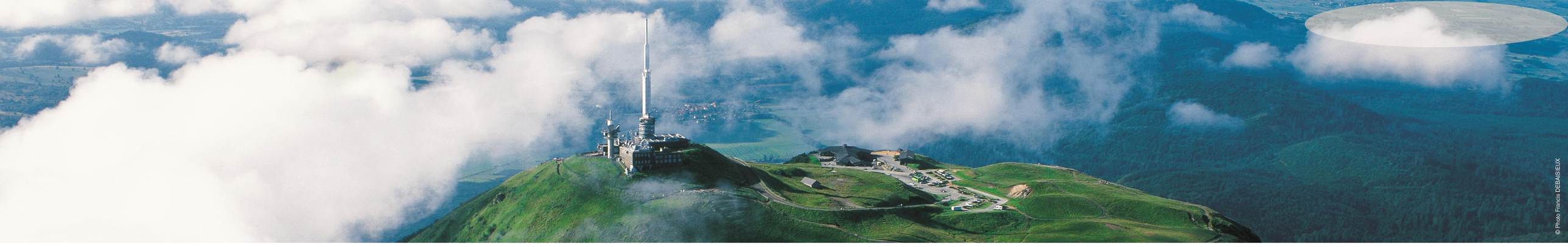

Volatile Organic Compounds at the puy de Dôme (PUY Global GAW) station (France. 1465m a.s.l.) since 2010.

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ABSTRACT : The high altitude puy de Dôme research station is located in central France (45° 46' N, 2° 57' E, 1465 m a.s.l.), 16km away from the city of Clermont-Ferrand. This station is a Global GAW station (ID: PUY), and is part of ACTRIS-2 Integrating Activities (H2020). At the summit, meteorological parameters including wind speed and direction, temperature, pressure, relative humidity and radiation, atmospheric trace gases (O3, NOx, SO2, CO2, CO), and aerosol physical, optical and chemical properties (particle size, black carbon, mass...) are measured since years. Selected volatile organic compounds (VOCs, including a large set of non-methane hydrocarbons and some terpenes (isoprene, α-pinene) were measured during summer 2010, spring 2011, summer 2011, winter 2012, winter 2013, summer 2013, summer 2015. The analysis of VOCs collected on Tenax/Carbosieve III cartridges was achieved by using thermo-desorption coupled gas-chromatography with mass spectrometry (GC-MS).

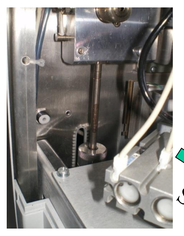
The results presented here are discussed in terms of observed levels seasonal variation, (i). Comparison with Hohenpeissenberg and Monte Cimone (ii). air mass origins (iii) impact of boundary layer height (iv) and sources of these gaseous pollutants using PCA (principal component analysis) method (v).

ANALYTICAL PROCEDURES

- **VOCs Sampling** on cartridges (Tenax TA)

VOC Analyses with an ATD-GC-MS
(Automatic Thermal Desorption – Gas Chromatography -Mass Spectrometer)

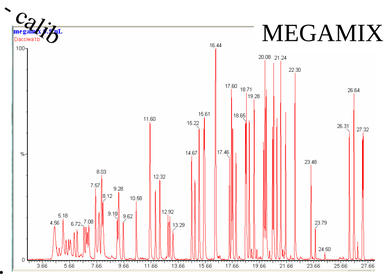
SAMPLING



DESORPTION

Standard - calib

MEGAMIX



ATD (Turbomatrix):
- desorption temperature of 300°C during 25 min.
- cryofocussing on 20 mg Carbosieve/Carbotrap at –10°C
-flash injection from –10°C to 300°C

GC-MS from Perkin Elmer : separation onto a RTX-5MS column (60m. 0.25 mm i.d.. 0.25 µm film thickness).
-Temp.program (GC): 30°C during 5 min. 5°C/min rise up to 160 °C, 40°/Min rise up to 250°C. Run time: 34 min
-Mass detection :electronic impact (70 eV. scanning 35 - 350 amu).

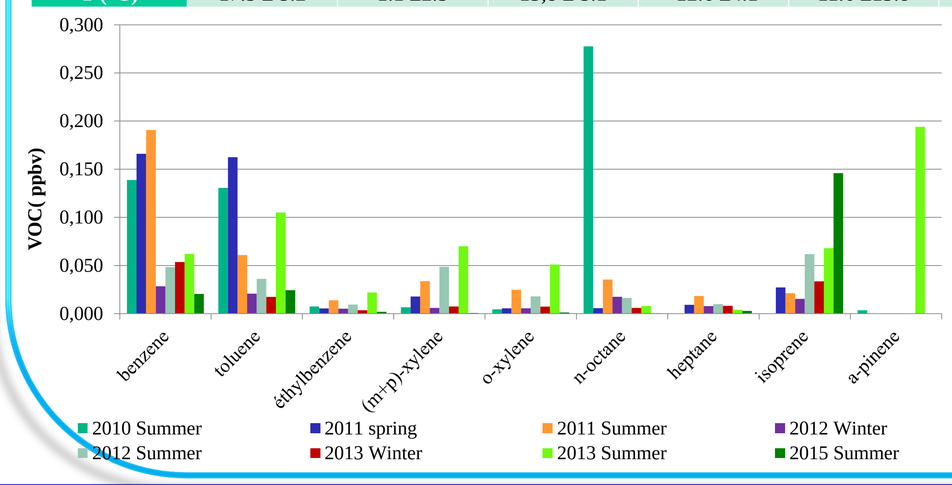
- **NOx measurement** with a TEI 42 CTL using ozone chemiluminescence method. and since 2012 a blue light converter for « true » NO2.

- ACTRIS intercomparison- Round Robin experiments for VOC and NOx (2012),
- GAW audit for Ozone (2016)
- **Ozone measurement** with a TEI 49i using UV absorption ..

i) OBSERVED LEVELS (VOCs)

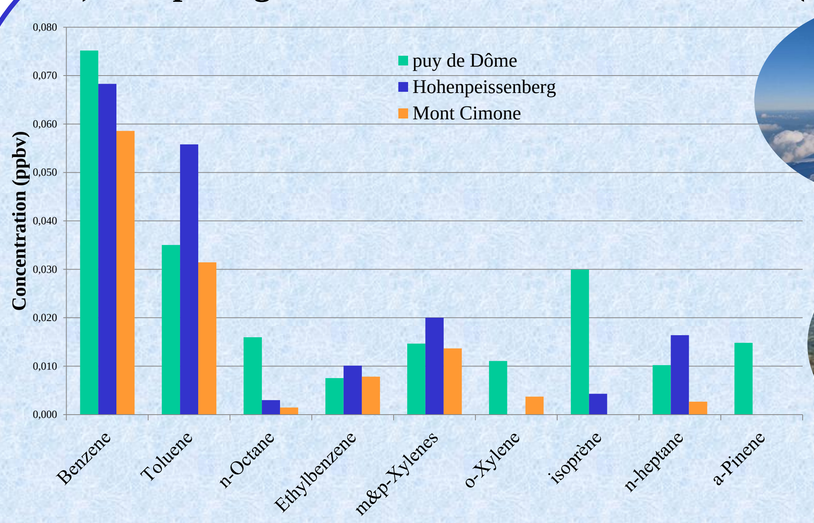
Mean and standard deviation mixing ratio of the measured compounds during the ACTRIS test campaigns .

VOC (ppb)	2010 Summer (nb : 48)	2011 Spring (nb : 20)	2011 Summer (nb : 72)	2012 Winter (nb : 82)	2012 Summer (nb : 57)	2013 Winter (nb : 63)	2013 Summer (nb : 51)	2015 Summer (nb : 266)
Benzene	0.139 ± 0.134	0.166 ± 0.239	0.191 ± 0.127	0.028 ± 0.102	0.048 ± 0.525	0.054 ± 0.156	0.062 ± 0.165	0.020 ± 0.024
Toluene	0.131 ± 0.281	0.163 ± 0.339	0.061 ± 0.378	0.021 ± 0.092	0.036 ± 0.223	0.017 ± 0.023	0.105 ± 0.162	0.024 ± 0.158
Ethylbenzene	0.007 ± 0,032	0.005 ± 0.018	0,014 ± 0.230	0.005 ± 0.005	0.009 ± 0.159	0.003 ± 0.009	0.022 ± 0.074	0.002 ± 0.205
(m+p)-xylene	0.007 ± 0,051	0.018 ± 0.052	0,034 ± 0.654	0.006 ± 0.013	0.049 ±1.081	0.007 ± 0.028	0.070 ± 0.162	0.001 ± 0.237
o-xylene	0.004 ± 0,104	0.006 ± 0.017	0,025 ± 0.292	0.006 ± 0.007	0.018 ± 0.322	0.007 ± 0.025	0.051± 0.089	0.001± 0.100
Octane	0.278 ± 0,665	0.006 ± 0.005	0,035 ± 1.994	0.018 ± 0.050	0.016 ± 0.170	0.006 ± 0.019	0.008 ± 0.162	3.77E-04 ± 0.017
Heptane	-	0.009 ± 0.012	0,018 ± 0.465	0.008 ± 0.029	0.010 ± 0.050	0.008 ± 0.008	0.004 ± 0.136	0.003 ± 0.013
Isoprene	-	0.027 ± 0.433	0,021 ± 0.122	0.015 ± 0.059	0.062 ± 0.218	0.033 ± 0.048	0.068 ± 0.131	0.146 ±0.321
α-pinene	0.004 ± 0,003	-	-	-	-	-	0.194 ± 0.249	-
Ozone	66 ± 12	49 ± 4	51 ± 10	38 ± 8	39.8 ±9.9	40.1 ± 6.8	47.6 ± 11.8	40.4 ± 9.0
NO	0.089 ± 0,326	0.177 ± 0.537	0,103 ± 2.043	0.179 ± 2.625	0.100± 2.660	0.133 ± 1.369	0.126 ± 0.275	0.10, ± 0.266
NO_2	2.139 ± 0,771	1.723 ± 0.767	0,969 ± 1.842	2.980 ±2.895	0.609 ±1.341	0.709 ± 1.445	0.432 ± 0.193	0.609 ± 1.341
T (°C)	17.3 ± 5.2	1.1 ±2.3	13,8 ± 5.1	-12.6 ±4.1	11.6 ±13.8	-4.0 ± 4.2	12.5 ±4.3	11.6 ± 3.9



- Three compounds measured mainly during all periods are benzene, toluene and isoprene in summer.
- Work on the installation of the cogwheel train took place during the summer of 2010 to the end of June 2012. This work was able to bring local contamination during certain periods, such as the emission of BTEX (Benzene, toluene, Ethylbenzene, xylene).

ii) Comparing with other stations or observatoris (VOCs)

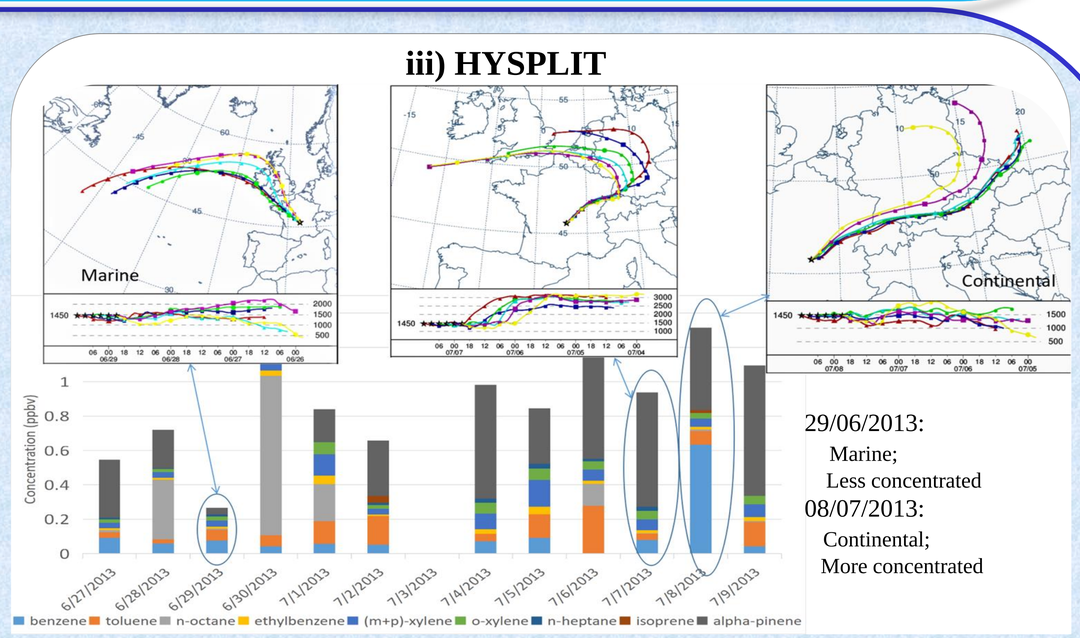


Monte Cimone

Hohenpeissenberg

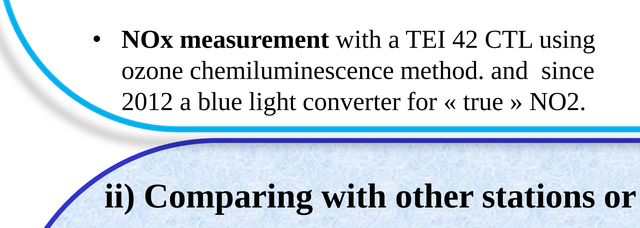
puy de Dôme

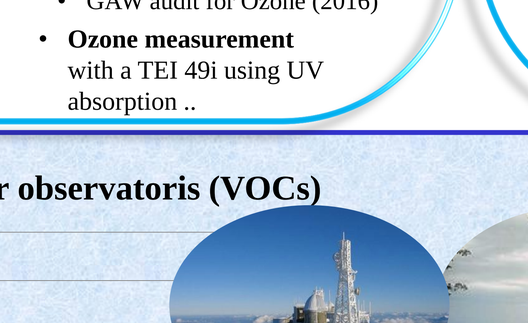
iii) HYSPLIT



29/06/2013:
Marine;
Less concentrated
08/07/2013:
Continental;
More concentrated

iv) Free Troposphere(FT)/ Boundary Layer (BL)

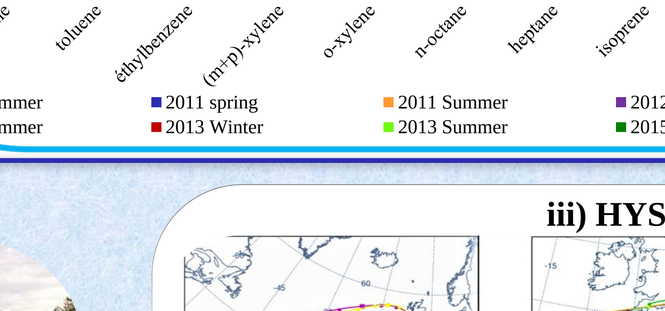




→Impact on BLH on VOC concentrations :
- ❖ FT: Low concentration, BL : High concentration except Ozone

→pdD over FT during night and in BL during day

→Isoprene concentration at the pdD station depends on :
- ❖Emission from plants/trees (higher during the day)
- ❖Boundary Layer Height



	F1	F2	F3	F4
Benzene	0,260	0,098	0,126	**0,340**
Toluene	**0,960**	0,004	0,006	0,003
n-Octane	**0,897**	0,005	0,023	0,038
Ethylbenzene	**0,943**	0,001	0,025	0,021
(m+p)-Xylene	**0,939**	0,001	0,026	0,023
o-Xylene	**0,937**	0,002	0,024	0,024
n-Heptane	**0,772**	0,039	0,013	0,079
Isoprene	0,041	0,153	**0,380**	0,173
Temperature	0,016	0,003	**0,658**	0,146
Ozone	0,028	0,011	**0,438**	0,318
NO	0,004	**0,807**	0,014	0,106
NO2	0,059	**0,759**	0,044	0,064

	D1	D2	D3	D4	D5
Benzene	0,054	0,000	0,000	**0,851**	0,059
Toluene	**0,861**	0,001	0,000	0,108	0,004
n-Octane	**0,956**	0,004	0,006	0,002	0,000
Ethylbenzene	**0,984**	0,002	0,001	0,008	0,000
(m+p)-Xylene	**0,986**	0,002	0,001	0,006	0,000
o-Xylene	**0,983**	0,002	0,002	0,006	0,000
n-Heptane	**0,529**	0,000	0,000	**0,360**	0,034
Isoprene	0,001	0,005	0,007	0,108	**0,809**
Temperature	0,002	0,006	**0,645**	0,010	**0,200**
Ozone	0,006	0,000	**0,893**	0,007	0,010
NO	0,000	**0,932**	0,002	0,002	0,000
NO2	0,021	**0,891**	0,012	0,003	0,002

v) Principal component analysis of Summer 2015

PCA is used to identify major factor that controls major trace gase concentrations including ambient VOC at puy de Dôme station.

After rotation →
D1: Anthropogenic source *(44.85% variability)*;
D2: Vehicle Source *(15.38% variability)*;
D3:Photochemical Source *(13.09% variability)*;
D4: Source "long distance transport" *(12.27% variability)*;
D5: Biogenic source *(9.32% variability)*.

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