Pollutants Adsorbed on Airborne Urban PM

A Source Apportionment Approach for Vehicular Emissions

by Valter Maurino, Ezio Pelizzetti and Claudio Minero

A tentative vehicular source apportionment was undertaken in order to estimate the impact of different vehicular sources to the organic micropollutants present on the urban airborne particulate matter (PM). Samples of PM were collected in Turin last year near a heavy-traffic urban street. The organic extracts of collected PM were fractionated and analyzed by GC-MS. To assess the contributions to organics contained in the urban PM from different vehicular sources, the particulate matter contained in several samples of gas exhausts from three different vehicles was collected and analyzed. Most of the contribution to organic pollutants adsorbed on PM is due to high emitter gasoline cars.

Air quality management in urban ambient is a very difficult task [1]. Prominent emission sources are the vehicular traffic [2] and, during the cold season, domestic heating. Industrial point emission could also have high impact on local and regional scale. The increase in periods of dry weather and the increased vehicular traffic lead to severe photochemical smog episodes in summer and high levels of CO, NO_x, BTEX, PM_{10} and other traffic-related primary pollutants during winter. This last condition happened in the winter 2001-2002 in several major cities of the North Italy.

Among the quoted pollutants, PM, and especially the fine fractions PM_{10} and $PM_{2.5}$ can have very adverse effects on human health. PM_{10} and, in the Usa, $PM_{2.5}$ are considered very important indicators of urban air quality, and included in regulatory policies [3]. Usually PM is grouped in the three so-called modes: ultrafine, fine, and coarse [4]. Coarse particles (>2.5 μm) are mainly of crustal origin and of scarce toxicological interest. The ultrafine particles (<0.12 μm) are chemically formed or condensed from hot vapors (e.g. diesel exhaust) and coagulate into fine particles. Defined as having an aerodynamic diameter less than 2.5 μm, the ultrafine and fine particles are predominantly of anthropogenic origin (primary and secondary). They vehiculate many toxic and mutagenic organic compounds [5], and are deposited with high probability in the lower part of the respiratory system. Thus they have the largest toxicological impact. Several recent toxicological studies have consistently reported increased daily mortality associated with the exposure to fine particulate air pollution [6, 7]. Different vehicle categories and heating systems, also in relation to their maintenance, have very different impact on air quality either for the direct emission of particulate or for the particular organic pollutants that are emitted. Nowadays, zero emission vehicles (ZEV, mainly electrical cars) with good fuel distance and competitive costs are not yet available. Moreover, an imposed sudden change of vehicle characteristics will have a high societal impact.

Corrective actions with low societal impact and good improvements of air quality should be taken after a careful analysis of the various *vehicular* emission sources, and their influence on the whole urban air quality.

This work reports the methodological approaches that can be used, and a preliminary estimation of the impacts that *different vehicle category* have on the *organic fraction* of airborne particulate matter sampled nearby a heavy traffic road. The vehicular source apportionment was assessed through a chemical mass balance model.

Air quality models for source apportionment

Regulatory actions and policies to improve the air quality can be formulated when good estimates of the impact of source emissions are known. To achieve this task, reliable air quality models are required.

The source apportionment can be performed in two complementary ways. The traditional approach is the *dispersion modeling* [8, 9], in which a pollutant emission rate and meteorological information are input to a mathematical model that disperses (and may also chemically transform) the emitted pollutant,

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generating a *prediction* of the resulting pollutant concentration at a point in space and time. The inputs may be measured quantities, although they need not to be. In this case the modeling is a simulation of different scenarios, depending on source positions and emission rates. Dispersion models require as inputs meteorological data, land use and landscape patterns in order to obtain reliable results. Dispersion models can be local, modeling pollutant dispersion due to traffic in limited urban zones (street canyons), or regional, modeling 3D diffuse and/or point sources with complex eulerian or lagrangian approaches in order to solve the fluid dynamic equations, eventually with chemical processes. For a review see the web site of the Italian National Agency for Environmental Protection (Agenzia Nazionale di Protezione Ambientale, Anpa) [10].

The alternative approach is the *receptor modeling* [11-14], which is a mathematical procedure for identifying and quantifying the sources of ambient air contaminants at a *receptor* (ambient air, airborne particulate matter etc.) primarily based on the concentration measurements at that receptor. The concentration measurements can involve chemical or physical properties characteristic of particular source emissions.

Receptor modeling is diagnostic, whereas dispersion modeling is also prognostic. Moreover, receptor modeling is directly based on measurements and cannot be performed without them. It does not need meteorological and landscape data, and depending on the mathematical implementation, it does not require emission databases. While source apportionment embraces in principle both modeling approaches, in the common usage it is often taken as synonymous of receptor modeling.

The first article published on receptor modeling dates back to 1972 [15]. There Frielander described the first chemical mass balance receptor model. Whereas dispersion models have been applied mainly to gaseous pollutants, which are by far simpler to model through fluid dynamics and chemical reactivity than particulate matter, the receptor model was originally applied to apportion source contributions to atmospheric aerosol samples.

The receptor models may be classified as single-sample or multivariate. The first type of modeling analysis is performed independently on each available sample. The simplest example of this is the "tracer element or compound" method, in which a particular chemical species is known to be uniquely associated with a specific source. Under this approach the total ambient mass impact of the source may be estimated by dividing the measured ambient concentration of the compound by the compound's abundance in the source's emissions.

Table 1/1 - Compounds identified through GC-MS analysis in the organic extracts (diclorometHane) of PM from receptor and sources

#	*RT (min.)*	*Compound*	*MW*	*Isomer*
1	19.05	1,2,3-Trimethyl-1H-indene	158	
2	19.06	Acenaphthene	154	
3	19.18	4-methoxy-3-methyl-1(3H)-isobenzofuranone	178	
4	19.32	1,3-Dimethyl-2-butenyl-benzene	160	
5	19.39	3-Hydroxy-4-methoxy-benzaldehyde	152	
6	19.79	Dimethylnaphthalene	156	B
7	19.82	Dimethylquinoline	157	
8	20.34	Methyl hydroxybenzoate	152	
9	20.45	Diterbutylbenzoquinone	220	
10	20.53	Acenaphthylene	152	
11	20.78	Dimethoxy-dimethylbenzene	166	
12	20.83	Methyl-1-1'-biphenyl	168	A
13	20.87	Methyl-1-1'-biphenyl	168	B
14	21.02	Methyl-1-1'-biphenyl	168	C
15	21.08	1,1-Bis(1-dimethylethyl)-4-methyl-phenol	220	
16	21.17	1-Naphtaldehyde	156	
17	21.18	Diterbutylphenol	206	
18	21.23	1-Naphthol	144	
19	21.30	Hydroxybiphenyl	170	
20	21.37	Dibenzofuran	168	
21	21.39	Ethyl ethoxybenzoate	194	
22	21.40	1,2-bis-(phenyl)-ethane	182	
23	21.41	Fluorene	166	
24	21.62	p-Nitrophenol	139	
25	21.84	Trimethylnaphthalene	170	
26	22.35	Dimethyl-1-1'-biphenyl	182	
27	22.78	1-Phenyl-1-methyl-2-phenyl-etane	196	A
28	22.86	1-Methyl-3-[4-methyl-phenyl-methyl])benzene	196	
29	22.93	Hydroxybenzoic acid	138	
30	22.98	1-Phenyl-1-methyl-2-phenyl-etane	196	B
31	22.99	Benzophenone	182	
32	23.11	1-Methyl-3-[4-methyl-phenyl-methyl])benzene	196	A
33	23.46	1-Methyl-3-[4-methyl-phenyl-methyl])benzene	196	B
34	23.65	Acenaphthenone	168	
35	23.74	1-Methyl-3-[4-methyl-phenyl-methyl])benzene	196	C
36	23.92	1-Methyl-3-[4-methyl-phenyl-methyl])benzene	196	D
37	23.54	Diisopropylnaphthalene	212	A
38	23.65	Diisopropylnaphthalene	212	B
39	23.75	Diisopropylnaphthalene	212	C
40	23.93	Carboxyaldehyde-1-1'-biphenyl	182	
41	24.10	Methyl-fluorene	180	
42	24.09	1-Methyl-3-[4-methyl-phenyl-methyl])benzene	196	E
43	24.01	1,2,3,4-Tetraidro-9,10-dimethylanthracene	210	
44	24.18	Diisopropylnaphthalene	212	D
45	24.23	Isopropyl-dimethylazulene	198	
46	24.29	Benzo[b]nafto[2,3-d]tiophene	264	
47	24.36	Diisopropylnaphthalene	212	E
48	24.43	Benz[a]azulene	178	
49	24.47	Butyltetrahydroanthracene	238	
50	24.50	9H-Fluorenone	180	
51	24.52	1-Methyl-3-[4-methyl-phenyl-methyl]benzene	196	F
52	24.66	1-Methyl-3-[4-methyl-phenyl-methyl]benzene	196	G
53	24.76	3,5-Di-butyl-4-hydroxybenzaldehyde	234	
54	24.82	Dibenzothiophene	184	
55	24.82	Tetramethylnaphthalene	184	
56	24.89	Ethylnitronaphthalene	201	
57	25.01	Tetramethyl-1-1'-biphenyl	210	
58	25.18	Phenanthrene	178	
59	25.30	Anthracene	178	
60	25.36	Methyl-benzofluorenone	196	
61	25.63	Acridine	179	
62	25.70	9,9-Dimethyl-9H-fluorene	194	

Table 1/2 - Compounds identified through GC-MS analysis in the organic extracts (dicloromethane) of PM from receptor and sources

#	RT (min.)	Compound	MW	Isomer
63	25.72	Anthrone	194	
64	25.92	Cyclopenta [g]-2-benzopyran	258	A
65	26.02	Cyclopenta [g]-2-benzopyran	258	B
66	26.51	6,7-Dihydrocrysene	230	A
67	26.56	9-Hydroxymethyl-9H-fluorene	196	
68	26.79	Phenalen-1-one	180	
69	27.00	Dihydrocrysene	230	B
70	27.11	Tetramethylacenaphthylene	208	
71	27.36	Dimethoxyphenylacetophenone	256	
72	27.37	Dimethylnaphthothiophene	212	
73	27.42	3-Methyl-2,2-Diphenylaziridine	209	
74	27.58	Anthraquinone	208	
75	27.86	1,1,3,3-Tetramethyl-butyl-phenol	206	
76	27.55	Phenathrenol	194	A
77	28.01	Thiophenone	100	
78	28.18	Phenathrenol	194	B
79	28.27	Phenathrenol	194	C
80	28.29	1-[4-(2-Phenyletenil)phenyl]-ethanone	222	
81	28.32	Dimethylphenanthrene	206	
82	28.71	Cyclopenta(def)phenanthrenone	204	
83	28.80	1-1'-Biphenyl-1-propen-2-thiol	226	
84	28.86	bis(1-Methylethyl)-biphenyl	238	
85	28.86	Methylcrysene	242	A
86	28.71	Fluoranthene	202	
87	28.92	2,3-Dihydro-1H-cyclopentaphenanthrene	218	
88	29.15	Benzo[a]acenaphthylene	202	
89	29.30	Benzo[b]acenaphthylene	202	
90	29.06	Methylcrysene	242	B
91	29.50	Pyrene	202	
92	29.52	Anthraldehyde	206	
93	29.56	Hydroxypyrene	218	A
94	29.71	Trimethylphenanthrene	220	A
95	29.89	1,1-Diphenylcyclohexane	236	
96	29.90	Hydroxypyrene	218	B
97	30.36	Diphenylcyclohexane	236	
98	30.87	Trimethylphenanthrene	220	B
99	30.15	Methylpyrene or Methylfluoranthene	216	A
100	30.45	Methylpyrene or Methylfluoranthene	216	B
101	30.68	Methylpyrene or Methylfluoranthene	216	C
102	30.96	Methylpyrene or Methylfluoranthene	216	D
103	31.05	Methylpyrene or Methylfluoranthene	216	E
104	31.21	2,3,5,6,-Tetrahydro-3,3,4,5,5, 8-esamethyl-indecen-1,7-dione	270	
105	31.84	Tetramethylphenanthrene	216	A
106	31.89	Benzanthrone	230	
107	32.24	Tetramethylphenanthrene	234	B
108	32.39	Cyclopenta[c,d]pyrene	226	
109	32.31	Benzo[a]dibenzothiophene	234	
110	32.55	Tetramethylphenanthrene	234	C
111	33.00	Benz[a]antracene	228	
112	33.02	Dimethylpyrene	230	
113	33.05	Cyclopentapyrene or cyclopentafluoranthene	226	
114	34.30	Methyl-benz[a]anthracene	242	
115	35.44	Butene-2,3-bis(1-naphthyl)	308	
116	35.54	2,4-Bis(1-methyl-1-phenylethyl)phenol	330	
117	36.08	Benzo[a]pyrene	252	
118	36.34	Benzopyrene or benzofluoranthene	252	A
119	36.76	Benzopyrene or benzofluoranthene	252	B
120	36.89	Benzopyrene or benzofluoranthene	252	C
121	37.11	Benzopyrene or benzofluoranthene	252	D
122	39.81	Benzoperilene isomer	276	
123	40.66	Benzo[ghi]perylene	276	
124	46.40	Coronene	300	

Obviously, it is very difficult to find unique tracers that have statistical stable abundance in the source. Even if the compound is not uniquely associated with a source of interest, but its abundance in that source is known, then the method can be used to provide an upper limit for the source's impact. For example, the ^{14}C content of an ambient sample can be used to estimate the fraction of carbon in the sample that is biogenic.

The best-known example of single-sample receptor modeling is the *chemical mass balance* (CMB). CMB model removes the need for unique tracers of sources, but still requires that the abundance of the chemical components of each source (source profiles) are known. The basic idea of CMB modeling is that composition patterns of emissions from various classes of sources are different enough that one can identify their contributions by measuring concentration of many species in samples collected at a receptor site. The observed concentration profile of an atmospheric PM sample would be a linear combination of the source emission profiles, each weighed by a source strength term [11, 13]. A software based on a CMB model together with emission inventory databases is currently used and distributed by Us Epa [16] for identifying and apportioning the emission sources of airborne PM.

Multivariate receptor models [17] require the input of data from multiple samples. They extract the source apportionment information from all of the sample data simultaneously. These models are able to estimate not only the source contributions, but the source compositions (profiles) as well, and, in principle, source emission profiles are no longer required. The simplest example of a multivariate method is "tracer element/multiple linear regression". This method requires tracers that are uniquely associated with the sources of interest, but it does not require their abundances to be known. Multivariate receptor models include (a) absolute principal component analysis, (b) specific rotation factor analysis, (c) target transformation factor analysis, (d) three-mode factor analysis, (e) source profiles by unique ratios (SPUR), (f) receptor model applied to patterns in space (RMAPS), (g) UNMIX [18], and (h) positive matrix factorization (PMF) [18, 19]. Most of these models are based on factor analysis, or the closely related principal component analysis. The basic assumption of these methods is the absence of spatial and temporal correlation between emissions from different sources. Emissions from correlated sources (e.g. different vehicular sources, which are highly correlated in time) are unresolved from each other. In comparison with CMB modeling, far less is understood about the behavior and validity of these multivariate models. Criticisms have been directed at specific models, in addition to the general criticism to the factor analysis-based models that do not make use of additional constraints to limit the solution space.

Weaknesses of receptor models are the limited capability to treat the formation of secondary aerosols, which is far more important for the finer fraction of PM, and the chemical reactivity of the aerosol components. In the CMB models that require source profiles, the secondary PM is introduced as a virtual emission source [10-12].

Early applications of receptor modeling, especially CMB, used elemental PM composition in order to apportion emission sources. Actual research topics, funded by many regulatory agencies worldwide, involve the study of the organic compounds of size-fractionated PM in order to establish more detailed source-receptor relationship and discover new source/processes [8, 17, 20-27].

PM sampling extraction, fractionation, and analysis

Airborne PM was sampled at a distance of 10 meters from a heavy-traffic urban road in Turin (C.so Massimo d'Azeglio, in November-December 2001). An air sampling pump mod. Charlie (TCR Tecora, Milan, Italy) was equipped with a glass-fiber filter (Gelman Science, Ann Arbor, Michigan USA, 37-mm diameter, pretreated at 500 °C) and operated at a sampling flux of 10 Liter/min. The filter inlet was placed at a height of 1 meter above ground. 27 samples integrated over 24 hours interval (9 a.m.-9 a.m.) have been collected.

The gas exhausts from the three vehicles, selected as representatives of the circulating fleet (HS, LS, DE, see below), were sampled with the same apparatus in order to characterize the source emission profile. The filter inlet was placed 5 cm inside the silencer. Sampling was carried out driving the vehicle for 15 minutes in an urban ring comprehensive of the point of air sampling.

Eleven samples of diesel exhaust have been collected due to the generally assumed relationship between PM pollution and the emission of diesel powdered vehicles; 5 and 3 samples have been collected for HS and LS gasoline vehicles, respectively. The 46 samples were extracted with dichloromethane (Suprasolv, Merck) in a microwave extraction apparatus (Sohxwave, Prolabo, France). After solvent evaporation, the extracts were fractionated on a silica gel column (Kieselgel 60, Merck, Darmstadt, Germany, methanol washed and activated overnight at 120 °C) to simplify the subsequent gas-chromatographic analysis. Five fractions from each sample were obtained, eluting the silica gel column with: A - pentane 100% (Suprasolv, Merck); B - pentane 70% and dichloromethane 30%; C - dichloromethane 100%; D - dichloromethane 90% and methanol 10% (Suprasolv, Merck); E - methanol 100%. The first fraction contains apolar compounds with scarce toxicological effects (mainly alkanes), so it was discarded.

Fractions B, C, D and E, for a total of 184 fractions, after solvent evaporation under gentle N_2 stream, were redissolved in 1.0 ml of a solution of Chrysene D-12 (internal standard) in dichlorometane at 20 µg/L. They have been analyzed by a GC-MS apparatus (a TRACE GC 2000 gas-chromatograph coupled with a GCQ ion trap mass spectrometer, Thermo-Finnigan, Germany) equipped with a Programmable Temperature Vaporizer (PTV) inlet and a DB5-MS capillary column (30 m length, 0.25 mm I.D., 0.25 µm film thickness, J&W Scientific, Koln, Germany). Instrumental conditions were: programmed temperature injection of 50 µL sample with solvent evaporation phase (initial inlet temperature at 35 °C for 3 minutes with split valve open, then to 300 °C at 100 °C/sec. with split valve closed); carrier gas He at 1 ml/min. constant flow; initial column temperature 50 °C for 6 minutes, then to 300 °C at 10 °C/min.; the ion trap mass spectrometer was operated in scan mode from 29 to 400 amu, with the transfer line held

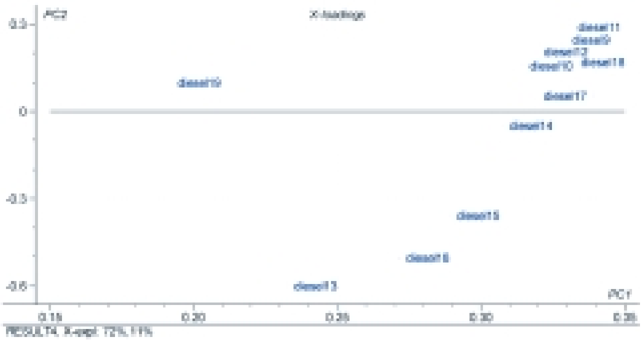

Figure 1 - PCA analysis on diesel samples, showing that some outliers are present

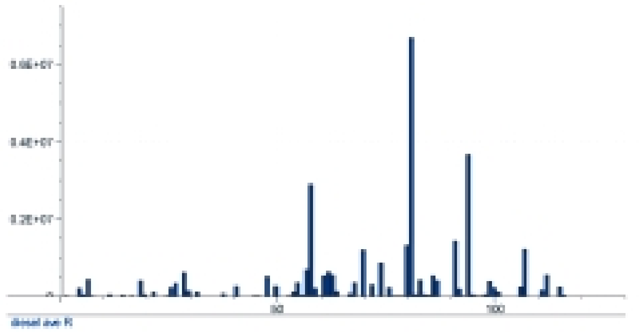

Figure 2 - Source emission profile for the diesel powered vehicle. Numbers in the abscissa refer to different compounds (see Table 1). Compounds are ordered following increasing retention times in the GC-MS analysis (roughly decreasing volatility). Relative concentration values are given in pg/m³ of gas exhaust assuming the response factor of the internal standard (Chrysene-D12)

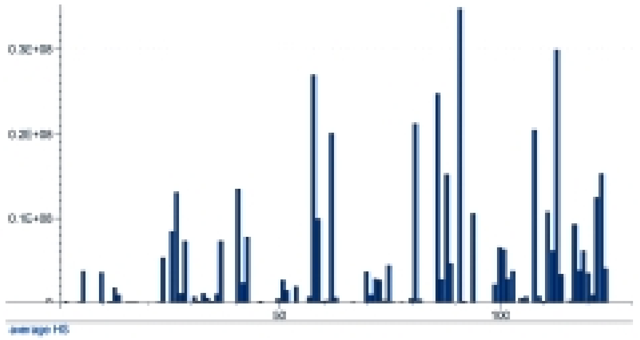

Figure 3 - Source emission profile for the HS gasoline powered vehicle

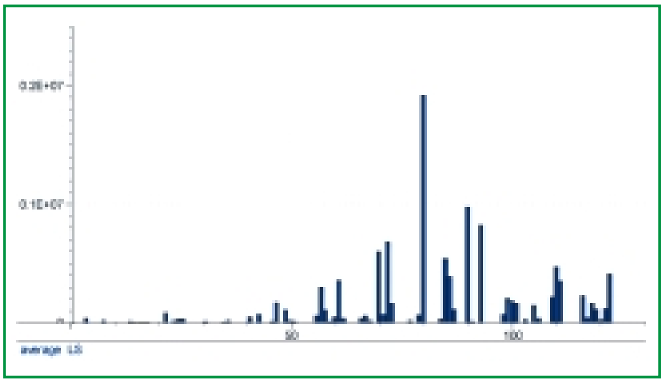

Figure 4 - Source emission profile for the LS gasoline powered vehicle

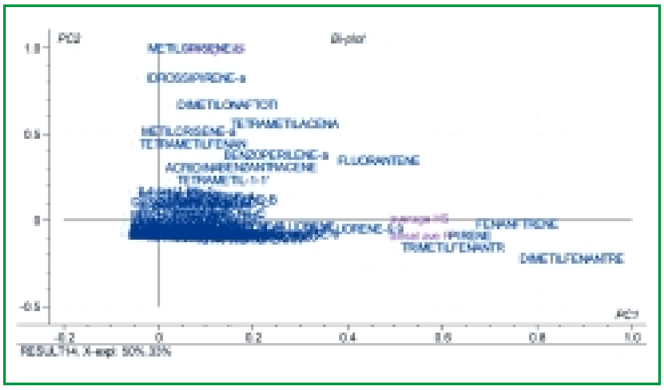

Figure 5 - Biplot of sample loadings (pink) and scores (blue) from the principal component analysis among the averaged emission profiles of the vehicular sources. See the text for details

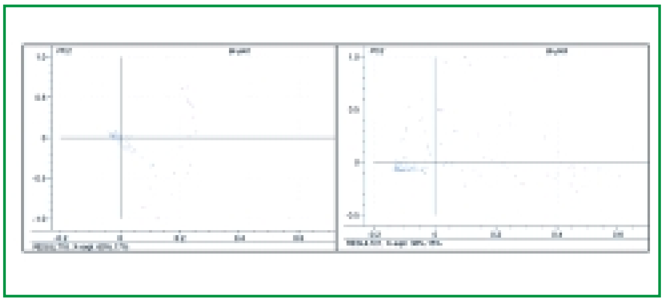

Figure 6 - Biplots of sample loadings (pink) and scores (blue) from the principal component analysis among the receptor samples. See the text for details

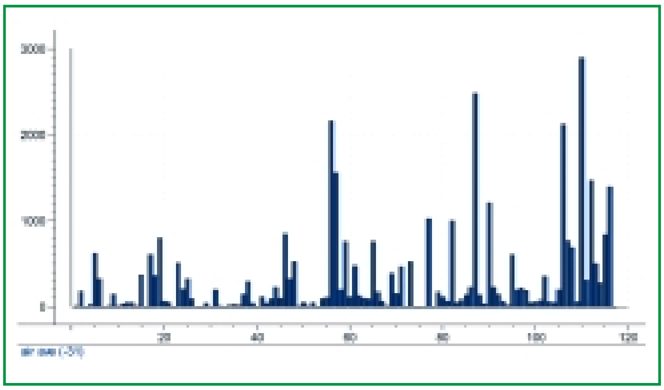

Figure 7 - Receptor profile concerning the extractable organic fraction of the airborne particulate matter

at 280 °C and the ion source at 200 °C. Compounds identified with the help of Nist 98 spectral library were quantified integrating the peak of the ion currents characteristic of the given compound assuming response factors equal to that of the internal standard. Concentrations reported are thus in pg m^{-3} equivalent to the internal standard. Analytical data are referred to the total volume of air or exhaust sampled. Table 1 reports all the organic compounds identified on PM from the considered vehicular sources and the receptor. The reported quantification obviously results in incorrect concentration values for the identified compounds in both the air and exhaust samples. A proper quantification is possible with use of response factors for authentic standards, but it is unnecessary to the following analysis, since analytical data concerning sources and receptors are obtained with the same procedure, assuring internal consistency of the entire data set.

Chemometric analyses

Using the software package Unscrambler (Camo Asa, Oslo Norway) did elaboration of data with chemometric methods (Principal Component Analysis, PCA, and Multiple Linear Regression, MLR). This software computes PCA with a Nipals algorithm and the MLR with a singular value decomposition algorithm.

Source characterization

Accurate chemical mass balance estimation of source impacts require accurate emission profiles of the relevant emission sources. As the Italian vehicular fleet is concerned (passenger cars, 1997 data in [28], page 12), the percentage of non catalyzed, catalyzed, diesel and GPL vehicles are 59.5, 26, 10.5 and 4%, over a total number of 31 millions vehicles. Commercial vehicles (van, buses, and trucks) are mainly diesel powered and amount to 3.3 millions. Motorcycles are also of concern (7.8 millions). However, due to the sampling season (winter), they were not considered.

To date no emission data concerning the organic fraction of PM from different vehicular sources are available in Italian emission inventories [28, 29]. Average mass emission factors for PM are reported only for diesel vehicles (average value of 0.4-1.2 g/kg of fuel burned), with no indication on the organic and elemental carbon contents ([28], page 89). It is generally recognized that diesel powered vehicles emits a PM mass 20-30 times greater than that emitted from gasoline vehicles [30]. However, diesel PM contains a greater quantity of elemental carbon with respect to gasoline vehicles. Organic carbon associated to diesel PM is composed mainly of 2-4 rings PAH, whereas gasoline vehicles emit greater quantities of 5-6 rings PAH (benzopyrenes, benzo[ghi]perylene, indeno[cd]pyrene, coronene). However, emission factors for non-methane organic compounds are larger for gasoline vehicles, particularly when pre-1992 vehicles are considered [28].

The above considerations show that the choice of representative vehicular sources is not so straightforward. Moreover, the percentages of gasoline vehicles, which are catalyst equipped, should be significantly increased since 1997. In this preliminary study three vehicular sources were considered suitable to study the contribution of organic pollutants to PM, to avoid excessive number of measurements. The three source are a low maintenance high emitter gasoline car, complying ECE 15/04 norm (pre 1984, high smoker, HS, representative of low maintenance and non catalyzed vehicles),

Table 2 - MLR analysis summary of the source and receptor model calculation according to Eq. 1

Source	b_i	*p*	*Averaged values (M)*	b_i *normalized*	$b_i \times M$ *normalized*
b_o	134.2	0.000	-		43.0%
Gasoline HS	4.97×10^{-5}	0.000	3.20×10^{6}	14.6%	49.6%
Gasoline LS	1.46×10^{-4}	0.48	3.94×10^{4}	58.6%	1.7%
Diesel	4.11×10^{-5}	0.44	2.53×10^{5}	25.8%	5.7%

and two normal emitters, namely a diesel engine van (DE, catalyst equipped, complying 94/12/ECC norm) and a gasoline car (complying 94/12/EEC, low smoker, LS). The DE emitter is taken as representative of both light duty and heavy duty diesel vehicles (scarce in the urban traffic).

The raw data from 11 diesel samples, 5 HS gasoline and 3 LS gasoline sample have been preprocessed by PCA to detect eventual samples and variables (chemical compounds) outliers. An example of the procedure is shown in Figure 1, where samples diesel 19, 13, 16, 15 are outliers. Including these samples the explained variance is 72% and 11% by the first two PCs, while without them the explained variance is 88% and 5%, respectively. Thus the experimental set was reduced to 7 diesel samples. Since all the 7 samples are statistically significant, their values have been averaged. The emission profile of DE emitter is reported in Figure 2.

The same data preprocessing was carried out on gasoline samples. The 5 HS samples are all statistically homogeneous and significant (explained variance 85% and 8% by PC1 and PC2, respectively). The same holds for the 3 LS samples (explained variance 84% and 12% by PC1 and PC2, respectively). Since all the samples are statistically significant, their values have been averaged. The emission profiles of HS and LS emitters are reported in Figure 3 and 4. It is worth of note that: i) the gasoline HS emitter shows concentration levels of particle-phase organic compounds 10-40 times and 5 times the levels found on PM from gasoline LS and diesel emitters, respectively; ii) emission profiles from gasoline LS and diesel vehicles are quite different, the first being characterized by 5-6 ring PAHs, methylchrysenes and hydroxypyrenes, whereas the second contains almost no 5-6 ring PAHs and contains phenanthrene, methylated phenantrenes and pyrene according to [29]; iii) the emission profile of the gasoline HS seems to be a mix of the preceding two. These emission profiles are also important in the evaluation of the toxicological impacts of these PM sources: some five ring PAH (e.g. benzo[a]pyrene) show high indirect mutagenic activities and are recognized as human carcinogens [3]. The above considerations are confirmed by a PCA analysis on the three emission profiles. The results (score and loading plots) are reported in Figure 5. As expected, on the two first PCs the gasoline LS and the diesel emitters show poor correlation. The DE and HS emitters show correlation. The score plot of the compositional variable substantiate the observations on the emission profiles, confirming that compounds noted as tracer of diesel (high scores on PC1) are different from gasoline LS (high scores on PC2).The PCA analysis confirms, by a statistical argument, the existence of significant differences on the two source profiles, assuring the possibility to differentiate their contributions on the receptor. Moreover, the number of compositional variables could be reduced, because the discriminating variables are those having high scores on one of the two PCs.

This further reduction was not carried out.

Receptor characterization and estimation of source impacts

The receptor position, near an heavy traffic urban road, together with the typical winter microclimate assures that prominent impacts on the sampled PM come from vehicular traffic. Contribution from other sources, either traffic related or not (industrial, domestic heating, secondary PM, natural emissions), could not be excluded.

The raw data from 27 air samples have been preprocessed by PCA to detect eventual samples and variables (chemical compounds) outliers. The raw processing is reported in Figure 6 left. The samples except sample air-31 are all significant, but some compounds are outliers, namely benzo[b]nafto[2,3-d]tiophene, dimethoxyphenylacetophenone, benz[a]azulene, 1-[4-(2-phenyletenyl)phenyl]-ethanone, two isomers of cyclopentapyrene (MW 226), 2,3-bis(1-naphthyl)butene, butyltetrahydroanthracene. Thus the experimental set was reduced to 116 variables. Since from Figure 6 right all the samples and variables are statistically significant, their values have been averaged. The receptor profile (air) is reported in Figure 7. Gas phase concentrations of the particle-phase organic compounds identified are roughly 500-15,000 times lower than the concentration levels found in the source gas exhausts. If the compounds on the receptor are totally derived from the selected sources, this range of concentration ratios gives an estimate of the dilution factor of the source gas exhaust at the receptor.

At a first glance the receptor profile slightly differs from the source profiles in the distribution of high molecular weight compounds (5 ring PAHs) and in the first 20 compounds (high volatility). As the high molecular weight compounds are concerned, this can be a sampling artifact, due to the longer sampling period for the receptor samples (24 hours) with respect to the emitter samples (15 minutes). Alternatively, the high molecular weight compounds are obviously more efficiently adsorbed on PM and the lighter compounds are best dispersed in the vapor phase and concurrently can be transported from other locations. The source profile that better correspond to the high MW profile is that of the HS emitter. This implies that toxicity of PM is not directly related to its major emission sources (DE), but to compounds that are emitted by high smoker's vehicles.

This analysis is confirmed by MLR analysis of sources and receptor averaged data. The relationship between the receptor variable values (vector of concentrations in air Y) and the vectors of variable values (X_i) associated to the sources i is:

$$Y = b_o + \Sigma_i b_i X_i \qquad (1)$$

where b_o is the part of the receptor variables not modeled by X_i. b_o is a contribution of other sources, either point sources (other component of the vehicular fleet distribution), or area and volume sources like those that led to secondary pollutants and aerosols. MLR analysis according to Eq. 1 leads to the values of parameter reported in Table 2.

The p-value measures the probability that a parameter estimated from experimental data should be as large as it is, if the real (theoretical, non-observable) value of that parameter were actually zero. Thus, p-value is used to assess the significance of observed effects or variations. The usual limit used in the interpretation of a p-value is 0.05 (or 5%). If p-value <0.05, the observed effect is not due to random variations.

Table 2 shows that only the HS emitter and the unknown sources are statistically significant. Surprisingly the HS contribution to the air pollution is more significant that the diesel emission. Anyway, observing that the a-dimensional b_i values are the volume fractions of the exhaust gases in the urban air, the inverse of their sum gives the dilution factor (DF).

Such a calculation led to DF = 3,850. This means that along an urban road, actually at the sampling point, one breaths the equivalent PM present in 1 liter of gas exhaust diluted to roughly 4 m^3. The ratio of b_i to their sum is equivalent to the fraction of volume for emission of the different sources. Although only for the HS source the data are statistically significant, the values reported in Table 2 are grossly consistent with the vehicular fleet distribution. In fact diesel vehicles account for 12-15% and LS are the majority of the circulating fleet [29].

The average concentration values for each sources multiplied by the corresponding volume fractions gives the average mass of each pollutant in the urban air attributable to a specific source i. The normalization over the total mass are reported in the last column of Table 2. About 50% of the organic compounds adsorbed on PM are due to HS vehicles. This value has high statistical significance.

Although values for diesel and LS sources are not statistically significant, the values are consistent with the previous observations. Although the percentages of DE cars in the vehicular fleet is 15% and they mostly contributed to the total PM load of urban air, their contribution to the amount of organic compounds adsorbed on PM is only about 6%.

Unfortunately, the other half of mass contribution is due to unknown sources. This can be due to limited number of emitter chosen and to secondary pollutant formation, on which further studies are under development worldwide [21-27].

Although limited in their statistical significance, these results show: i) the approach outlined in this paper could be conveniently used to model and apportion vehicular source impacts on urban air quality; ii) further research work is needed to model, classify and identify other relevant pollution sources, including domestic heating and industrial sources; iii) the results of such studies could be beneficial a) to regulatory policies for pollution control and abatement, and b) to properly tune the actions for limiting severe case of urban air pollution, as air quality indicators, traffic limitation to selected classes of cars, more efficient control on emissions [32], and increased vehicles fleet turnover.

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[32] Such controls are known in Italy as "bollino blu".

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