Kumar, A and Bofinger, Neville and Ayoko, Godwin (2007) Characterisation of soluble Inorganic PM10 aerosols in Brisbane. In *Proceedings 14th International IUAPPA World Congress*, Brisbane, Australia.

Characterisation of soluble Inorganic PM10 aerosols in Brisbane

A.U. Wathsala Kumar[1], Neville D. Bofinger[1] and Godwin A. Ayoko[2]
[1] School of Natural Resource Sciences Queensland University of Technology, QLD., 4001, Australia
w.kumar@qut.com.au
[2] School of Physical and Sciences, Queensland University of Technology, QLD., 4001, Australia g.ayoko@qut.com.au

Abstract

PM10 samples were collected from three sites in Brisbane over a period of 20 months. These samples were analysed for water soluble ionic species (Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-,NO_3^-, SO_4^{2-}, F^-, Br^-, NO_2^-, PO_4^{-3}) using Inductively coupled plasma optical emission spectrometer (ICP_OES)and Ion exchange chromatography (IC). Metallic species (Zn, Cu, Pb, Fe, Mn, Al) that are soluble in acid were also analysed using ICP-OES. Na^+ and Cl^- concentrations were high in all samples. Principal Components Analysis (PCA) was used to identify seasonal differences and weekend/weekday trends of the sample concentrations. This showed that seasonal variation played a major role in the soluble aerosol concentrations of the samples. PCA was also used to identify the sources of the samples and it could be concluded that sea salt is the major source of these aerosol samples.

Keywords: PM10; Water Soluble ions; Brisbane; ICP_OES; IC

1. Introduction

Atmospheric particles which are less < 10 µm in diameter (PM10) has been related to urban health issues (e.g. Dockery and Pope, 1994) and climate change problems (Jennings, 1993). Ionic composition of aerosols have been studied comprehensively because water soluble ions are found to be major components of atmospheric aerosols as they can comprise up to 60%-70% of particulate mass(Ali-Mohamed, 1991).

Compared with cities such as Los Angeles, Mexico City and Bangkok air pollution in Australian cities such as Brisbane is low. However, there are days where the PM10 concentration of aerosols exceeds the national standard which is maximum 50µg/m^3 average over one day. Therefore it is important to monitor aerosol concentration in these cities.

Over the years there have been many studies done on particulate matter in Brisbane (e.g. Verrall, 1986 and Chan et al, 1997). However none of these studies have looked comprehensively at water soluble ions in particulate matter. This study investigates water soluble ion concentration in PM10 in Brisbane during the period of December 2002 to August 2004. This project also investigates the acid soluble fraction of metallic species such as Pb as they are anthropogenic aerosols that are useful tracer of environmental pollution.

2. Experimetal Methods

2.1. Sampling and Sampling sites

Particulate samples were collected using High volume PM10 samplers. Samples were collected at three air monitoring stations within the South East Queensland air quality network. These stations are Rocklea, Woolloongabba and Eagle farm (figure 1)

Four sets of aerosol samples were analysed for this project. Table 1 has a summary of these aerosols samples. The first three sets of samples were supplied Queensland Environmental Protection Agency. These samples were collected on Teflon filter using a standard PM10 high volume sampler. The samples were collected every sixth day for 24 hours. Samples from December 2002 to January 2004 from both Rocklea and Woolloongaba stations were analysed. Samples December 2002 to March 2003 were analysed from the Eagle farm station. Only one half of these filter samples were used for this study.

Samples were also collected for 12 months using GF/A filters. These samples were collected at the Rocklea air monitoring station from September 2003 to August 2004. Here 7 samples and blanks were collected every 6 weeks. One quarter of each filter were analysed for soluble inorganic ions and one quarter of each filter was analysed for acid extracted elements. The other half of the sample was used to determine polyaromatic hydrocarbons (PAHs) concentrations, which are not reported in this paper.

A fraction of the samples from Rocklea September 2003 to August 2004 was also analysed for Pb, Al, Zn, Cu and Mn using hot acid extraction where HCl/HNO_3 acid for 30 minutes. These samples were then diluted where the final solution concentration is 3% HNO3/ 8% HCl then analysed using ICP_OES (Varian, Liberty 100).

Sample blanks, laboratory blanks and spiked samples were used for quality control and quality assurance. Detection Limits (DL) were calculated as three times the standard deviation of the field blanks.

Table 1: Summary of particulate sampling

Sampling Station	Sampling Period	Filter Type	Sampling sequence	Filter Fractions used
Eagle Farm	Dec2002 to Mar 2003	Teflon	Every 6th Day	½Water soluble ions
Rocklea	Dec2002 to Jan 2004	Teflon	Every 6th Day	½ Water soluble ions
Woolloongabba	Dec2002 to Jan 2004	Teflon	Every 6th Day	½ Water soluble ions
Rocklea	Sep2003 to Aug 2004	GF/A	Every 6 weeks for a week	¼ Water soluble ions ¼ acid soluble ions

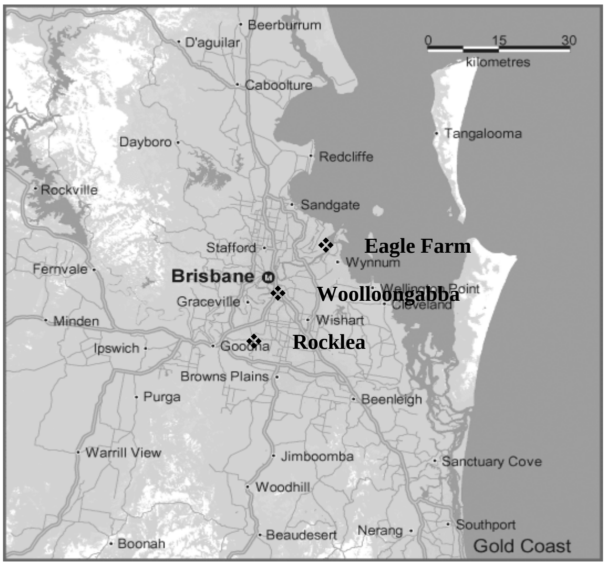


Figure 1. Brisbane airshed and Sampling sites

(Source: Vodafone, 2007)

2.2. Chemical Analysis

Collected aerosol samples were cut into different portions and analysed. The fraction for water soluble ion analysis was extracted ultrasonically with 100ml of ultra pure water for 60minutes. These samples were then analysed using Ion chromatograph (Dionex Bio LC) for Cl^-, NO_3^-, SO_4^{2-}, F^-, Br^-, NO_2^- and PO_4^{-3} using AS9HC column. CS12 Column was used to analyse NH_4^+ ions. Inductively coupled plasma optical emission spectrometer (Varian Liberty 100) was used to analyse Na^+, K^+, Mg^{2+} and Ca^{2+} ions.

3. Results and Discussion

3.1. Ion concentration in aerosol samples

A total of 195 samples were collected from the three stations from December 2002 to August 2004.

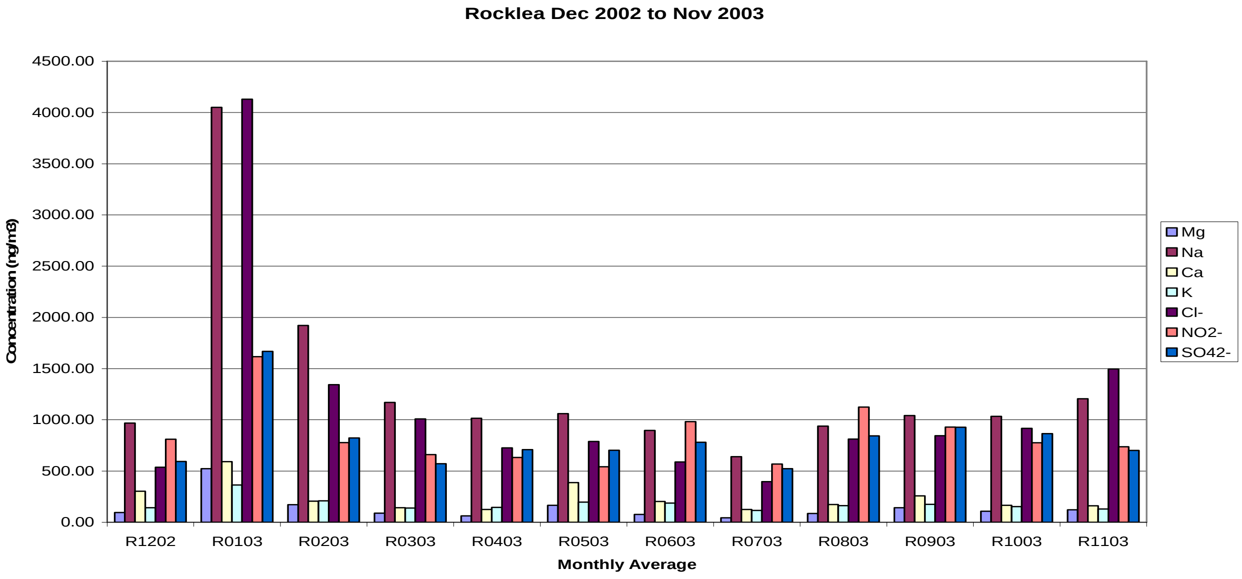
Cl^-,NO_3-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+} were high in concentration and found in all the samples. F^-, Br-, NO_2^-, PO_4^{-3} and NH_4^+ ions were determined in some samples only.

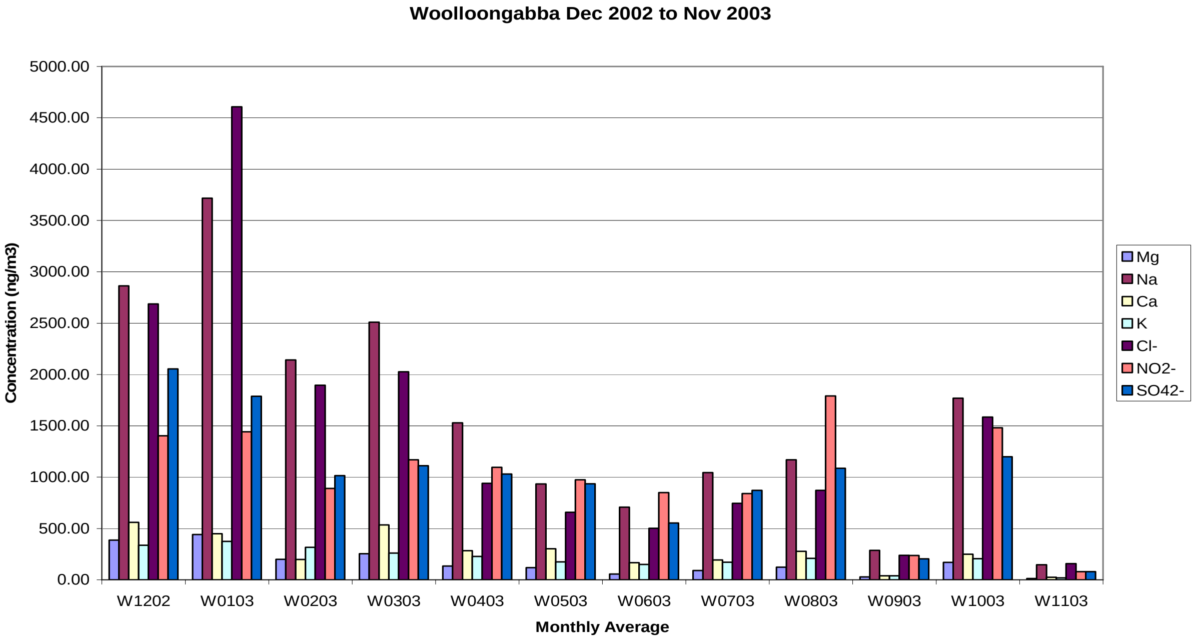
The average monthly concentration of Cl^-,NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+} soluble ions at the three stations from December 2002 to November 2003 is compared in Figure 2. There is a number of interesting features displayed by this data. It could be seen that Na^+ and Cl^- is high in summer months, especially in January in 2003. The nitrate concentrations seem to be high in winter months.

It is also obvious that Na^+ and Cl^- are found in higher concentrations than the other ions. This indicates that Brisbane's Soluble PM10 aerosols are strongly influenced by sea salts.

The average concentration of soluble ions of all stations is compared in Table 2. It also compares these results of this study with other similar studies. The average concentrations indicate that Woolloongabba and Eagle farm stations have higher concentrations of these ions than Rocklea. This could be because these stations are closer the sea and the Brisbane river that the Rocklea Station.

Compared to the levels reported in a previous study the current levels of the metallic species, especially Pb is generally low, reflecting the phasing out of leaded petrol and decreasing levels of other anthropogenic sources of aerosols in Brisbane.





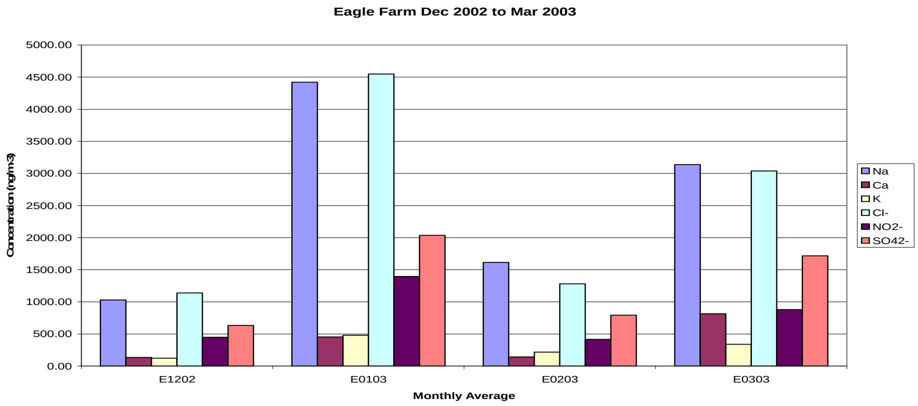


Figure 2. Comparison of average monthly concentration of major Ions in all three sites Dec 2002 Nov 2003

Table 2: Average Concentration (µg/m3)

	Rocklea	Woolloongabba	Eagle Farm	Brisbane Chan et al 1997 (Calculated)	Auckland Wang 2002
Cl^-	1202.78	1409.56	2501.54	1330	3376
NO_3^-	885.38	927.80	786.10		736
SO_4^{2-}	857.76	994.43	1295.11		1291
F^-	51.30	53.93	59.26		
Br^-	7.15	23.15	3.61		
NO_2^-	38.45	33.41	35.25		
PO_4^{-3}	1.26	2.07	Below detection		
NH_4^+	25	19	28		19
Na^+	1388.25	1567.71	2551.99	1224	2266
K^+	181.58	206.91	289.85	104	112
Ca^{2+}	237.76	273.27	386.21	431	167
Mg^{2+}	146.37	167.97	276.10	186	245
Zn	53.85	Not Analysed	Not Analysed	64	
Cu	3.13	Not Analysed	Not Analysed		
Pb	40.4	Not Analysed	Not Analysed	106	
Al	22.80	Not Analysed	Not Analysed	585	
Fe	40.61	Not Analysed	Not Analysed	452	

3.2. Multivariate analysis

Part of the aims of this study was to determine trends of the data and identify the sources of the inorganic constituents of the air samples from the sites. Principal Components Analysis (PCA) was used to identify patterns in daily and seasonal variations of the chemical species. PCA effects multivariate data reduction by transforming the data into orthogonal components that are linear combinations of the original variables. Therefore, PC reduces multidimensional data into fewer dimensions. The theory of PCA is well documented elsewhere (Wold et al, 1987; Jolliffe, 1986).

3.2.1. Seasonal Variations

The monthly average of all the chemical species were used to determine if there is a seasonal pattern in the data. The meteorological data such as wind speed, humidity, rainfall and temperature, supplied by the QLD EPA for each of the sites was also used for this process. The scores plot obtained from the PCA (Figure 3) illustrates how warmer months cluster together and colder months cluster together. There is an outlier in the data which is January 2003. It can be concluded that there are seasonal variations in the soluble inorganic aerosols in Brisbane.

The loadings plot (Figure 4) identifies the relationship between the chemical species and the meteorological information. There are two definite clusters that are negatively correlated on Principal Component 2. The chemical species that are clustered together are major components of sea salts (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- ,NO_{3-} and SO_4^{2-}). Thus, the loadings plot indicates that the main source of soluble aerosols in these samples is marine aerosols.

In addition, most meteorological data are clustered together showing that these parameters negatively affect the concentrations of sea salts at these sites.

3.2.2. Weekend and Weekday

PCA was also used to investigate the Weekend and Weekday relationships in the samples. Figure 5 is a scores plot of all the samples from the Woolloongabba. There are no predominant clusters that can be seen in the samples. This indicates that soluble inorganic aerosol concentrations of the samples cannot used to identify difference between weekend day and weekend samples. This could be because major constituent of the soluble inorganic aerosol fraction is sea salt and day of the week would not affect it.

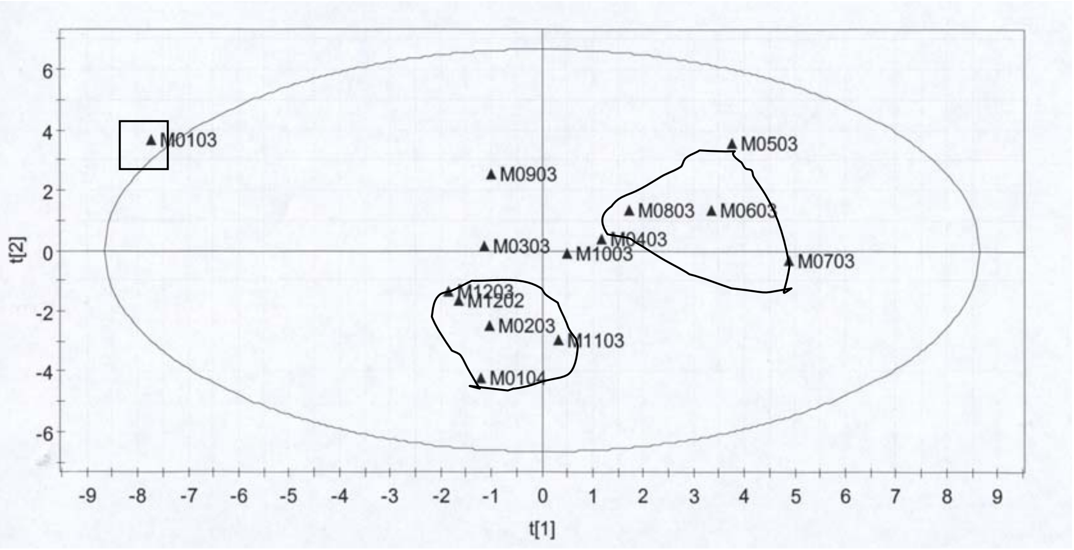


Figure: 3: Scores Plot on Monthly average of all sites form Dec 2002 to Jan 2004

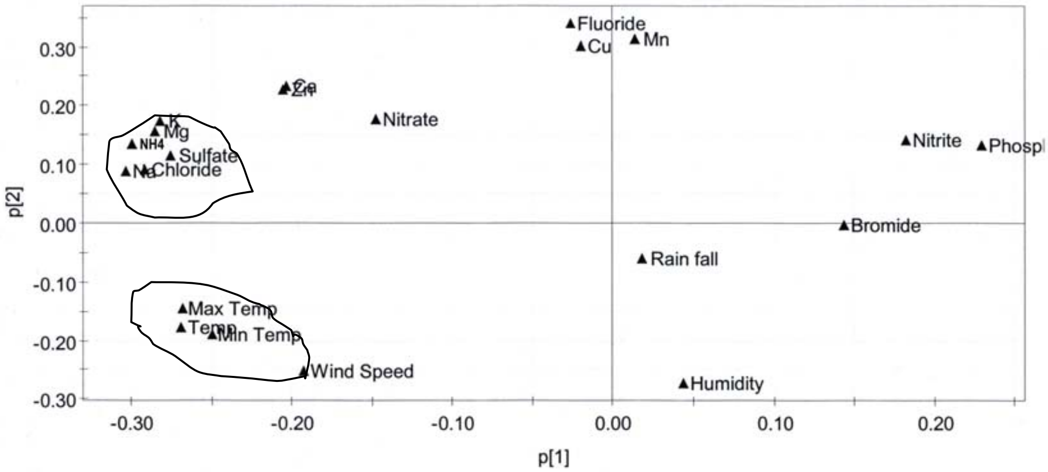


Figure.4: Loadings Plot on Monthly average of all sites form Dec 2002 to Jan 2004

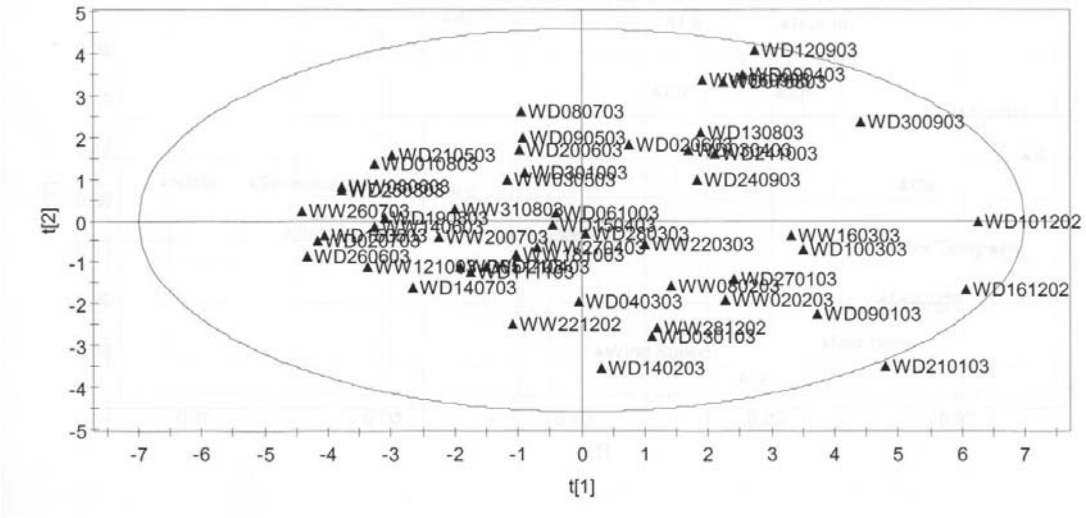


Figure.5: Scores Plot on of all samples in Woolloongabba station Dec 2002 to Nov 2003

4. Conclusion

This study investigated the soluble inorganic fraction of PM10 aerosol at three sites in Brisbane. All major anions and cations were found in the aerosols collected from the three sampling sites between December 2002 and August 2004.

The results clearly indicated that sampling site closer to the sea had higher concentrations of PM10 aerosols and that the concentrations of showed seasonal variations.. There were no trends in the variation of the concentrations of the chemical species with the day of the week. This is possibly because the main source of the aerosols does not show regular daily variations in source strengths. The metallic species that were analysed which were Zn, Cu, Pb, Fe, Mn and Al were low in concentration, indicating that decreasing strengths of anthropogenic sources of PM10 aerosols in Brisbane. Overall, Na^+ and Cl^- concentrations were higher than concentrations of the other ions in the samples. This indicates that Brisbane's Soluble PM10 aerosols are strongly influenced by sea salts.

Acknowledgments

Queensland Environmental Protection Agency and QUT.

References

Ali-Mohamed, A.Y., 1991. Estimation of inorganic particulate matter in the atmosphere of Isa Town, Bahrain, by dry deposition. *Atmospheric Environment B* 25, 397–405.

Chan, Y. C., Simpson, R. W. Mctainsh, G. H., Vowles, P. D., Cohen, D. D. and Bailey, G. M. (1997) Characterisation of chemical species in PM2.5 and PM10 aerosols in Brisbane, Australia. *Atmospheric Environment* 31(22), 3237-3250.

Dockery, D.W. and Pope, C.A. (1994) Acute Respiratory effects of particulate pollution. *Annual reviews of Public Health* 15, 107-132

Jennings, S.G. (Ed.), 1993. *Aerosol Effects on Climate*. The University of Arizona Press, Tucson.

Jolliffe, I. T. (1986). *Principal component analysis*. Kent, Springer- Velage

Verrall, K.A., Muller, W.A., Kingston, P.A., Rose, H.C. and Rafferty, N.A (1986). Identification of sources contributing to Total Suspended Particles in Brisbane. *Clean Air Congress '86*

Vodafone (2007), Queensland Coverage Map Brisbane and Gold Coast, http://vic.vodafone.com.au/coverage/qld.asp?detail=59%20Brisbane%20and%20Gold%20Coast

Wang, H. and Shooter, D. (2001). Water soluble ions of atmospheric aerosols in three New Zealand cities: seasonal changes and sources. *Atmospheric Environment* 35(34): 6031-6040.

Wold, S., Essensen, K. and Geladi, P. (1987). Principal component analysis, *Chemometrics and Intelligent Laboratory systems* 2: 37- 52.