A Chemical Mass Balance approach for impact assessment in urban areas

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Keywords: particulate matter, air quality, receptor models, PAH, metals

1 Introduction

Optimisation of air quality strategies can be by obtained establishing source-receptor relationships and source apportionment[1]. Receptor modelling has been applied to ambient data collected in two European urban areas (Milan and Paris). A matrix of profiles of major traffic source, together with stationary source profiles taken from literature data, was prepared for metals and Polyciclic Aromatic Hydrocarbons (PAH) to perform a Chemical Mass Balance.

2 Experimental

Two monitoring campaigns have been conducted in 1999 in Milan (March 16th - April 1st) and Paris (April 22nd – May 13th) by a mobile laboratory located in heavily trafficked areas, close to two stations of the monitoring network (Viale Marche, Milan and Porte d'Auteuil-Blvd périphérique, Paris). Manual counting of the number of heavy-duty vehicles, passenger cars and motorcycles has been performed. Fleet composition was available (Paris: CITEPA 1996; Milan: ACI 1998). Meteorological conditions were recorded in both sites.
The analytical procedures for organic PAH and derivatives are reported elsewhere[2].
In Paris, PM2.5 was collected during weekdays every two hours during daylight and for 12 hours overnight. Filters from the Dekati impactor were analysed for metal species (from Na to Pb, almost 18 species) by Particle Induced X-ray Emission (PIXE).

3 Results

Air quality reflects the higher diesel portion of the traffic flux in Paris. In fact NO_x average concentrations, measured in the two sites, are higher in Paris than in Milan, while CO levels are comparable. An unexpected high PM10 concentration, that is generally attributed to diesel emissions, is measured in Milan because of industrial emission contributions[3]. Higher benzene concentration and its relative abundance versus aromatics like toluene and the xylenes, supports the effect of fleet composition and fuel type[4-6]. Pyrene, Anthracene and B(a)Pyrene, as well as total PAH, averaged during the sampling dates, are higher in the Paris location. That is again suggesting that relative traffic source intensities are different.
The major components of the fine fraction of the atmospheric aerosol appear to be sulphate, nitrate and iron. Total concentration of elements resulted higher in Milan than in Paris whilst anions show a different distribution, with sulphates lower in Milan.

3.1 Chemical mass balance (CMB) modelling

The CMB receptor model consists of a solution of linear equations, defining each receptor chemical concentration as the linear sum of the products of source profile abundance and contributions. The source profile abundance (i.e., the mass fraction of a chemical or other property in the emissions from each source type) and the receptor concentrations, with appropriate uncertainty estimates, serve as input data to the software. The output consists of the amount contributed by each source type represented by a profile to the total mass and each chemical species.

CMB has been applied to chemically characterised PM10 and PM2.5, to metals and to PAH separately. Starting from measurements performed in the emission testing, a set of metals and PAH profiles per each kind of traffic source (light duty diesel, heavy duty diesel, gasoline vehicles equipped with or without catalytic device) were available.

3.1.1 PAH

On the basis of the PAH fingerprints, source differentiation is possible between cat and non-cat gasoline engines but not between HD and LDD.
Deviation from CMB assumption – receptor is directly connected to sources - is expected due to reactivity of PAH. Decay factors[7] were used to modify the source profiles that were used for the apportionment.
The fitting was obtained when HDD, cat and not cat gasoline engines were included in the balance both in Milan and in Paris with 11 compounds. The time series for Milan are shown in Fig. 1 where very stable source apportionment data are obtained. Underprediction of higher molecular weight PAH is observed. Averaged Diesel contribution is 14%. Diesel accounts for about 20% of total PAH in Paris (previous data[4] from 1986 were 30%).

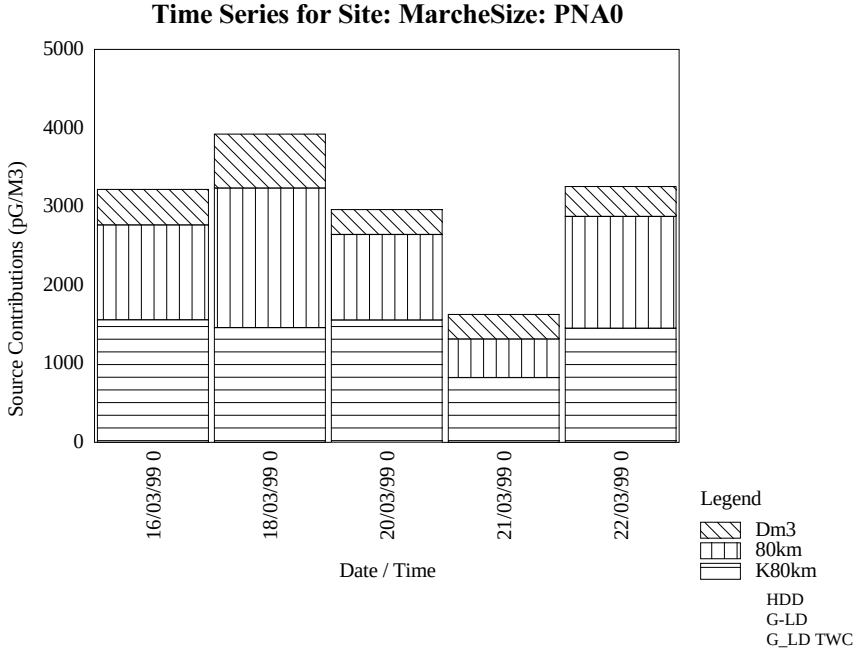

Fig. 1 Apportionment of PAH in Milan. Legend: HDD= Heavy Duty Diesel; G-LD= Gasoline Light Duty; G-LD TWC= Gasoline Light Duty with Three Way Catalyst.

The comparison of source contributions calculated for the two sites (Fig.2) shows a slightly higher contribution of PAH from diesel in Paris, compatible with local fleet composition.
In both sites PAH diesel emissions account for only about 15% of total PAH. The last result suggests that on-the-road emission of PAH by gasoline vehicles is higher than expected. It appears that a deeper insight on reference fuel and on the fingerprints used in the balance for gasoline engines is required.

PM apportionment was tentatively performed using PAH/PM ratios at the exhaust, leading for Paris and Milan to a PM_{10} traffic contribution with a ratio 7:3 between diesel and gasoline. PM_{10} calculated concentrations account for 25% and 55% of averaged experimental data in Milan and Paris respectively.

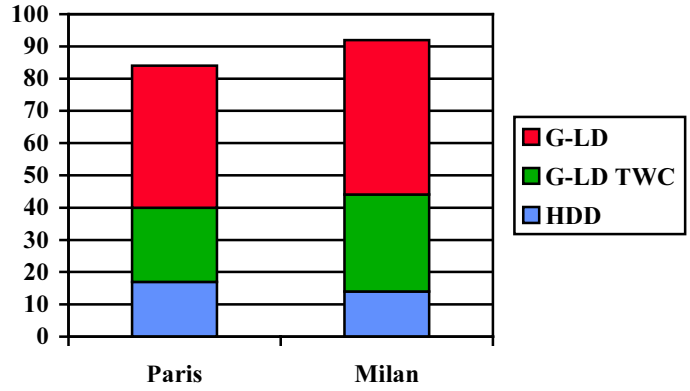

Fig. 2 Source apportionment of PAH in Milan and Paris, expressed as percentage of total PAH.

3.1.2 Metals

By measurements performed at tail pipe exit, fingerprints for vehicular sources were available but no distinction between LDD and HDD metal profiles nor cat and no-cat is possible due to correlation among fingerprints. Non-vehicular exhausts profiles, as those related to soil, traffic related source and combustion processes, were taken from the literature[1,3].

Ambient data were divided into two categories: wind direction from N (that favours transport from the Boulevard towards the mobile laboratory) and wind direction from SE or no prevailing wind. When wind was coming from North, traffic sources were the most relevant: diesel fingerprint accounted for 40 % and total traffic sources for more than 60 % of total metal concentrations. The average contribution attributed to soil is 37%. When a combustion source was introduced (Fig. 3) traffic related sources weighted only about 30%, whereas the diesel contribution was still predominant.

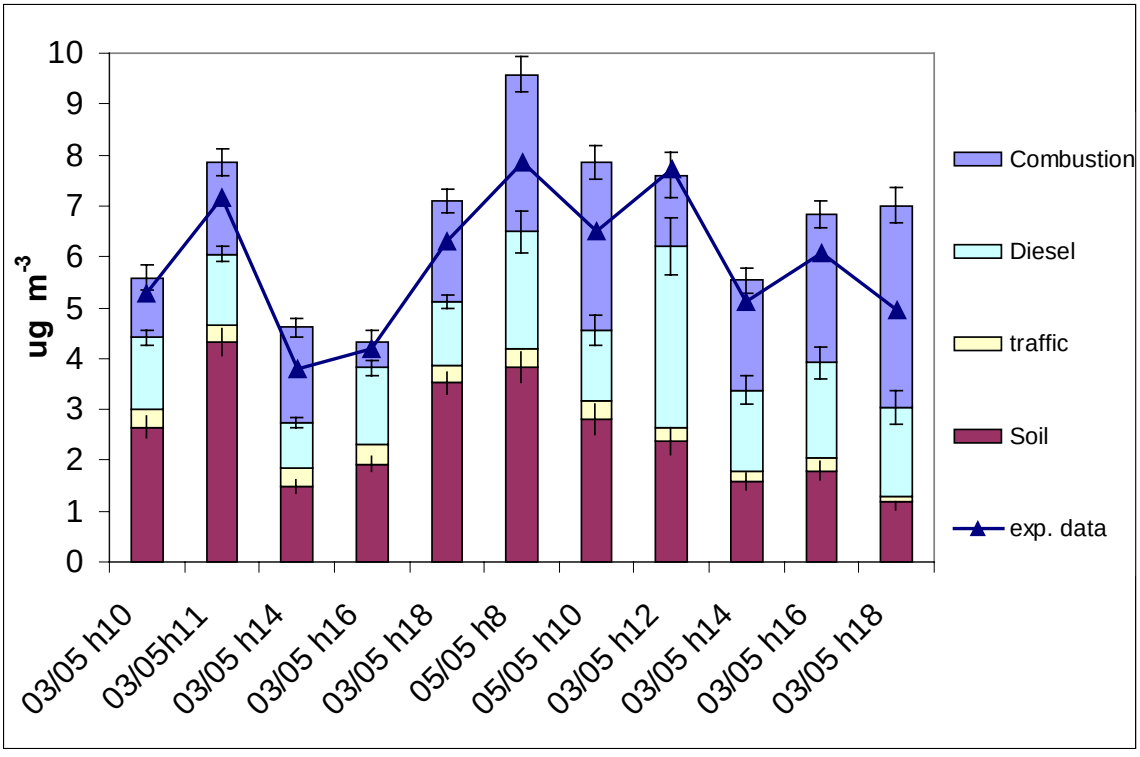

Fig. 3 Source apportionment (3rd –5th April: no prevailing wind).

4 Conclusions

CMB is a powerful technique to identify major contributors to ambient concentrations, especially for the condensed matter. Fingerprints obtained in exhaust emission testing are essential for source recognition nevertheless on-road traffic profiles are affected by reactivity, level of maintenance of vehicle fleet and non-exhaust traffic emission (like brake and tyre wear).
Relative contributions between gasoline and diesel vehicles were quantified based on PAH, whilst diesel contribution and the influence of stationary sources from the surroundings of the receptor site were detected by metal apportionment.
PAH measured in particulate matter (PM_{10}) are dominated by gasoline pattern both in Milan and Paris.

Acknowledgements

This work was funded by GERTH (Joule III) and it shouldn't have been possible without the technical support of B. Martin, M. Pasquereau, G.B Dementhon (IFP), F.Giavazzi (Euron) for emission characterisations; F. Lucarelli (INFN Florence) for PIXE analysis and B. Larsen (JRC) for PAH measurements in atmospheric samples. The authors thank EniTecnologie colleagues F. Petrucci and R. Collili who performed the monitoring campaigns.

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