

**Particulate Matter (PM) Source Attribution in the Paso del
Norte Air Basin using Multivariate Analysis of Organic
Speciation Data**

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ABSTRACT

The Paso del Norte air basin, encompassing the Juarez-El Paso metroplex, is among the most polluted and complicated airsheds along the US-Mexico border. PM filter samples were collected at 11 different receptor sites in this region and 57 organic PM constituents were identified by Thermal Desorption (TD)-GC/MS. Based on the knowledge that sources unique to this region contribute to these samples, various local source samples, including cooking, trash burning, brick kiln, and bridge traffic emissions, were collected and analyzed using TD-GC/MS and compared with available literature data. By applying Principal Component Analysis (PCA) with Varimax as well as graphical factor rotation methods to the various receptor/source and data sets, a limited number of components were numerically extracted which highlight the chemical relationships between sources and receptors. The 11 PM receptor profiles are found to exhibit characteristic series of chemical compounds, and for the US sites these compound series are reasonably well explained by the available source literature data. Yet, some prominent compound series for the Mexican sites, viz. soot-like polynuclear aromatics and long chain aliphatics are less explained by published PM source profiles. Addition of the above mentioned local source profiles is shown to better explain the Mexican receptor patterns.

INTRODUCTION

The ability of combined gas chromatography/mass spectrometry (GC/MS) techniques to provide detailed information about the chemical composition and provenance, as well as potential health and environmental impacts, of complex environmental samples has been widely recognized for more than 40 years. Solvent extraction (SX)-GC/MS has been the standard method for GC/MS analysis of particulate matter (PM) samples. However, this method requires large quantities of ambient PM (typically on the order of 10-100 mg) and the laboratory operations involved tend to be slow and laborious. In addition, large quantities of solvents are consumed, thus having potential environmental as well as health and safety impacts.

In previous exploratory chemical analysis of the organic constituents in selected PM₁₀ receptor samples from the El Paso/Juarez area of the US/Mexico border, a combination of conventional solvent extraction (SX)-GC/MS procedures as well as a newly developed solvent-free thermal desorption (TD)-GC/MS method resulted in a good correlation ($R^2=0.821$) between the two methods. This suggests that for studies requiring fast results or for PM samples in the microgram rather than in milligram range the solvent-based GC/MS analysis of filter samples can be replaced by the simpler and faster solvent-free thermal-desorption (TD)-GC/MS method. Also, in previous studies, systematic comparisons between GC/MS data on temporally and spatially resolved PM₁₀ samples from the same airshed by means of multivariate statistical analysis methods suggest that the dominant PM₁₀ sources tend to be vehicular exhaust emissions, urban dust, biomass combustion, waste burning and plant debris. In this study, PM₁₀ samples from 11 receptor sites, 5 in Juarez and 6 in El Paso, and 4 local sources (cooking, brick kiln, trash burning, bridge traffic) were analyzed using TD-GC/MS.

The purpose of the study was to: (1) characterize the nature of PM₁₀ by determining the chemical compositions of receptor samples and local sources; (2) perform source attribution of PM₁₀ particles using sources from literature and combined literature/local sources; and (3) identify possible sources that are still missing, thus providing direction and guidance for more definitive, quantitative source apportionment studies.

EXPERIMENTAL METHODS

The PM₁₀ sampling system used for 2hr sample collection represents the combination of a standard PM₁₀ sampling tower such as used for dichotomous (dichot) samplers with a single, specially machined QF filter holder. Sample air was drawn through the filter by use of a small, portable, membrane-type air sampling pump with an attached pressure gauge. The air stream, at a flow rate of 16.7 L/min, was directed onto two stacked (primary and backup) 21-mm diameter QF filters, which were supported by a stainless steel screen. Eleven samples were collected on Jan. 15th 2001 at eleven sites—5 on Mexican side, 6 on US side, as shown in Figure 1.

Filter strips were cut to introduce and position inside a special glass reaction tube which is lined with a ferromagnetic foil characterized by the Curie-point temperature of 315 °C for desorption and placed into a Curie-point desorption reactor for desorption of volatile and semivolatile organic compounds. In Curie-point type desorption, a high frequency induction coil surrounds the glass tube and heats the foil by induction. The foil heats up till its Curie point is reached (this is the temperature at which the wire becomes paramagnetic, and its energy intake drops, thus holding the temperature of the foil at this point). Flash desorption of organic compounds from the ambient particles immobilized by the quartz fiber filter strips is achieved using a total heating time of 10 s under a continuous flow of He carrier. The continuous flow of He transfers the analytes from the reaction zone into a fused silica capillary column of a gas chromatograph, coupled to a mass spectrometer.

Subsequent to sample desorption, the compounds were introduced into a fused silica capillary column, and a temperature programmed separation of analytes coupled with simultaneous MS monitoring, was initialized. The GC analysis for the TD method was carried out on a Hewlett-Packard (HP) Model 5890 gas chromatograph using an HP-5MS column with 25 m long 0.20 mm I.D. fused silica capillary coated with a 0.33- μ m-thick film equipped with thermal desorption inlet. The oven was temperature programmed from 50 °C to 320 °C at a rate of 3~15 °C/min.

Compound identification and peak area integration were conducted using quadrupole type Mass Selective Detectors (MSD 5972 or MSD 5973 from Hewlett Packard) operated in the electron impact mode with electron energy of 70 eV. A group of target compounds were identified by an initial qualitative analysis of representative GC/MS runs from the data file. Selected ion chromatograms of indicative m/z ratios from these potential compounds of interest were used to obtain retention times and relative intensity of target compounds.

Data were reduced, interpreted, and evaluated with the technique of multivariate data analysis. The multivariate data analysis techniques used are primarily based on an exploratory PCA data

analysis approach with subsequent orthogonal rotation of the PCA components using the Varimax technique. PCA is a data analysis tool that is used to reduce the dimensionality of a large number of interrelated variables while retaining as much of the information (variance) as possible. PCA calculates a non-correlated set of variables ("factors" or "components") which are ordered so that the first few retain most of the variance present in the original variables. The first step in PCA is usually to create an autoscaled data matrix, by subtracting the variable mean and dividing by the standard deviation. A commercially available NCSS statistical software package (NCSS, Utah, U.S.) was used to perform PCA in this study.

RESULTS AND DISCUSSIONS

Factor analysis of TD-GC/MS profiles containing 57 organic compounds representing 11 different PM receptor sites (5 on the Mexican and 6 on the US side of the border) produced the following results.

The first few factors show strongly correlated behavior within chemical compound groups such as normal alkanes, fatty acids, polynuclear aromatics and fossil terpenoids. In many cases further differentiation between chemical subgroups, such as shorter and longer chain n-alkanes or fatty acids, as well as smaller and larger polynuclear aromatics were also found (Table 1).

Due to the fact that most chemical compound (sub) groups occur in PM emissions from multiple sources, some of which naturally correlated (e.g. traffic and road dust), few if any chemical component vectors in factor space are truly orthogonal, thereby interpretation of factors found by orthogonal rotation procedures such as Varimax rotation may be misleading and non-orthogonal graphical rotation methods was used to overcome this.

The combined loading and score plot of Factor 1 and Factor 4 (Figure 2 and Figure 3) revealed a general trend where PM samples from the Juarez (Mexican) sites tend to be dominated by polynuclear aromatics (large and small) as well as fatty acids (characteristic of meat cooking) and long chain alkanes, believed to represent the burning of plastic waste. Samples from El Paso (US) sites tend to have higher proportions of terpenoids and wood burning related oxygen compounds (methoxyphenols, alcohols, and ketones). The relative strength of combustion sources on the receptor sites can be obtained (Table 2).

Whereas most of the PM receptor profiles from US sites can be reasonably well attributed to published source profiles, the Mexican profiles were less clearly explained, indicating that additional local source profiles information, i.e. on brick kilns and trash burning, were needed.

To better explained the receptor data, especially Mexican receptor profiles, five published literature source profiles, namely cooking, tire wear and road dust, catalytic autos, diesel trucks, firewood (pine & oak) and cigarettes, which are believed to be important in this region were selected. Based on the natural correlation and similarities between tire wear and road dust, they were grouped as one with 20 percent of tire wear and 80 % of road dust. In addition, four local sources: cooking, brick kiln, bridge traffic, trash-burning samples were taken in this region and were analyzed using GC-MS. For cooking, both literature and local source were available, the

average of the two was used, yielding 8 source profiles in total. PCA was performed on this combined receptor/source data set. Factor 2 and Factor 4 (Figure 4 & Figure 5) explained 25 % of the total variance and showed three trends: automotive emissions, relatively strongly characterized by fossil terpenoids; biomass burning, related to alkanols and ketones, as well as benzaldehydes and amyris; and waste burning, related to large alkanes (C27-C 33).

It is clear from the score plot, after the addition of local sources, the brick kiln seems to be strong in Advanced Transformer site and Zenco related to trash burning.

The source profiles do not cover the space of the receptors, suggesting that gaps with regard to available source profiles exist. For example, Lindbergh, and Tillman are believed to be agriculture areas. These sources must be determined before a more quantitative source apportionment can be attempted.

CONCLUSIONS

Principal component Analysis (PCA) on eleven receptor data showed strong PM10 contributions from combustion sources. Most of the PM receptor profiles from U S sites can be relatively well attributed to published source profiles, while the Mexican profiles are less clearly explained.

The addition of published source profiles and specific local source profiles to the published source profiles resulted in improved correlations between Mexican PM receptor and source profiles. Source profiles, including agricultural sources, are needed before a more quantitative source apportionment can be attempted.

ACKNOWLEDGEMENTS

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Figure 1. El Paso/Juarez satellite map of the US/Mexico border showing the locations for collection of PM for 11 samples for TD GC/MS analysis.

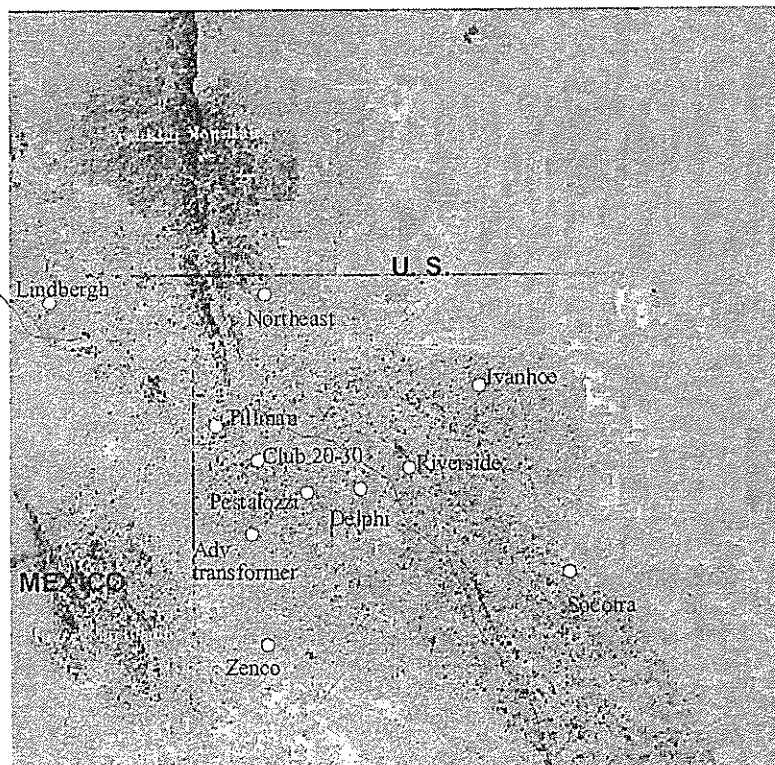


Figure 2. Plot of factor loadings of factor 1 vs factor 4 of 11 PM receptor samples

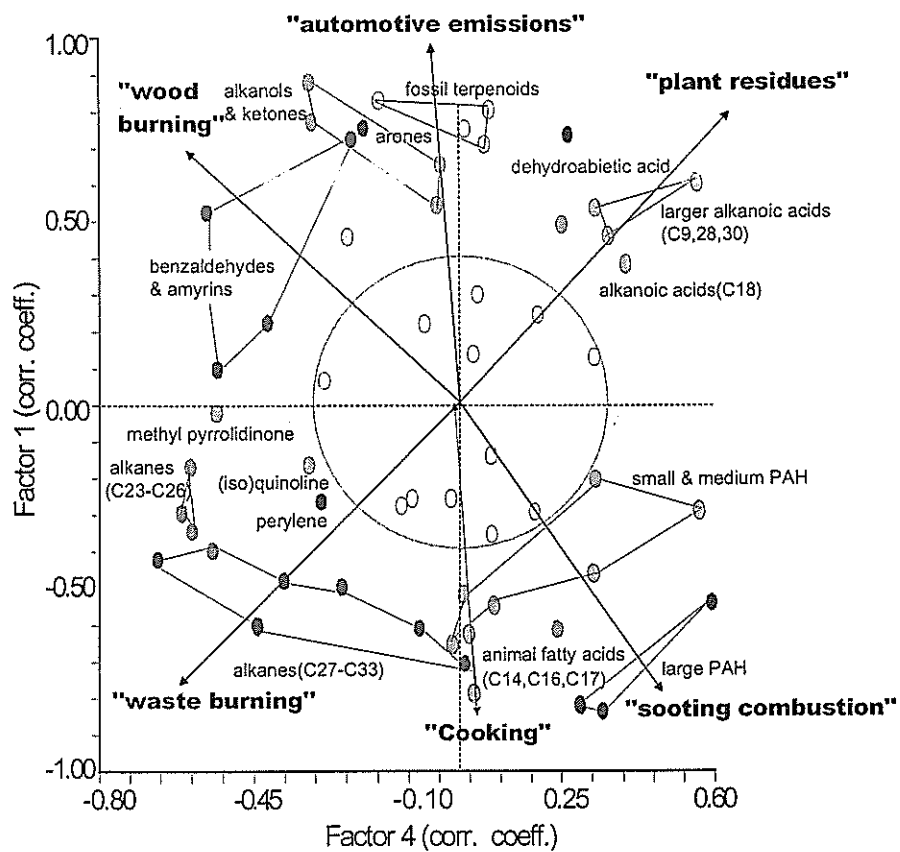


Figure 3. Plot of Factor scores of factor 1 vs factor 4 for 11 receptor PM 10 samples.

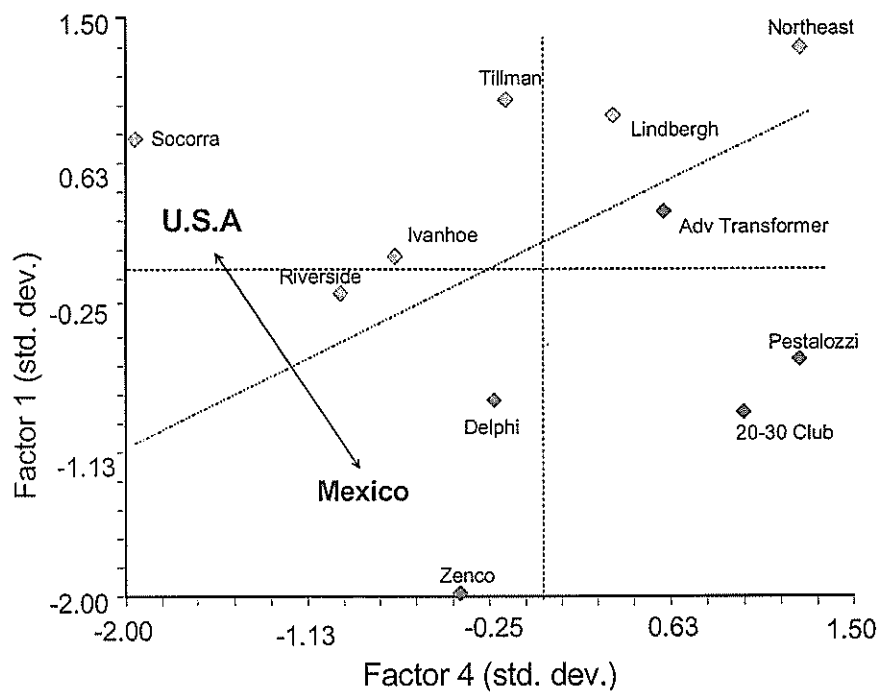


Figure 4. Loading plot of factor 2 vs factor 4 of 11 PM receptor samples and 8 sources

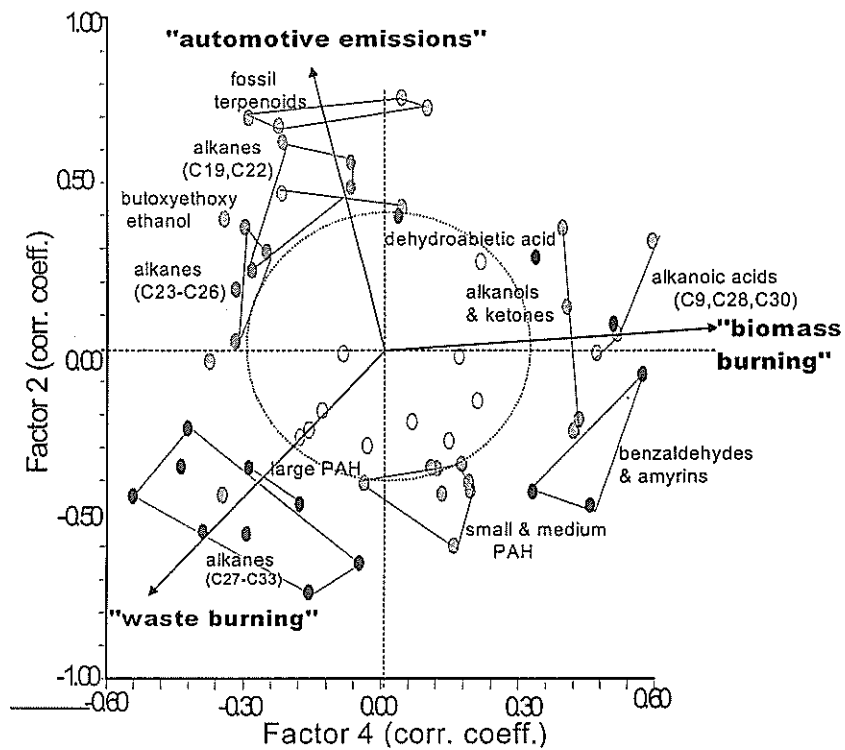


Figure 5. Plot of Factor scores of factor 2 vs factor 4 for 11 receptor PM 10 samples and 8 sources.

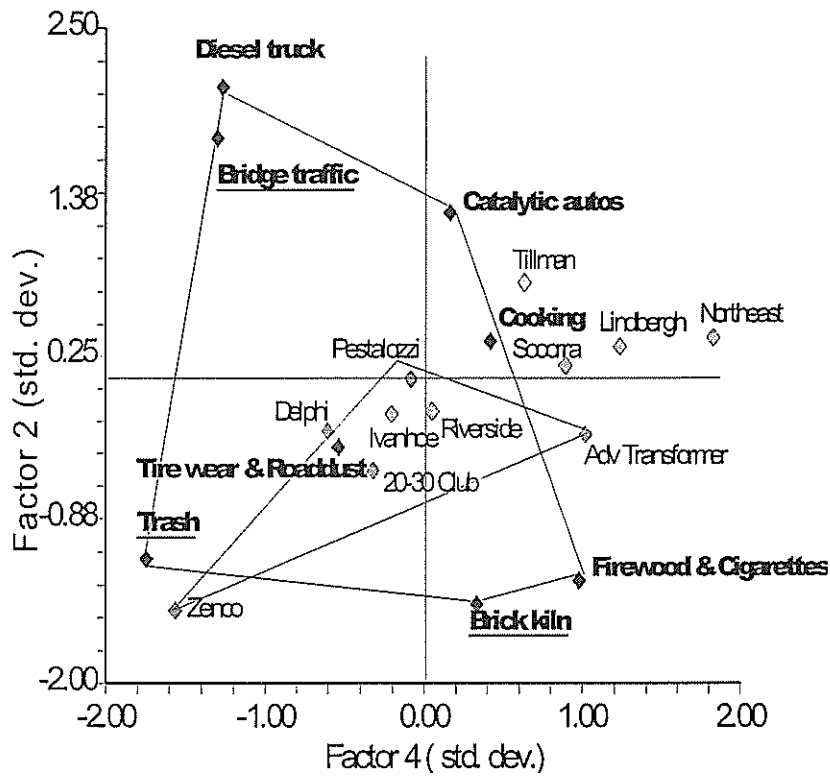


Table 1. Groups of organic compounds and factor loadings of 11 receptors and combined data set

groups	Compounds	11 receptor				11receptor8sources			
		Factor1	Factor2	Factor3	Factor4	Factor1	Factor2	Factor3	Factor4
1 alkanes (C19-22)	1 n-nonadecane (19)	-0.613	-0.663	0.1225	0.24	-0.353	0.234	-0.123	-0.283
	2 n-eicosane (20)	0.245	-0.464	-0.565	0.196	-0.273	0.6223	0.0423	-0.216
	3 n-heneicosane (21)	0.3	-0.472	-0.665	0.059	-0.426	0.5603	-0.208	-0.067
	4 n-docosane (22)	0.22	-0.034	-0.936	-0.064	-0.631	0.4854	-0.249	-0.067
2 alkanes (C23-26)	5 n-tricosane (23)	-0.255	0.316	-0.778	-0.092	-0.753	0.3652	-0.125	-0.298
	6 n-tetracosane (24)	-0.295	0.295	-0.427	-0.614	-0.801	0.1758	-0.307	-0.317
	7 n-pentacosane (25)	-0.169	0.605	-0.028	-0.595	-0.677	0.2887	-0.312	-0.25
	8 n-hexacosane (26)	-0.344	0.568	0.082	-0.589	-0.719	0.0218	-0.405	-0.319
3 alkanes (C27-33)	9 n-heptacosane (27)	-0.396	0.228	0.2692	-0.544	-0.417	-0.241	-0.434	-0.424
	10 n-octacosane (28)	-0.421	0.199	0.1602	-0.668	-0.403	-0.359	-0.456	-0.438
	11 n-nonacosane (29)	-0.598	0.131	0.2647	-0.443	-0.203	-0.562	-0.499	-0.294
	12 n-triacontane (30)	-0.609	0.524	0.427	-0.074	-0.285	-0.446	-0.254	-0.543
	13 n-hentriacontane (31)	-0.481	-0.026	0.0172	-0.382	-0.161	-0.65	-0.489	-0.048
	14 n-dotriacontane (32)	-0.497	-0.22	0.4801	-0.25	0.007	-0.554	-0.316	-0.39
	15 n-tritriacontane (33)	-0.707	-0.357	0.175	0.028	0.264	-0.739	-0.33	-0.158
4 alkanic acids (10,12,13,18)	17 n-decanoic acid(10)	0.129	-0.712	-0.427	0.325	-0.22	0.4243	0.1224	0.0462
	18 n-dodecanoic acid(12)	-0.255	-0.766	-0.379	-0.003	-0.073	-0.039	-0.463	-0.375
	19 n-tridecanoic acid(13)	0.065	-0.598	-0.248	-0.291	0.385	0.4674	0.1435	-0.218
	23 n-octadecanoic acid(18)	0.375	-0.039	0.6704	0.406	0.771	-0.024	-0.056	0.1702
5 alkanic acids (14,16,17)	20 n-tetradecanoic acid(14)	-0.276	-0.831	0.3142	-0.116	0.338	-0.189	-0.492	-0.13
	21 n-hexadecanoic acid(16)	-0.623	-0.532	0.3842	0.037	0.604	-0.445	-0.391	-0.346
	22 n-heptadecanoic acid(17)	-0.794	-0.374	0.3456	0.049	0.885	-0.27	-0.033	-0.178
6 alkanic acids (9, 28,30)	16 n-nonanoic acid(9)	0.606	0.214	0.2524	0.56	-0.156	0.3226	-0.099	0.595
	24 n-octacosanoic acid(28)	0.457	-0.212	0.6887	0.357	0.048	-0.014	-0.361	0.4713
	25 n-triacontanoic acid(30)	0.536	0.009	0.5053	0.328	-0.076	0.0428	-0.372	0.5159
7 alcohols & ketones	26 hexadecanol	0.879	0.279	-0.102	-0.323	-0.168	-0.249	-0.647	0.4204
	27 docosanol	0.543	0.616	-0.018	-0.035	-0.304	-0.215	-0.436	0.4326
	28 nonanal	0.656	0.012	0.2367	-0.026	0.123	0.1235	0.0368	0.4061
	29 tridecanal	0.771	-0.077	-0.357	-0.318	-0.385	0.3615	-0.396	0.397
8	30 dehydrobiotic acid	0.734	0.47	0.3196	0.267	0.552	-0.223	-0.052	0.067
9 benzaldehyde & amyrrin	32 3-methoxy-4-hydroxybenzaldehyde	0.725	-0.135	0.116	-0.227	0.033	-0.474	0.2673	0.4568
	33 trimethylbenzaldehyde	0.223	-0.392	0.4227	-0.419	-0.194	0.3966	-0.175	0.0382
	34 4-hydroxy-dimethoxybenzaldehyde	0.097	-0.56	0.2071	-0.533	0.207	-0.433	0.0209	0.3309
	35 S-amyrrin (olean-12-en-3-ol)	0.524	0.143	-0.15	-0.555	-0.285	-0.079	-0.462	0.5725
10 small & Medium PAH	36 phenanthrene	0.5	-0.034	-0.352	0.248	-0.333	-0.35	0.7305	0.1754
	37 1-methyl-7-isopropylphenanthrene	-0.459	0.041	-0.124	0.323	-0.602	-0.279	-0.359	0.1485
	38 fluoranthene	-0.139	-0.292	0.824	0.088	-0.333	-0.363	0.7353	0.1208
	39 pyrene	-0.292	0.067	0.797	0.188	-0.336	-0.36	0.7518	0.1084
	40 benz[a]anthracene	-0.516	0.518	-0.544	0.025	-0.683	-0.408	0.1429	-0.038
	41 chrysene/triphenylene	-0.655	0.547	-0.195	7E-04	-0.499	-0.599	-0.122	0.1584
	42 benzo[j]fluoranthene	-0.547	0.782	0.0261	0.096	-0.784	-0.44	0.0532	0.1335
	43 benzo[e]pyrene	-0.287	0.616	0.4046	0.563	-0.594	-0.431	0.4923	0.1938
44 benzo[a]pyrene	-0.203	0.884	0.0233	0.328	-0.615	-0.405	0.5416	0.191	
11 large PAH	45 perylene	-0.264	-0.225	0.3998	-0.298	-0.316	-0.249	0.3995	-0.159

	groups	Compounds	11 receptor				11receptorBsources			
			Factor1	Factor2	Factor3	Factor4	Factor1	Factor2	Factor3	Factor4
		46 indeno[1,2,3-cd]pyrene	0.838	0.013	-0.175	0.344	-0.455	-0.36	0.5815	-0.289
		47 indeno[1,2,3-cd]fluoranthene	0.921	0.347	0.0096	0.291	-0.581	-0.473	0.4493	-0.179
		48 benzo[ghi]perylene	-0.546	0.385	-0.119	0.59	-0.539	-0.295	0.7023	-0.031
12	arones	49 1H-phenalen-1-one	0.742	-0.389	-0.337	-0.212	-0.476	0.0735	-0.455	0.509
		50 9,10-anthracenedione	0.138	0.41	-0.8	0.048	-0.589	0.2597	-0.185	0.2179
13	terpenoids	51 (20S and R)-cholestanes	0.77	0.164	0.1623	0.103	-0.323	0.7267	-0.103	0.1023
		52 22,29,30-trisnorneohopane	0.71	0.624	0.1379	0.074	-0.156	0.7584	0.0362	0.0451
		53 17"(H), 21\$(H)-29-norhopane	0.752	-0.108	0.3775	0.03	-0.133	0.6705	0.3501	-0.224
		54 17"(H), 21\$(H)-hopane	0.831	0.273	-0.095	-0.165	-0.025	0.698	0.4554	-0.289
14	N&O containing	55 quinoline/isoquinoline	-0.163	-0.51	0.2048	-0.326	-0.326	-0.018	-0.387	-0.084
15		56 1-methyl-2-pyrrolidinone	-0.023	0.58	0.1746	-0.534	-0.596	-0.16	-0.196	0.2092
16		57 2-(2-butoxyethoxy)ethanol	-0.352	0.02	-0.397	0.09	-0.24	0.3886	0.2034	-0.343
17		31 benzoic acid	0.458	0.413	-0.077	-0.236	-0.373	0.2734	0.1109	0.3372

Table 2. Strongest PM 10 Contributions form combustion sources on Jan. 15th, 2001

		Organic PM 10 Sources				
		automotive	waste	cooking	Wood	Other Biomass
MX	Zenco	-----	+++	+++	-----	-----
	Adv Transformer	-----	-----	-----	-----	++
	Club 20/30	-----	-----	+++	-----	+
	Pestalozzi	-----	-----	+++	-----	++
	Delphi	-----	+	+	-----	-----
US	Lindbergh	++	-----	-----	-----	++
	Tillman	++	-----	-----	-----	-----
	Riverside	-----	++	-----	+	-----
	Socorro	+	++	-----	+++	-----
	Northeast	+++	-----	-----	-----	++
	Ivanhoe	-----	+	-----	+	-----