

Semicontinuous GC analysis and receptor modelling for source apportionment of ozone precursor hydrocarbons in Bresso, Milan, 2003

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Abstract

The European Ozone Directive 2002/3/EC specifies the analysis of 30 individual C₂–C₉ hydrocarbons in urban air with the attribution of emission sources to pollution concentrations as a major objective. In the present study, we investigate an approach for source apportionment of these ozone precursor hydrocarbons in urban air based on reliable semi continuous volatile organic compound (VOC) analysis in the field and in vehicle emission laboratory combined with multivariate receptor modeling. The GC system relies on an hourly analytical cycle based on a trap sample enrichment phase followed by a dual column gas chromatographic flame ionisation detector (FID) analysis and has successfully been tested during an air monitoring campaign at an urban site (Milan, Italy, September 2003) and in the vehicle laboratory performing exhaust emission measurements while running driving cycles on a chassis dynamometer (mopeds, gasoline and diesel cars). The receptor modeling relies on two complementary principles. The chemical mass balance (CMB) modeling apportions well characterized source profiles for the 30 individual C₂–C₉ hydrocarbons in the Ozone Directive to the concentrations in ambient air and produces source contribution estimates (SCE) as output. The positive matrix factorization (PMF) analyses variability in the ambient air concentration data and searches for latent variables consisting of co-varying hydrocarbons and produces profiles as output, which in this study could be attributed to known emission sources. Both CMB and PMF rely on an estimated uncertainty for each input data. A new approach is presented, by which the uncertainty is allowed to float as function of the photochemical reactivity of the atmosphere and the stability of each individual compound.

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1. Introduction

Environmental air samples typically comprise a complex mixture of low concentration compounds requiring enrichment procedures and high resolution chromatography for accurate analysis. The wide volatility and polarity range of organic compounds present in the atmosphere, whether petrochemical or any natural matrix, requires adequate resolution or selective detection. In finding the 'needle in the haystack' with a selective detector, a major role is today played by

mass spectrometric detectors (MSD) that, provided specific fragment ions (m/z) are available for each co-eluting compound, can, in principle, cope with poor single GC column separations. Nevertheless, selective detection has application limits and coupling together analytical columns with appropriate selectivity, is the ultimate solution for the speciation of complex samples.

Since ground-level ozone was one of the air pollutants of most concern in Europe in the summer of 2003, a topical subject is nowadays the determination of the C₂–C₉ ozone precursor hydrocarbons (two-dimensional gas chromatographic (2D-GC) with dual flame ionisation detector (FID) detection), both with respect to characterizing emission sources and to monitoring ambient air quality. The new Ozone Directive 2002/3/EC, which has been in force as of 9 September

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Table 1
The 30 ozone precursors hydrocarbons recommended for measurements in the Ozone Directive 2002/3/EC

| | | | |
|------------------|------------------------|-------------------|-----------------------------|
| Ethane | <i>trans</i> -2-Butene | <i>n</i> -Hexane | <i>m</i> + <i>p</i> -Xylene |
| Ethene | <i>cis</i> -2-Butene | Isohexane | <i>o</i> -Xylene |
| Ethyne | 1,3-Butadiene | <i>n</i> -Heptane | 1,2,4-Trimethylbenzene |
| Propane | <i>n</i> -Pentane | <i>n</i> -Octane | 1,2,3-Trimethylbenzene |
| Propene | Isopentane | Isooctane | 1,3,5-Trimethylbenzene |
| <i>n</i> -Butane | 1-Pentene | Benzene | |
| Isobutane | 2-Pentene | Toluene | |
| 1-Butene | Isoprene | Ethylbenzene | |

2003, obliges member states in the future not only to monitor ozone itself but also its photo-chemically reactive precursors in the air, namely nitrogen oxides and 31 volatile organic compounds (VOCs) (Table 1).

One of the major objectives of this directive is to assist in the attribution of emission sources to pollution concentrations. Each volatile organic compound reacts in the air at a different rate and with different reaction mechanisms and thus, VOCs can differ significantly in their influence on ozone formation. A sensitive and selective analytical technique, reliable also in-the-field is essential for source apportionment. The use of cryogen-free gas chromatographs facilitates real-time air monitoring at remote locations [1] for short periods of time and on a continual basis, throughout the year [2,3] in urban areas. In the latter case, the most important contributor to ozone precursors is road traffic [4], thus the investigation of ozone precursor VOCs in vehicle emissions is of great concern.

For the present study, we have combined ambient air monitoring of an urban air mass (Milan, September 2003) and vehicle emission measurements of 30 individual C₂–C₉ hydrocarbons specified in the Ozone Directive with multivariate receptor modeling using the chemical mass balance (CMB) modeling and positive matrix factorization (PMF).

Finally we have calculated the potential impact of the identified and quantified sources on ozone formation through the maximum incremental reactivity (MIR) approach, developed by W.P.L. Carter and used in “low emission vehicles and clean fuels” regulations in California [5]. The MIR is the ozone variation, caused by adding a small amount of test VOC to the emission in a photochemical smog episode, divided by the amount of test VOC added. It can be used to assess the impact of changing emissions of an individual VOC on ozone formation. A coherent relationship between traffic emissions and ambient air concentrations was aimed for in the present study by using the same analytical technique for analysis of the atmospheric air-shed and emission characterization.

2. Experimental

2.1. Urban site

Hourly samples of 800 ml of ambient air were collected and analyzed from 13 September to 1 October 2003 at Bresso,

an urban site in the outskirts of Milan (Italy, 45°32'.4N, 9°12'.1E; 146 m asl). Bresso has 27.000 inhabitants and borders onto a large green park area (Parco Nord) surrounded by major traffic ores, the major one being a highway at the distance of approximately 1 km.

2.2. Vehicles emissions facilities

All the driving tests were performed in the Vehicle Emission Laboratory (VELA) of the EU Joint Research Centre, at Ispra, for the characterization of the emissions of all types of on road and non road vehicles. For the present study, passenger cars and mopeds were driven on a chassis dynamometer (Zoellner GmbH) with a constant volume sampler (flow 7.5 m³/min). The VOC emissions from four mopeds (two-stroke, two-stroke with oxidative catalyst, two-stroke with direct injection, and two-stroke with liquified petroleum gas) were compared with EURO3 gasoline and diesel cars. Driving cycles, adapted for each vehicle category were run, as follows: New European Test Cycle (NEDC, equivalent to ECE15 + EUDC but without the initial 40 s idle time) for the gasoline and diesel cars and ECE47 for mopeds. Approximate distances for the test cycles were 10 km for NEDC and 6UDC + EUDC and 6 km for ECE47. Commercially available fuel was used for all the tests.

Ten litres of vehicles exhaust samples were collected in TedlarTM bags and successively connected to the analyzer inlet. Only a limited sample volume of 80 ml was collected and analyzed for each driving test allowing replicated analysis if necessary.

2.3. Instrumentation

2.3.1. Sample enrichment and thermal desorption module

A thermal desorption unit (UNITYTM) and an auxiliary sampling device (Air ServerTM) from Markes International (Pontyclun, UK) were used to collect samples from ambient air or Tedlar bags of exhaust gases. Sample enrichment proceeds at –15 °C (two stages Peltier cold element) on a “Ozone precursor/Freons Trap” (Markes) multilayer adsorbent trap (12 cm × 2 mm i.d.): porous polymer (5 mm), graphitized carbon black (8 mm), carbon molecular sieve 1 (15 mm) and a carbon molecular sieve 2 (30 mm). Sample volume is electronically driven by a mass flow controller (MFC). A whole-sample thermodesorption/injection step follows the sampling (sample re-collection option disabled) and the released compounds are injected into the gas chromatograph via a heated transfer line (130 °C) lined with uncoated, deactivated fused silica. Collection of the next sample proceeds as chromatographic analysis of the previous sample continues. Automated cyclic trap reconditioning with carrier gas flow is performed between subsequent runs. All the instrumental parameters (sampling and analysis, Table 2) are set and monitored with a dedicated software interface (Markes International Pontyclun, UK).

Table 2
Sampling and thermal desorption settings

| Analyzer parameter | Sample type | |
|---|-------------|---------------------|
| | Urban air | Vehicle emission |
| Sampling flow (ml/min) | 40 | 40 |
| Sampling time (min) | 20 | 2 |
| Sampling temperature (°C) | –15 | –15 |
| Recollection split tube | Not used | Not used |
| Nafion dryer | Used | Used |
| Desorption flow (ml/min) | 20 | 20 |
| Desorption temperature (°C) | 320 | 320 |
| Transfer line temperature (°C) | 130 | 130 |
| Purging flow (ml/min) | 20 | 20 |
| Purging time (min) | 5 | 5 |
| Purging temperature (°C) | –15 | –15 |
| Total cycle time (min) (sampling, TD/GC, purging) | 60 | (Manual single run) |

2.3.2. 2D-GC analysis module

Analysis were performed with a gas chromatograph (6890, Agilent, Wilmington, DE, USA) equipped with dual flame ionisation detector. VOCs were separated on a WCOT and a PLOT (DB-1 and Al₂O₃/KCl both from Agilent, Waldbronn, Germany). A certified standard mixture with the 31 ozone precursors VOCs (approximately 0.5–10 ppbV each, SIAD Bergamo, Italy) was used for calibration runs. Details are reported in Table 3. GC control and data acquisition (ChemStation, Agilent, Wilmington, DE, USA) software is run in parallel to the sampling and desorption application on the same PC.

3. Results and discussion

3.1. The analyzer

The ozone precursors VOC analyzer were commercially available since early 90s [6–8] and since then have been improved with the contemporary available technology [1,9–11]; however, the presence of water vapor in real samples is still a major issue as it affects both the pre-concentration and the separation phases. The often proposed use of drying devices is controversial with respect to the sample integrity, and its applicability is highly compound dependent. A second issue is the peaks' identity that completely relies on the widely used PLOT columns' selectivity, retention time sta-

bility [12] and a well known elution order in the operating conditions.

3.1.1. Sample enrichment and thermal desorption module

The Nafion™ dryer devices consist of an inner semi-permeable tube of Nafion™ (copolymer of tetrafluoroethylene and fluorosulfonyl monomer (perfluoro 3,6-dioxo-4methyl-7-octenesulphonic acid)) where the wet ambient air sample is flowing, surrounded by an outer tube of various inert materials. The water vapor is selectively absorbed into the walls of the inner Nafion™ tube and transferred to the outer volume where a dry purge gas stream flows or a static desiccant (magnesium perchlorate, 13× molecular sieve) is present [13] to carry off moisture. This transfer is driven by the difference in the partial pressures of the water vapor on opposing sides. Although suitability of the Nafion™ dryer for permanent gases and some halocarbon [13] has been reported, comparison of non-methane hydrocarbons, paraffin, olefin and aromatic concentration for canister samples (heavy trafficked road tunnel) [14] analyzed with and without dryer showed a difference ranging from 4 to 30%. A careful use of this device must be done to minimize polar compounds losses, monoterpenes rearrangements and possible contamination [11,15–17]. Compounds like isobutylene, methyl-*tert*-butyl ether, 2-methyl-1-pentene for example, has been reported as almost entirely removed from the chromatogram [12 PG18]. However, the stripping out of polar and other compounds is, to some extent, a useful side effect of the dryer in this application resulting in a simplified chromatogram, and preventing columns contamination. It would be very difficult to assess peaks identity of real samples relying solely on non-selective FID detection even with the resolving power of the dual-column Deans' switch system. When the Nafion™ option is used, calibration samples must necessarily be "dried" as real samples. If no drying device is used, small sampled volume and carrier gas preflushing of the adsorbent trap prior to desorption represent the best compromise between acceptable detection limits and system (sampling and analysis) reliability. Influence of water vapour on the preconcentration phase can be limited selecting a proper combination of carbonaceous and polymer adsorbents in a multilayer trap, detailed discussions have been extensively reported [18–22].

The adsorption/desorption trap efficiency of our system in the C₂–C₇ range is summarized in Table 4 along with the corresponding statistical results, data were obtained

Table 3
GC settings and column specifications

| GC settings and programming | | Capillary columns | | |
|-----------------------------|-------------------------------|-------------------------|-----------------------|--|
| Carrier gas (CG) | He | | (1) WCOT (DB1) | (2) PLOT (Al ₂ O ₃) |
| Oven | 40 °C × 2 min (ramp at 7 °C) | Stationary phase | Polidimethyl-siloxane | Al ₂ O ₃ /KCl |
| | 120 °C × 3 min (ramp at 7 °C) | Length (m) | 50 | 50 |
| | 200 °C × 35 min | Internal diameter (mm) | 0.32 | 0.32 |
| | | Phase thickness (μm) | 1.2 | 8 |
| | | CG lin. velocity (cm/s) | 27 | 29 |

Table 4
Performance of the trap

| Compound | Boiling point (°C) | Cone (ppb mol) | Correlation coeff. (R^2) | Relative standard deviation (%) | | | | | |
|------------------------|--------------------|----------------|------------------------------|---------------------------------|-----|-----|----------------|------|------|
| | | | | Peak area | | | Retention time | | |
| Ethene | −103.7 | 9.31 | 0.9989 | 0.9 | 1.1 | 1.0 | 0.54 | 0.19 | 0.11 |
| Ethyne | −84.0 | 7.75 | 0.9970 | 1.4 | 1.1 | 1.5 | 0.38 | 0.12 | 0.05 |
| Propane | −42.1 | 2.25 | 0.9973 | 4.9 | 1.5 | 1.9 | 0.28 | 0.03 | 0.02 |
| <i>trans</i> -2-Butene | 0.9 | 1.94 | 0.9973 | 3.2 | 0.7 | 2.0 | 0.18 | 0.05 | 0.03 |
| 1,3-Butadiene | −4.4 | 4.66 | 0.9969 | 1.5 | 0.4 | 2.8 | 0.12 | 0.05 | 0.02 |
| Heptane | 98.4 | 2.43 | 0.9955 | 2.0 | 3.1 | 2.0 | 0.04 | 0.06 | 0.05 |
| Toluene | 111 | 2.82 | 0.9962 | 4.3 | 3.5 | 1.0 | 0.07 | 0.04 | 0.03 |
| Sampled volume (ml) | | | | 200 | 400 | 600 | 200 | 400 | 600 |
| Replicates (n) | | | | 5 | 5 | 3 | 5 | 5 | 3 |

using a dry reference mixture (only seven compounds shown).

In the table, the obtained peak areas are shown for seven hydrocarbons (C_2 – C_7 range) in triplicate analysis of a certified gas standard at ppb level. The correlation coefficient R^2 refers to the linear regression of the peak area versus sampled volume in the range of 0–600 ml, 3 not shown) of all replicates (13) for each compound. The good performance reported in Table 4 relies on the electrically-cooled sorbent trap that eliminates the risk of ice from humid samples blocking the sample flow path, furthermore inconvenience and high running costs associated with liquid cryogen are reduced. Sample and data integrity are ensured with stringent leak test of every tube prior to desorption without heat or gas flow applied. A pre-desorption purge phase with carrier gas to remove air prevents the sorbent/analyte oxidation and artifact formation. The analytical sensitivity is optimized with a splitless (100%) transfer of analytes to the first high-resolution capillary GC column at flows down to 2–2.5 ml/min. The direct connection to the column via a uniformly-heated capillary line, without going through a GC injector eliminates cold spots and prevents band broadening, allowing the extension of the analyte boiling range to nC_{30} and above.

System operation is PC controlled and indication of the actual status is available as a simple flow path schematic on the screen. For precision and repeatability of real-time continuous analysis of ambient air and offline Tedlar bags exhaust samples, the air server (AS) accessory is needed to control the sampling flow using a MFC driven by the desorber software. The AS allows also the automated interchange between sample, zero and calibration gas streams. All parts of the sample flow path are automatically swept with carrier gas between samples to minimize the risk of carryover.

3.1.2. 2D-GC analysis module

Dual column systems range from simple two column configurations coupled together in series, to adjust the overall selectivity of the paired stationary phases, to the more complex two dimensional (2D) arrangement of a comprehensive 2D-GC (GC \times GC) [23–25] which will allow the user to take full advantage of the available peak resolution from each coupled column. Commercial multidimensional kits are available

today [26] to upgrade almost any GC to a basic 2D-GC–GC system commonly referred as Deans' switch system [27–30]. The main advantage of this interface is the lack of any moving part or sample pathway to cross (e.g. the body of conventional low dead volume switching valves) between columns. In the case of a sample containing a mixture of compounds covering a wide range of volatility or polarity, a combination of two capillary columns (WCOT, PLOT, Molsieve) jointed with a proper "tee" unions system, represents an extremely efficient two-dimensional gas chromatographic analyzer that only needs standard detection (e.g. thermal conductivity detector, FID) as reported in Fig. 1.

As it appears in Fig. 1, VOCs eluting from the first column (COL1, e.g. WCOT) can be diverted alternatively to the second column (COL2, e.g. PLOT) or the first detector simply applying an auxiliary carrier gas (ACG) flow to one end or the opposite (T2 or T3) of the midpoint branch with a tree way solenoid valve (SV). The pressure at the first column inlet and the midpoint branch is set via electronic pressure controllers (EPC) 1 and 2, respectively. The midpoint is connected to the first detector with a deactivated fused silica capillary with the same pressure drop of the second column. Both midpoint branch ends are short-circuited with a restrictor (R).

As reported in the schematic representation of Fig. 1, the analytes eluting from column 1 can move to one end of the midpoint branch (T2), or the opposite (T3), according to the auxiliary carrier gas flow direction defined by the

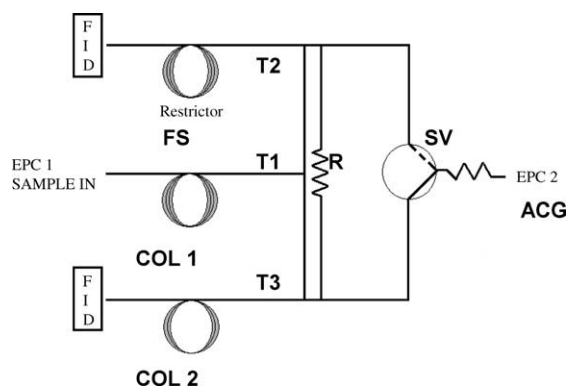


Fig. 1. Schematic of the 2D-GC Deans' switched system.

SV position. However, peak broadening of the compounds flowing in the “tee” connections to detector 1 (T2) or to column 2 (T3) can occur in the ACG inactive line (i.e. toward the SV). The presence of the restrictor (R) ensure a minimal flow in the “tee” connection to prevent such disadvantages, furthermore the contemporary electronic control can easily handle the varying flows in the switching interface between columns providing the required pneumatic stability to avoid, or minimize, the risk of back diffusion of the sample into the switching lines causing carry over effects. Mixtures of permanent gases, or extremely volatile compounds, together with relatively less volatile components can be efficiently separated with this arrangement of columns, provided the more volatile compounds are effectively non-retained on the first column. Analogous configurations can be developed for mixtures of compounds with different polarity instead of volatility. The specific column set described in this case fits the requirements of many applications: natural gas analysis (calculation of calorific values), process control in the chlorine (vinyl chloride monomer production) as well petroleum (oxy-compounds in gasoline) industries to cite a few.

The analysis of a C₂–C₉ mixture of hydrocarbons, with the proper resolution of the lighter as well the heavier fraction, requires the choice of a WCOT column for the C₆–C₉ range (i.e. suitable for the separation of aromatic compounds) followed by an alumina PLOT column, with a high selectivity for lighter C₂–C₅ hydrocarbons (HC). Both of them can be chosen from several possibilities according to the target compounds to be speciated. However, the use of an Al₂O₃ deactivated with KCl is frequently reported for ambient air analysis [31–33]. Whatever the PLOT column of choice, the system requires no cooling of the oven for the separation of C₂–C₅ hydrocarbons, no refocusing of the sample at its inlet

after the switch actuation (provided a sufficiently low start temperature (e.g. 40 °C) can be reached in the GC oven) and it allows to the dual column analysis to be carried out in a single GC oven. However, a multi-column separation of a C₂–C₉ mixture can also be obtained with parallel injection and analysis on the PLOT and WCOT columns [34]. Furthermore a simpler direct coupling of a PLOT (Al₂O₃/KCl) followed by a WCOT (SE54) column is effective in shortening the analysis time (increased initial oven temperature, 70 °C) for automated remote monitoring, with a smaller resolution power compared to the 2D combination of the same two columns.

The activated Al₂O₃ is a solid stationary phase with a high degree of porosity. The deactivation degree of its polar surface and deactivating agent (typically sodium sulfate or potassium chloride) affects the property of the column and the elution order of unsaturated hydrocarbons. As demonstrated in Table 5 different relative elution of ethyne and propyne with respect to C₄–C₅ alkanes is usually presented to underline the major difference between them. A fine tuning of selectivity for the separation of light hydrocarbons is provided by proprietary deactivations of the alumina phase [35], or by using a silica PLOT column [9] if resolution of chlorinated hydrocarbons is required. However relative retention of compounds separated on a solid Al₂O₃ stationary phase depends also on the linear velocity and the nature of the carrier gas in the column [36–38]. Contrasting elution order for the *i*C₄/propadiene/*n*C₄ and *i*C₅/1,3-butadiene/*n*C₅ triplets for example has been reported [36,39–42].

Optimal adjustment of analysis parameters like carrier gas type and linear velocity, column stationary phase and phase ratio, oven program, etc. is critical and requires the understanding of the properties of each parameter as they are key factors in determining the elution order on very selective

Table 5
Elution order of C₃–C₅ hydrocarbons on Al₂O₃/KCl PLOT capillary column

| | This paper (He ^a) | Rudlein et al. [19] (He ^a) | Lofgren et al. [45] (He ^a) | Jemma et al. [38] (H ₂ ^a) | Schaeffer [48] (N ₂ ^a) | Schaeffer [48] (He ^a) |
|------------------------|----------------------------------|---|---|---|--|--------------------------------------|
| Propene | 1 | 1 | 1 | 1 | 1 | 1 |
| Ethyne | 2 | 2 | 2 | 3 | 2 | 2 |
| Isobutane | 3 | 3 | 3 | 2 | 3 | 3 |
| Propadiene | 4 | 4 | 4 | 5 | 4 | – |
| <i>n</i> -Butane | 5 | 5 | 5 | 4 | 5 | 4 |
| <i>trans</i> -2-Butene | 6 | 6 | 6 | 6 | 6 | 5 |
| 1-Butene | 7 | 7 | 7 | 7 | 7 | – |
| Isobutene | 8 | 8 | 8 | 8 | 8 | 6 |
| <i>cis</i> -2-Butene | 9 | 9 | 9 | 9 | 9 | 7 |
| Propyne | 10 | 11 | 11 | 12 | 11 | – |
| Isopentane | 11 | 10 | 10 | 10 | 10 | – |
| 1,3-Butadiene | 12 | 13 | 13 | 13 | 13 | – |
| <i>n</i> -Pentane | 13 | 12 | 12 | 11 | 12 | 8 |
| 2-Methylpentane | 14 | 14 | – | 14 | – | – |
| 3-Methylpentane | 15 | (16) | – | 15 | – | – |
| Isoprene | 17 | 15 | – | 17 | – | – |
| <i>n</i> -Hexane | 16 | (17) | – | 16 | – | – |

See references for the original papers.

^a Carrier gas

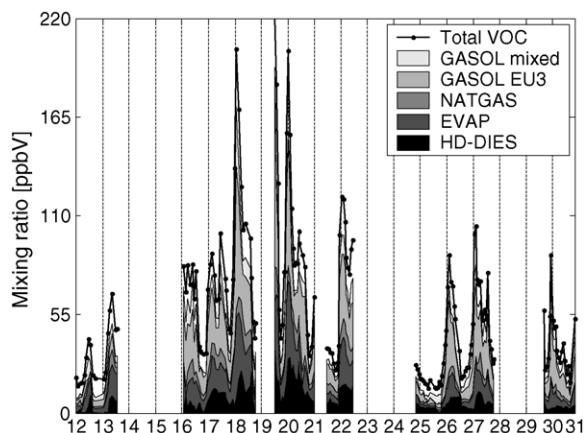


Fig. 2. Total VOC mixing ratios and the source contributions in Bresso, Milan, Italy, from 12 September to 31 September 2003. See Chapter 3.4 for explanations.

columns. If selective detection (e.g. PID for the alkenes) is not used misidentification of the compounds can occur.

3.2. Urban air hourly monitoring

The sampling of 30 ozone precursor VOCs was carried out during September 2003 (from 13 September to 1 October) at Bresso. The daily variation of the sum of VOCs is shown in Fig. 2. The normal concentration levels for the sum of VOCs at this site ranged from 60 to 90 ppbV. However, on the 18–20th of September particular meteorological conditions (zero wind during a high pressure episode) entrapped the air over the city and the concentrations rose to 200 ppbV. High concentrations of ozone (>100 ppb) were also measured during this episode (data not shown). The average contribution of each individual compound ($\pm 95\%$ confidential interval) to the sum of VOCs is shown in Table 6. For all samples taken during this campaign, the individual VOC compounds were highly inter-correlated pointing to one dominating source type (traffic). Only on a few days spikes of individual compounds were observed, which indicated sporadic contributions from other sources (acetylene, *n*-butane, *n*-heptane, toluene).

In order to investigate the contribution from individual traffic sources to the 30 ozone precursor hydrocarbons found in the air over Bresso emission measurements were conducted during 2003 and 2004 in our Vehicle Emission Testing Laboratory (VELA) for a number of vehicles using the same semicontinuous analyzer as for the air measurements.

3.3. Vehicles emission characterization

Semicontinuous analysis of ozone precursor hydrocarbons with cryogen-free sampling and dual column Dean switching was conducted on VOC emissions from vehicles representative for traffic in Milan. The vehicles consisted of four EURO2–EURO3 gasoline cars (1.6–1.9 L engine displacement), six EURO3 diesel cars with 1.9–2.3 L engine dis-

placement) and four two-stroke mopeds (50 cc with and without oxidative catalyst, with direct injection, and with LGP as fuel instead of traditional two-stroke fuel). The vehicle testing was performed on a chassis dynamometer (Zoellner GmbH) with a constant volume sampler (flow 7.5 m³/min) with the following driving cycles adapted for each vehicle category: New European Test Cycle (NEDC, equivalent ECE15 + EUDC without 40 s idle time) for the gasoline and diesel cars and ECE47 for mopeds. Approximate distances for the test cycles were 10 km for NEDC and 6UDC + EUDC and 6 km for ECE47. Commercially available fuel was used for all the tests. In addition, the cars were tested for evaporative emissions in a 50 m³ sealed test chamber according to the European Commission Directive on measures to be taken against air pollution by emissions from motor vehicles (98/69/EC). An example of a chromatogram is shown in Fig. 3.

The qualitative difference between the exhaust chromatograms was very evident. The most particular chromatograms were obtained for liquefied petroleum gas engines, which are rich in C₂–C₄ compounds most likely deriving from non-combusted fuel components. Two-stroke engines emit large quantities of C₂–C₇ compounds and the exhaust contains high levels of the most toxic of the VOCs, i.e. 1,3-butadiene. The chromatograms from four-stroke gasoline engines resembled those of two-stroke engines but with a higher proportion of non-combusted aromatics. The chromatograms from EURO3 diesel engines were much simpler and contains mainly very light hydrocarbons (see data in Table 6).

The relative contribution of each individual VOC to the potential ozone formation can be estimated by the maximum incremental reactivity approach [5]. The technical background for this approach is as the following: Carter (1994) used a chemically detailed box model to quantify the ozone formed from 180 different VOC in 39 cities across the United States. Eighteen different reactivity scales were developed from those model calculations. The scales differ in the assumptions about the levels of NO_x and the measure of ozone impact (such as impact on the peak ozone versus integrated impact over time). One scale, the maximum incremental reactivity scale, was chosen for regulatory application in California. MIR values for individual VOCs are calculated in 10-h box model simulations and are defined as the maximum sensitivity of the peak ozone concentration ($[O_3]_p$) to a small increase in the initial conditions and emissions of the VOC (E_i). MIR is determined for the input ratio of VOC to NO_x that leads to the maximum sensitivity to VOC: $MIR_i = \max(\Delta([O_3]_p)/\Delta E_i)$ over all VOC/NO_x.

The average relative contribution of the individual VOCs to the potential ozone formation at the sampling site Bresso (Milan) is shown in Table 6 and show a dominance of ethene, toluene and C₈–C₉ aromatics. The potential ozone formation from the exhaust of six classes of engine technologies were estimated by the MIR approach and ranged from 0.1 to 0.5 g O₃/km for diesel and gasoline engines (with catalyst)

Table 6
Ambient air mixing ratios and source profiles for ozone precursor VOCs

| | ^a Air (ppbV) | Contribution to ozone formation (%) | ^b GASOL-EU3 (%) | ^c GASOL-mixed (%) | ^d HD-DIES (%) | ^e EVAP (%) | ^f NATGAS (%) |
|-----------------------------|-------------------------|---|----------------------------|------------------------------|--------------------------|-----------------------|-------------------------|
| 1. Ethane | 4.8 ± 0.5 | 0.3 ± 0.1 | 3.4 ± 0.7 | 8.2 ± 2.4 | 1.7 ± 0.8 | 0.2 ± 0.1 | 76.3 ± 15.3 |
| 2. Ethene | 8.5 ± 1.5 | 13.3 ± 4.3 | 31.8 ± 6.4 | 20.4 ± 8.9 | 13.7 ± 3.9 | 1.8 ± 2.5 | 0.2 ± 0.2 |
| 3. Propane | 2.2 ± 0.3 | 0.4 ± 0.1 | 0.2 ± 0.0 | 0.2 ± 0.1 | 3.1 ± 1.5 | 6.5 ± 9.0 | 15.4 ± 3.1 |
| 4. Propene | 1.5 ± 0.6 | 4.5 ± 2.6 | 9.5 ± 1.9 | 6.3 ± 2.8 | 5.5 ± 1.3 | 0.7 ± 0.8 | 0.2 ± 0.2 |
| 5. Acetylene | 1.4 ± 0.2 | 0.3 ± 0.2 | 5.5 ± 1.3 | 7.4 ± 3.9 | 3.5 ± 2.4 | 0.0 ± 0.0 | 0.2 ± 0.2 |
| 6. Isobutane | 2.9 ± 0.4 | 1.5 ± 0.6 | 0.9 ± 0.5 | 0.7 ± 0.4 | 0.4 ± 0.4 | 6.3 ± 3.3 | 2.2 ± 0.4 |
| 7. <i>n</i> -Butane | 3.2 ± 0.4 | 1.5 ± 0.6 | 1.8 ± 0.4 | 1.9 ± 0.9 | 0.9 ± 2.2 | 13.4 ± 3.9 | 3.7 ± 0.7 |
| 8. <i>trans</i> -2-Butene | 0.6 ± 3.6 | 3.6 ± 2.3 | 3.2 ± 4.6 | 0.5 ± 0.2 | 0.3 ± 0.6 | 0.8 ± 0.5 | 0.2 ± 0.2 |
| 9. 1-Butene | 0.2 ± 0.3 | <0.1 | 0.6 ± 0.1 | 0.8 ± 0.3 | 4.1 ± 0.8 | 0.9 ± 0.5 | 0.2 ± 0.2 |
| 10. Isobutene | 1.2 ± 3.8 | 3.8 ± 3.6 | 2.5 ± 0.5 | 0.2 ± 0.2 | 1.4 ± 0.3 | 1.9 ± 2.7 | 0.2 ± 0.2 |
| 11. <i>cis</i> -2-Butene | 0.1 ± 1.7 | 0.4 ± 0.6 | 0.4 ± 0.1 | 0.3 ± 0.2 | 0.4 ± 0.2 | 1.6 ± 1.8 | 0.2 ± 0.2 |
| 12. Propyne | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.6 ± 0.2 | 0.2 ± 0.2 | 0.8 ± 0.8 | 0.0 ± 0.0 | 0.2 ± 0.2 |
| 13. Isopentane | 4.0 ± 0.5 | 2.3 ± 0.9 | 7.8 ± 3.1 | 7.8 ± 3.6 | 1.8 ± 4.8 | 15.5 ± 5.5 | 1.3 ± 0.3 |
| 14. 1,3-Butadiene | 0.5 ± 8.7 | 2.5 ± 3.6 | 3.8 ± 2.3 | 0.9 ± 0.4 | 4.1 ± 2.8 | 0.0 ± 0.0 | 0.2 ± 0.2 |
| 15. <i>n</i> -Pentane | 3.8 ± 0.6 | 2.5 ± 0.4 | 3.0 ± 1.6 | 1.8 ± 0.9 | 2.1 ± 1.8 | 18.4 ± 7.8 | 1.2 ± 0.3 |
| 16. <i>trans</i> -2-Pentene | 0.1 ± 3.0 | <0.1 | 0.2 ± 0.1 | 0.2 ± 0.1 | 0.5 ± 0.5 | 0.8 ± 0.9 | 0.2 ± 0.2 |
| 17. <i>cis</i> -2-Pentene | 0.4 ± 7.9 | 1.8 ± 2.8 | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.4 ± 0.3 | 0.3 ± 0.3 | 0.2 ± 0.2 |
| 18. Methylpentanes | 3.3 ± 0.5 | 3.2 ± 1.5 | 16.0 ± 3.2 | 1.9 ± 1.0 | 4.3 ± 2.9 | 19.9 ± 14.1 | 0.2 ± 0.2 |
| 19. Isoprene | 0.1 ± 29.8 | 2.4 ± 3.1 | 0.2 ± 0.1 | 0.3 ± 0.1 | 0.5 ± 0.4 | 0.5 ± 0.8 | 0.2 ± 0.2 |
| 20. <i>n</i> -Hexane | 0.4 ± 0.1 | 0.4 ± 0.2 | 0.3 ± 0.1 | 0.4 ± 0.2 | 1.3 ± 0.8 | 1.3 ± 1.3 | 0.2 ± 0.2 |
| 21. <i>n</i> -Heptane | 0.6 ± 0.2 | 0.5 ± 0.6 | 1.0 ± 1.0 | 0.9 ± 0.4 | 0.8 ± 0.4 | 0.9 ± 0.5 | 0.2 ± 0.2 |
| 22. Benzene | 0.8 ± 0.1 | 0.3 ± 0.1 | 1.5 ± 0.9 | 8.7 ± 3.5 | 4.4 ± 2.1 | 0.7 ± 0.3 | 0.2 ± 0.2 |
| 23. Toluene | 3.9 ± 0.7 | 8.9 ± 4.6 | 2.9 ± 1.1 | 14.7 ± 6.4 | 6.3 ± 5.1 | 3.6 ± 0.9 | 0.2 ± 0.2 |
| 24. Ethylbenzene | 1.2 ± 0.3 | 2.3 ± 1.0 | 0.5 ± 0.2 | 2.3 ± 1.0 | 4.0 ± 2.8 | 1.4 ± 2.3 | 0.2 ± 0.2 |
| 25. <i>m/p</i> -Xylene | 2.4 ± 0.3 | 17.3 ± 5.5 | 0.7 ± 0.2 | 7.6 ± 3.4 | 15.3 ± 9.5 | 2.2 ± 3.5 | 0.2 ± 0.2 |
| 26. <i>o</i> -Xylene | 1.2 ± 0.2 | 6.2 ± 1.8 | 0.3 ± 0.1 | 2.9 ± 1.3 | 5.2 ± 3.2 | 0.6 ± 1.0 | 0.2 ± 0.2 |
| 27. 1,3,5-Trimethylbenz. | 0.8 ± 13.3 | 7.4 ± 3.4 | 0.3 ± 0.3 | 0.6 ± 0.3 | 2.9 ± 1.5 | 0.0 ± 0.0 | 0.2 ± 0.2 |
| 28. 1,2,4-Trimethylbenz. | 2.0 ± 3.0 | 12.3 ± 3.9 | 0.9 ± 0.9 | 1.9 ± 0.8 | 10.4 ± 6.4 | 0.0 ± 0.0 | 0.2 ± 0.2 |
| Sum of VOCs | 58.4 ± 5.9 | 100 | 100 | 100 | 100 | 100 | 100 |

^a Mean ± average uncertainty (see text).

^b Mean ± SD from exhaust of six EURO3 vehicles.

^c Mean ± SD from exhaust of six EURO1–EURO2 vehicles [2,3].

^d Mean ± uncertainty of heavy-duty diesel exhaust in tunnel [43].

^e Mean ± SD of evaporative emissions from five EURO2–EURO3 vehicles.

^f Mean ± SD of natural gas [44].

and from 1 to 10 g O₃/km for two-stroke engines. Ethene and propene are responsible for 40–60% of the potential ozone formation from two-stroke engines and catalyzed four-stroke gasoline engines and even more than 90% for EURO3 diesel engines. This fact highlights the importance of the performance of VOC analyzers in the C₂–C₃ range.

3.4. Source apportionment by receptor modelling

Two receptor models (chemical mass balance and positive matrix factorization) were used to identify the major sources and estimate their contributions to ozone precursor hydrocarbons at Bresso, Milan.

The chemical mass balance model is a least squares model that utilizes source profiles and ambient concentration data to calculate source contribution estimates (SCE) where the species in the profiles are limited to those monitored at the receptor. CMB is an effective variance weighted least squares estimation method that uses the uncertainties in the ambient concentrations and the source profile data to generate source

contribution estimates and SCE uncertainties. Thus great care should be taken in estimating the uncertainties in the ambient concentrations, which is not merely a function of the analytical precision and accuracy. Accordingly, for compounds with low atmospheric half-lives the most important factor influencing the uncertainty is the photo-chemical reactivity of the compound and the atmosphere at any given moment of sampling. The CMB receptor model has previously been applied successfully for VOC source apportionment [43]. The version CMB8 of this model [45] was applied to the 163 VOC samples obtained by the semi continuous VOC analyzer in September 2003 at Bresso (Milan) together with a series of source profiles measured in our VELA laboratory and collected from literature.

The uncertainty ($U_{i,j}$) was attributed to the measured mixing ratio ($C_{i,j}$) for each individual hydrocarbon (i) and each individual sample (j) based on a 10% analytical reproducibility, a 0.05 ppbV detection limit and a floating photochemical stability ($S_{i,j}$) of the given compounds in function of the photochemical reactivity of the atmosphere:

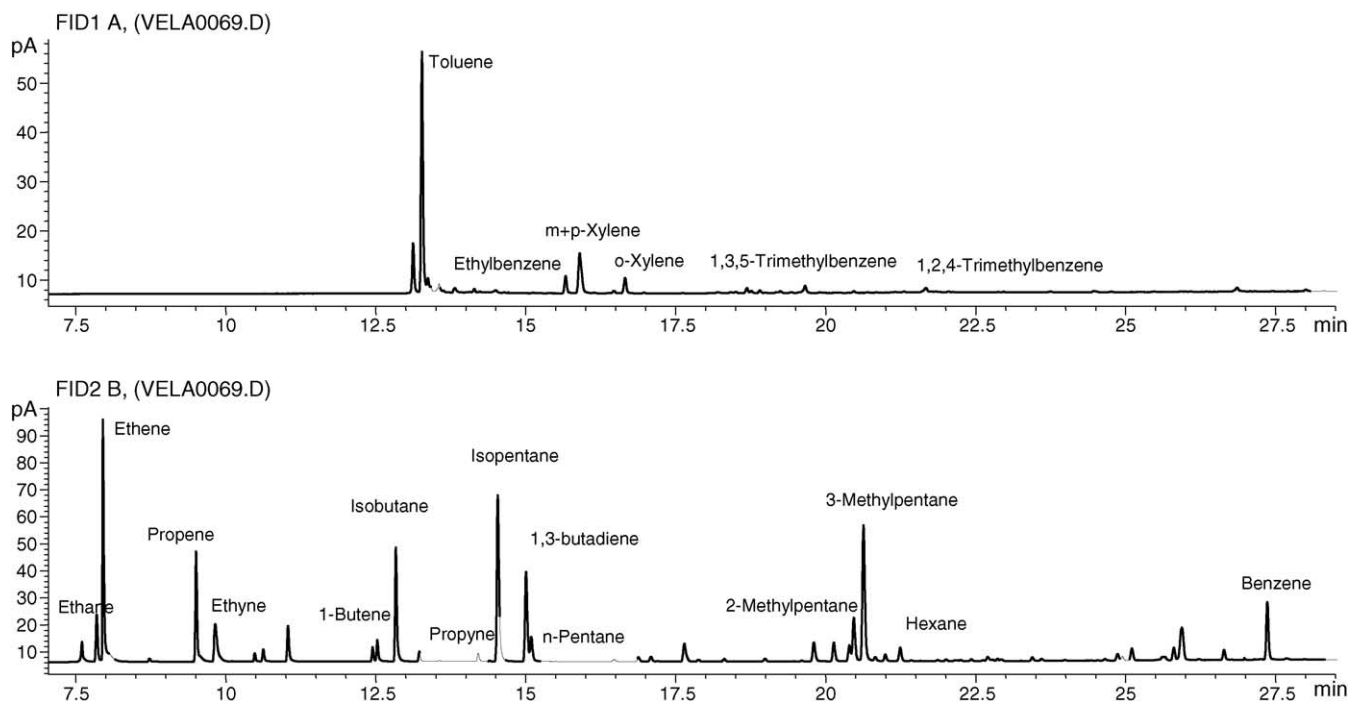


Fig. 3. Chromatogram of exhaust emissions from a gasoline engine with a three-way catalyst. Upper traces WCOT, lower traces PLOT.

$U_{ij} = (0.1 C_{ij} + 0.05)/S_{ij}$. The photochemical stability was calculated from pseudo-first order reaction kinetics [46] and measured ozone concentrations (running average of past 24 h) assuming proportionality between ozone and OH radical concentrations ($[\text{OH}]_{\text{mol/cm}} = 27\,000[\text{O}_3]_{\text{ppbv}}$) and assuming constant NO_3 radical concentrations of 1 ppt at night time:

$$S_{ij} = \prod_{n=1}^3 [\Omega_n]_i e^{-k_i \Omega_n j t}$$

where k_i denotes the pseudo-first-order reaction rate for each combination of individual hydrocarbon (i) and photo-oxidant (Ω_n) i.e. O_3 , OH and NO_3 .

A simpler approach has been used by Fujita et al. (1994), which was to exclude hydrocarbons more reactive than toluene and attribute a fixed uncertainty for each individual compound. The advantage of the new approach used for the present study is that it does not exclude information collected for any compound but generates higher uncertainties for the most reactive compounds from midday to late afternoon, when high concentrations of photo-oxidants are present and thus lowering their weight in the calculations at these moments. However, at night time when the concentrations of these compounds are higher, they are allowed a certain weight in the calculations.

A total of 15 source profiles (average and uncertainty) were considered for the CMB calculations. The profiles included the set of vehicles tested in VELA and profiles extracted from literature data such as heavy-duty diesel exhaust from the Ft. McHenry tunnel [43], natural gas [44], and exhaust measurements of light duty diesel and gasoline vehicles representative of the French 2003 fleet [2,3].

In order to use all profiles published in literature the data of 2-methylpentane and 3-methylpentane was pooled into “methylpentanes” since not all profiles published differentiates between these two isomers. After screening for colinearity between these two isomers. After screening for colinearity by multi-linear regression analysis 11 profiles were kept for the calculations. The CMB8 interface allows for instant source apportionment calculations for a series of individual receptor samples and shows statistical performance indicators as the output. The higher the number of source profiles included in a calculation, the better is the fit of the calculated hydrocarbon concentrations to the measured ones. However, increasing the number of source profiles also reduces their intrinsic statistical significance due the lower number of degrees of freedom available for estimation of each profile. The CMB approach followed a manual iterative process in which a number of combinations of source profiles were tested for all 163 individual receptor samples. A number of combinations gave good solutions and often one source could be replaced by another one coming from the same category with only a small reduction in the CMB performance criteria (e.g. heavy-duty diesel and EURO1 diesel). However, the inclusion of both source profiles from the same category would be discarded by the CMB software. The optimum combination was found to include the five source profiles listed in Table 6. With these profiles and average of 80.4% of the total hydrocarbon concentration was explained and the fit of the calculated hydrocarbon concentrations to the measured ones had an average regression constant (r^2) of 0.83. The best agreements were obtained (in decreasing order) for ethane, propane, ethene, acetylene, isopentane, methylpentanes, the xylenes, ethylbenzene, n -pentane, n -heptane, and

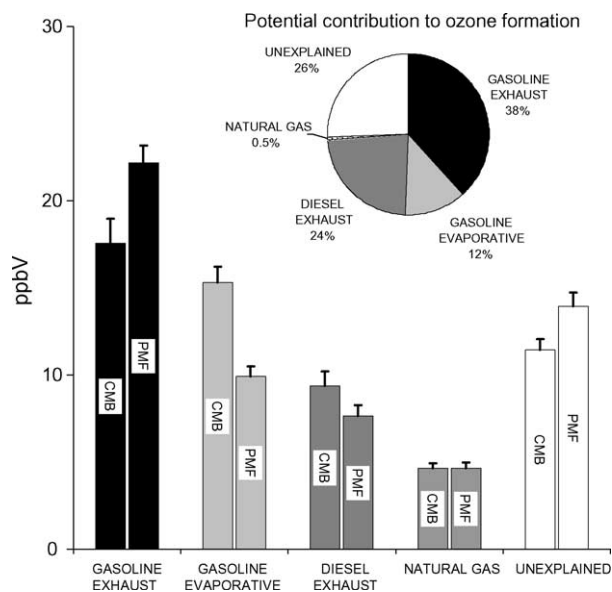


Fig. 4. Source contribution estimates (mean \pm 95% confidential interval) from chemical mass balance (CMB) and positive matrix factorization (PMF) modeling of 163 VOC measurements in Milan (Bresso) September 2003. Bars show contributions to the mixing ratio (sum of VOCs) and the pie shows the potential contribution to ozone formation calculated from the MIR approach [5].

isobutene. Toluene and the trimethylbenzenes were systematically underestimated by approximately 20%. A high degree of scattering was observed for the compounds present in sub-ppb mixing ratios. In more than 90% of the samples all five sources were detected at the 90% significance level and four out of five sources were detected at the 95% significance level. The average SCE \pm 95% confidence interval of all 163 source apportionments is shown in Fig. 4. Not surprisingly the dominating source contribution came from gasoline exhaust (the sum of SCEs from the profiles GASOL-EU3 and GASOL-mixed in Table 6) and gasoline evaporation, which together accounts for 60% of the measured ozone precursor hydrocarbons. Another 20% comes derived from diesel exhaust (calculated as heavy-duty) and 8% from presumed leakage of natural gas. Although the contribution from diesel is calculated as heavy-duty diesel, which can easily be explained by the vehicle distribution at the highway passing by at approximately 1 km distance, it may also include light duty diesels and private diesel cars. The resolution by CMB in this study does not allow distinguishing between these categories of traffic sources. When the potential contribution to ozone formation is calculated by the maximum incremental reactivity approach [5] the impact of hydrocarbons from gasoline sources is estimated to be 50% and the impact of diesel exhaust to 25%.

The model of positive matrix factorization is a variant of factor analysis, described in detail by Paatero and Tapper (1994), which has found application in source apportionment studies of atmospheric pollutants [47,48]. It distinguishes itself from other factor analysis models such as,

e.g. principle component analysis in the fact that it produces non-negative factor loadings and scores. An important aspect of PMF is that it does not rely on information from the correlation matrix but utilizes a point-by-point least-squares minimization scheme. Therefore, the profiles produced can be directly compared to the input matrix without transformation. The CMB approach initiates with the characterization of the sources, which are considered important for air mass of concern thereby running the intrinsic risk of overlooking one or more sources. PMF is the ideal complementary statistical approach to CMB for source apportionment of ozone precursor hydrocarbons, since it analyses variability in the ambient air concentration data and searches for latent variables consisting of co-varying hydrocarbons. By combining the two approaches the potential distortion of the emission profiles by photochemical degradation of the most reactive of these compounds can be addressed. The PMF calculations were implemented as a ME2 multi-linear engine script running in the robust mode with the error model $EM = -14$ for data above 0.2 ppbV and $EM = -16$ for data below 0.2 ppbV [49]. The calculations were carried out for the 163×56 matrix of hydrocarbon mixing ratios and uncertainties for the samples obtained by the semi continuous VOC analyzer in September 2003 at Bresso (Milan).

In PMF, the choice of the number of factors; using too few factor will combine sources of different nature together and using too many factors will make a factor closely resembling a real source profile dissociate into two or more non-existing sources [47,48]. In the present study calculations were done for a broad range of factors and the degree of fitting of the produced factor profiles to realistic traffic source profiles was used as assessment criteria for determining the most appropriate number of factors. The five- or six-factor model was found to generate the most reasonable results. Switching to lower number of factors produced outputs with in which it was impossible to distinguish between profiles. In all cases, abnormalities were found for the hydrocarbons ethane, propane, butane and isobutene. These are key components of natural gas. However, none of the produced profiles bore a resemblance to a clean profile for natural gas (Table 6). Therefore, the specific option of forcing a factor in the multi-linear engine was used. The NATGAS profile (Table 6) was forced in as factor while allowing ME2 to vary its composition within its intrinsic uncertainty levels. The composition of the factors in the five-factor solution (NATGAS plus four) is shown in Fig. 5. A striking resemblance is evident between the PMF factors and the best fitting source profiles from the CMB calculations, which lends confidence in the combined source apportionment result.

Also by PMF, the best agreements between modeled and measured concentrations were obtained (in decreasing order) for ethane, propane, ethene, acetylene, isopentane, methylpentanes, the xylenes, ethylbenzene, *n*-pentane, *n*-heptane, and isobutene. Again, toluene and the trimethylbenzenes were systematically underestimated by approximately 20% and a high degree of scattering was observed for the

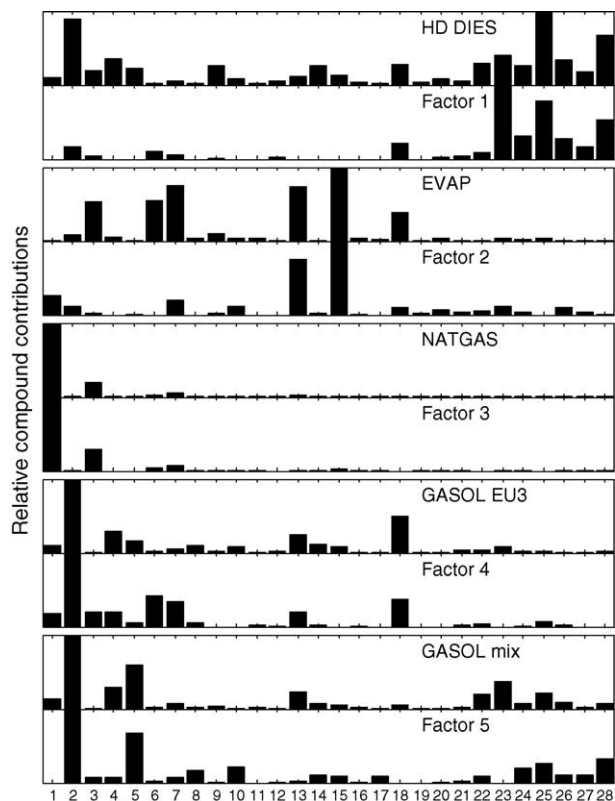


Fig. 5. Comparison of the five factors revealed by PMF and the five source profiles found by CMB to contribute with more than 80% to the total mixing ratio of the 28 hydrocarbons (numbers in Table 6) in Bresso, Milan, September 2003.

compounds present in sub-pbb mixing ratios. Of the total hydrocarbon mixing ratio 76.1% was explained by the five factors and the fit of the calculated hydrocarbon concentrations to the measured ones had a regression constant (r^2) of 0.91. The average contribution of the five factors (sources) \pm the 95% confidence interval of all 163 source apportionments is compared to that of the CMB calculations in Fig. 4. PMF confirms gasoline exhaust (the sum of the factors resembling the profiles GASOL-EU3 and GASOL-mixed in Table 6) and gasoline evaporation as the dominating source for the ozone precursor hydrocarbons specified in the Ozone Directive, albeit gasoline exhausts by PMF is estimated to be a slightly stronger source than by CMB and vice versa for gasoline evaporation. Approximately 20% is again estimated to derive from a factor similar to the profile for diesel exhaust. The 8% estimate of presumed leakage of natural gas by CMB did not change by allowing ME2 to vary the source profile within its intrinsic uncertainty levels.

4. Conclusion

The present study demonstrates how combined ambient air monitoring of an urban air mass (Milan, September 2003) and vehicle emission measurements of individual C₂–C₉ hy-

drocarbons specified in the Ozone Directive 2002/3/EC can be used as the basis for source apportionment with multivariate receptor modeling.

The semicontinuous analysis of ozone precursor hydrocarbons in air and vehicle exhaust with cryogen-free, on-line sampling and dual column Deans' switch chromatography has been operated for approximately 12 months in our field and main laboratories for routine air quality measurements and vehicle emission characterization. The results acquired to date, point to the fact that the C₂ and C₃ hydrocarbons together with aromatic compounds are the main ozone precursors. This study has shown a, robust and practical (cryogen-free) technology for on-line monitoring of ozone precursors in field and laboratory applications at the levels required for both ambient air and vehicle emissions testing. However, care is still required both for initial set up (optimizing performance) and for on-going monitoring of system performance to ensure that valid data continues to be produced for compliance with the requirements of the Ozone Directive.

The use of two multivariate receptor models (CMB and PMF) which are fundamentally different and complementary is essential for the source apportionment of ozone precursor hydrocarbons. One (CMB) initiates its calculations from the assumed knowledge of the main source profiles for the Bresso air mass and calculates their contribution to the air pollution. The other (PMF) takes its starting point in the statistical analysis of the variability in the ambient air concentration data and identifies latent variables (factors) consisting of co-varying hydrocarbons, which in this study could be attributed to the major emission sources, namely gasoline exhaust (30–38%), gasoline evaporation (17–26%), diesel exhaust (13–16%) and natural gas leakage (around 8%). Both CMB and PMF rely on an estimated uncertainty for each input data. The successful source apportionment calculations was attained due to use of a new approach, by which the uncertainty is allowed to float as a function of the photochemical reactivity of the atmosphere and the stability of each individual compound.

The maximum incremental reactivity calculation of the potential ozone formation of the emitted ozone precursor hydrocarbons points to a 50% contribution to the ozone in the Bresso air mass by gasoline vehicles and 50% by diesel vehicles.

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