Volatile Organic Compounds (VOCs) sources apportionment in Paris based on measurements : focus on the road traffic and solvent sources

Alexia Baudic[1], Valérie Gros[1], Stéphane Sauvage[2], Nadine Lecoge[2], Olivier Perrussel[3], Nicolas Marchand[4], Irène Xueref-Remy[1], Lamia Ammoura[1], Roland Sarda-Estève[1], Cerise Kalogridis[1], Nicolas Bonnaire[1], Dominique Baisnée[1], Bernard Bonsang[1], Hervé Petetin[3], Olivier Sanchez[3], Amandine Rosso[3] and Jean Sciare[1]

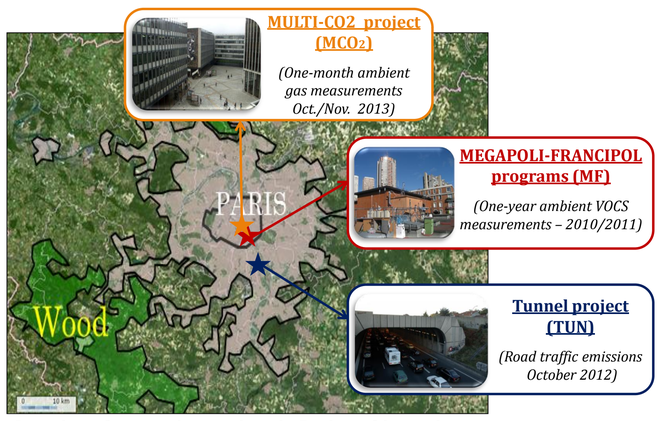
[1]*Laboratoire des Sciences du Climat et de l'Environnement, LSCE, UMR CNRS-CEA-UVSQ, Gif-sur-Yvette, Ile-de-France, 91191, France*
[2] *Ecole Nationale Supérieure des Mines de Douai, Département Sciences de l'Atmosphère et Génie de l'Environnement, Douai, Nord-Pas-De-Calais, 59500, France*
[3]*AIRPARIF, Paris, Ile-de-France, 75004, France*
[3]*Aix Marseille Université, CNRS LCE FRE 3416, Marseille, Bouches-du-Rhône, 13331, France*

Presenting author email : **alexia.baudic@lsce.ipsl.fr**

Abstract

Currently, cities remain seriously confronted with recurrent pollution issues. Volatile Organic Compounds (VOCs) are well-known outdoor air species, acting thus as precursors of secondary pollutants, such as ground-level ozone (O_3) and Secondary Organic Aerosols (SOA). In Paris, quality objectives settled by European standards are subject to regular over thresholds affecting about 3 million inhabitants; hence the growing importance of characterizing VOCs emissions in this town. Within this context, one-year 'real-time' selected VOCs measurements were performed in downtown Paris (2010-2011). A sources apportionment analysis using the 'source-receptor' statistical model Positive Matrix Factorization (PMF) was achieved. This approach allowed to identify five main VOCs sources (with one of them mixed) and their respective contributions. The main emission source is related with road traffic activities (approximately 50%), both in agreement with a preliminary study (Gaimoz et al., 2011) and with the local 2010 emission inventory provided by the air quality network AIRPARIF. Based on this PMF study, solvent use also appears as a substantive source in Paris, but still probably over-estimated in the inventory. On account of the significance of these two sources, specific additional measurements (within a tunnel and outdoor ambient air) were carried out in order to help to constrain their respective identification.

Material & Methods



Location of measuring stations in Paris and its region

Instrumental deployed during measurement campaigns

Instruments	Parameters	Time resolution	Campaigns
Gas measurements			
GC-FID	Light & Heavy NMHC (C2C6-C6C12)	30 min	MF, MCO_2, TUN
GC-MS	Aromatics & Halocarbons	2 h	MF, MCO_2
PTR-MS	Aromatic & Oxygenated VOCs	10 min	MF, MCO_2, TUN
Picarro	CO, CO_2	5 s	MF, MCO_2, TUN
Gas analyzers	NO, NO_2, O_3	1 min	MF, TUN
Aerosols measurements			
ACSM	Org, NH_4, SO_4, NO_3, Chl	10 min	TUN
Aethalometer 7-λ	Black Carbon	1 min	MF, TUN
WAD-IC	Hcl, HONO, HNO_3, SO_2	15 min	MF
Meteorological data	Temperature, Wind speed/direction…	#	MF, MCO_2

The 'source-receptor' **Positive Matrix Factorization (PMF)** statistical method (V.3, EPA, 2008)

(Model developed by Paatero & Tapper in 1994)

$$X = F * G + E$$

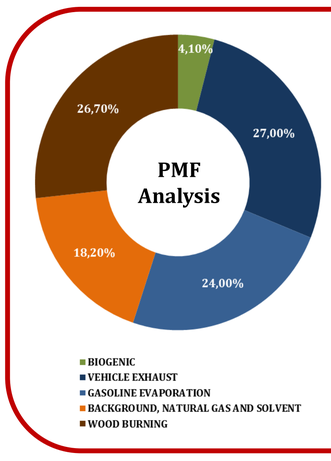
X : PMF Input data Concentrations — 17 VOCs & 3 294 samples*
F : Sources Contributions
G : Sources Profiles
E : Residual Matrix

Alkanes : ethane, propane, i/n-butane, i/n-pentane, hexane
Alkenes : ethylene, propene, acetylene, isoprene
Aromatics : benzene, toluene, xylenes + C8
Oxygenated VOCs : methanol, acetaldehyde, acetone, MAK+MVK

** Data from 15th January to 22nd November 2010 (2h mean)*

Results

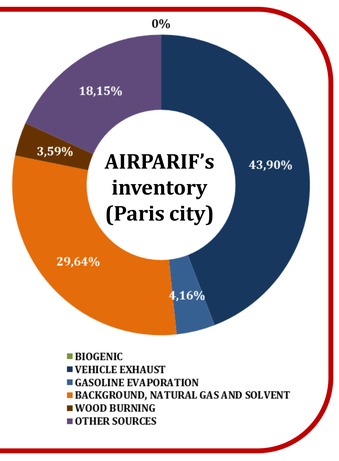
Identification of 5 main VOCs sources by PMF analysis & Comparison with the local emission inventory (2010)



- **Road traffic related emissions are the predominant source of VOCs (~ 50 %), in agreement with Gaimoz et al. 2011**
- The 'wood burning' source shows a significant contribution (~ 27 %), mainly in winter
- **The 'solvent' source couldn't be accurately isolated from background and natural gas sources (~ 18 % overall)**
- The 'biogenic' source has a minor impact (~ 4%), but still significant in spring and summer

Road traffic activities appear as the main VOCs source for both observations & inventory, but the contributions of exhaust and gasoline evaporation still completely disparate

Inventory seems to over-estimate the 'solvent' source



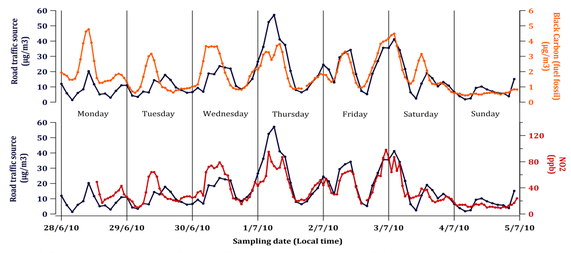
Focus on the road traffic & solvent sources

Consistent with road traffic fingerprint

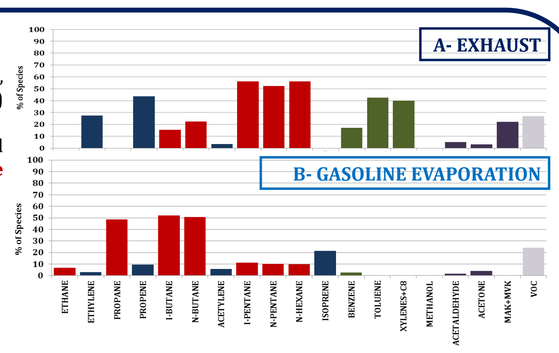
'Road traffic' source

A/ Exhaust : Profile mainly represented by **alkanes** (**pentanes**, hexane), **aromatics** (**toluene**, C8) and **alkenes** (**ethylene**, propene)

B/ Gasoline evaporation: Profile especially dominated by **alkanes** : **propane and i/n-butane**



Weekly time series of traffic source, NO_2 and Black Carbon (fuel fossil)

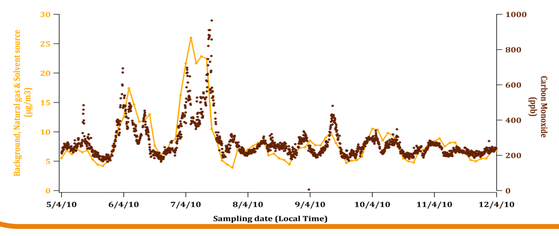


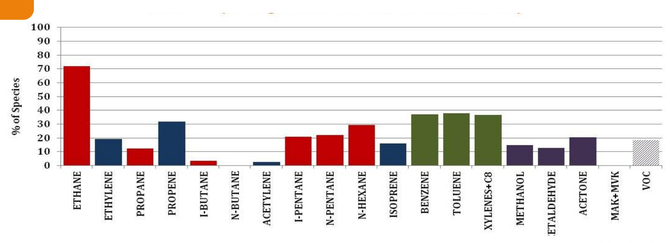
✓ **A good co-variation between the traffic source and several independent tracers, such as NO/NO2, CO or BC was observed**

✓ **Weekday/Weekend differences in concentrations of air pollutants**

Background, Natural Gas and Solvent

Combination profile drived by :
Alkanes : **ethane** and **propane** proving background & natural gas emissions, for which ones **pentanes** and n-hexane are typical compounds
Aromatics (benzene, toluene and xylenes)
Oxygenated compounds (**acetone**)

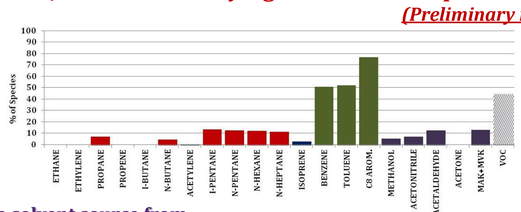


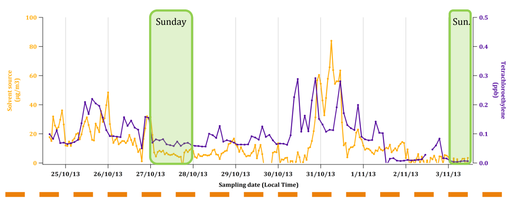


✓ **Combined source profile widely represented by a continental background, explaining thus a good co-variation with CO (long life-time compound)**

New profile helping to isolate solvent source from background & natural gas sources

✓ **A fairly good agreement between the solvent source and industrial tracers, such as tetrachloroethylene (widely used as *'dry-cleaning fluid'*) was found**



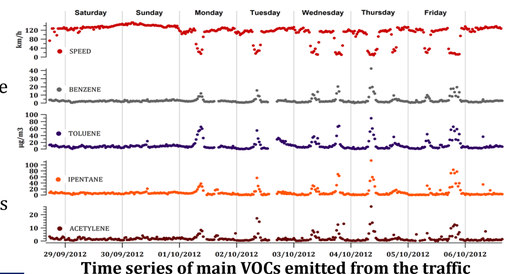


Tunnel experiment (October 2012)

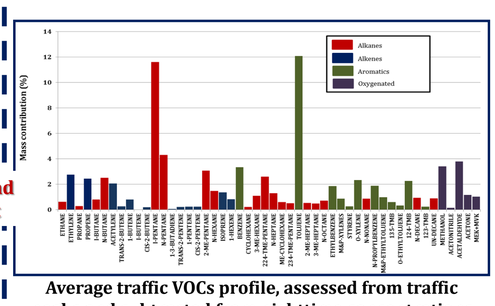
MAIN OBJECTIVE : Displaying an average typical VOCs profile of vehicular emissions

✓ Diurnal cycle characterized by a first increase of VOCs concentrations at ~ 8-9 am and a second increase at ~ 5-7 pm, corresponding to periods of traffic jam (vehicle speed < 30 km/h)

✓ Weekly cycle dominated by higher VOCs concentrations during weekdays than weekend periods



Time series of main VOCs emitted from the traffic

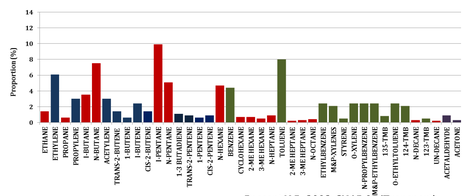


Average traffic VOCs profile, assessed from traffic peaks and subtracted from nighttime concentrations

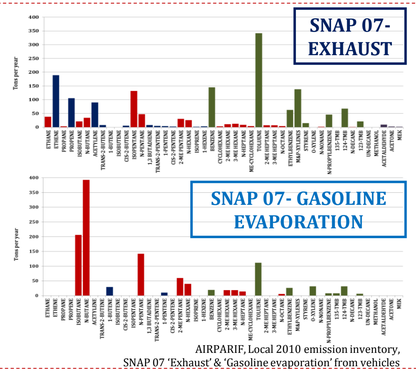
Profile mainly dominated by **toluene** and **isopentane**; secondarily by light **alkenes** (**ethylene**, propene, acetylene), some **aromatics** (benzene, xylenes, TMB) and **oxygenated** compounds (methanol, acetaldehyde)

∑ **Exhaust** & **Gasoline evaporation** profiles

Comparison with emission inventories



Passant N.R, 2002, SNAP 07 'Transport'



AIRPARIF, Local 2010 emission inventory, SNAP 07 'Exhaust' & 'Gasoline evaporation' from vehicles

Rather good agreement between observations and inventories

- ✓ Similar majority VOCs : **isopentane**, **toluene**
- ✓ **Ethylene** is dominant in inventories
- ✓ Gasoline evaporation : **butanes**; few propane
- ✓ Few **oxygenated compounds** in inventories

Multi-CO2 project (Oct./Nov. 2013)

OBJECTIVE : Identifying a solvent VOCs profile using PMF & halocarbons measurements

(Preliminary results)

Profile mostly represented by **aromatics** (**C8, toluene, benzene**), some **alkanes** (**pentanes, hexane,** propane, butane) and **oxygenated compounds** (methanol)

Conclusions

- **Road-traffic activities appear as the dominant VOCs emission source in megacities** (Hellén H. et al., 2003 ; Niedojadlo A. et al. 2007; Lanz V.A. et al., 2008)
- **Additional measurements (within a tunnel or outdoor ambient air) have helped to a better characterization of road trafic and solvent source profiles (PMF approach more robust when combined with source profiles studies)**
  - ➢ *Future processings with the PMF model will be performed (using several error estimation techniques…) in order to assess the robustness of our current results*
- **Significant improvement on the solvent source identification, which must be further consolidated**
  - ✓ *Source profile in agreement with N.R Passant (2002) and the AIRPARIF's inventory (2010)*

Acknowledgements

This work was supported by the CEA, CNRS, IPSL, Ile-de-France region funds, the PRIMEQUAL FRANCIPOL/PREQUALIF projects and the EU-ANR MEGAPOLI. T. Le Priol and J.F Le Petit (CEREMA) are also acknowledged for the logistical assistance in the tunnel campaign organization. A. Baudic gratefully thanks all teams working within these projects, as well as the CEA for her doctoral grant.

AIRPARIF (2013), Local 2010 emission inventory for Paris city, www.airparif.asso.fr.

Ammoura L. et al. (2014), Atmospheric measurements of ratios between CO_2 and co-emitted species from traffic: a tunnel study in the Paris megacity and a comparison with the regional emission inventory (submitted in ACPD)

Gaimoz C. et al. (2011), Volatile Organic Compounds (VOC) sources in Paris in spring 2007. Part II: Source apportionment, Environmental Chemistry, 8, 91-103.

Passant N.R. (2002), Speciation of UK emissions of non-methane organic compounds, AEAT, Report n°0545, Issue 1, 289 p.