Multi-criteria ranking and source apportionment of fine particulate matter in Brisbane, Australia

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Environmental context. There are serious global concerns about the environmental and health effects of atmospheric air pollutants. However, estimates of pollutants from measurements made in the proximity of a source do not always represent the ultimate atmospheric concentrations. Therefore alternative methods of attributing pollutants to sources, and estimating their contributions to atmospheric concentrations, as demonstrated in the current work, will become an increasingly important area of environmental research.

Abstract. This paper reports the application of multicriteria decision making techniques, PROMETHEE and GAIA, and receptor models, PCA/APCS and PMF, to data from an air monitoring site located on the campus of Queensland University of Technology in Brisbane, Australia and operated by Queensland Environmental Protection Agency (QEPA). The data consisted of the concentrations of 21 chemical species and meteorological data collected between 1995 and 2003. PROMETHEE/GAIA separated the samples into those collected when leaded and unleaded petrol were used to power vehicles in the region. The number and source profiles of the factors obtained from PCA/APCS and PMF analyses were compared. There are noticeable differences in the outcomes possibly because of the non-negative constraints imposed on the PMF analysis. While PCA/APCS identified 6 sources, PMF reduced the data to 9 factors. Each factor had distinctive compositions that suggested that motor vehicle emissions, controlled burning of forests, secondary sulphate, sea salt and road dust/soil were the most important sources of fine particulate matter at the site. The most plausible locations of the sources were identified by combining the results obtained from the receptor models with meteorological data. The study demonstrated the potential benefits of combining results from multi-criteria decision making analysis with those from receptor models in order to gain insights into information that could enhance the development of air pollution control measures.

Keywords: Air Quality, Source Identification, Receptor Models, PMF.

Introduction

Air pollution can produce serious problems, such as visibility degradation, and adverse effects on human health, vegetation, materials and global climate.[1-4] The association between fine particulate matter and adverse health effects such as respiratory and cardiovascular diseases, and increased absence from work and hospitalization is well documented.[5] Thus there is a global resolve to tackle air pollution through research, legislation, and education. This has led to the promulgation of air quality standards in many nations, including Australia, where the National Environmental Protection Measures for Air Quality were implemented in 1998. Subsequent amendments to the measures led to a standard that required particulate matter with aerodynamic diameter <2.5μm ($PM_{2.5}$) not to exceed 25μg/m^3 averaged over one day and 8 μg/m^3 averaged over 1 year.[6] To ensure compliance and establish long-term trends, state governments usually monitor and report the quality of air at various sites under their jurisdictions.

As a part of this program, Queensland Environmental Protection Agency (QEPA) has several air monitoring stations which includes the Brisbane Central Business District station that is located within the Gardens Point Campus of Queensland University of Technology. Among other pollutants, this station measured airborne fine particulate matter over the city between 1995 and 2003. Once this data is collected, the number of times (if any) the national standards are exceeded are examined and time series analysis conducted to evaluate seasonal variations and trends. Because some of the pollutants may have more than one source, time series analysis alone is unable to reveal the sources of the pollutants, their compositional profiles, possible locations and seasonal source strengths. Therefore, we describe in

this paper additional analyses that could enhance the understanding of the nature of the pollutants and facilitate the development of air management strategies.

Multi-criteria decision making methods, Preference METHods for Enrichment Evaluation (PROMETHEE) and Graphical Analysis for Interactive Assistance (GAIA) are powerful tools that can provide guidance for decision makers who are faced with complex options. In addition to providing the best compromise solution, they provide the rationale for the solution. These methods have not, as far as we are aware, been extensively applied to ambient air quality data. Apart from their application to indoor and outdoor air quality in the micro-environments of residential houses in Brisbane,[7] they have been used to study the chemical composition of ambient air in Brisbane.[8] However, these methods have not been applied in the literature to large air quality data matrices such as the one described in this study.

PROMETHEE is a non-parametric method for obtaining ranking information about objects. In the current study, unlike time series analysis, which is usually applied to one chemical species at a time, PROMETHEE can be used to examine and rank objects on the basis of the different chemical species found in the particulate matter. GAIA, on the other hand, displays PROMETHEE results in the form of a special PCA biplot that contains a decision axis, which assist in understanding the decision. The analysis can also provide information on the possible sources, but not on the locations of the sources or the contributions of each source to the air pollution at the sampling site.

In order to understand the sources of particulate matter and develop appropriate measures for controlling and reducing the potential effects of air pollution, it is necessary to know the sources of the chemical species in the particulate matter, the contributions of each source to the air quality at a site and plausible locations of the

sources. Thus literature is replete with information on receptor models that can be used to achieve these goals.[9-14] Two of such models, Principal Component Analysis/Absolute Principal Component Scores (PCA/APCS) and Positive Matrix Factorization (PMF) have been used in this paper. PCA/APCS calculates orthogonal factors using eigenvector-eigenvalue analysis and determines the number of appropriate factors based on the percentage of the variance explained by the results. The results provide information on the compositional profile and the variation with time and meteorology so that the factor can be associated with a source. This analysis has been applied to air quality data in many locations.[11, 15-17] PMF,[18] on the other hand, addresses the receptor model problem by weighting data points individually, applying a non-negativity constraint to promote more physically reasonable results, and use a least-squares technique to resolve the optimal solutions. PMF has also been used to examine air quality data in various locations.[14, 16, 19-21] Compared to PMF, PCA/APCS is simpler to use but as will be shown later in this paper, it produces less realistic outcomes and resolves less sources than PMF.

Receptor models have only had limited application to air quality data collected in Brisbane, and this has only involved the use of target transformation factor analysis combined with PCA.[22] Therefore an important aim of this work is to use receptor models to determine the sources of the chemical species found in fine particulate at the receptor site, quantitatively evaluate the contributions of each source to the site and calculate the possible locations of these sources by Conditional Probability Function (CPF) analysis. The comprehensive information from the PROMETHEE/GAIA analyses, receptor modelling and conditional probability analyses are useful for the formulation of air pollution control strategies.

Experimental

Sample collection and analysis

Data was collected at a Queensland Environmental Protection Agency air monitoring site located at the Gardens Point campus of the Queensland University of Technology (QUT) in the Central Business District (CBD) of Brisbane (Figure I). The site is located at latitude -27.4774 and longitude 153.0281 in a building that is close to the Brisbane River. The terrain in the greater Brisbane area consists of some large hills and the city is situated on a low-lying floodplain.[23]

The fine particulate matter was collected on Teflon filters by QEPA while chemical characterisation by Ion Beam Analysis and laser techniques was undertaken by Australian Nuclear Science and Technology Organisation (ANSTO) in Sydney. The samples were collected twice a week between April 1995 and December 2003. A weekday sample was collected on Wednesday and a weekend sample collected on Sunday over a total of 914 days.

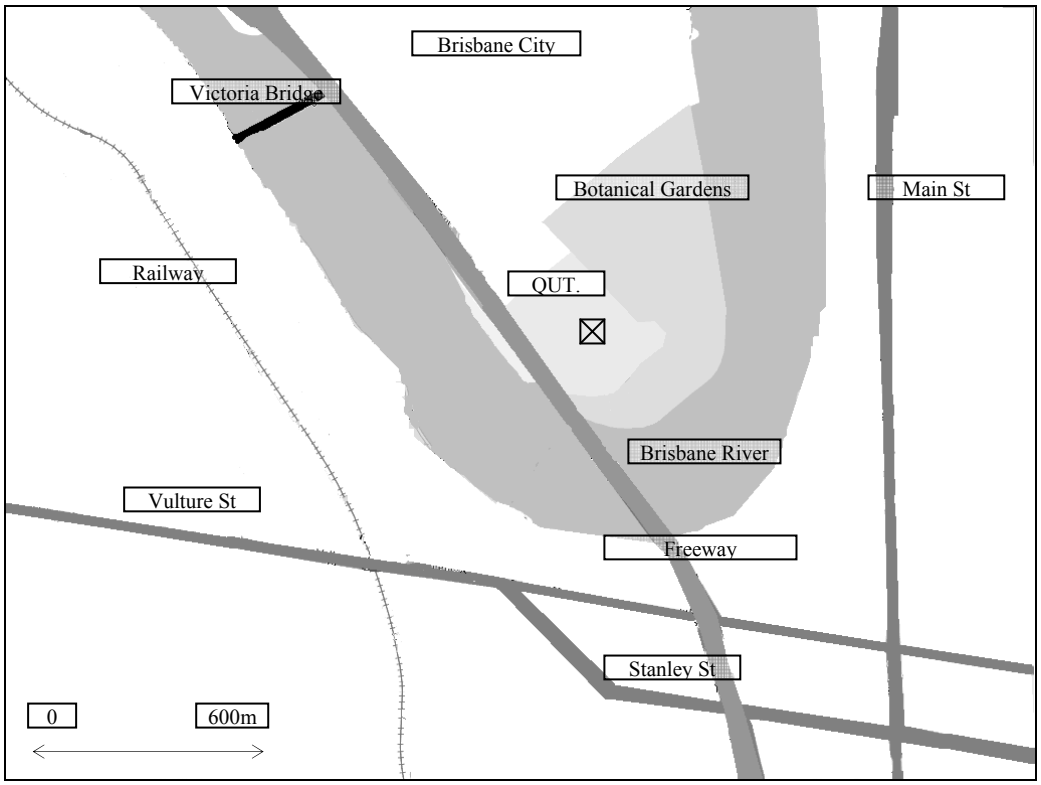

Figure I: Location of QUT Sampling Site.

Data analysis

PROMETHEE/GAIA

The PROMETHEE/GAIA analysis was performed using Visual Decision Lab 2000 software.[24] The years the sampling was conducted were treated as objects in the matrix, and the annual mean concentrations (restricted by processing power) of each of the chemical species were regarded as the variables. Thus the data matrix consisted of 9 objects and 21 variables. Being a non-parametric method, PROMETHEE is able to handle such a matrix effectively and facilitate the ranking of the objects on the basis of the measured variables.[25] The method requires each variable to be separately modelled and optimised (i.e. ranked top-down (maximised) or bottom-up (minimised)). In this study, the concentrations of the pollutants were "minimised" and the V-shaped preference function was applied to each variable as described by Lim et al.[8] All objects were compared pairwise based on each variable and this resulted in a difference, d, for each comparison. The preference function was then used to allocate a preference value for each difference and to establish a preference table so that the sum of the preference values of an object for all variables is given as a preference index (π). To refine the selection of objects, positive and negative outranking flows were calculated in such a way that the net outranking flow $\Phi = \Phi^+ + \Phi^-$ where Φ^+ shows how an object outranks all other objects and Φ^- shows how it is outranked be other objects.[26] Thus the object with the highest Φ value is considered the best and vice versa.

The GAIA plane is a special type of PCA that provides information on the variable responsible for the ranking in PROMETHEE and the interrelations between objects and variables. PROMETHEE/GAIA can provide information on the possible

sources, but not on the locations or the contributions of each source to the air pollution at the sampling site.

Receptor Modelling

Different receptor models used in air pollution research are based on a conservation of mass equation:

$$\chi_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad \text{i} = 1,\ldots,n; \text{ j} = 1,\ldots,m; \text{ k} = 1,\ldots,p \quad (1)$$

Where χ_{ij} is the jth species concentration in the ith sample, g_{ik} is the particulate mass concentration from the kth source contributing to the ith sample, f_{kj} is the jth species mass fraction from the kth source, e_{ij} is residual associated with the jth species concentration measured in the ith sample.[27] In practical terms, the modelling can be performed for m chemical species from p independent sources and n samples.

Principal Component Analysis/Absolute Principal Component Scores

An eigenvector-eigenvalue analysis was carried out to determine the number of factors and produce two sets of results: the scores (g_{ik}), and the loadings (f_{kj}). Statistical Package for Social Sciences (SPSS) software[28] was used to complete this analysis as described by Guo et. al.[11, 15, 29] Sensitivity analysis was also performed by identifying and removing the outliers from the data.

The major disadvantage of the method is that it can produce negative source contributions. This is unreasonable for an environmental system. Also, the scaling methods commonly used in PCA can distort the results.[30]

Positive Matrix Factorization

PMF2[18] analysis uses a least squares method and applies non-negative constraints to the data and the results to produce more reasonable outcomes than PCA/APCS analysis. The data points can be weighted individually depending on their estimated

errors. For this study, the EPA approach was used to estimate the uncertainty associated with each data point.[31] A sample was excluded if all of the elemental concentrations were missing. Missing concentration values for other samples were replaced by the geometric mean of the species.[32]

Prior to PMF analysis further data pre-treatment was carried out as follows. The signal -to- noise ratios (S/N) of all variables were examined (Table I). They were then divided into 3 categories: "strong" if the S/N values are greater than 2, "weak" if the S/N values are between 0.2 and 2, and "bad" if less than 0.2.[33] Chemical species categorised as "bad" were removed from the data set, while "weak" species were down-weighted in the PMF model by multiplying the uncertainties by 3.[33] 18 species (H, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Co, Ni, Cu, Zn, Br, Pb, and EC) were considered as good variables, and 3 weak variables, (Na, V, and Cr) were downweighted by 3 (Table I).

A plot of the measured mass concentration obtained from the receptor site against the mass concentration predicted by the model is shown in Accessory Materials AM VII. The R^2 value (0.87 ±0.01) obtained for the plot indicates that the relationship between the measured and predicted $PM_{2.5}$ mass concentrations is close to linearity.

Conditional Probability Function

CPF attempts to identify the likely location of the sources of the species detected at a receptor site. This is achieved by combining the source contribution results produced from the PMF analysis with the wind speed and direction data measured at the receptor site as described in Lee, 2006.[34] The parameters used for this analysis included: 75% percentile was used for the conditional probability, 24 degrees was used for the wind direction bins and if insufficient samples were contained within a bin, it was discarded.

Results and Discussion

Table I provides the summary statistics for the chemical species examined in this study. An assessment of the air quality data revealed that nine days exceeded the National Environmental Protection Measures standard [6] during the sampling period, with only one year (1995) exceeding the yearly average. Thus the air quality at the station was generally good.

QUT Sampling Site (ng/m^3)					
Species	**Arithmetic Mean**	**Median**	**% Missing**	**r^2**	**S/N Ratio**
H	245.3	190.9	0%	0.82	4.2
Na	207.0	139.5	46.8%	0.39	1.8
Al	34.5	15.5	0.1%	0.96	5.0
Si	90.2	44.6	0%	0.94	4.8
P	5.4	4.0	5.7%	0.98	4.8
S	360.0	320.8	0%	0.55	3.1
Cl	235.8	136.9	0.6%	0.91	5.0
K	81.1	47.0	0%	0.03	4.9
Ca	34.3	24.7	0%	0.68	3.9
Ti	6.3	3.4	0.2%	0.81	4.9
V	0.6	0.4	28.1%	0.09	1.9
Cr	0.6	0.4	22.7%	0.43	1.9
Mn	2.9	1.8	3.2%	0.72	4.9
Fe	57.6	36.9	0%	0.98	4.7
Co	0.4	0.2	40.7%	0.07	2.2
Ni	0.5	0.2	34.2%	0.99	4.0
Cu	3.9	2.4	1.1%	1	4.9
Zn	23.4	11.6	0.1%	1	5.0
Br	11.0	7.0	1.7%	0.95	4.9
Pb	32.9	21.6	2.8%	0.94	5.0
EC	1859.9	1443.6	0%	0.86	3.7

Table I: Summary Statistics for the species concentrations at the receptor site.

PROMETHEE/GAIA Analysis of QUT site

PROMETHEE / GAIA analysis was performed on 9 objects and the 21 elements, and the PROMETHEE II complete ranking result is shown in Figure II. It is evident from the figure that based on all of the measured chemical species, the highest ranked year (i.e. one with least pollution) was 2003, and the lowest ranked year was 1995. Thus the best air quality at the site was generally observed in 2000, 2001, 2002 and 2003 while the worst was from 1995-1999.

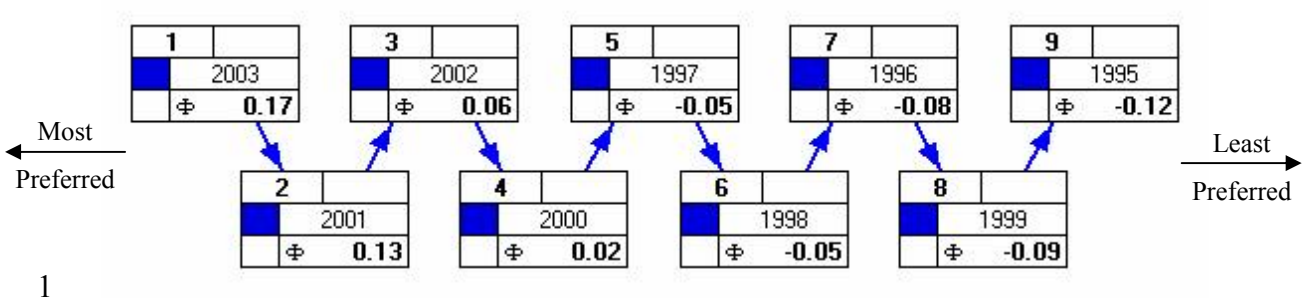

Figure II: PROMETHEE II Complete Ranking of data matrix sampling site data.

GAIA (Figure III) shows the relationships among the objects and the variables, and the position of the decision axis (i.e. direction in which the most preferred objects are positioned). The relationship between the objects and variables is reversed because pollutant concentrations were "minimised". This means that when the elements are in the same direction as the sampling year, the species is lower during that year. It also showed that the sampling period was separated into two clusters on PC1 viz: 1995-1999 and 2000-2003. The decision axis, pi, points towards 2000-2003; this complements the PROMETHEE ranking information and confirmed that the best air quality was obtained during these years. As stated in ref 7 and references therein, the longer the vector for a particular variable, the more of the data variances it accounts for. Therefore because of their long vectors in the GAIA plane, the most important species influencing the ranking are lead, bromine, aluminium and silicon. Also in keeping with the guidelines for interpreting GAIA results (stated in Ref 7), elements such as Br, Pb, EC, Ni, Cu and Cr which are oriented in the direction of measurements made in 2000-2003 are strongly associated with those years.

Motor vehicle emissions are usually characterised by Pb and Br.[35] Thus the gradual phasing out of leaded fuel which occurred during the sampling period contributed significantly to the lowering of Pb and Br in the samples and markedly affected the air quality at the site. Such multi-criteria ranking provides information that can assist the formulation and prioritisation of mitigating measures.

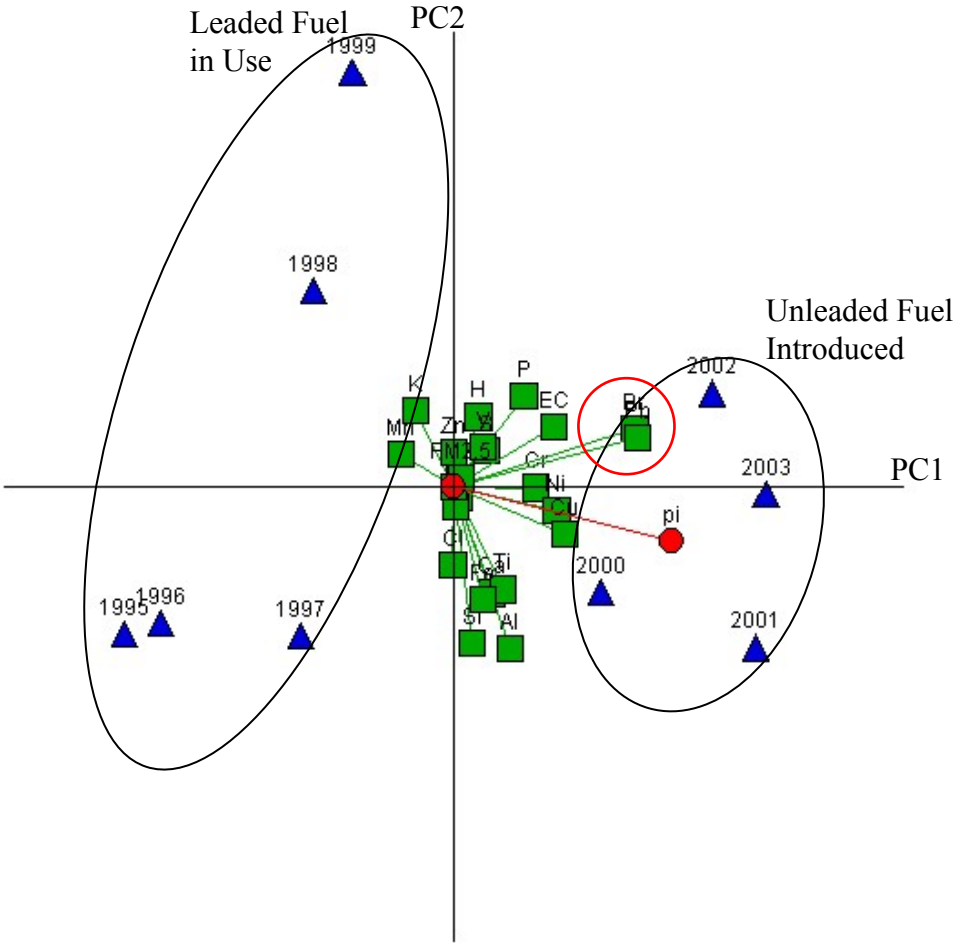

Figure III: GAIA Plane for the sampling site data showing the decision axis, pi, and the first two PCs that explained 75.2 percent of the data variance.

The GAIA plane also provided information on the possible sources of the chemical species. For example, the vectors for Pb and Br correlate closely, suggesting motor vehicle emissions as a source at the site. Similarly, the vectors for Si, Al, Ti, Ca and Fe correlate (with positive PC1 and negative PC2 coordinates), indicating that soil is also a pollution source at the site.

PROMETHEE/GAIA, however, does not supply any quantitative data on the contributions from these sources to the concentrations of pollutants detected at the receptor site. Such information can, however, be obtained by combining the PCA analysis with Absolute Principal Component Scores.

Principal Component Analysis / Absolute Principal Component Scores

Table II shows that six factors were identified (based on eigenvalues greater than 1) by the SPSS program used for this analysis. (The source profiles, source contributions, and CPF plot are presented as Accessory Materials, AM II, AM III and AM IV.)

Factor	Source Assignment	Characteristic Elements	Seasonal Variation	Weekly Variation	Direction of Source (CPF)	Percentage Source Contribution
1	Soil	Al, Si, Ca, Ti, Fe	Winter	Weekday	Gardens/ Parklands	8.5%
2	Motor Vehicle	Br, Pb, EC	Winter	Weekday	Highway	16.6%
3	Secondary Sulphate	S	Constant	Constant	Power Plant	52.2%
4	Zn Smelter	Zn, Mn	Constant	Weekday	Smelter	1.7%
5	Metal Smelter	Cu, K, V, Cr, Pb, Ti, Cl	Constant	Constant	Smelter	3.1%
6	Sea Salt	Na, Cl	Summer	Constant	River/Ocean	17.9%

Table II: Summary of results for the PCA/APCS analysis.

The first source was identified as soil based on its composition of elements such as aluminium, silicon, calcium, titanium and iron.[20] These species had the highest concentrations in the profile; however Ni and V are also present in the source profile and this could indicate that there is some contribution from oil combustion residue. Infrequent peaks were identified in the source contribution analysis of this source and the seasonal variation of the source contributions showed a significantly higher contribution in winter. In Brisbane, winter is the driest period of the year, thus it is associated with more wind-blown dust. The weekday and weekend variation identified a lower weekend factor value. The CPF analysis found that this source is likely to be located to the northeast and the west of the receptor site. Brisbane City

Botanical Gardens are located to the northeast, and South Bank parklands and Riverside freeway are located to the west of the site. However, the absence of strong fractions of BC, Pb and Br from the source profile suggests that there are limited contributions of road dusts to this source. Therefore the peak oriented in the western direction may be from the parkland rather than the freeway. The percentage contribution of this source to the total $PM_{2.5}$ mass found at this site was 8.5%.

Bromine, lead, and elemental carbon were identified as the major components of factor 2 and suggests that the second source might be motor vehicle emissions.[16] The source contribution indicated that the emissions detected at the receptor site decreased over the sampling period. A high winter, low summer variation pattern also appears to be present. This is attributable to the existence of stable weather conditions during the cooler months of the year, which are unfavourable to the dispersion of pollutants. Weekly variation identified the weekday average of the source contributions are higher than the weekend. The large peaks to the south in the CPF analysis point to a highway located 210m from the receptor site. 16.6% of the total mass detected at the site was apportioned to this source. It is the third highest contributor which indicates that vehicular traffic is one of the more significant sources for this site.

The third source was identified as secondary sulphate by the high composition of sulphur.[14, 20] The source contribution indicates that the average contributions for the seasons are very similar. A slight weekday variation was identified in the weekly variation. The largest sources of SO_2 are the power generation plant and the refinery which are located to the west and northeast of the site respectively, and the CPF results are consistent with these relatively near rather than regional sources of secondary sulphate. 52.2% contribution is attributed to this factor.

The fourth source shows zinc and manganese as well as other metals indicating that the likely source is Zn smelting.[34] The source contributions indicated that there was very little difference across the sampling period. The weekly variation indicates that the contributions are higher during the weekday. Peaks to the south and northeast identified the possible locations for the source and are directed toward significant smelters in the area. The percentage composition was only 1.7%.

The fifth source has a composition consisting of Cl, K, Ti, V, Cr, Cu, S and Pb. These elements indicate that the source is possibly metal smelting.[34] The presence of sulphur in such industrial emissions is not unusual.[36] The percentage contribution is 3.1%. Sporadic peaks were found throughout the sampling period in the source contribution. A slightly higher summer average was observed for the seasonal variation. The weekly variation did not identify a significant difference between the weekdays and weekends, and the CPF analysis indicated that the source is located to the northwest of the sampling site where a significant metal smelter is situated.

Finally, the sixth source consists of sodium and chlorine indicating a sea salt source.[14, 21] Given the presence of sulphur in the source profile, some contributions from aged sea salt cannot be ruled out. 18% was found for the percentage contribution and the Brisbane River was identified in the CPF analysis as the source. The seasonal variation pattern indicated a higher summer than winter contribution.

Positive Matrix Factorization analysis of QUT site

The optimum number of sources was determined to be nine, based on the Q value, the physically reasonable results, and the standardised residuals. Multiple linear regression of the $PM_{2.5}$ mass against the source contributions was performed to determine scaling coefficients used to estimate the source profile and source contribution in the appropriate units.

Table III presents the summary of the PMF2 results, Accessory Material AM V shows the source profile, Accessory Material AM VI shows the source contribution plot for the PMF analysis and the CPF is presented as Accessory Material AM VII.

Factor	Assigned Source	Characteristic Elements	Seasonal Variation	Weekly Variation	Direction of Source (CPF)	Percentage Source Contribution
1	Road dust	Si, K, Ca, Ti, EC	Winter	Weekday	Highway	11.1%
2	Biomass Burning	H, K, EC	Winter	Weekend	West	36.3%
3	Aged Sea Salt	Na, S, EC	Summer	None	River/Ocean	17.8%
4	Oil	Ni, V	None	None	Refinery	0.8%
5	Motor Vehicle	EC, Pb, Zn, Br	Winter	Weekday	Highway	3.5%
6	Soil	Al, Si, K, Ca, Ti, Fe	Winter	Weekday	Parklands	8.3%
7	Secondary Sulphate	S	None	None	Power Plant /Refinery	12.1%
8	Metal Smelter	Cu, Zn, K, Ca, Cr, Fe, Ni, H, S	Winter	None	Smelter	1.0%
9	Sea Salt	Na, Cl	Summer	None	River/Ocean	9.0%

Table III: Summary of the results for the PMF analysis.

The first factor is characterised by very high EC with Zn, but also has Si, Ca, K, Fe, Ti, and H. The second group of chemical species are indicators for a soil source, but the presence of high EC and Zn suggest a motor vehicle contribution. Thus the combination of the two groups is characteristic of a road dust source.[16] A large peak in late 2000 and a slightly high winter variation pattern were identified in the source contribution analysis. The weekly variation clearly identified a much higher contributions during the weekday rather than the weekend while the CPF analysis indicated that the source is located south/southeast of the receptor site and this

possibly implies the Riverside Expressway, a significant highway in the area. 11.1% percentage contribution for this source was identified.

The second source has high amounts of EC, K, and H which are the distinctive elements of biomass burning and the source accounts for 36.3% of the total $PM_{2.5}$ mass concentration.[14, 16] This percentage contribution is clearly the highest of the sources and according to the State of the Environment 2003 report,[37] controlled burning is the highest source of particulate matter in Brisbane. The two types of fires (controlled/uncontrolled burning) occur at different times of the year. Uncontrolled burning occurs during the hot summer time while controlled burning is performed during the winter months. Uncontrolled burning is rare during this time of year. The Queensland Bureau of Meteorology record the significant weather for each month and there was only one large bushfire during the winter sampling months and a corresponding peak was found in the source contributions. Indoor heating is limited because the temperature does not get too cold. The seasonal variation identified a winter trend while the weekly variation showed that weekend contributions were higher and the CPF analysis identified the source as coming from mostly West-Northwest, where more significant forest areas are located.

The chemical species with major contributions in the third source included sodium, sulphur and elemental carbon. With the sodium as high as the sulphur, it is possible that this source is aged sea salt which is manifested by the replacement of Cl and by S due to the following reaction:[35]

$2NaCl(p) + H_2SO_4(ag) \rightarrow Na_2SO_4(p) + 2HCl(g)$.

The source contribution showed a higher summer than winter variation pattern that is possibly due to formation of the aged sea salt from fresh sea salt. There was no obvious weekly variation pattern and the CPF showed that the source is located east

of the sampling site where the Pacific Ocean is located. In addition, there were indications from the CPF values that some of the aged sea salt came from the Brisbane River. This source accounted for 17.8% of the total $PM_{2.5}$ mass concentration.

Nickel and vanadium are present in the fourth source and they are tracer chemical species for an oil source.[20, 38] This source only accounts for 0.81% of the total mass. The source contribution and seasonal variation plot did not show any significant seasonal variation pattern. The weekly variation also did not show any significant trends. CPF analysis identified high CPF values in several directions, one of which points towards an oil refinery to the northeast of the site.

Source five has strong peaks for Zn, Br, Pb, and EC, which are distinctively associated with motor vehicle emissions.[35, 39] The percentage contribution from this source to the total mass is only 3.5%, which is similar to that reported (3.2%) for Queens College in New York City.[39] However, the combined contribution from motor vehicle/road dust is 14.6%, and this is fairly consistent with the percentage of vehicle related emissions obtained in many urban studies. A significant high winter - low summer variation pattern was identified in the source contribution. It also appears that the source is decreasing each year until it has almost completely disappeared by the year 2000. An attempt at analysis by separating the two time periods was made but the examination was not completed because valid results were not produced. The weekday contribution appeared to be higher than the weekend. A highway around the south of the receptor site was the main direction found in the CPF analysis. This source seems to be associated with leaded petrol powered vehicles that were present in the 1990s and the removal of the lead explains why overall it has a low contribution, particularly in the new millennium.

The chemical species Al, Si, S, K, Ca, Ti, and Fe present in the sixth source are clearly dominant and are characteristic of a soil source.[20] The source contributions identified some large contributing days at different times throughout the sampling period. A higher winter level was found in the seasonal variation and may be due to the stable atmospheric conditions during this time of year. Weekdays were identified in the weekly variation as having higher contributions than weekends possibly suggesting a contribution from road dust. Parklands located to the west appear to be the source of the soil. 8.3% was identified as the percentage of the total $PM_{2.5}$ mass.

The seventh source has significantly high sulphur composition and so is likely to be due to secondary sulphate formation.[20] Coal refining and power generation are the major sources of SO_2 that is the basis of the formation of secondary sulphate. 12.1% for the percentage contribution indicates it as one of the most important sources. This percentage contribution is significantly lower than that obtained by PCA/APCS but considerable variability in the results obtained by different models is quite common.[16,38,42] The source contributions did not show any significantly unusual days and the seasonal variation identified the source as consistent throughout the year. A slightly higher weekday average was found in the weekly variation and the location of the source appears to be from the power plant to the west and oil refinery to the northeast.

The eighth source has high values for H, S, K, Ca, Cr, Fe, Ni, Cu, and Zn. The combination of copper and zinc with some of the minor metals indicates that this source could be metal processing.[27] Source contribution results identified that there were just a few scattered days that had a significant contribution. Combining this information with the percentage contribution of only 1% indicates that this is a minor source. The seasonal variation found that there was a higher contribution in the winter

than in summer. There was only a slightly higher contribution from the weekdays than the weekends and the CPF values point to the southwest where a metal smelter is located, with a smaller point towards the southeast.

Sodium and chloride are the major chemical species present in the ninth source. This is very characteristic of sea salt.[20, 40] This source contributed 9% of the total mass. No significant days of high concentration were identified in the source contribution analysis and the seasonal variation indicates a summer relationship. There is no weekly variation for this source and the CPF direction points toward the river to the east of the receptor site and is consistent with the source identification.

Each of the methods used in this paper has its advantages and disadvantages. The PROMETHEE/GAIA analysis provides unique results that allow users to rank the quality of the air monitored in different years on the basis of their chemical compositions. Information on the chemical species responsible for the ranking as well as their possible sources can also be obtained from the PROMETHEE/GAIA results. However, no quantitative information on the sources of the pollutants can be determined from the analysis. PCA/APCS, on the other hand, provides a quick and easy method for the determination of the number of possible sources of pollutants and the contribution of each source to the atmospheric concentration. The major disadvantage of this method is that it sometimes produces negative concentrations and contributions for some sources, which are unreasonable for an environmental study. In addition, compared to PMF, fewer factors are determined from PCA/APCS studies. [41, 42] Finally, in the PMF analysis, pollutant concentrations are weighted individually using their analytical precisions, missing and outlier values are adjusted for, and the optimum number of sources resolved. The combination of the three methods provides a unique ranking analysis result, a quick result that indicates the

possible sources and a more refined analysis that offers more reliable source apportionment of pollutants in the atmosphere. Such comprehensive information has a greater potential to facilitate the development of source control strategies than those obtained from any one of these methods.

Conclusion

Species concentration data for $PM_{2.5}$ samples at a Brisbane air monitoring site were analysed using PROMETHEE/GAIA, and two receptor models, PCA/APCS and PMF. PROMETHEE and GAIA provided net ranking information necessary to select one sampling period in preference to all others, on the basis of the chemical species. Such ranking analysis has not previously been applied to ambient fine particle data. This method appears to offer a useful tool in ranking air quality at multiple sites and prioritizing control strategies to focus on the highest emitting sources. The patterns in GAIA plane analysis assisted the identification of the plausible sources of the pollutants and provided information on variables that strongly influence the discrimination of the objects. Both PCA/APCS and PMF provided quantitative information on the sources, source compositional profiles and source contributions. Broadly similar source profiles were identified by these receptor models, with soil, sea salt, vehicle emission, secondary sulphate and metal smelting as the common sources. However, PCA/APCS identified fewer sources than PMF, and as previously noted by other researchers who compared the source compositional profiles obtained by different receptor models,[16, 42] there are considerable differences in the contributions obtained for the common sources. EC dominated the profiles assessed during the analysis and this may have affected the sources. Also, the absence of NO_3^- and Organic Carbon (OC) from the monitoring limited the possibility of assessing the

presence of sources containing these species in the area. Cohen[43] indicated that hydrogen can be identified as coming from organic matter when examining the profiles. Any attempt to develop control strategies must use the comprehensive information from all of these analyses along side those obtained from the CPF values.

Acknowledgements

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Accessory Materials Available

Information on source profiles, sources contributions and Conditional Probability Function analysis are presented as additional figures in the Accessory Materials section.

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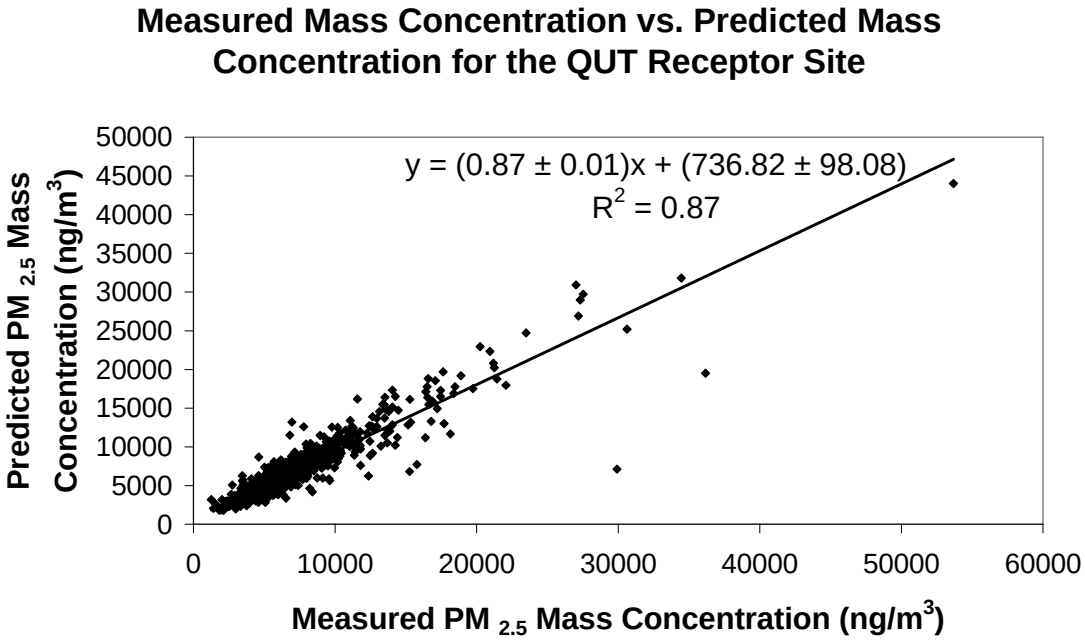
Cover Sheet for Accessory Materials

Authors: Adrian J. Friend and Godwin A. Ayoko

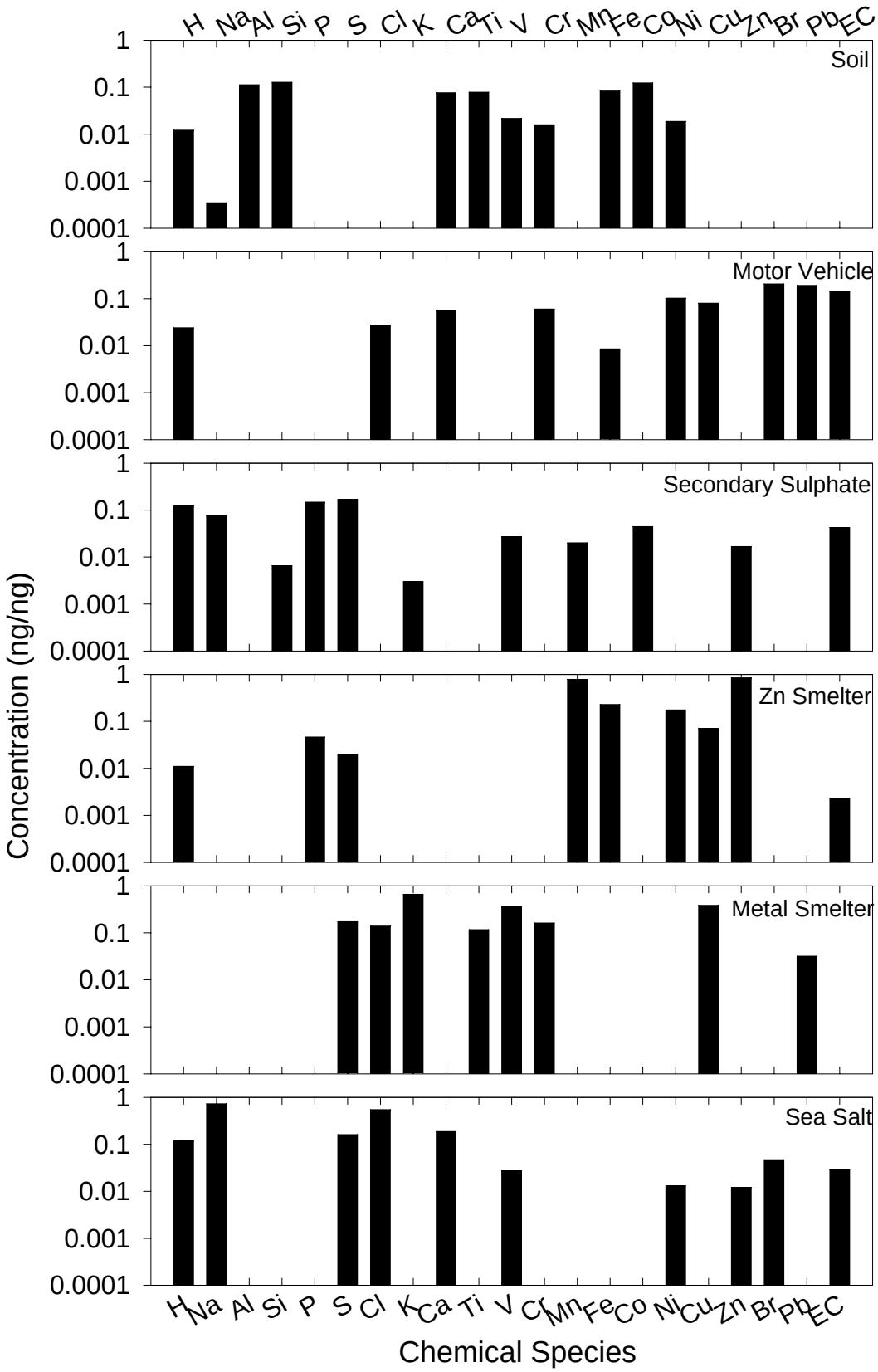
Title: Multi-criteria ranking and source apportionment of fine particulate matter at an air monitoring station in Brisbane, Australia

Number of pages: **7**

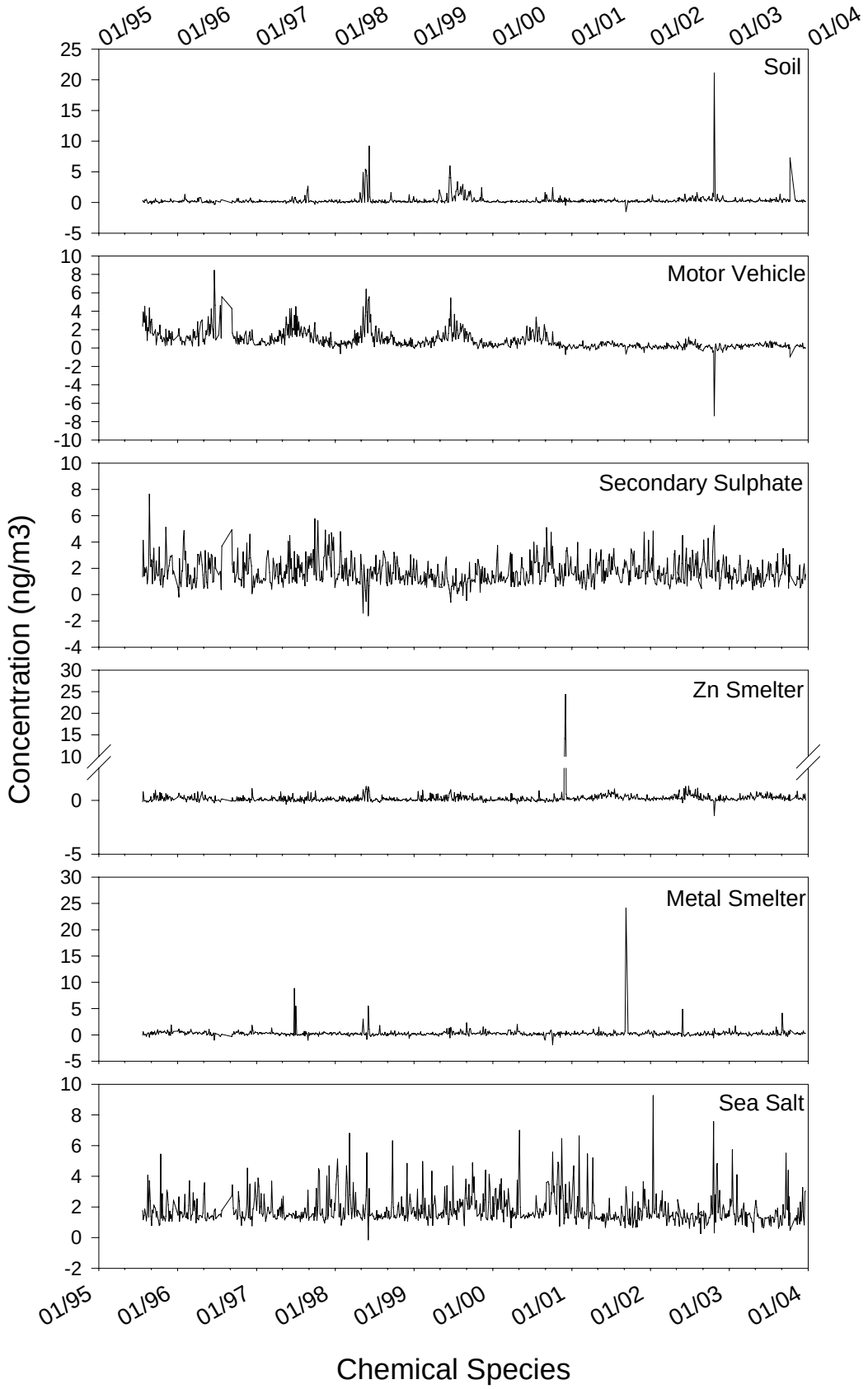
Number of Figures: **7**



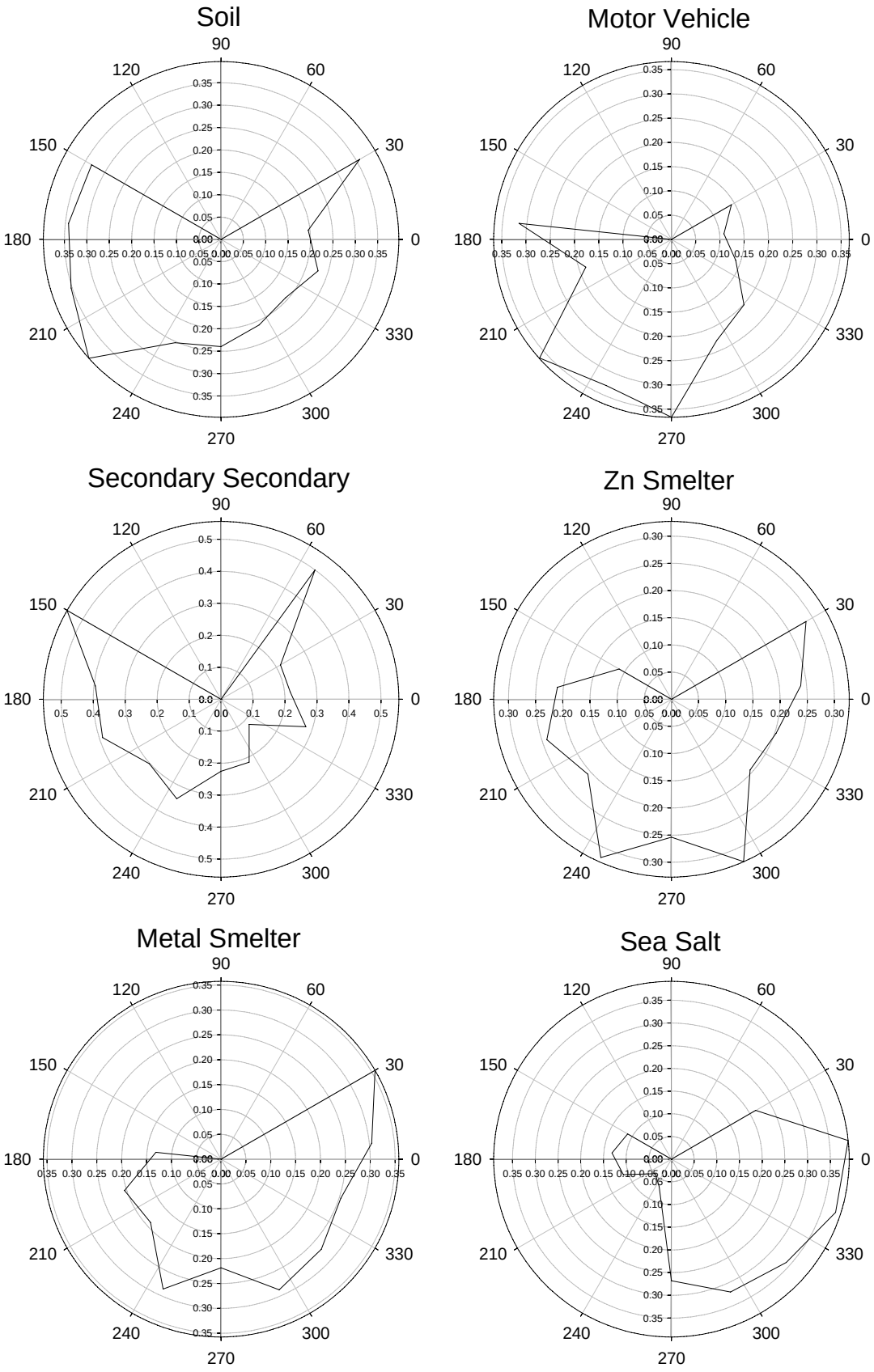
AM I: Measured verses predicted PM $_{2.5}$ mass concentration for the site.



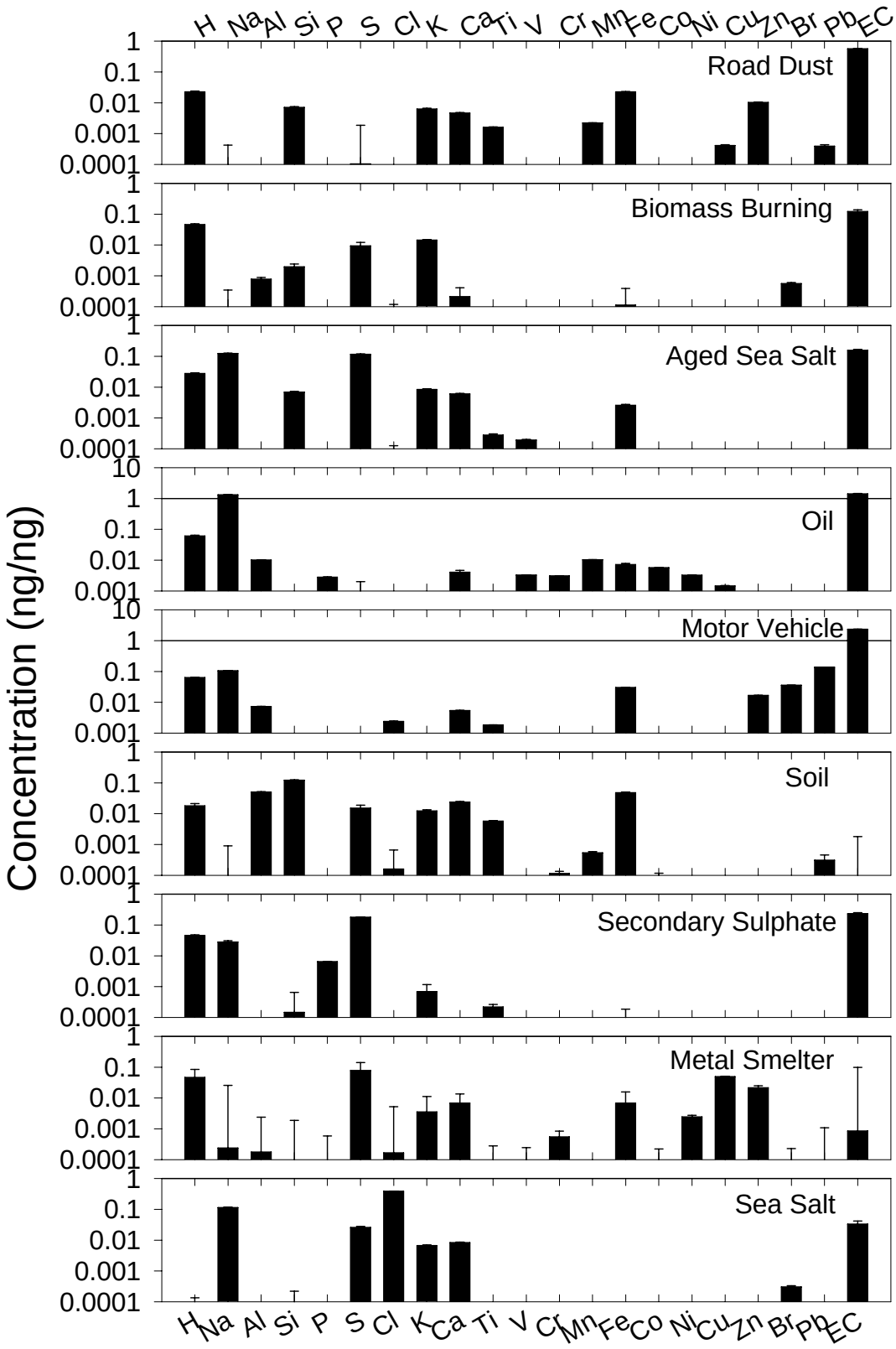
AM II: Source profile plot for the PCA/APCS analysis of the QUT receptor site.



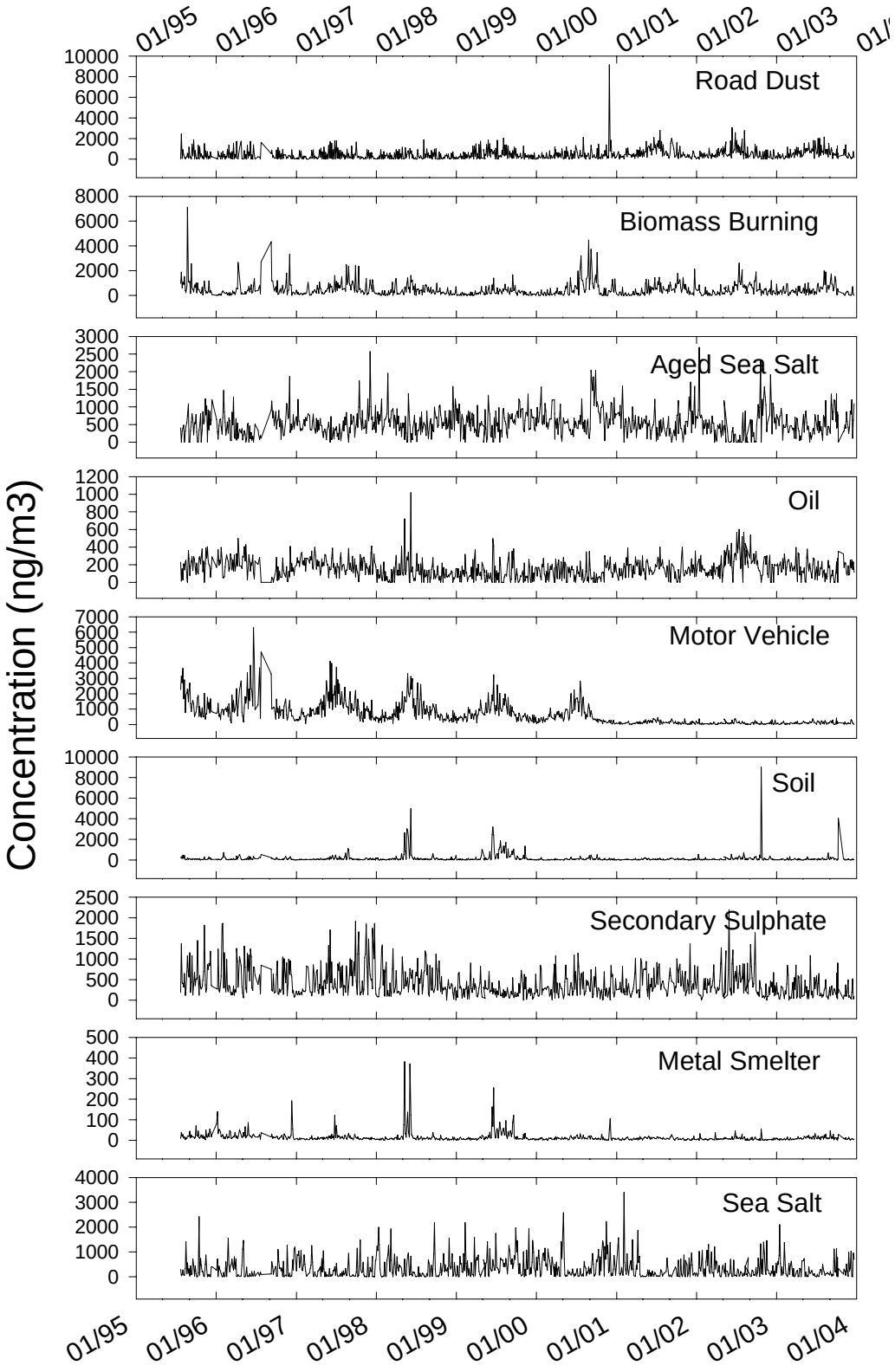
AM III: Source contribution plot for PCA/APCS analysis of QUT receptor site.



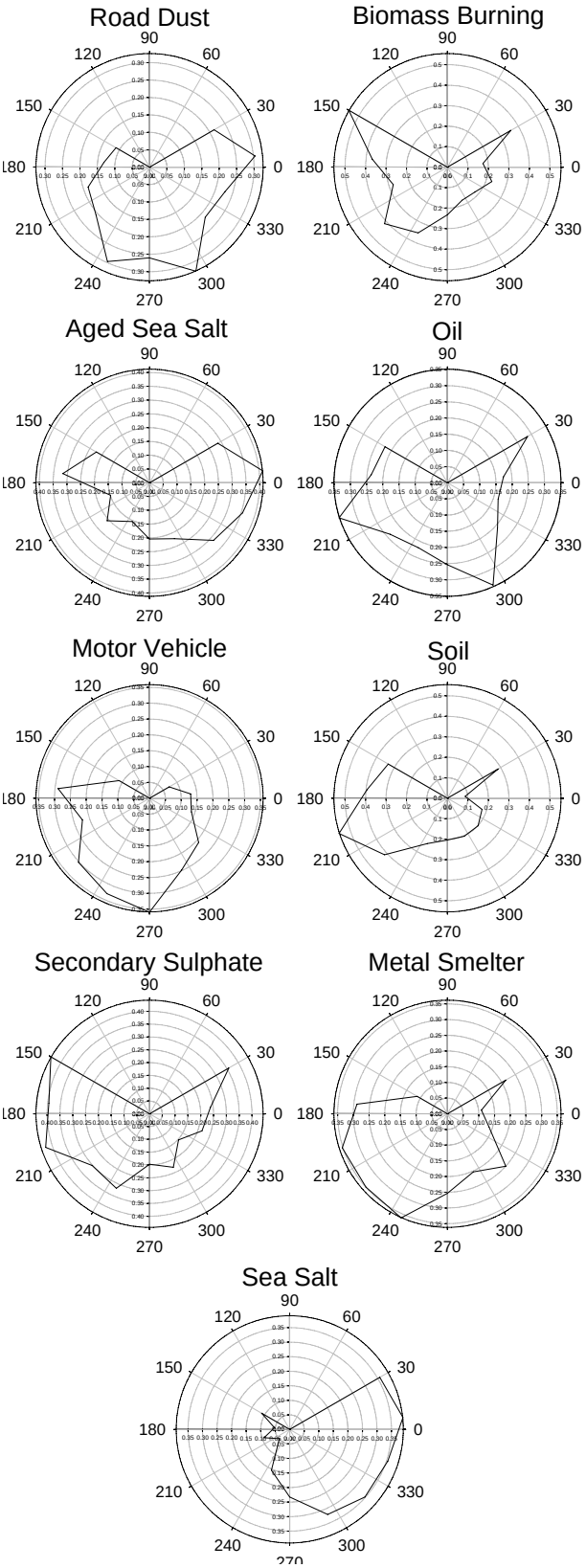
AM IV: CPF results based on the source contribution obtained from the PCA/APCS analysis.



AM V: Source profile plot for the PMF analysis. X-axis denotes chemical species



AM VI: Source contribution plots for PMF analysis. X-axis denotes sampling date.



AM VII: CPF results based on the source contribution obtained from PMF analysis.