

DEVELOPING CHEMICAL SOURCE PROFILES FOR GREATER CAIRO, USING POSITIVE MATRIX FACTORIZATION (PMF) RECEPTOR MODELING

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ABSTRACT

The purpose of this paper is to demonstrate that Positive Matrix Factorization (PMF) can model factors and calculate source attributions from ambient data sets, where limited chemical source profiles are available. It also demonstrates a procedure for the derivation of modeled profiles which can be applied in subsequent Chemical Mass Balance (CMB) receptor modeling.

Various receptor models including Positive Matrix Factorization (PMF) and Chemical Mass Balance (CMB) were applied in order to calculate the source attributions. Chemically analyzed ambient data sets from Cairo were collected at several sites, representing short time intervals during 1999-2002. PMF source factors modeled from the Cairo data sets contain clear signatures of motor vehicle emissions, vegetative burning, marine salt, ferro-manganese plant emissions, oil fired power plant, cement plant, secondary ammonium chloride, geological dust, lead smelter, and a copper zinc smelter. Variable amounts of secondary ammonium sulfate and ammonium nitrate are contained in most of the modeled factors. Application of the PMF model was able to calculate source attributions as well as overcome the issues inherent to the application of the CMB receptor model. Source profiles were derived from PMF factors, which could serve as input to the CMB modeling.

INTRODUCTION

Cairo, Egypt suffers from high ambient concentrations of atmospheric pollutants. In order to reduce ambient pollution, the U.S. Agency for International Development (USAID) and the Egyptian Environmental Affairs Agency (EEAA) have supported the Cairo Air Improvement Project (CAIP) [1]

One of the CAIP initiatives was a source attribution study (SAS) to determine contributions from various sources to the observed pollutant levels. As part of the SAS, intensive monitoring studies were carried out during the periods of February/March and October/November 1999 and June 2002. PM_{10} , $PM_{2.5}$, polycyclic aromatic hydrocarbons (PAHs), and volatile organic compounds (VOCs) were measured on a 24-hour basis at sites representing background levels, mobile source impacts, industrial impacts, and residential exposure. Source attribution results using measured source profiles, ambient samples, and the Chemical Mass Balance (CMB) receptor model are presented in another paper by Gertler *et al.* [2] at this meeting.

This paper presents results of Positive Matrix Factorization (PMF) receptor modeling using the same ambient data set as above. PMF is a variant of Factor Analysis with non-negative factor coefficients. It calculates factors from an ambient air data set, which can be shown to be substituted for measured chemical source profiles. PMF modeling differs from Chemical Mass Balance (CMB) receptor modeling in that no measured source profiles are required, only a reasonably large (>100 samples) ambient data set. One of the assumptions of the CMB model [3] is that the chemical compositions of the sources remain consistently the same between when measured at the source until sampled in the ambient atmosphere at the

receptor site. This is seldom the case, and in many instances it is difficult to apply the CMB model when dealing with reactive source components such as motor vehicle emissions or vegetative burning. Over time, and depending on prevailing meteorological conditions, as well as the presence and concentrations of reactive chemical components (reactive hydrocarbons, NO_x, SO₂, O₃) in the ambient atmosphere, profiles modeled at the receptor site may no longer be representative of the original measured chemical profiles at the source. In many instances appropriate chemical profiles are unavailable, especially from non-point sources such as garbage and vegetative burning, geological and road dust, or motor vehicle emissions. Chemical source profiles for the impacting sources are often also difficult and expensive to acquire, or not available. For the above reasons, receptor models such as the PMF [4], and UNMIX [5, 6] were developed, also as improvements to other multivariate procedures such as Factor Analysis (FA) and Principal Components Analysis (PCA) [7].

This paper focused on identifying major source types and calculating average PMF modeled source attributions for the 1999- 2002 period. The paper also demonstrates the ability of PMF to develop chemical source profiles for CMB receptor modeling, for Cairo.

CAIRO AMBIENT DATA SET

A data set of 360 samples was assembled from five subsets as described elsewhere [8, 2]. Two of the sample subsets were described as being source samples. These were collected in the proximity of major sources, such as at road tunnels and burning garbage dumps, near steel plants and cement factories, and not directly at the point of emissions. In such instances the source samples are diluted with ambient air already polluted by other sources, and are for this modeling exercise considered to be a source enriched ambient samples. In the course of subsequent PCA and PMF this would lead to a bias of the modeled results towards elevated species concentrations from such source enriched ambient samples. The PMF modeling was performed on the complete data set (360 samples) as well as on the PM_{2.5} (195 samples) and PM₁₀ (165 samples) sample subsets.

For this analysis the inorganic elements and ions, as well as the eight carbon species on front as well as backing filters were considered (50 species in total). With the exploratory rounds of analysis, all species were subjected to PCA using SAS[®] data analysis software. No missing or zero values in this data set were replaced, and subsequently the PCA was performed only on those samples without missing values. Several iterations of PCA were conducted, in order to identify and eliminate species that do not contribute substantially (< 0.1 as factor coefficient) to the total variance of the sample set. From the PCA as well as previous CMB [1] and preliminary PMF, the following 34 species were identified for the final PMF receptor modeling: Cl⁻, NO₃⁻, SO₄⁼, NH₄⁺, Na⁺, K⁺, OC₁₋₄, OPT, EC₁₋₃, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Br, Sb, Ba, Pb, and Mass. In this case and prior to the PMF modeling each of the zeros and negative values in the data set were replaced by the smallest measured positive value for that species, and the corresponding uncertainties by half this value.

RESULTS

The selection of the number of factors (Factor 1-9) (Figure 1) for the PMF modeling was based on the PCA results and experience from similar studies [9]. The PCA also showed that at least six factors are required to account for more than 95 percent of the total variance in the data set.

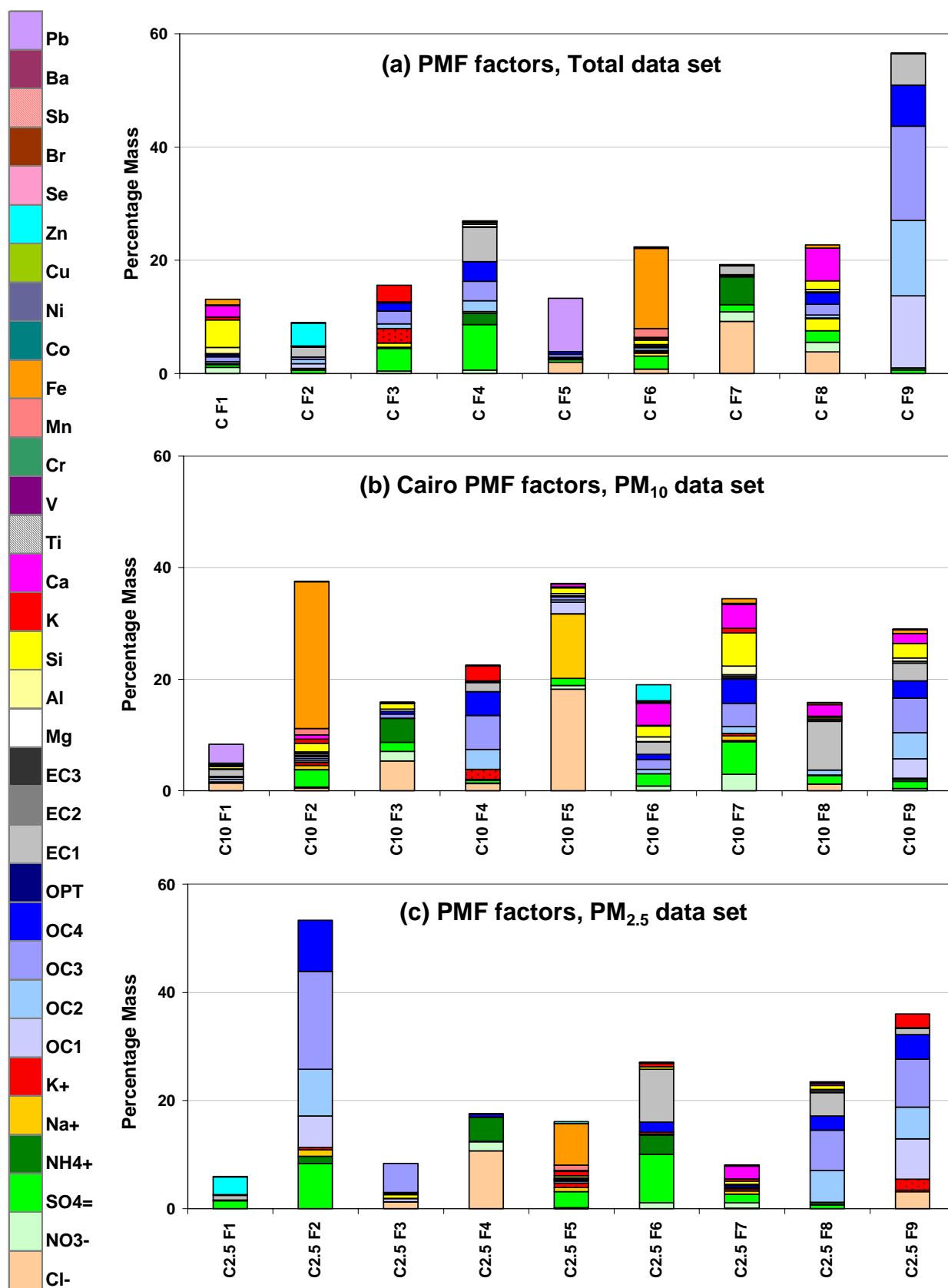


Figure 1. PMF modeled source profiles for the total data set (a), as well as for the PM₁₀ and the PM_{2.5} (c) data subsets, for Cairo.

So as to better resolve amongst the sources of fine (e.g. combustion, smelter) and coarse (e.g. geological, road, cement plant) dust, three individual subsets of results were modeled, one being complete data set of 360 samples (Figure 1a), and the other two the PM_{2.5} (Figure 1b) and PM₁₀ (Figure 1c) sample subsets. The PMF modeled factors for each data set or subset are presented by bar charts showing the relative mass proportions of the modeled species. Since the data set includes samples at or close to sources, and in other instances for certain periods of the year, this source attribution may not be representative of the annual average Cairo ambient atmosphere. Also grouped in these figures are the major sources represented by each of the nine factors. *It should be noted that each factor seldom represents a single source, but often a combination of a major and one or more minor and trace source types.*

Source Profiles from PMF Modeled Factors

The modeled PMF factors often also contain secondary ammonium and sea salt. Minor profiles such as marine salt, secondary ammonium nitrate, ammonium chloride and ammonium sulfate were subsequently subtracted from the modeled PMF factors. Of the 27 modeled factors (nine for each of the three sample sets), nine identified as containing major sources, were selected. The criteria applied in this selection step included the abundance (attribution) of the factor, the contribution of a major source to that factor, together with the amount of secondary ammonium and other ions to be subtracted to provide a “clean” source profile. Table 1 lists the nine selected factors from which the nine chemical source profiles were extracted.

Table 1. PMF modeled factors selected for the extraction of source profiles.

Profile Extracted	PMF Modeled Factor Number	PMF Modeled Data Set
Geological dust	CF1	PM _{2.5} + PM ₁₀
Heavy oil combustion (Mazut)	CF4	PM _{2.5} + PM ₁₀
Cement plant	CF8	PM _{2.5} + PM ₁₀
Motor vehicle emissions	CF9	PM _{2.5} + PM ₁₀
Copper-zinc smelter	C2.5 F1	PM _{2.5}
Diesel vehicle emissions	C2.5 F8	PM _{2.5}
Vegetative burning	C2.5 F9	PM _{2.5}
Lead-zinc smelter	C10 F1	PM ₁₀
Ferro-manganese industry	C10 F2	PM ₁₀

The “cleaned” PMF modeled source compositions were normalized to the sums of the analyzed species. Mass totals were calculated from ion balances and converting elements to oxides, as well as recalculating the organic carbon species to hydrocarbons. (reconstituted mass) applying multiplication factors (Table 2) which were previously calculated for each measured source type in Cairo. These differ from the empirical value of 1.4 applied in the case of the IMPROVE data sets [9]. The assumption is that the sum of the species was 100 percent and that the difference in mass between the analyzed and non analyzed species is ascribed to hydrogen and oxygen bound to organic compounds.

$$\text{Hydrocarbon mass} = \text{Multiplier} * (\text{OC1} + \text{OC2} + \text{OC3} + \text{OC4} + \text{OPT})$$

By comparison of major species ratios and trace element markers with measured profiles in Cairo by Lowenthal *et al.* [1] and elsewhere by Engelbrecht *et al.* [10], Watson *et al.* [11], and Maykut *et al.* [12], the following cleaned modeled source profiles were identified (Figure 2, Table 3).

Table 2. Multiplier for OC calculated from “source” samples for each source types.

Source Type	*Multiplier
Geological dust	3.33
Heavy oil combustion (Mazut)	1.43
Cement plant	1.41
Motor vehicle emissions	1.16
Copper-zinc smelter	2.08 est.
Diesel vehicle emissions	1.13
Vegetative burning	1.88
Lead-zinc smelter	2.08
Ferro-manganese industry	2.12

1. Heavy Oil Combustion (Mazut)

The profile contains as major species, increasing amounts of OC2, OC3, OC4, and EC1, as well as Mg. From the carbon fractions ratios and the range of trace elements (V, Ni, Ba, Sb, Br, Cr and Co), this profile was identified as being from heavy industrial oil combustion, *i.e.* Mazut, often used at oil fired power plants

2. Motor vehicle Emissions

The profile contains major, nearly equal amounts of OC1, OC2, OC3, and slightly less OC4 and EC1. Leaded gasoline has not been identified as such, because of all the Pb being classed with the lead-zinc smelter profile. Leaded gasoline was also phased out in Cairo in 1997 and it was not expected to show up in this profile.

3. Diesel Vehicle Emissions

This profile is characterized by large amounts of OC2, OC3, OC4 and EC1, with some EC2. It also contains some trace amounts of V, Cu, Zn, Br, Sb, and Ba. The Si, Al, K, Ca and Ti in this profile may be from road dust.

4. Vegetative Burning

This profile is composed of large amounts of all four OC fractions (OC1, OC2, OC3, OC4), together with a high concentration (3.77%) of soluble K^+ , typical of vegetative burning. It also contains some EC1.

5. Geological Dust

The soil profile is simple to identify, being composed of the regular geological species such as Al, Si, Ca, and Fe, as well as some insoluble K and soluble K^+ . The carbon fractions are considered to be part of the soil profile.

6. Cement Plant

The Ca, together with amounts of Si, Al, and Fe, and OC2, OC3 and OC4 points to this being a cement plant profile.

7. Copper-zinc Smelter

This is a predominantly a zinc profile, with some copper. Because of the volatility of zinc, this metal is often emitted in great abundance by metallurgical processes, including sulfide reduction and arc furnaces. There is also a high concentration of EC1 associated with this profile, which is ascribed to the metallurgical sulfide reduction process.

8. Lead-zinc Smelter

This predominantly Pb profile contains some Zn, and also EC1 which is interpreted as being from the lead smelting process. This profile has minor geological species, which can be ascribed to geological dust.

9. Ferro-manganese Industry

This is a very definite ferro-manganese profile representative of the iron and steel industry in Cairo. The crustal species such as Al, Si, K and Ca, as well as the carbon species are considered to be part of this profile.

Table 3a. Cairo PMF Modeled Source Profiles (excluding anions and cations other than K+)

Species	PM Oil fired power plant			PM Motor vehicle emissions			PM _{2.5} Diesel vehicle emissions			PM _{2.5} Vegetative Burning		
	% Species	±	% Unc.	% Species	±	% Unc.	% Species	±	% Unc.	% Species	±	% Unc.
Cl-	0.000	±	0.004	0.000	±	0.000	0.000	±	0.160	0.000	±	5.080
NO3-	0.000	±	0.062	0.000	±	0.000	0.000	±	0.208	0.000	±	0.330
SO4=	0.000	±	0.258	0.000	±	0.024	0.000	±	6.739	0.000	±	0.904
NH4+	0.000	±	0.065	0.000	±	0.016	0.000	±	4.123	0.000	±	0.254
Na+	0.000	±	0.024	0.000	±	0.002	0.000	±	0.077	0.000	±	0.033
K+	0.008	±	0.022	0.000	±	0.004	0.000	±	0.069	3.770	±	1.437
OC1	0.000	±	0.009	20.058	±	0.249	0.171	±	3.132	13.780	±	11.961
OC2	8.974	±	0.243	20.874	±	0.277	22.648	±	12.213	10.816	±	11.247
OC3	16.372	±	0.420	26.103	±	0.452	29.002	±	23.620	16.384	±	17.595
OC4	16.467	±	0.319	11.381	±	0.182	10.222	±	13.438	8.271	±	10.346
OPT	0.019	±	0.002	0.000	±	0.000	0.002	±	0.028	0.000	±	0.015
EC1	29.165	±	0.383	8.737	±	0.175	16.923	±	12.866	2.187	±	5.741
EC2	0.243	±	0.030	0.086	±	0.011	1.260	±	2.400	0.073	±	0.319
EC3	0.008	±	0.000	0.000	±	0.000	0.001	±	0.006	0.000	±	0.001
Mg	3.494	±	0.021	0.000	±	0.000	0.000	±	0.020	0.000	±	0.003
Al	0.022	±	0.017	0.044	±	0.004	1.086	±	0.802	0.051	±	0.166
Si	1.351	±	0.033	0.056	±	0.002	2.787	±	1.149	0.050	±	0.092
K	0.103	±	0.025	0.000	±	0.002	0.030	±	0.481	0.974	±	1.520
Ca	0.204	±	0.020	0.000	±	0.001	1.328	±	0.638	0.000	±	0.069
Ti	0.000	±	0.001	0.000	±	0.000	0.003	±	0.016	0.000	±	0.001
V	0.177	±	0.003	0.000	±	0.000	0.002	±	0.009	0.000	±	0.001
Cr	0.001	±	0.000	0.000	±	0.000	0.000	±	0.001	0.000	±	0.000
Mn	0.014	±	0.001	0.000	±	0.000	0.000	±	0.005	0.000	±	0.002
Fe	0.613	±	0.013	0.008	±	0.000	1.186	±	0.473	0.002	±	0.012
Co	0.000	±	0.000	0.000	±	0.000	0.000	±	0.001	0.000	±	0.000
Ni	0.070	±	0.000	0.000	±	0.000	0.000	±	0.001	0.000	±	0.000
Cu	0.095	±	0.001	0.000	±	0.000	0.070	±	0.047	0.000	±	0.000
Zn	0.097	±	0.004	0.001	±	0.000	0.012	±	0.112	0.001	±	0.006
Se	0.000	±	0.000	0.000	±	0.000	0.000	±	0.001	0.000	±	0.000
Br	0.001	±	0.000	0.000	±	0.000	0.000	±	0.002	0.000	±	0.002
Sb	0.001	±	0.000	0.000	±	0.000	0.000	±	0.003	0.000	±	0.000
Ba	0.007	±	0.000	0.000	±	0.000	0.001	±	0.009	0.000	±	0.001
Pb	0.100	±	0.004	0.000	±	0.000	0.000	±	0.013	0.000	±	0.001
Total	77.607			87.348			86.736			56.357		

Table 3b. Cairo PMF modeled source profiles (excluding anions and cations other than K+).

	PM Geological dust		PM Cement plant		PM2.5 Copper-zinc smelter		PM10 Lead-zinc smelter		PM10 industry	Ferro-manganese
Species	% Species	% Unc.	% Species	% Unc.	% Species	% Unc.	% Species	% Unc.	% Species	% Unc.
Cl-	0.000	0.024	0.000	0.130	0.000	0.095	0.000	0.544	0.000	0.053
NO3-	0.000	0.079	0.000	0.110	0.000	0.143	0.000	0.017	0.000	0.014
SO4=	0.000	0.175	0.000	0.216	0.000	11.380	0.000	0.303	0.000	0.159
NH4+	0.000	0.002	0.000	0.001	0.000	0.917	0.000	0.163	0.000	0.009
Na+	0.000	0.021	0.000	0.059	0.000	1.267	0.000	0.055	0.000	0.030
K+	0.737	0.017	0.119	0.019	0.001	0.774	0.183	0.034	1.052	0.027
OC1	0.000	0.009	0.000	0.008	1.236	11.267	4.730	0.276	0.690	0.066
OC2	1.470	0.164	2.652	0.159	0.004	1.250	4.646	0.337	0.886	0.088
OC3	3.906	0.351	9.644	0.354	0.026	7.584	1.969	0.534	0.607	0.156
OC4	1.201	0.259	10.497	0.303	0.050	10.128	0.002	0.109	0.495	0.089
OPT	0.000	0.001	0.001	0.001	0.000	0.037	0.033	0.024	0.028	0.012
EC1	0.494	0.193	0.001	0.033	19.395	11.145	15.477	1.079	0.000	0.017
EC2	0.801	0.031	0.734	0.034	0.000	0.051	0.144	0.037	0.663	0.044
EC3	0.001	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.000
Mg	0.000	0.000	0.087	0.003	0.220	0.332	0.001	0.040	0.000	0.000
Al	4.727	0.089	2.314	0.057	0.002	0.486	0.316	0.412	0.641	0.077
Si	21.404	0.263	7.825	0.105	0.000	0.101	5.462	1.640	3.230	0.383
K	1.500	0.055	0.000	0.023	0.000	0.170	0.000	0.150	0.449	0.123
Ca	8.792	0.153	29.697	0.162	0.203	0.523	0.897	0.694	1.536	0.118
Ti	0.638	0.005	0.000	0.000	0.000	0.004	0.002	0.001	0.000	0.000
V	0.000	0.000	0.001	0.000	0.000	0.003	0.065	0.004	0.000	0.000
Cr	0.000	0.000	0.000	0.000	0.000	0.001	0.021	0.002	0.000	0.000
Mn	0.009	0.001	0.000	0.001	0.042	0.066	0.396	0.009	2.364	0.026
Fe	4.397	0.040	2.864	0.032	0.676	0.625	1.903	0.127	54.424	0.608
Co	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.001	0.000	0.001
Ni	0.000	0.000	0.000	0.000	0.000	0.001	0.047	0.001	0.000	0.000
Cu	0.021	0.001	0.006	0.001	0.992	0.078	0.047	0.002	0.000	0.000
Zn	0.000	0.003	0.088	0.003	72.899	2.300	3.035	0.076	0.001	0.012
Se	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000
Br	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sb	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000
Ba	0.000	0.000	0.001	0.000	0.000	0.007	0.001	0.001	0.000	0.000
Pb	0.000	0.002	0.000	0.000	2.289	0.466	40.342	0.280	0.127	0.003
Total	50.099		66.534		98.034		79.722		67.195	

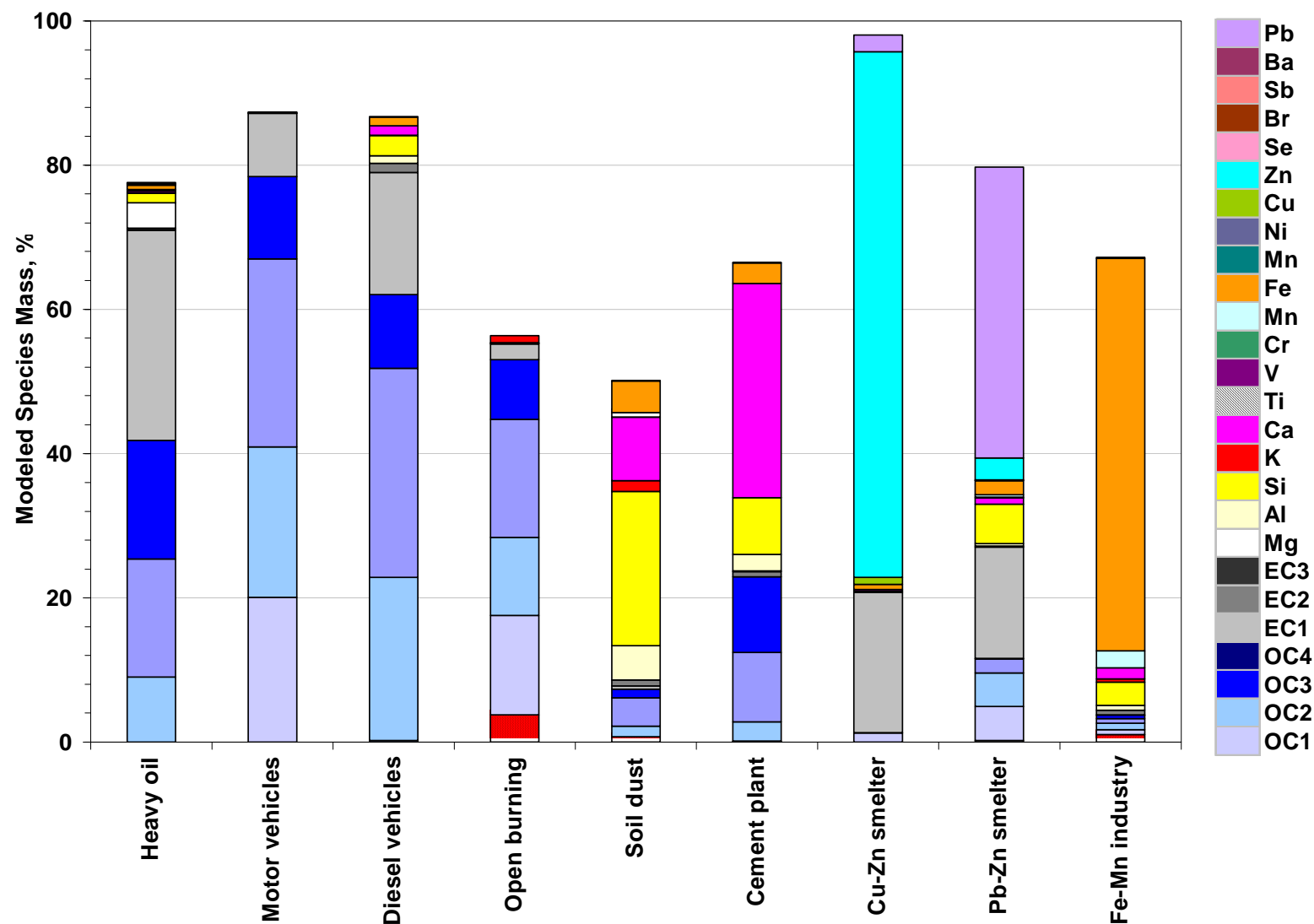


Figure 2. Cleaned PMF modeled chemical source profiles for application as input to the CMB receptor model.

CONCLUSIONS

The data matrix of 360 samples and 50 species, together with their uncertainties were assembled for this study. The elements and ions, together with the carbon fractions were explored by PCA and modeled by PMF. The chemically analyzed ambient data set from Cairo was collected at several sites, representing spring and fall samples collected during 1999-2002. The data set was found to be adequate to perform PMF receptor modeling and to model the nine source profiles. The total data set of 360 samples as well as the individual PM_{2.5} (195 samples) and PM₁₀ (165 samples) sample subsets were analyzed, using 34 species in each run. The modeling showed that each PMF factor represented one major source type, together with one or more minor and trace sources. The PM_{2.5} modeled results better resolved the combustion process profiles such as the heavy oil combustion, motor vehicle emissions and vegetative burning while the PM₁₀ modeled results emphasized coarse processes such as geological dust and ferro-manganese plant emissions. Major source factors and average attributions modeled from the three data sets in this PMF study include, motor vehicle emissions (13-28%), vegetative burning (8-18%), marine salt (17%), ferro-manganese plant emissions (8-17%), oil fired power plant (14-16%), cement plant (4-11%), secondary ammonium chloride (7-10%), geological dust (7-16%), lead smelter (4-7%), and copper zinc smelter (3-13%). Variable amounts of secondary ammonium sulfate and ammonium nitrate were found to be contained in most of the modeled factors

The factors (1-9) were re-calculated, so as to extract the major source profiles and to remove the contributions from the minor and trace profiles, specifically secondary ions and marine salt. Nine “cleaned” PMF factors, representing matured regional chemical source profiles were extracted. These include geological dust, cement plant dust, heavy oil combustion emissions, composite motor vehicle emissions, diesel vehicle emissions, vegetative burning, ferro-manganese industry, lead-zinc smelter, and copper-zinc smelter emissions. These modeled profiles can be applied in Chemical Mass Balance (CMB) receptor modeling and future source apportionment studies.

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