7.02   ASSESSING THE IMPACT OF PARTICULATE MATTER SOURCES IN THE MILAN URBAN AREA

Stefano Mossetti[1], Silvana P. Angius[1], Elisabetta Angelino[1]
[1]Regional Environmental Protection Agency of Lombardy (ARPA Lombardia), Milan, Italy

INTRODUCTION
High concentrations of fine particulate matter currently represent the main air quality problem in Lombardy, and in order to develop effective control strategies it is necessary to estimate the contributions of different sources to the ambient air quality. The application of receptor models for source apportionment can provide useful insight into this problem.
The US-EPA CMB7 receptor model (US-EPA, 1989) was applied to a set of data collected in the city of Milano for the PUMI (Particolato Urbano MIlanese) project (ARPA, 2002), with the goal of estimating the relative impact of different local emission sources on particulate concentrations, of quantifying the contribution of sources not included in emission inventories, such as resuspension due to vehicular traffic, and of investigating the dependence of source contributions on meteorological conditions, such as rain and wind.
Since the chemical mass balance method also requires source profiles to be known, a traffic profile was estimated, starting from local tunnel data, which can be considered to include all traffic contributions, such as exhaust emissions, brake and tire wear, and resuspension.

THE CHEMICAL MASS BALANCE APPROACH FOR SOURCE APPORTIONMENT
Receptor models use ambient concentrations, and sometimes source chemical fingerprints, to apportion sources of particulate matter to ambient air. The approach is based on the assumption that mass is conserved and that the measured mass concentration is the sum of separate contributions from any number of independent sources. The chemical mass balance method, as applied in the US-EPA CMB (Chemical Mass Balance) model, uses an effective variance-weighted least-square solution to a set of linear equations that express the receptor concentration of a chemical species as the sum of the products of source contributions and source compositions. A large number of species must therefore be measured in the ambient samples. Key to successful application of the CMB model is that all important sources be identified, that accurate source profiles be known, and reasonable uncertainties be estimated for both ambient concentrations and source fingerprints. The best results are therefore obtained when profiles representative of the actual sources in the area are used.
Outputs of the model include an estimate of source contributions with associated uncertainties, in addition to a number of statistical parameters to help in the evaluation of the results.
While CMB7 assumes that no changes occur in aerosol composition between source and receptor, secondary aerosols can contribute significantly to ambient concentrations, especially of fine particles and under some meteorological conditions. For such cases, a technique has been suggested (Watson et al.,1994) where a secondary particulate 'source' can be introduced to apportion that part of ambient particulate that is not accounted for by the primary sources included in the calculations. The technique can give at least an upper estimate of the contribution of secondary aerosol.
The results of the application of a receptor model represent an important piece of evidence to help build the cause-effect link between source emissions and receptor concentrations that is essential for a better understanding of the causes of air pollution. They can also help

modellers estimate the accuracy of emission inventories and quantify sources not considered in inventories.

DATA

CMB7 was applied to ambient PM10 concentrations obtained during a campaign performed in Milan during the PUMI project. The samples were taken in via Messina, an urban site not directly affected by local sources, using a Tecora PM10 sampler with a flow rate of 16,67 l/min.

The available data set includes measurements of daily average PM_{10} concentrations, element concentrations (Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Pb), measured with XRF and atomic absorption methods, and concentrations of nitrates (NO_3^-), sulphates (SO_4^{2-}), and ammonium ions (NH_4^+).

In addition, local tunnel data, acquired during the same project, were used to estimate a traffic profile. The tunnel, joining Viale Brianza and Viale Lunigiana, next to the Central railway station, is about 200 m long, with two traffic lanes in each direction, and has no forced ventilation system. The traffic in the tunnel is typically heavy, and composed of passenger cars, light and heavy-duty vehicles. The traffic profile estimated from the tunnel measurements can therefore be assumed to be inclusive of all traffic contributions typical of the area.

APPLICATION OF THE CMB MODEL

In order to identify the main particulate sources contributing to ambient PM10 concentrations, the correlations between the measured chemical elements were analyses, in addition to local emissions inventories. Previous studies (Marcazzan et al., 2001) were able to identify correlations among groups of elements originating from a common source. Our own analysis mostly confirmed the results, indicating that soil, mainly characterised by the Al, Si, Ca group, vehicular traffic, with Fe, Cu, Br, Pb as main tracer elements, and stack emissions (industrial, power plant, and incinerator) with Mn, Zn, K, are among the main groups of sources to be taken into account. These three sources, in addition to a 'secondary' source introduced to quantify the contributions of secondary aerosol to the measured concentrations, were used for the model application.

The source chemical profiles introduced are described in table 1. The soil dust and general industry fingerprints were taken from the US-EPA Speciate ver. 3.2 database. The secondary source, including only Sulphate and Nitrate, was characterised according to Watson et al., while an ad-hoc profile was derived from local tunnel data to characterise traffic emissions.

Table 1. References for the source profiles

Source	Reference
Soil dust	Speciate 3.2 US-EPA
Industry	Speciate 3.2 US-EPA
Secondary	Watson e al., 1994
Traffic	This work

The traffic profile therefore describes all traffic contributions, including exhaust emissions from different vehicles, brake, tire, and asphalt wear, and re-suspension. One anomaly was observed in the calculated chemical fingerprint, due to the presence of a considerable amount of iron, probably caused by the nearby train tracks.

The chemical profiles of the sources introduced in the model are shown in table 2.

The model was applied to the set of data available for the period between April and July 2002. The winter data were excluded from this initial application, since a reliable chemical profile describing heating sources was not available.

Table 2. Source profiles

Species	Soil dust		Industry		Amsul		Amnit		Traffic	
	%	U	%	U	%	U	%	U	%	U
Al	5.732	0.424	1.784	1.310	0.000	0.000	0.000	0.000	0.329	0.033
Si	16.898	1.092	3.574	3.000	0.000	0.000	0.000	0.000	1.570	0.157
S	0.351	0.126	4.369	1.992	24.300	2.430	0.000	0.000	1.080	0.108
K	0.936	0.279	2.184	1.761	0.000	0.000	0.000	0.000	0.268	0.027
Ca	4.349	0.217	2.767	1.203	0.000	0.000	0.000	0.000	2.380	0.238
Ti	0.362	0.032	0.075	0.083	0.000	0.000	0.000	0.000	0.138	0.014
V	0.015	0.002	0.031	0.024	0.000	0.000	0.000	0.000	0.008	0.001
Cr	0.013	0.004	0.177	0.266	0.000	0.000	0.000	0.000	0.033	0.003
Mn	0.103	0.011	0.666	0.420	0.000	0.000	0.000	0.000	0.049	0.005
Fe	3.246	0.247	3.089	1.318	0.000	0.000	0.000	0.000	6.228	0.623
Ni	0.004	0.003	0.135	0.067	0.000	0.000	0.000	0.000	0.006	0.001
Cu	0.050	0.006	2.079	1.219	0.000	0.000	0.000	0.000	0.319	0.032
Zn	0.045	0.007	3.322	1.456	0.000	0.000	0.000	0.000	0.201	0.020
Br	0.005	0.006	0.048	0.043	0.000	0.000	0.000	0.000	0.079	0.008
Pb	0.044	0.026	4.939	2.624	0.000	0.000	0.000	0.000	0.206	0.021
$SO_4^=$	0.008	0.007	9.053	5.107	72.700	0.727	0.000	0.000	0.004	0.001
NO_3^-	0.003	0.057	0.208	0.522	0.000	0.000	77.500	7.800	0.007	0.001
NH_4^+	0.000	0.000	0.000	0.000	27.300	2.730	22.600	2.300	0.000	0.000

In order to minimize the uncertainty, the samples were divided according to the meteorological characteristics of the day in which they were taken, and average PM10 and chemical species concentrations were calculated for each group of samples. Out of a total of 55 samples, 37 were selected to calculate an average no-precipitation day, 15 for typical rainy conditions, one was used to characterise heavy rain (43 mm of rain during 14 hours). The effects of wind were evaluated on a sample taken during a strong foehn episode, with winds over 5 m/s throughout the whole day.

RESULTS
The model results were verified against the statistical validation targets suggested in the EPA "Model validation protocol". In all the cases discussed in this paper, the results satisfied the prescribed conditions: $R^2 > 0.8$, $\chi^2 < 4$, % total mass between 80 and 120 %. In addition, the calculated PM10 concentrations reproduce the measured values within ± 18% in all four cases, as shown in figure 1. The measured concentrations for the four cases considered are: 55 µg/m³ for days without rain, 41 µg/m³ for rainy days, 28 µg/m³ in the case of heavy rain, 33 µg/m³ with strong wind.

A summary of the results obtained for the four meteorological conditions examined is shown in table 3, where mass concentrations and associated uncertainties are reported. For each source, PM10 concentrations and the associated model uncertainties are shown. The contribution to the total PM10 concentrations from each source is shown in figure 2. Vehicular traffic is clearly the main contributor to PM10 concentrations with a 55% contribution, followed by secondary particulate (26%), to the formation of which traffic also contributes, by soil, at 15%, and industry with 4%. Meteorological conditions, especially the

extreme ones, strongly affect both total ambient particulate concentrations and the relative contributions of various sources to the measured concentrations.
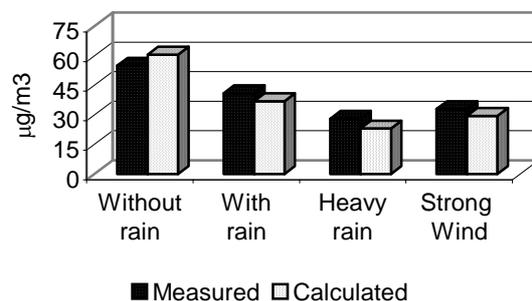

Figure 1. Comparison between measured and calculated PM10 concentrations

Table 3. Estimated contributions for the different PM10 sources with associated uncertainties

Source	Without rain		With rain		Heavy rain		Strong wind	
	Mass	Unc.	Mass	Unc.	Mass	Unc.	Mass	Unc.
	(µg/m3)	(µg/m3)	(µg/m3)	(µg/m3)	(µg/m3)	(µg/m3)	(µg/m3)	(µg/m3)
Traffic	33.058	± 5.757	22.420	± 3.952	16.307	± 3.659	10.189	± 3.464
Soil dust	9.265	± 0.973	4.341	± 0.624	2.143	± 0.742	18.032	± 1.363
Industry	2.329	± 0.691	2.557	± 0.683	4.514	± 1.001	0.860	± 0.264
Secondary	15.954	± 2.792	7.549	± 1.445	0.144	± 0.037	0.429	± 0.166

The strong wind situation analysed is, as mentioned earlier, a foehn event (northern wind from the Alps) that typically transports masses of clean air from the mountains. In this case, the soil source becomes the main contributor, as shown also by the percentage increase of the concentrations of Al, Si, Ca and Ti, whose contribution as a group to PM10 concentrations increases from 3.8 µg/m³ (7% of the total) during an average summer day to 6.2 µg/m³ (19% of the total) on the windy day. Strong wind and hard rain also affect secondary particulate formation, that is strongly reduced by both conditions.
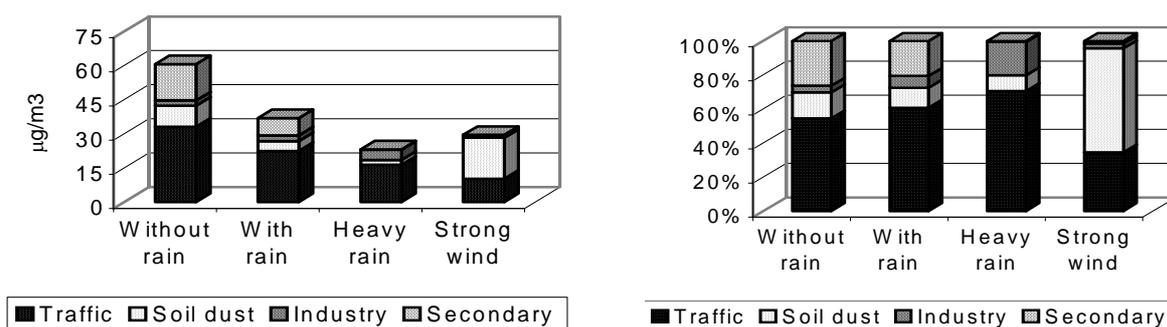

Figure 2. Mass and percentage contributions of PM10 sources to ambient concentrations

CONCLUSIONS

CMB7 was applied to a set of PM10 data sampled at an urban site in Milano. The application of the model to PM concentrations measured in summer months resulted in the identification of four main particulate sources: road traffic which, with a 55% contribution, represents the main source; secondary aerosols with 26%, soil dust at 15% and a contribution of about 4% from stack emissions.

Model analysis of selected groups of samples clearly showed the influence of rain and wind on the contributions from different sources.

Future developments of the work include extending the application of the model to the winter data in order to estimate the contribution of heating sources to particulate concentrations and the extent of the impact of secondary aerosols in the cold season. To this goal, specific source profiles will have to be developed to characterize local heating sources, as profiles taken from literature have not given satisfactory results.

A more detailed description of traffic source is also currently under study, to chemically characterize and distinguish different contributions to traffic emissions such as brake and tire wear, re-suspension, exhaust emissions from diesel and gasoline vehicles.

In addition, the application of a receptor model is being extended to PM2.5 data, which are becoming available for the site.

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