.001	319.1	1.5	0.1	0.2	151.8	3.0	0.2	
06/03/2013	Q0261203	1.9	2.0	0.0	0.6	0.0	4.2	15.5	0.2	10.41	0.01	0.373	0.001	373.4	1.5	0.2	0.1	119.6	6.4	0.1	
09/03/2013	Q0261202	2.9	1.6	0.0	0.0	1.9	6.4	7.7	0.4	8.80	0.01	0.519	0.001	518.7	1.5	0.1	0.1	149.5	2.2	0.4	
15/03/2013	Q0261201	1.8	3.8	0.0	0.7	0.0	2.9	9.2	0.3	4.85	0.02	0.304	0.001	304.2	1.5	0.1	0.1	85.5	3.8	0.2	
18/03/2013	Q0262998	2.4	0.4	0.0	0.1	2.1	4.9	4.6	0.6	2.68	0.03	0.339	0.001	339.3	1.5	0.2	0.1	103.4	2.4	0.5	
21/03/2013	Q0262997	7.0	0.4	2.7	1.3	0.0	9.0	4.4	0.5	7.00	0.01	1.422	0.001	1422.3	1.5	1.0	0.2	152.4	2.0	0.5	
24/03/2013	Q0262996	2.4	0.8	0.0	0.9	0.0	6.3	3.0	0.9	7.24	0.01	0.270	0.001	269.7	1.5	0.1	0.0	47.9	0.9	0.9	
27/03/2013	Q0262995	3.6	1.0	0.2	0.1	2.3	6.3	6.2	0.4	9.60	0.01	1.491	0.001	1491.5	1.5	1.0	0.1	150.0	2.4	0.3	
30/03/2013	Q0262994	2.1	0.5	0.0	0.5	0.0	4.2	6.8	0.3	10.65	0.01	0.427	0.001	426.7	1.5	0.3	0.1	134.5	2.1	0.2	
02/04/2013	Q0262993	2.0	1.4	0.0	0.9	0.0	3.6	10.3	0.2	8.96	0.01	0.283	0.001	283.4	1.5	0.2	0.1	116.0	4.7	0.2	
05/04/2013	Q0262991	4.3	0.3	1.0	0.5	0.0	9.5	9.0	0.2	11.30	0.01	1.435	0.001	1434.7	1.5	1.0	0.1	149.1	4.1	0.2	
08/04/2013	Q0262990	8.2	0.4	4.5	2.1	1.7	4.4	6.2	0.3	5.10	0.01	1.284	0.001	1284.2	1.5	0.8	0.1	144.6	3.1	0.2	
11/04/2013	Q0262989	10.3	0.4	6.5	3.1	8.8	5.7	11.6	0.2	13.33	0.01	1.791	0.001	1791.2	1.5	1.2	0.2	153.7	5.4	0.1	

Date	ID																			
14/04/2013	Q0262988	2.8	0.3	0.0	0.2	0.0	6.0	5.9	0.3	4.29	0.02	0.465	0.001	464.7	1.5	0.2	0.1	110.2	3.3	0.1
17/04/2013	Q0262987	3.8	0.6	1.0	0.5	3.6	6.9	2.0	1.2	4.19	0.01	0.608	0.001	607.8	1.5	0.2	0.1	107.7	1.0	0.4
20/04/2013	Q0262982	2.1	1.2	0.0	0.7	0.0	7.4	0.9	3.9	2.99	0.01	0.162	0.002	162.4	1.7	0.1	0.1	71.4	0.1	3.9
23/04/2013	Q0262981	1.9	0.7	0.0	0.0	3.8	4.9	9.1	0.2	12.20	0.01	0.313	0.001	313.3	1.5	0.2	0.1	117.1	2.5	0.2
26/04/2013	Q0262980	3.8	0.5	0.5	0.2	1.3	6.3	9.5	0.5	12.48	0.01	1.023	0.001	1022.6	1.5	0.5	0.1	139.7	1.8	0.5
29/04/2013	Q0262979	29.3	1.0	0.0	0.4	2.0	5.5	25.6	0.1	22.33	0.01	0.465	0.001	465.0	1.5	0.3	0.1	141.3	7.9	0.1
02/05/2013	Q0262978	3.5	0.1	5.7	2.7	2.3	5.4	14.0	0.1	12.04	0.01	1.843	0.001	1842.5	1.5	1.3	0.2	158.3	7.7	0.1
04/05/2013	Q0262977	20.4	0.7	16.2	7.7	9.9	7.6	15.0	0.1	15.58	0.01	3.246	0.001	3245.6	1.5	3.0	0.2	195.1	10.0	0.1
06/05/2013	Q0262976	3.1	1.0	0.2	0.1	3.2	5.5	6.7	0.4	5.51	0.02	0.783	0.001	783.1	1.5	0.5	0.1	105.5	2.8	0.3
08/05/2013	Q0262975	28.9	1.1	25.4	12.1	16.2	6.4	14.2	0.1	22.93	0.01	4.558	0.001	4557.7	1.5	3.7	0.2	209.9	9.3	0.0
10/05/2013	Q0262974	3.1	0.6	0.0	0.5	1.6	3.9	12.8	0.1	14.07	0.01	0.635	0.001	634.8	1.5	0.3	0.1	136.6	4.0	0.1
12/05/2013	Q0262973	19.6	0.8	16.9	8.1	14.3	6.2	21.2	0.1	23.07	0.01	3.368	0.001	3368.5	1.5	2.5	0.2	178.0	11.8	0.1
14/05/2013	Q0262972	3.1	0.8	0.0	0.0	0.0	7.8	14.6	0.1	14.78	0.01	1.079	0.001	1078.6	1.5	0.6	0.1	143.4	5.8	0.1
16/05/2013	Q0262971	19.2	1.1	14.2	6.8					20.23	0.01	3.547	0.001	3546.8	1.5					
18/05/2013	Q0262970	16.9	0.6	15.4	7.3	15.6	5.9	10.8	0.2	11.29	0.01	1.916	0.001	1916.4	1.5	1.3	0.2	154.4	5.6	0.1
20/05/2013	Q0262969	17.3	0.7	13.7	6.5	8.6	6.7	17.7	0.1	18.88	0.01	3.754	0.001	3754.5	1.5	3.3	0.2	199.6	10.3	0.1
22/05/2013	Q0262967	10.3	0.4	8.5	4.0	8.2	4.6	7.9	0.2	10.36	0.01	2.141	0.001	2140.8	1.5	1.5	0.1	141.0	3.1	0.2
24/05/2013	Q0262966	10.4	0.4	7.0	3.3					10.36	0.01	2.267	0.001	2267.1	1.5					
26/05/2013	Q0262965	1.6	0.1	0.7	0.4	0.0	3.1	9.0	0.2	10.44	0.01	0.597	0.001	597.3	1.5	0.3	0.1	116.5	2.5	0.2
28/05/2013	Q0262963	2.9	0.1	0.0	0.0	1.5	5.0	2.6	2.5	5.33	0.01	0.407	0.001	407.0	1.5	0.2	0.1	102.3	0.1	2.4
30/05/2013	Q0262962	40.8	2.1	32.1	15.3	10.4	7.6	19.9	0.0	28.07	0.01	5.082	0.001	5082.2	1.5	4.3	0.2	223.3	13.9	0.0
01/06/2013	Q0262961	3.2	0.5	0.5	0.2	1.4	4.8	11.0	0.1	10.38	0.01	0.877	0.001	876.5	1.5	0.4	0.1	117.9	3.4	0.1
03/06/2013	Q0262960	2.3	0.5	0.0	0.1	1.9	3.9	9.6	0.3	10.21	0.01	0.758	0.001	758.2	1.5	0.5	0.1	121.9	2.2	0.2
05/06/2013	Q0262959	2.0	0.1	0.0	0.4	3.2	4.6	7.9	0.4	7.81	0.01	0.339	0.001	339.0	1.5	0.2	0.1	114.4	2.2	0.3
07/06/2013	Q0262958	34.6	1.3	30.1	14.3	24.2	8.7	18.3	0.1	25.48	0.01	4.553	0.001	4552.9	1.5	4.0	0.2	214.7	13.5	0.0
09/06/2013	Q0262957	16.0	1.0	11.5	5.5	3.1	5.4	5.3	0.5	9.93	0.01	2.576	0.001	2576.3	1.5	1.7	0.1	143.0	3.9	0.1
11/06/2013	Q0262956	10.6	0.4	5.2	2.5	4.4	4.6	6.8	0.3	8.34	0.01	1.877	0.001	1876.8	1.5	1.0	0.1	127.6	2.3	0.2
13/06/2013	Q0262955	11.1	0.4	6.7	3.2	8.4	4.3	6.6	0.2	9.31	0.01	2.486	0.001	2485.7	1.5	1.7	0.1	143.0	4.0	0.1
15/06/2013	Q0262954	24.2	1.3	18.9	9.0	7.4	5.6	9.9	0.3	17.57	0.01	4.202	0.001	4202.2	1.5	2.4	0.2	158.0	7.5	0.1
17/06/2013	Q0262953	5.6	0.3	2.2	1.1	0.0	4.6	6.0	0.2	8.27	0.01	1.219	0.001	1218.9	1.5	0.6	0.1	121.9	2.4	0.2
19/06/2013	Q0262951	9.3	0.6	6.5	3.1	0.0	9.6	7.7	0.3	6.79	0.01	1.775	0.001	1775.3	1.5	1.3	0.1	134.7	4.0	0.2
23/06/2013	Q0262950	24.4	0.9	15.0	7.1	11.4	6.2	14.2	0.2	18.39	0.01	3.658	0.001	3658.2	1.5	2.9	0.2	187.6	8.4	0.1
25/06/2013	Q0262949	53.2	2.0	44.1	21.0	36.5	11.2	20.0	0.3	32.11	0.01	5.697	0.001	5696.7	1.5	4.8	0.3	253.6	15.8	0.0
27/06/2013	Q0262948	22.4	1.0	16.7	7.9	12.7	5.4	13.8	0.1	16.38	0.01	3.206	0.001	3206.3	1.5	2.0	0.2	166.7	8.4	0.1
29/06/2013	Q0262947	30.4	1.3	23.4	11.1	9.0	5.2	11.9	0.2	25.61	0.01	4.308	0.001	4308.1	1.5	2.0	0.2	160.1	6.3	0.2
01/07/2013	Q0262946	2.7	0.5	0.7	0.4	0.0	5.4	7.1	0.4	9.41	0.01	1.219	0.001	1218.9	1.5	0.7	0.1	141.5	1.9	0.3
03/07/2013	Q0262943	2.0	0.8	0.0	0.8	0.0	5.4	3.3	0.4	9.73	0.01	0.329	0.001	329.0	1.5	0.2	0.1	134.5	1.5	0.3
05/07/2013	Q0262942	5.8	0.4	3.2	1.5	4.1	4.5	5.6	0.3	11.76	0.01	1.390	0.001	1390.2	1.5	0.8	0.1	142.0	1.7	0.3
07/07/2013	Q0262941	3.9	0.1	0.0	0.0	0.0	4.4	11.2	0.4	19.61	0.01	0.988	0.001	988.3	1.5	0.5	0.1	138.5	2.2	0.4
09/07/2013	Q0262940	13.8	0.6	9.5	4.5	16.6	5.7	10.6	0.2	11.12	0.01	2.711	0.001	2711.2	1.5	2.0	0.2	166.6	6.2	0.1
11/07/2013	Q0262939	1.3	0.2	0.0	0.5	0.0	9.7	4.6	0.4	3.31	0.02	0.365	0.001	365.5	1.5	0.1	0.1	71.8	1.3	0.3
13/07/2013	Q0262938	11.2	0.4	7.5	3.6	2.6	5.9	7.5	0.6	10.35	0.01	2.417	0.001	2416.6	1.5	1.7	0.2	158.8	6.2	0.1
15/07/2013	Q0262937	2.1	0.5	0.0	0.5	0.0	6.1	7.9	0.4	7.62	0.01	0.410	0.001	410.3	1.5	0.2	0.1	95.8	3.0	0.3
17/07/2013	Q0262936	1.4	0.2	0.0	0.2	0.0	5.9	11.1	0.2	12.51	0.01	0.754	0.001	754.0	1.5	0.4	0.1	120.3	4.7	0.2
19/07/2013	Q0262935	12.7	0.7	9.0	4.3	8.9	5.1	11.0	0.2	13.81	0.01	3.099	0.001	3099.2	1.5	2.3	0.2	171.4	5.3	0.2
21/07/2013	Q0262934	1.2	0.4	0.0	0.7	0.0	6.7	9.1	0.2	4.30	0.02	0.326	0.001	325.8	1.5	0.3	0.1	107.5	3.8	0.2
23/07/2013	Q0262933	2.6	0.5	0.5	0.2	2.0	5.8	7.5	0.3	5.51	0.02	1.014	0.001	1013.9	1.5	0.6	0.1	120.3	4.1	0.3
25/07/2013	Q0262932	5.7	0.2	2.0	0.9	0.0	6.4	12.8	0.1	10.28	0.01	1.732	0.001	1731.7	1.5	1.1	0.1	137.8	5.8	0.1
27/07/2013	Q0262931	4.5	0.2	1.5	0.7	1.9	4.4	11.1	0.2	9.37	0.01	1.763	0.001	1762.8	1.5	0.9	0.1	143.7	4.3	0.1
29/07/2013	Q0262930	43.4	1.9	37.4	17.8	28.9	7.7	14.4	0.4	23.28	0.01	4.776	0.001	4776.2	1.5	4.0	0.2	229.6	11.7	0.1
31/07/2013	Q0262928	6.2	0.3	3.0	1.4	5.3	4.0	7.9	0.2	7.45	0.01	1.221	0.001	1220.8	1.5	0.8	0.1	124.2	4.4	0.1
02/08/2013	Q0262927	10.2	0.4	6.5	3.1	0.0	8.5	6.4	0.4	9.47	0.01	2.034	0.001	2033.7	1.5	1.4	0.2	157.7	4.9	0.1
04/08/2013	Q0262926	2.2	0.5	3.2	1.5	0.0	6.8	2.2	1.8	4.04	0.02	0.897	0.001	896.5	1.5	0.5	0.1	103.5	2.0	0.3
06/08/2013	Q0262925	5.1	0.3	0.0	0.5	0.0	4.3	10.5	0.3	10.91	0.01	0.541	0.001	541.5	1.5	0.3	0.1	136.7	2.5	0.3
08/08/2013	Q0262924	2.4	0.5	0.0	0.0	0.0	7.2	7.1	0.6	9.32	0.01	0.496	0.001	496.5	1.5	0.1	0.1	89.7	1.1	0.5
10/08/2013	Q0262923	9.6	0.5	4.7	2.3	0.0	5.9	3.2	0.4	7.19	0.01	1.848	0.001	1848.1	1.5	0.4	0.1	131.6	1.7	0.3
12/08/2013	Q0262922	1.6	0.2	0.2	0.1	0.0	7.0	8.4	0.1	7.55	0.01	0.581	0.001	581.4	1.5	0.3	0.1	96.7	2.6	0.4
14/08/2013	Q0262920	16.7	0.7	9.5	4.5	9.9	6.1	12.2	0.1	15.51	0.01	2.768	0.001	2768.4	1.5	1.7	0.2	161.2	5.7	0.1
16/08/2013	Q0262919	0.0	0.0	0.0	0.2	4.2	4.6	5.7	0.1	6.11	0.01	0.398	0.001	398.1	1.5	0.7	0.1	137.6	2.5	0.1
18/08/2013	Q0262918	6.4	0.5	2.5	1.2	3.7	4.6	5.8	0.4	5.95	0.01	0.977	0.001	977.0	1.5	0.5	0.1	106.2	3.4	0.1
20/08/2013	Q0262917	17.4	1.2	11.7	5.6	12.3	5.4	7.6	0.4	12.31	0.01	2.846	0.001	2845.7	1.5	1.8	0.2	159.6	4.6	0.3
22/08/2013	Q0262916	1.8	0.1	0.0	0.6	2.3	3.7	1.8	1.7	4.63	0.02	0.806	0.001	805.9	1.5	0.3	0.1	95.2	0.4	1.6
24/08/2013	Q0262915	4.7	0.3	2.2	1.1	3.0	4.8	4.2	0.6	7.65	0.01	1.283	0.001	1283.0	1.5	0.4	0.1	124.8	2.0	0.4
26/08/2013	Q0262914	14.6	0.6	8.7	4.1	12.4	5.6	8.2	0.2	12.33	0.01	2.478	0.001	2478.4	1.5	2.4	0.2	178.0	4.5	0.1
28/08/2013	Q0262913	1.4	0.1	0.0	0.6	1.0	2.9	3.4	0.4	9.72	0.01	0.498	0.001	497.9	1.5	0.1	0.1	85.9	1.3	0.4
30/08/2013	Q0262912	0.9	0.1	0.0	0.0	0.0	6.2	4.8	1.0	7.11	0.01	0.427	0.001	427.0	1.5	0.2	0.1	96.7	0.9	1.0

03/09/2013	Q0262910	18.9	1.8	13.2	6.3	9.7	5.8	2.8	2.6	9.51	0.01	2.445	0.001	2444.7	1.5	1.5	0.2	154.5	2.4	0.1
05/09/2013	Q0262909	1.2	0.2	0.0	0.2	1.5	3.9	6.5	0.2	11.44	0.01	0.411	0.001	410.8	1.5	0.3	0.1	99.8	2.9	0.2
08/09/2013	Q0262908	1.4	0.4	0.0	0.9	0.0	6.0	14.2	0.3	16.62	0.01	0.523	0.001	522.8	1.5	0.2	0.1	112.0	2.5	0.3
11/09/2013	Q0262907	1.2	0.7	0.7	0.4	0.0	4.9	13.8	0.1	14.19	0.01	0.649	0.001	648.9	1.5	0.3	0.1	99.3	3.6	0.1
14/09/2013	Q0262906	4.1	0.4	1.7	0.8	4.9	6.9	3.0	1.8	6.79	0.01	1.287	0.001	1287.5	1.5	0.6	0.1	116.3	0.5	1.7
17/09/2013	Q0262905	7.7	0.4	4.2	2.0	1.4	8.9	9.3	0.1	11.32	0.01	1.206	0.001	1206.4	1.5	0.6	0.1	111.9	3.7	0.1
20/09/2013	Q0262904	0.8	0.2	0.0	0.2	0.0	6.2	9.3	0.3	10.38	0.01	0.472	0.001	471.6	1.5	0.3	0.1	98.7	2.7	0.2
23/09/2013	Q0262903	2.5	0.3	0.2	0.1	0.0	4.9	6.1	0.6	10.81	0.01	0.984	0.001	984.0	1.5	0.5	0.1	109.2	1.5	0.6
26/09/2013	Q0262902	2.9	0.6	1.0	0.5	3.6	4.0	6.1	0.8	9.80	0.01	0.928	0.001	928.5	1.5	0.5	0.1	102.1	1.4	0.8
29/09/2013	Q0262901	2.3	0.6	1.7	0.8	0.0	3.7	8.0	0.7	10.32	0.01	0.509	0.001	509.2	1.5	0.3	0.1	95.8	1.6	0.7
02/10/2013	Q0306699	0.6	0.5	0.0	0.2	0.0	3.5	9.9	0.3	11.38	0.01	0.296	0.001	295.8	1.5	0.1	0.1	92.3	2.9	0.3
05/10/2013	Q0306697	1.3	1.0	0.0	0.7	0.0	4.6	1.5	3.5	4.21	0.01	0.643	0.001	642.8	1.5	0.3	0.1	99.1	1.4	0.5
08/10/2013	Q0306696	1.6	0.6	0.0	0.2	0.0	7.3	9.1	0.1	8.79	0.01	0.875	0.001	874.8	1.5	0.8	0.1	117.5	3.9	0.1
11/10/2013	Q0306695	7.4	0.9	3.0	1.4	1.4	8.2	5.3	0.4	7.48	0.01	1.250	0.001	1249.5	1.5	0.8	0.1	111.7	1.7	0.3
14/10/2013	Q0306694	1.9	0.2	0.0	0.7	3.1	4.5	15.3	0.1	17.58	0.01	0.260	0.001	259.6	1.5	0.2	0.1	107.1	4.3	0.1
17/10/2013	Q0306693	0.8	0.4	0.0	1.2	0.0	5.8	10.9	0.2	17.12	0.01	0.378	0.001	378.0	1.5	0.2	0.1	92.7	4.6	0.2
20/10/2013	Q0306692	0.3	0.2	0.0	0.5	0.0	3.7	15.8	0.3	19.87	0.01	0.305	0.001	305.0	1.5	0.1	0.1	59.6	2.8	0.2
23/10/2013	Q0306691	1.4	0.4	0.0	0.5	2.2	4.5	5.9	0.3	4.19	0.02	0.487	0.001	486.7	1.5	0.3	0.2	155.6	2.9	0.3
26/10/2013	Q0306690	0.5	0.3	0.0	0.5	1.9	5.0	21.9	0.1	19.48	0.01	0.232	0.002	231.6	1.5	0.1	0.1	101.0	5.3	0.1
29/10/2013	Q0306689	2.1	0.6	0.0	0.0	3.7	4.1	7.2	0.3	7.20	0.01	0.719	0.001	719.3	1.5	0.3	0.1	106.6	2.2	0.3

APPENDIX 5: DATA ANALYSIS - ANOVA RESULTS

Anova: Single Factor   **IBA vs Both Years**

SUMMARY

Groups	Count	Sum	Average	Variance
2011-2012	110	482.7	4.4	68.0
2012-2013	137	429.3	3.2	31.4

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	96.0	1	96.0	2.0	0.2	3.9
Within Groups	11675.8	245	47.7			
Total	11771.8	246				

Anova: Single Factor   **XRF vs Both years**

SUMMARY

Groups	Count	Sum	Average	Variance
2011-2012	139	763.5	5.5	104.4
2012-2013	137	525.3	3.8	57.8

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	189.8	1	189.8	2.3	0.1	3.9
Within Groups	22266.7	274	81.3			
Total	22456.5	275				

GF-AAS vs Both Years

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
2011 - 2012	139	1048.2	7.5	81.8
2012 - 2013	137	911.9	6.7	83.1

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	54.0	1	54.0	0.7	0.4	3.9
Within Groups	22600.2	274	82.5			
Total	22654.2	275				

All Methods vs All Data

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
GF-AAS	247	1813.6	7.3	85.9
XRF	247	1205.0	4.9	83.6
IBA	247	912.0	3.7	47.9

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1712.9	2	856.5	11.8	8.88E-06	3.0
Within Groups	53486.2	738	72.5			
Total	55199.1	740				

GF-AAS & XRF vs All data

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
GF-AAS	247	1813.6	7.3	85.9
XRF	247	1205.0	4.9	83.6

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	749.9	1	749.9	8.8	0.003	3.9
Within Groups	41714.4	492	84.8			
Total	42464.3	493				

Winter 1 & 2 vs All Methods

Anova: Two-Factor With Replication

SUMMARY	GF-AAS	XRF	IBA	Total
Winter 1				
Count	60	60	60	180
Sum	793.6	673.0	410.9	1877.5
Average	**13.2**	**11.2**	**6.8**	**10.4**
Variance	109.4	156.1	107.1	130.0
Winter 2				
Count	60	60	60	180
Sum	665.8	460.7	334.7	1461.2
Average	**11.1**	**7.7**	**5.6**	**8.1**
Variance	136.0	102.1	57.2	102.5
Total				
Count	120	120	120	
Sum	1459.4	1133.7	745.6	
Average	**12.2**	**9.4**	**6.2**	
Variance	122.8	131.2	81.9	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Sample	481.4	1	481.4	4.32	0.04	3.87
Columns	2128.6	2	1064.3	9.56	0.00	3.02
Interaction	78.7	2	39.3	0.35	0.70	3.02
Within	39407.0	354	111.3			
Total	42095.7	359.0				