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Natural source contribution to background PM_{10} in Awatoto

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Executive Summary

Research was carried out to determine background concentrations of soil/ dust and sea spray to PM_{10} concentrations in Awatoto, a coastal settlement south of Napier in the Hawke's Bay region. The method used for the study is outlined in a previous report 'Scoping report -assessing natural sources contribution to PM_{10} '(Wilton, 2009).

The method involved estimating sea spray and soil contributions based on concentrations of Na (sea spray) and Si (silicon) and other minor elements in soil measured on a filter and is based on research undertaken by Cohen et al., (2004) and Gimsensius, (2000). This method is typically less robust than source apportionment but provides a reasonable indication of the approximate contributions of natural sources to measured PM_{10}.

The objectives of the study were:

1. Trial the method outlined in Wilton 2009 to determine its suitability for estimating natural sources contributions in New Zealand.
2. Evaluate the contribution of sea spray and dust (natural and quarry combined) to 24-hour average PM_{10} concentrations measured in Awatoto during the summer.

The results of the study showed that this method for estimating background contributions to PM_{10} concentrations worked well in this scenario. The strong correlation between Na and Cl allowed for robust sea spray estimations. The method for estimating soil contributions can be less certain because of the natural variability in soil composition across the country. Notwithstanding this, the first approximation method used showed good consistency with theoretical soil composition allowing a reasonable estimate of the contribution from this source.

For the 26 sample days from February to May the average sea spray contribution to PM_{10} concentrations at Awatoto was 31%, with a further 27% from soil. Around 42% of PM_{10} was from sources other than sea spray and soil on these days. The sample period included three days when PM_{10} concentrations exceeded 50 $\mu g\ m^{-3}$ (24-hour average). The relative contribution on these days was 28% sea spray, 31% soil and 41% other sources.

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1 Introduction

Research was undertaken to determine the natural source contribution of PM_{10} concentrations in Awatoto, a coastal location south of Napier in the Hawke's Bay region.

Determining the contribution of natural sources to measured PM_{10} concentrations is important for Regional Councils when deriving management measures to reduce concentrations of PM_{10}. If natural source contributions of PM_{10} are not accounted for when developing strategies, management measures are less likely to achieve the expected reductions.

In New Zealand the main natural sources contributing to concentrations of PM_{10} are soil/ dusts and sea spray (Wilton, et. al., 2007). The most common technique used to determine the contribution of natural sources to PM_{10} concentrations is to measure concentrations of elements on a gravimetric sampler and undertake statistical analysis using Positive Matrix Factorisation (PMF) or a similar statistical method. This is commonly referred to as source apportionment or receptor modelling.

One limitation of the method is that it requires a large number of filters from a PM_{10} sampler (typically 100+) and requires substantial resources and specialist expertise to undertake the statistical analysis to determine the relative contribution of sources, including natural sources. Although this is a comprehensive approach, it is costly.

An alternative more basic methodology that requires analysis of fewer filters and no PMF type analysis been applied in Asia for the determination of the natural sources (marine aerosol and soil) contribution (e.g., Cohen, et. al., 2004). The method estimates concentrations of natural sources based on key elements and relationships between these elements.

1.1 Objectives

The objectives of the study were:

1. Trial the alternative method for estimating sea spray and soil/ dust to determine its suitability for estimating natural sources contributions in New Zealand.
2. Evaluate the contribution of sea spray and dust (natural and quarry combined) to 24-hour average PM_{10} concentrations measured in Awatoto during the summer.

2 Background

2.1 Sea salt

The source profiles for sea spray in airborne particulate are largely characterised by the chemical composition of sea salt. The typical composition is Na (32%), chlorine (58%), Mg (4%), S (3%), Ca (1%) and K (1%) (Weast, 1977). On average, NaCl represents 86% of the dried weight of sea water so these elements alone could be useful as an indicator of the sea spray component (Gimsensius, 2000). For the other chemicals present in sea salt, these elements are normally present relative to Na in the following ratios: Ca=0.038, S=0.084, and K=0.036. Cohen et al 2004 found the following ratios in $PM_{2.5}$ concentrations measured at Cape Grimm: Ca=0.038, S=0.092 and K=0.032.

In Australia, Gimsensius et. al., (2000) found that sodium was a good indicator for sea salt in the fine particulate ($PM_{2.5}$.) mass and that the best approach to estimate the NaCl component was to use 2.54 times Na concentrations. Approaches that used Cl were not as reliable because there were other significant sources of Cl.

As the total sea salt content includes anions and cations in addition to Na and Cl adjustments are required to the equation to account for these. Cohen et al (2004) used 3.25*[Na] to estimate the contribution of total sea salt including Na^+, Mg^+, Ca_2^+, K^+, Cl^-, SO_4^{2-}, HCO_3^-.

These estimates require the assumption that all Na present on the filter is from sea spray or require some adjustment for non sea spray Na. Sodium is a small component of soil and this is a potential factor that may need accounting for. In Australia Cohen et. al. (2004) did not adjust for soil-based Na because the contributions of soil and sea spray to PM_{10} were similar for most source apportionment studies in Asia and because the Na contribution to soil was around 3%.

2.2 Soil

Soil profiles are dominated by Si and Al with contributions from elements such as Fe, S, K, Na and Mg. Estimates of soil are more complex because the oxygen component is not measured and because the composition can vary slightly between areas. Cohen el al, (2004) estimated the soil contribution based on least squares regression of Si to each of the above elements, once filters with other sources of the elements (e.g., sea salt K and smoke K) were removed. The ratios of each element to Si were then established for a soil profile and the soil concentration estimated based on the assumption that the elements were present in their most common oxide forms.

An evaluation of the relationship between Si concentrations and estimated soil contributions for the Hasting source apportionment study was undertaken by Wilton et. al., in 2007. Results indicated Si comprised 33% of total estimated soil contribution, on average. This is slightly higher than the 29% found in Cohen et. al., (2004) for the $PM_{2.5}$ size fraction and may occur because some soil (Si and Al) appears also in the motor vehicle profile, most probably representing road dust.

3 Method

3.1 Programme design

The programme was designed with the following parameters:

- One in three day sampling for the months February to May 2010 using a Gent sampler at the Ravensdown industrial monitoring site. A total of 34 samples were collected. However, eight samples were unable to be used because the sampler was not operated correctly. A further sample day was deleted because elemental mass was higher than measured mass.
- Teflon filters were used to sample PM_{10}.
- Gravimetric analysis of filters for mass on all sample days.
- PIXE/ PIGME analysis of filters for concentrations of elements.
- Co-incidental monitoring of PM_{10} concentrations using the existing BAM.
- HBRC staff undertook the sampling.

3.2 Site details

The Awatoto air quality monitoring site owned and operated by Ravensdown in Hawke's Bay was selected for this study because it has shown numerous exceedences of the NES for PM_{10} during the summer months and is very close to the coast.

At present a local industry operate a BAM at the site which measures continuous PM_{10} concentrations. The monitoring site is located at Winstone Aggregates next to a large gravel pile (Figure 3.1). Although this is far from ideal in terms of siting a typical monitoring station, a larger than usual soil contribution is unlikely to compromise the objectives of this study. The monitoring site is likely to have a number of influences:

- Sea spray
- Dusts from the quarry and gravel stockpiles
- Emissions from Ravensdown
- Windblown dusts from natural sources

Figure 3.1: Location of air quality monitoring site at Awatoto.

3.3 Data Analysis

The following method was used for this study:

- Sea spray
    - Evaluation of the relationship between Na and Cl to determine the potential for other sources.
    - Evaluation of the relationship between Na and Si to determine if Na from soils is likely to interfere with estimates of sea spray based on Na.
    - Estimate sea salt concentrations based on 2.54 times measured Na concentrations.
    - If filters are identified (from the linear relationships above) with high Na from soil exclude the filters from the analysis or find a way to correct for the soil contribution.

- Soil
  - Evaluation of the relationship of all soil elements to Si based on least square or RMA regression. This involves identifying the soil relationship from scatter plots and quantifying the relationship in terms of ratio of smaller element to Si.
  - Use Si mass from each filter to estimate the mass of minor elements based on the above relationships.
  - Estimate the mass of each element with the addition of oxides based on the most common oxide for each element.
  - Compare estimates made to those made using a simpler approach based on the proportion of Si in each filter based on other source apportionment studies (e.g., Hastings or Napier).

The approach described is generally less accurate than an estimate using source apportionment receptor modelling because the latter better accounts for the presence of Na and Si in other sources.

The main conditions that are required for this approach to be appropriate as an indicative method are that sea spray is the main source of Na and that soil is the main source of Si.

4 Analysis

4.1 Sea Spray

Figure 4.1 shows the relationship between Na and Si and between Na and Cl. The very strong relationship between Na and Cl means that there is little if any Na from soil that would interfere with the method for calculating the sea spray contribution. Estimates of sea spray were therefore made by multiplying Na concentrations by 2.54.

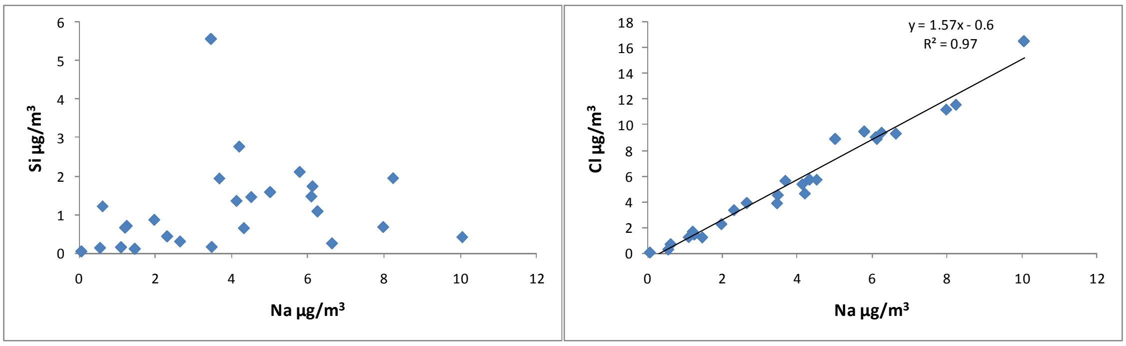

Figure 4.1: Relationship between Na and Si and between Na and Cl at Awatoto

4.2 Soil

4.2.1 Method one: Regression against Si and most common oxides

An equation commonly used as a first approximation for reconstructing soil mass based on elemental concentrations which account for the oxygen content not measured is shown below. This includes an additional multiplier of 1.16 to correct for the fact that three major oxide contributors (MgO, K_2O and Na_2O), carbonate and bound water are excluded from the equation (Davy, 2007).

Reconstructed soil mass = 2.2[Al] + 2.49[Si] + 1.63*[Ca] + 2.42*[Fe] + 1.94[Ti]

One limitation with this approach is that these elements may be present in other sources and therefore an overestimate of the soil contribution is possible. Cohen et. al., (2004) proposes linear regression of elements against Si to determine the appropriate adjustments that could be made to Si concentrations to estimate soil contributions.

Figure 4.2 shows a lot of variability between Si concentrations and sources of Ca, Mg and K suggesting other sources contribute to concentrations of these elements. Typically Si and Al were well correlated. The exception is two days when Al concentrations appeared to occur from a non soil source.

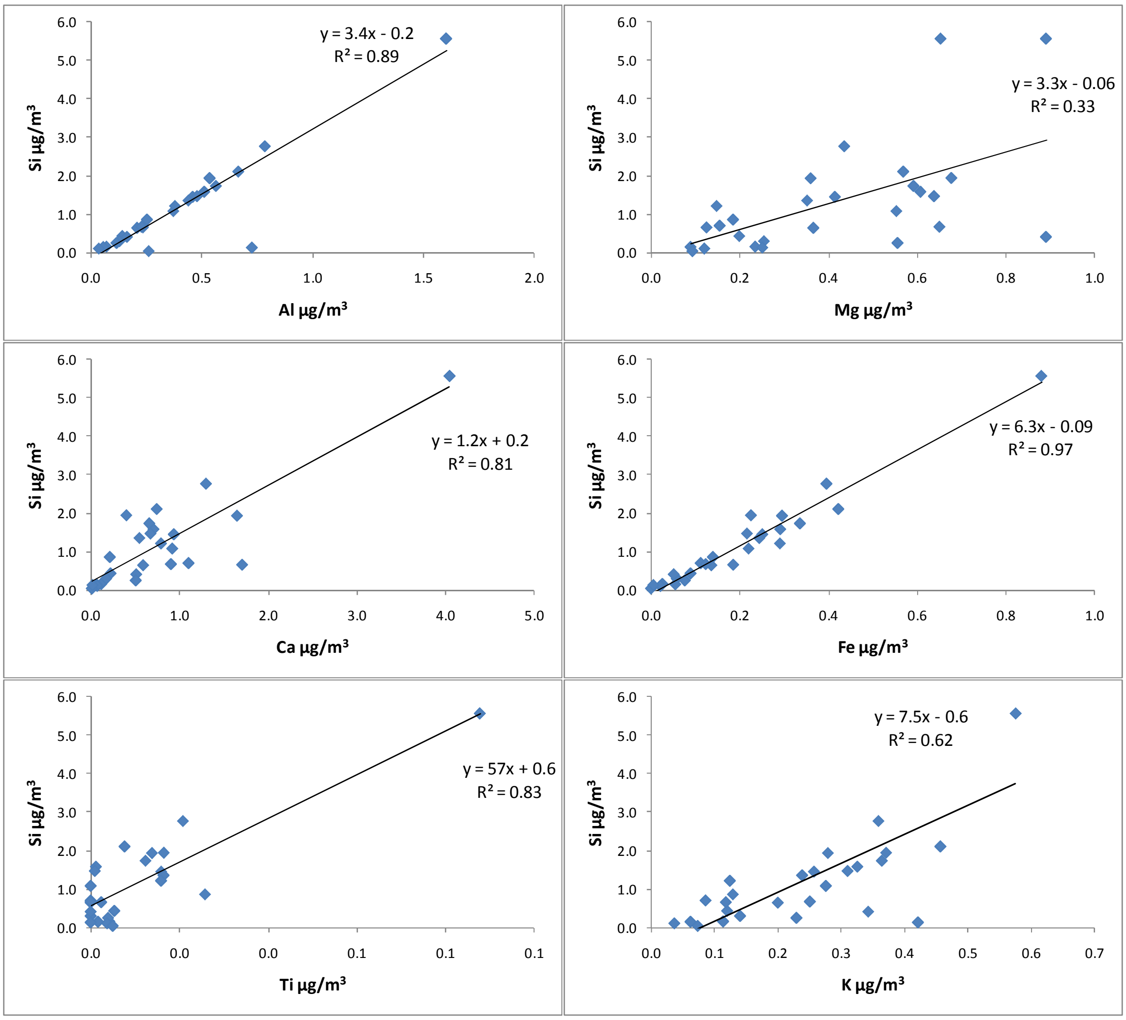

Figure 4.2: Linear regression of elements to Si based on measured elemental concentrations at Awatoto

Concentrations of soil were estimated for each day based on the measured elemental Si concentrations. Based on the regression equations, the following ratios to Si were used: Al – 0.29, Ca – 0.83, Fe – 0.16, Ti – 0.02, K – 0.13.

Table 4.1 compares the average elemental fractions in soil from this study to those reported in Cohen, et. al., (2004) from the ACE Asia sites and the theoretical amounts from "*Principals of Geochemistry*" (Mason and Moore, 1982). . The method used was least squares fits to each element relative to Silicon and assuming each element occurs as its common oxide. Results from this study are similar to Cohen et. al. (2004) and Mason and Moore (1982) with the exception of Ca which is about 4-5 times higher at the Awatoto site. This most likely reflecting a higher presence of calcium either in the phosphate rock used by Ravensdown or as a result of other local industry.

Table 4.1: Mean elemental fractions in soil from this study compared with Cohen et. al., (2004) for all ACE Asia sites and theoretical amounts from Mason and Moore (1982).

	Fraction	SD - plus or minus	Crustal Material	Soil - Awatoto
	Cohen et al 2004		Mason and Moore 1982	This study
AL	0.069	0.01	0.086	0.069
Si	0.215	0.039	0.294	0.234
K	0.041	0.006	0.027	0.031
Ca	0.046	0.014	0.039	0.19
Ti	0.0074	0.002	0.0047	0.004
Mn	0.003	0.002	0.001	n/a*
Fe	0.068	0.01	0.053	0.037
O	0.55	0.027	0.495	0.43

*Mn not included for this study because samples were largely below detection limit and consequently had poor correlation with Si (r^2=0.2)

4.2.2 Method two – use existing source apportionment soil profiles.

Figures 4.3 and 4.4 show the soil profiles from source apportionment studies conducted in Hastings (PM_{10} fraction) and Napier (coarse fraction). In Napier Si comprised around 36% of the elemental mass, compared with 43% in Hastings. The unmeasured component was higher in Napier than in Hastings. Figure 4.5 compares soil estimates at Awatoto based on the Si component and the Napier and Hastings soil profiles (including adjustments for the unmeasured component) and the method detailed in section 4.2.1 using regression of elements against Si concentrations at Awatoto. Results show the latter method and the Hastings soil profile give similar soil concentration estimates while estimates based on the Napier soil profile were slightly higher.

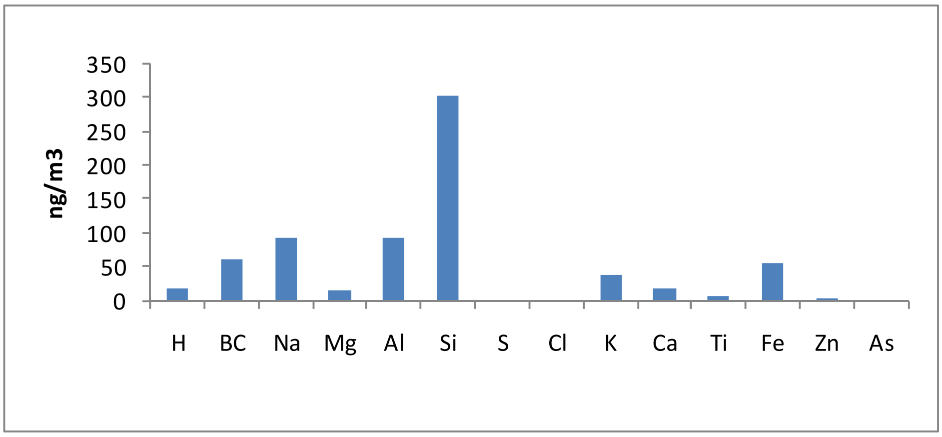

Figure 4.3: Composition of soil at Hastings from source apportionment analysis (Wilton, et. al., 2007)

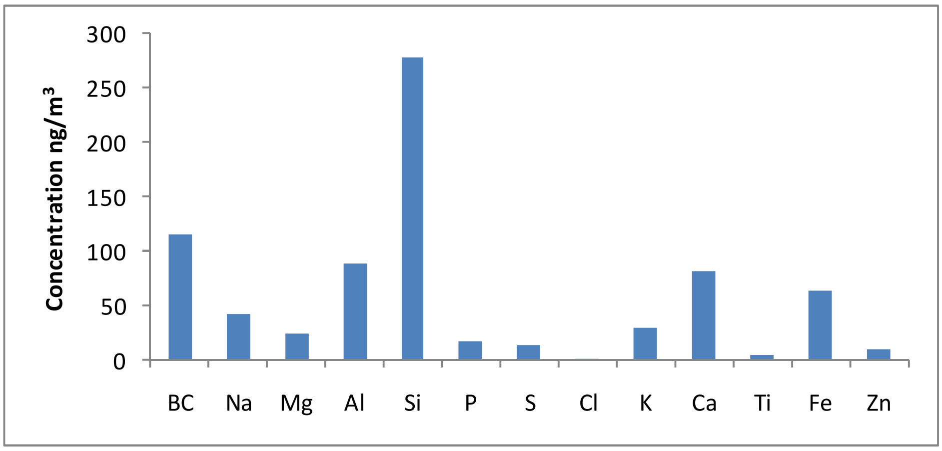

Figure 4.4: Composition of soil at Napier from source apportionment analysis (Wilton et. al., 2010)

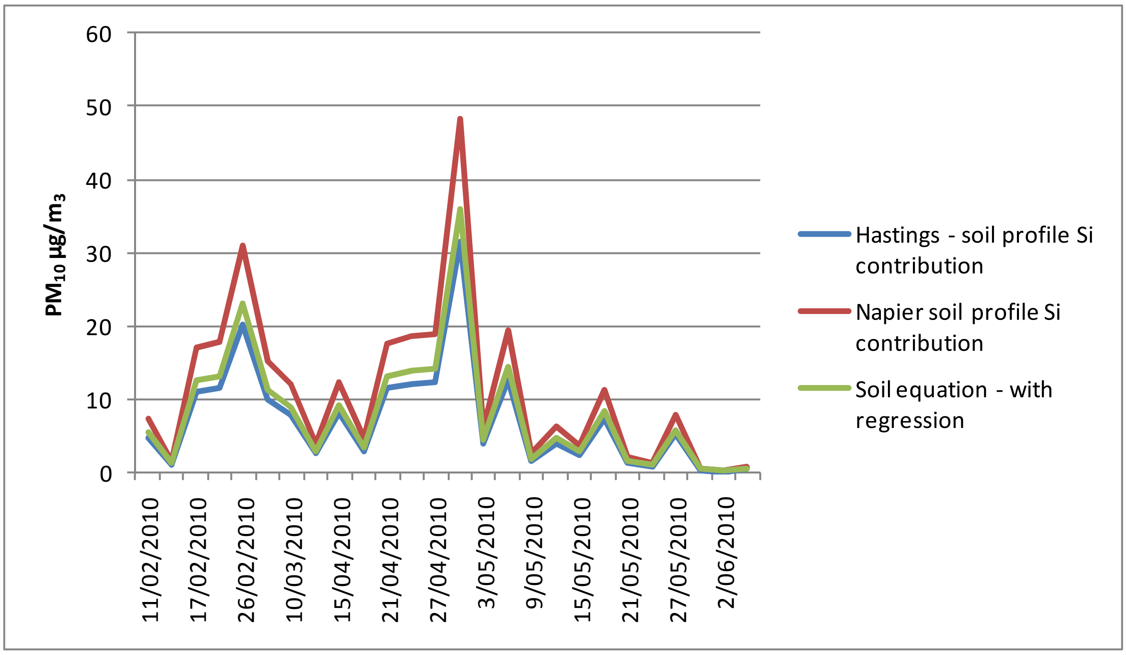

Figure 4.5: Comparison of estimated soil concentrations using Hastings soil profile, Napier soil profile and the regression of soil elements against Si method.

5 Contribution of sea spray and soil to PM_{10} in Awatoto

The relative contribution of sea spray and soil to PM_{10} concentrations in Awatoto for the sample days was estimated based on the method described in section 4.1 for sea spray and 4.2.1 for soil (regression against Si and assumption of common oxides). Figure 5.1 shows the relative contribution of each of these sources to PM_{10} concentrations for the sample days. Overall sea spray contributed 31%, soil/ dust 27% and other sources 42% of PM_{10} concentrations (Figure 5.2).

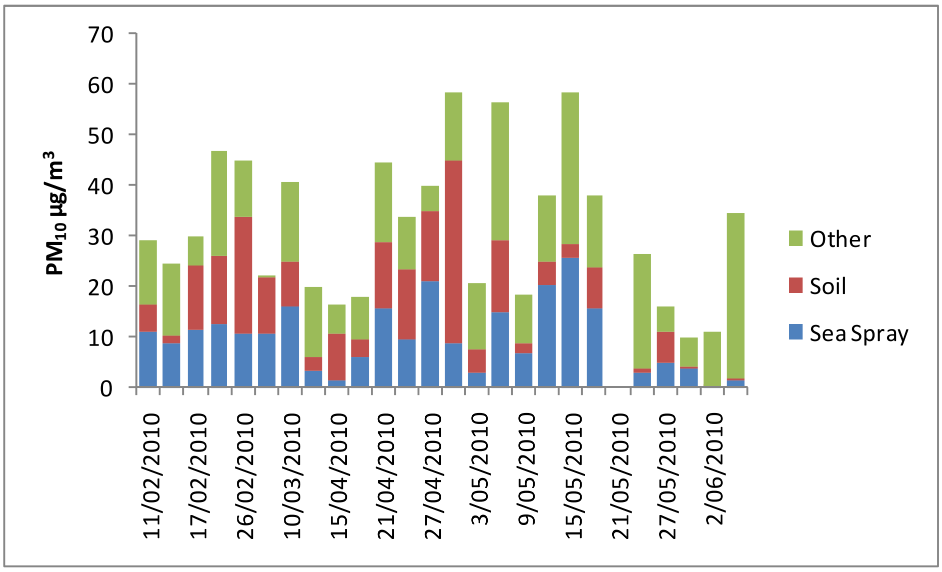

Figure 5.1: Estimated contributions of sea spray and soil/ dust to PM_{10} concentrations at Awatoto

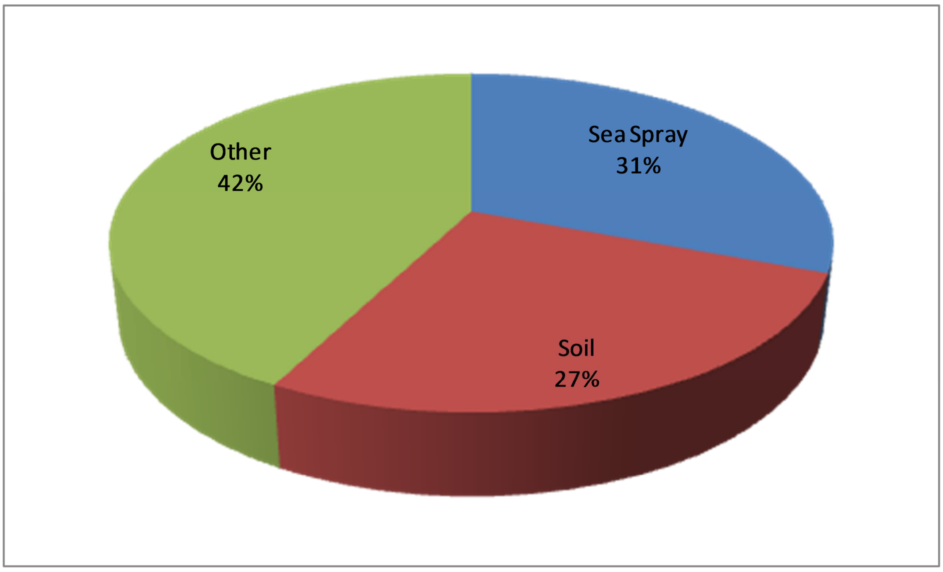

Figure 5.2: Average contributions of sea spray and soil/ dust to PM_{10} at Awatoto from February to May 2010.

During the sample days PM_{10} concentrations exceeded 50 µg m^{-3} (24-hour as measured by the GENT) on three days with concentrations of 56, 58 and 58 µg m^{-3}. The average relative contribution of sea spray and soil/ dust to PM_{10} concentrations on these days is shown in Figure 5.3. Results suggest that more than half of the PM_{10} concentrations on these days occur as a result of soil/ dust and sea spray.

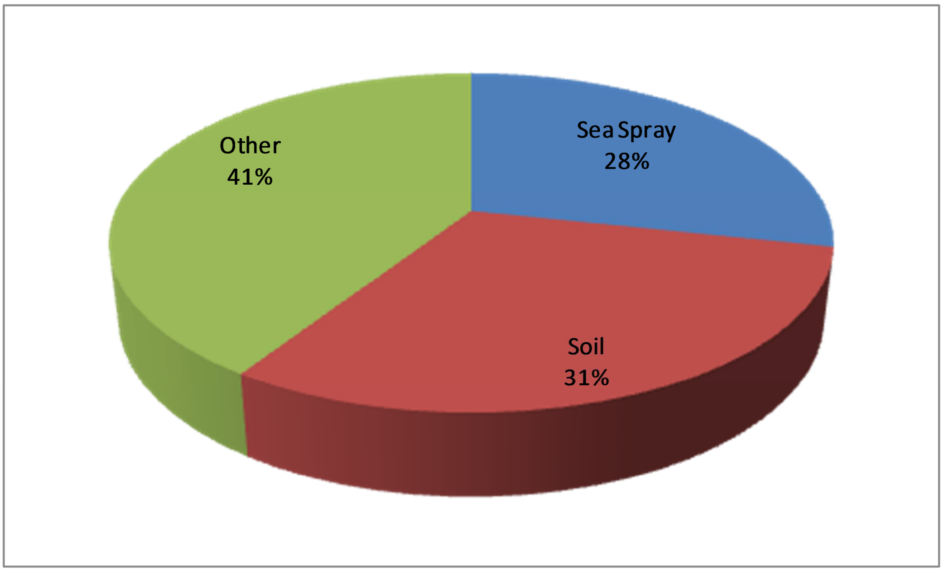

Figure 5.3: Average contribution of sea spray and soil/ dust to PM_{10} concentrations on three days when PM_{10} concentrations exceeded 50 µg m^{-3} at Awatoto (28 April, 4 and 13 May 2010)

6 Conclusion

The use of Na and Si concentrations to estimate sea spray and soil/ dust concentrations appears to be a cost effective method of establishing the natural sources contributions to PM_{10} concentrations.

The cost savings occur as a result of not having to carry out more detailed statistical analysis and potentially through reduced sample sizes, although a reasonable sample is required to give an average contribution for a given period.

The main limitation to use of this method would be if there were sources of Si that did not originate from soil/ dust or Na not from sea spray, particularly if these sources were present in most of the samples.

At the Winstone Aggregates monitoring site in Awatoto, sea spray was found to contribute 31% of the PM_{10} concentrations and soil/ dusts 27% of concentrations on the 26 sample days from February to May 2010. The distribution was slightly different on the three sample days when PM_{10} concentrations exceeded 50 $\mu g\ m^{-3}$ (24-hour average) with soil/ dust contributing 31% and sea spray 28%.

References

Cohen, D., Graton, D., Stelcer, E., Hawas, O., Wang, T., Poon, S., Kim, J., Choi, BC., Oh, SN., Shin, H., Ko, MY,Uematsu, M, 2004, Multielemental Analysis and characterisation of fine aerosols at several key ACE Asia sites, *Journal of Geophysical Research*, Vol 109, DI9SI2, 2004.

Davy, P.K., 2007, *Composition and Sources of Aerosol in the Wellington Region of New Zealand*, Submitted in fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at Victoria University of Wellington.

Gimsensius, A., Cohen, D. D., & Whitlow, H., 2000, Regional and Seasonal Variations of Fine Particle Sea salt near the New South Wales Coast during 1992 and 1993, *13th International Clean Air & Environment Conference*, Christchurch, New Zealand.

Mason, B., and C. B., Moore, 1982, *Principles of geochemistry, 4th Edition* John Wiley Hobeken N. J.

Scott, A., 2005, '*Source Apportionment and Chemical Characterisation of Airborne Fine Particulate Matter in Christchurch New Zealand*', A thesis submitted in partial fulfilment of the requirements for the Degree of Doctor of Philosophy at the University of Canterbury.

Weast, R. C., CRC *Handbook of Chemistry and Physics*, CRC Press (1977) 57th ed. Ohio USA page 203.

Wilton, E., Davy, P., Smith J., 2007, '*Source identification and apportionment of PM_{10} and $PM_{2.5}$ in Hastings and Auckland'*, NIWA Client Report, Foundation for Science, Research and Technology.

Wilton, E., and Trompetter, B., 2007, *Source Apportionment of PM_{10} in Blenheim.* Marlborough District Council, Foundation for Science, Research and Technology.

Wilton, 2009, *Scoping report –Assessing natural sources contributions to PM_{10}'*, Foundation for Science, Technology and Research.

Wilton, E., Baynes, M., Zawar Resa, P., 2010, Source apportionment of particulate in Napier. Hawkes Bay Regional Council report - Envirolink 869-HBRC130.