Section S1 – Characterization of road-traffic, residential wood-burning and domestic natural gas consumption sources from near-field measurements performed within the Paris region.

S1.1 – Highway tunnel experiment (2012).

Within the framework of the 'PRIMEQUAL/PREQUALIF' program, measurements of gas-phase and particulate-phase pollutants were conducted at the Guy Môquet tunnel (coordinates: 48°77'N, 02°39'E); a motorway (A86) tunnel which is located in Thiais (94, Val-de-Marne dept), about 20 kilometers southeast of inner Paris centre. A further description on the tunnel and the traffic situation is also available in Touaty and Bonsang (2000) and Ammoura et al. (2014).

Atmospheric measurements were performed within the longitudinal ventilation system located inside the tunnel. Contained in a galvanized steel duct (situated inside this vent outlet), the sampling lines were connected to the analyzers, which were installed in a rolltainer located on the roof of the tunnel. Air samplings were continuously measured from 28 September to 6 October 2012, representing 6 working days and 3 weekend days. A few VOC measurements outside the tunnel were also carried out on 2 October 2012. The analytical equipment has been previously described in Ammoura et al. (2014) and is therefore briefly mentioned only for VOCs.

Air samples extracted in-situ were continuously measured using two automated GCs-FID in order to quantify both light (C_2-C_6) and heavier (C_6-C_{12}) NMHCs emitted from vehicular emissions. An in-depth description of the instruments, sampling set up and technical information (sampling flows, preconcentration, desorption-heating times, types of traps and columns...) can be found in Gros et al. (2011). Around 42 hydrocarbons (including alkanes, alkenes, alkynes, dienes and aromatics) were measured with a time resolution of 30 minutes. One calibration was performed during the campaign (1 October 2012) and consisted of three injections of a NPL gas mixture. In addition, a PTR-MS was also installed near GCs-FID using the same main inlet line. Protonated masses from m/z 31.0 to 280.0 were measured with a resolution time of 5 minutes. The five selected masses for this study were m/z 33.0 (methanol), 42.0 (acetonitrile), 45.0 (acetaldehyde), 59.0 (acetone) and 71.0 (MVK+MACR+ISOPOOHs). The instrumental background was subtracted from the measured atmospheric signal and calibrations were performed with the GCU unit during the measurement campaign. The acquired atmospheric data were respectively delivered with ± 15 % (for GCs) and ± 20 % (for PTR-MS) uncertainties.

S1.2 – Wood combustion experiments (2013).

Within the framework of the ADEME (French Environment and Energy Management Agency) – 'CORTEA-CHAMPROBOIS' research project, wood combustion experiments were performed at INERIS in March 2013 using two kinds of Residential log Wood Stoves (RWS): old and modern technologies (primary *vs.* primary + secondary air inlets). Wood species used for combustion tests included pine (from pallet) and beech (logs, 12 % moisture).

Several fireplace experiments under combustion conditions (nominal and reduced outputs) were carried out for each wood species and each combustion device. For each combustion experiment, an undetermined amount of wood from pellet and about 4 kilograms of beech (2 logs) were burned. Measurements were performed in "controlled real" conditions in close field at about 20 m from emission exhaust of the RWS (dilution factor about 500). Combustion stoves were installed in the bottom vertical part of the INERIS' fire gallery, used as a dilution tunnel for this purpose. The fire gallery (size of about 3 x 3.5 x 50 m) has a controlled ventilation system that allows the extraction of combustion gases used for measurements. The system simulates dilution effects of the combustion emissions with the ambient air under constant operating conditions. Actual dilution ratios can be easily adjusted and determined using CO, CO_2 and air flow measurements. Samplings of diluted emissions allowed obtaining an average mixture of the exhausted gases for each combustion cycle. Each experiment lasted a couple of hours per day. Before each wood combustion test, the fire's gallery was ventilated with ambient air for about 2 hours. Details about these experiments can be found elsewhere (Albinet et al., 2015; Nalin et al., 2016).

For several experiments, an on-line PTR-MS was used for the measurement of VOC emissions at the close field sampling location. Isoprene (*m/z* 69.0), aromatics (*m/z* 79.0, 93.0 and 107.0) and oxygenated compounds (*m/z* 33.0, 42.0, 45.0, 59.0 and 71.0) were sequentially measured with a 1-min time resolution between 27th February and 06th March 2013. The instrumental background was subtracted from the measured atmospheric signal and calibrations were performed with the GCU unit after the measurement campaign.

Unfortunately, no on-line GC-FID instrument was available at the time of these measurements. For that reason, NMHC measurements have only been performed through the sampling of eight stainless-steel flasks (which have previously been evacuated and instantaneously filled in on site). Subsequently, they were analyzed using a Chrompack Varian 3400 GC-FID at the laboratory. An aliquot of air stored in the canister was analyzed by a two-step pre-concentration technique described in Bonsang and Kanakidou. (2001). Air samples were regularly calibrated by injecting 50 microliters (μl) of a standard mixture containing

approximately 100 ± 1.8 ppmv of major C_2-C_5 hydrocarbons. The injections of this certified gas mixture allowed verifying the reproducibility of the measurement (± 4 % on average) and calculating average response factors used to calibrate NMHCs.

S1.3 – Natural gas experiment (2015).

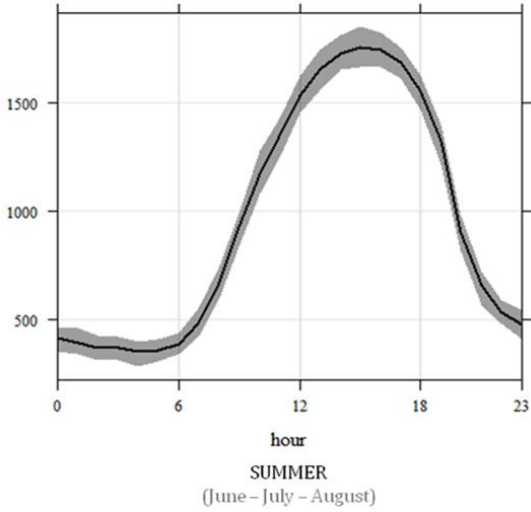
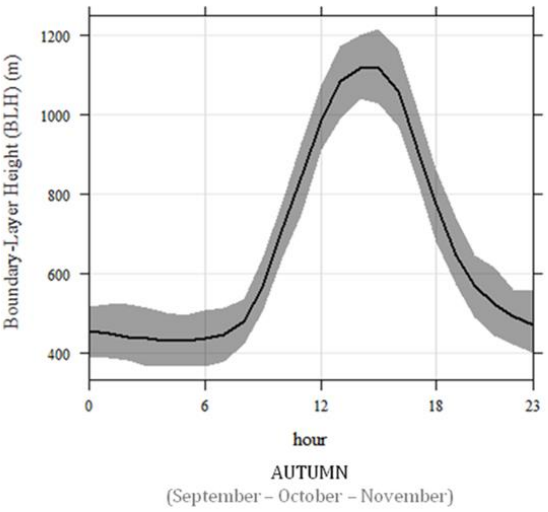
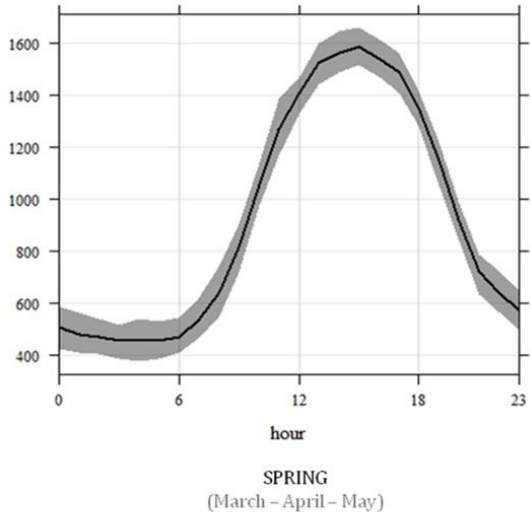
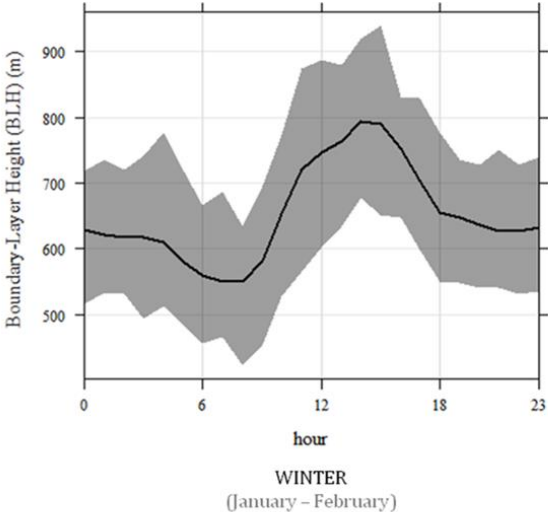
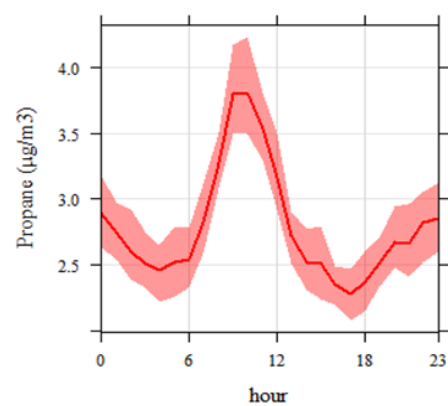
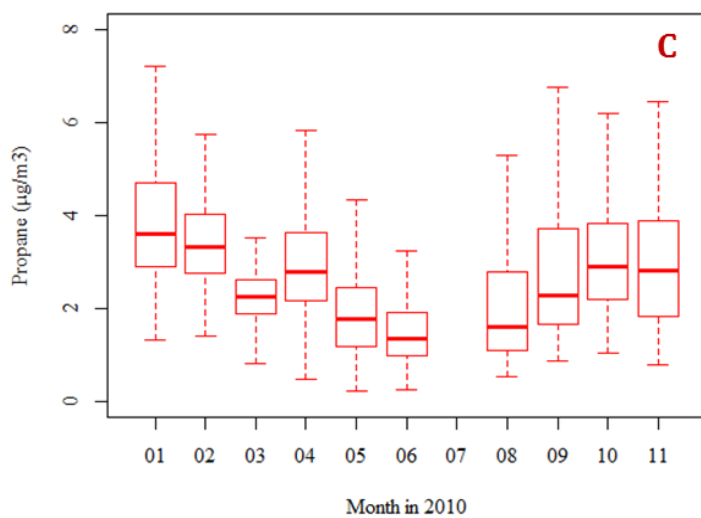
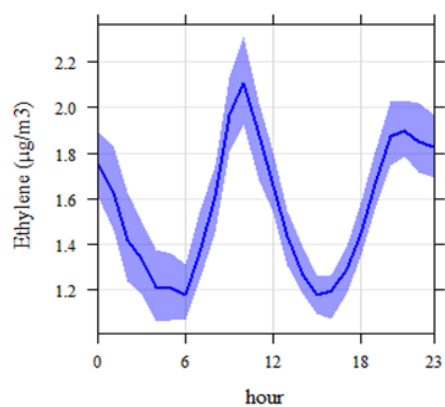
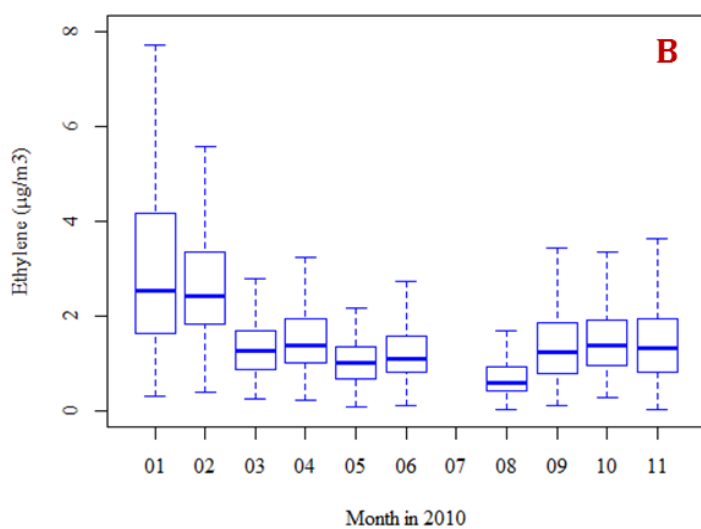
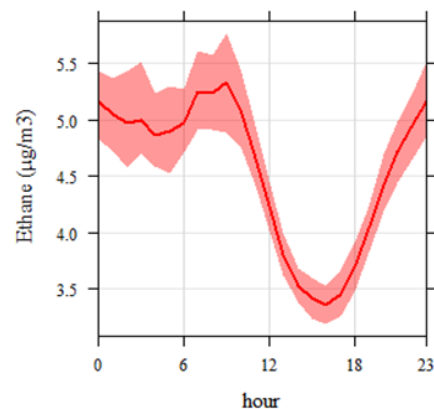
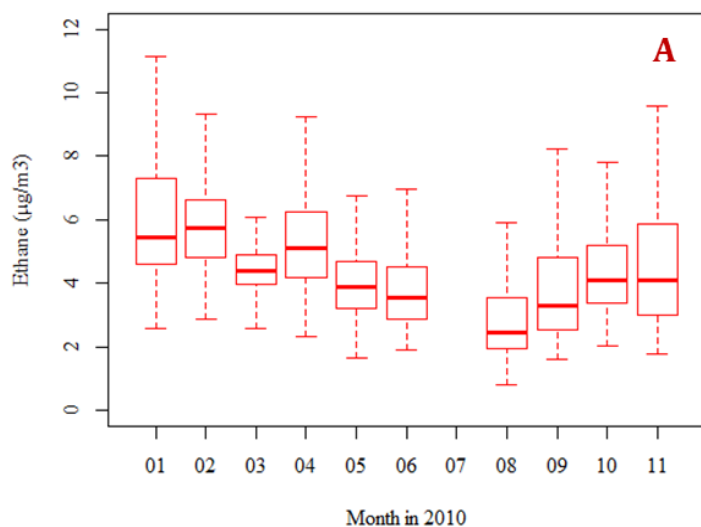
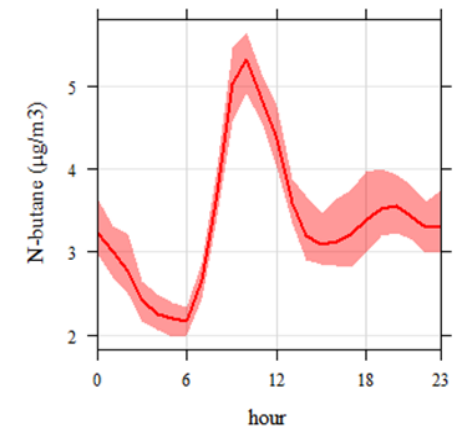
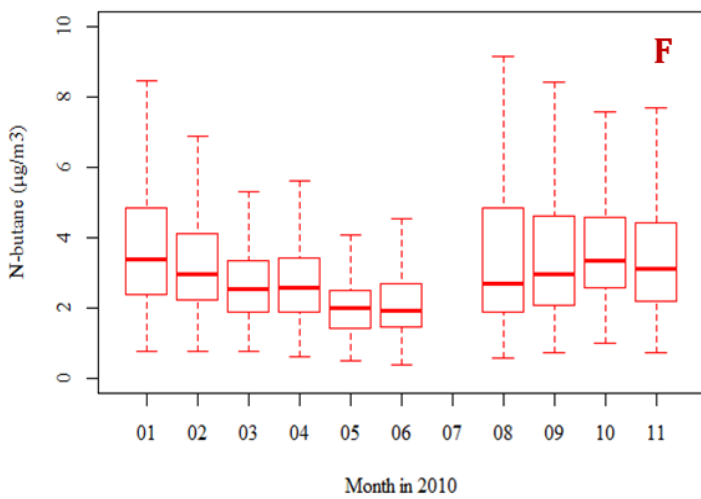
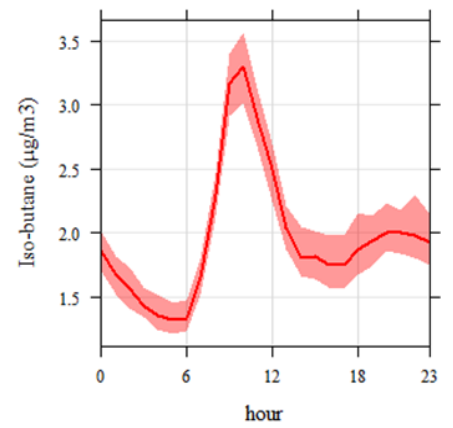
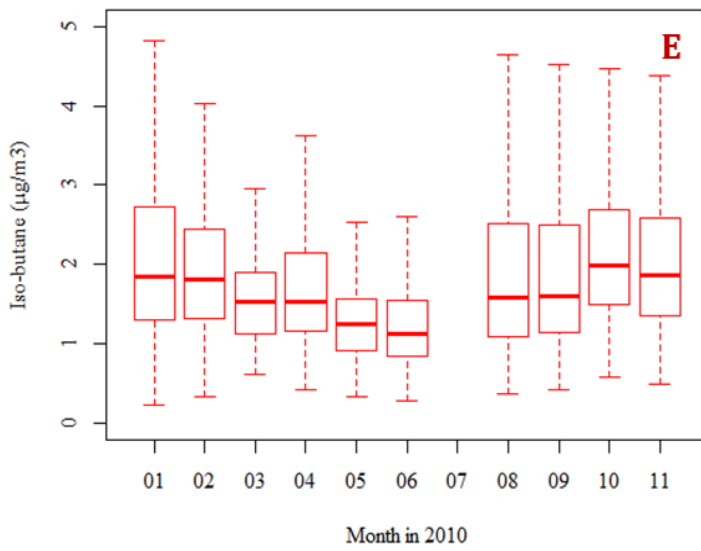
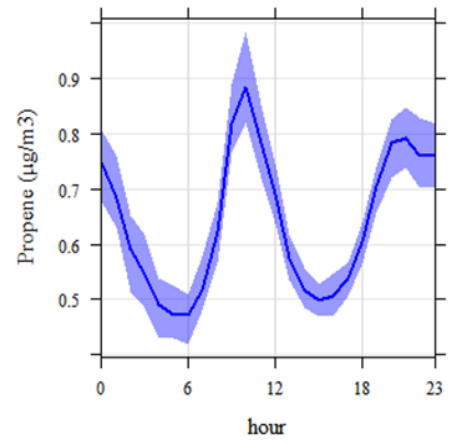
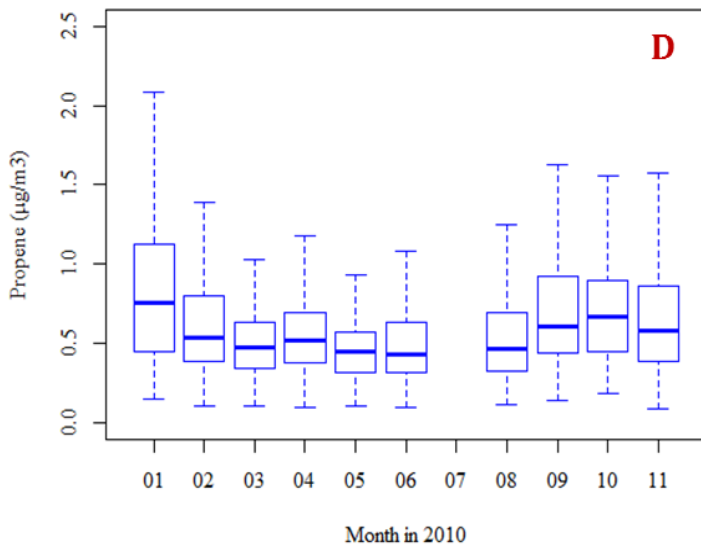
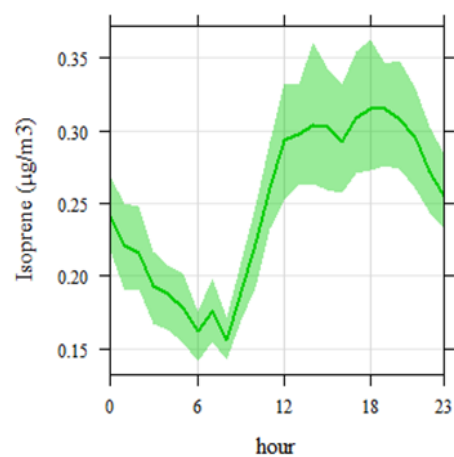
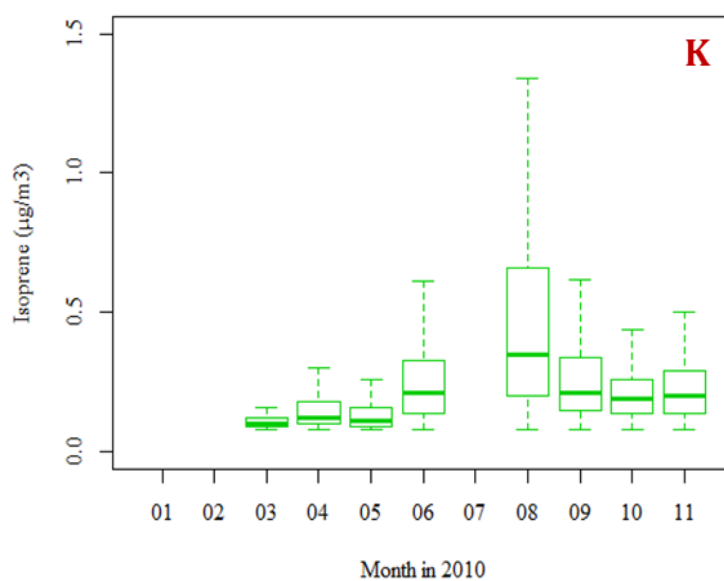
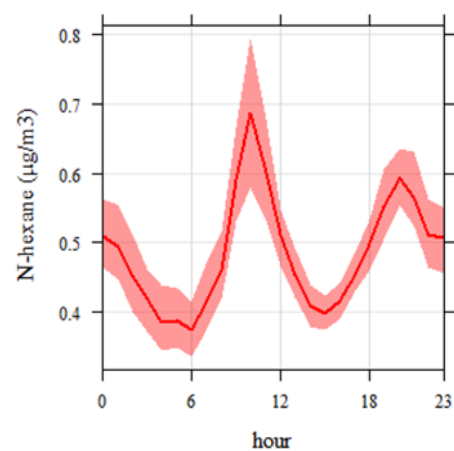
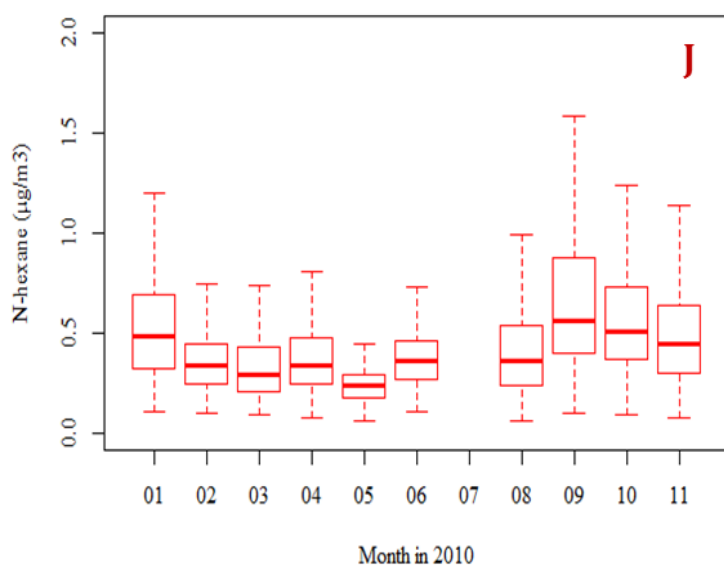
As a first approach to determine the NMHC composition of natural gas in Paris, near-field samplings were performed from a domestic gas flue using 3 stainless-steel flasks. They were analyzed during March 2015 with the laboratory GC-FID at LSCE.

Prior to analysis, these samples were diluted in order to obtain measurable concentrations within the linearity of the instrument. Typically, 0.5 ml of the gas stored in each canister was extracted with a syringe and diluted in 50 ml of ultra-pure helium. The final sample was then injected into the chromatographic system and analyzed under the standard operating conditions. 100 µl of the certified standard gas mixture were also used to calibrate these air samples.

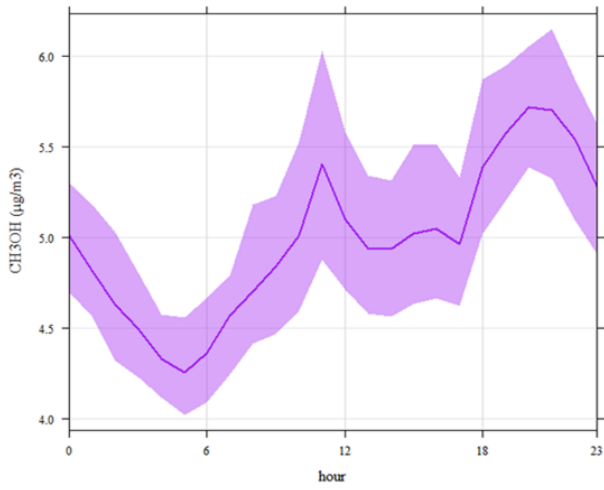
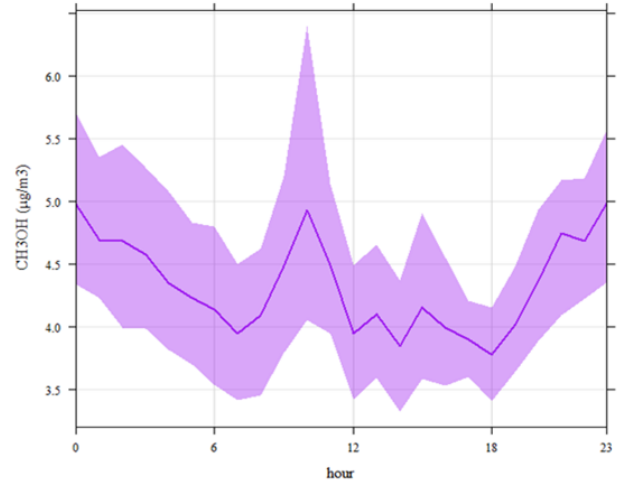
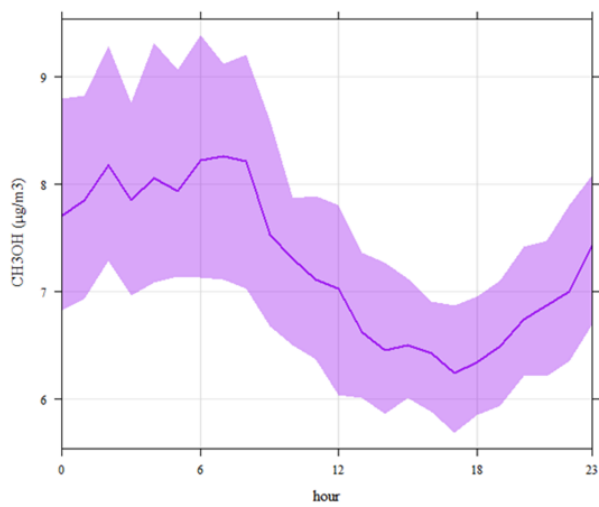
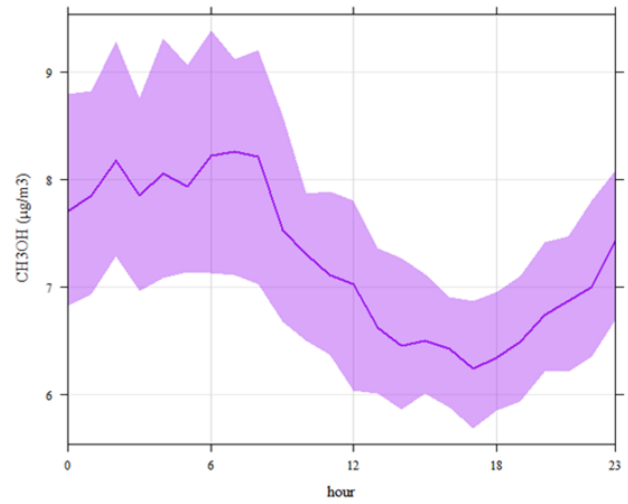
All aforementioned studies presented in this paper are summarized in **Table S1**.

Field Campaigns	Dates	Locations	Operating organism	On-line PTR-MS	On-line GC-FID	Off-line GC-FID	Additional data	References
Ambient EU-FP7 MEGAPOLI	January 15th – February 16th, 2010	LHVP	LCP LSCE	X	X		X	Dolgorouky et al. (2012)
Ambient PRIMEQUAL FRANCIPOL	March 24th – November 22nd, 2010	LHVP (on-line PTR-MS) 'Les Halles' station (on-line GC-FID)	LSCE AIRPARIF	X	X		X	
PRIMEQUAL PREQUALIF (Highway Tunnel)	September 28th – October 6th, 2012	Guy Môquet tunnel (Thiais)	LSCE	X	X		X	Ammoura et al. (2014)
ADEME – CORTEA CHAMPROBOIS (Fireplace)	March 5th – 6th, 2013	INERIS facility (Verneuil-en-Halatte)	LSCE INERIS	X		X	X	
Natural gas experiment	March 5th – 6th, 2015	Paris	LSCE			X		

Table S1 – Summary table restating the different field experiments presented in this study

Section S2 – Diurnal variations of the Boundary-Layer Height (BLH) per season. Solid lines correspond to hourly means and shaded areas indicate the 95 % confidence intervals of the mean.

Section S3 – Seasonal and diurnal variations of selected alkanes, alkenes, alkynes and dienes during the whole studied period.

(Left) Monthly box and whisker plots of ethane, ethylene, propane, propene, *iso*-butane, *n*-butane, acetylene, *iso*-pentane, *n*-pentane, *n*-hexane and isoprene (expressed as μg m^{-3}). Solid lines represent the median concentration and the box shows the InterQuartile Range (IQR). The bottom and top of the box depict the 25th (the first quartile) and the 75th (the third quartile) percentile. The ends of the whiskers correspond to the lowest and highest data still within 1.5 times the IQR of Q1 and Q3, respectively.
No VOC data was available in July (missing values) due to analytical problems on the operating GC-FID.

(Right) Diurnal variations of selected VOCs averaged over the whole sampling period.
Solid lines correspond to hourly means and shaded areas indicate the 95 % confidence intervals of the mean.

Section S3 – Diurnal variations of methanol per season.
Lines correspond to hourly means and shaded areas indicate the 95 % confidence intervals of the mean.

Section S4 – Correlation coefficients between the PMF modeled factors and independent parameters [CO, NO, NO$_2$, BC$_{ff}$, BC$_{wb}$, temperature and Total Volatile Organic Compounds (TVOCs) measured], based on the whole sampling campaigns.

Coefficients in bold represent strong correlations ($r > 0.5$) between PMF factors and independent parameters.

	B	WB	MVE	NGB	SOL	GE	CO	NO	NO$_2$	BC$_{ff}$	BC$_{wb}$	Temperature	t-VOCs
Biogenic source (B)	-	-0,30	0,15	-0,14	0,04	-0,14	-0,18	-0,13	-0,03	0,05	-0,23	**0,70**	0,20
Wood Burning (WB)		-	0,18	-0,19	0,23	0,05	**0,61**	0,30	0,29	0,19	**0,69**	-0,56	0,39
Motor Vehicle Exhaust (MVE)			-	-0,02	0,13	0,36	**0,53**	**0,54**	**0,64**	**0,52**	0,18	0,04	**0,60**
Natural Gas and Background (NGB)				-	0,00	-0,07	0,16	0,16	0,27	0,27	-0,04	-0,04	0,21
Solvents use (SOL)					-	-0,01	0,40	0,28	0,42	**0,50**	0,38	0,12	**0,66**
Gasoline Evaporation (GE)						-	0,23	0,35	0,26	0,07	-0,07	0,05	0,35

[1] Data available from 15 January to 10 September 2010.
Correlation coefficients were calculated for the whole campaign

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