

# Natural vs. anthropogenic: combined measurements of methane and volatile organic compounds (VOCs) for investigating sources of methane emissions

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## 1. Goal of the study

Methane is the second globally most abundant anthropogenic greenhouse gas, whose emissions contribute more than 1/3 of today's anthropogenic warming [1, 2]. Methane is emitted from the production and transport of coal and natural gas, as well as from livestock, agricultural practices and natural sources as well. Volatile organic compounds (VOCs) constitute less than 0.1% of the total atmospheric composition; however, their emissions and further atmospheric photo-oxidation reactions produce ozone and secondary organic aerosols which have adverse climate effects. Methane and VOCs can be co-emitted by the same natural or anthropogenic source. Here, measurements of methane and VOCs concentrations are combined to investigate the fingerprint of these sources.

## 2. Field site

The site is located in the countryside 40 km west of Paris (France, 45° 39'4.09"N). The agricultural field consists of 20 ha of land managed with a crop rotation of: corn, winter wheat, winter barley, mustard since the year 2000 and, this year, winter wheat. The cropland is surrounded by a farm (which houses dairy cattle, and a methaniser), other cultivated fields, towns (~1000 inhabitants) and roads.



## 3. Methods

Methane was measured with a quantum cascade laser (QCL) during the campaign of June-July 2016; whereas a cavity ring down spectroscopy instrument (CRDS, Picarro G2201-i) was used from October-November 2016. VOCs were measured by proton transfer reaction mass spectrometry (PTR-MS) and gas chromatography (GC-FID). The methane carbon isotopes were used to determine the isotopic fingerprint of methane and compared with some available literature.

## 4. Preliminary results

### 4.1 Campaign June-July 2016

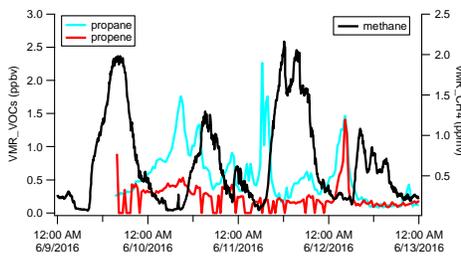


Fig.1. Methane and VOCs might have similar sources of emission.

### 4.2 VOCs Fingerprint of specific nearby sources

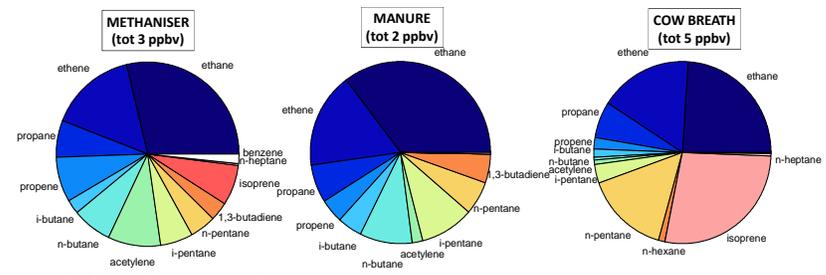


Fig.2. The VOCs fingerprint of specific sources of emission nearby the sampling site was investigated. Preliminary results show the variety of VOCs emitted by these sources.

### 4.3 Campaign Oct-Nov 2016: Ambient data of methane, C isotopes and VOCs

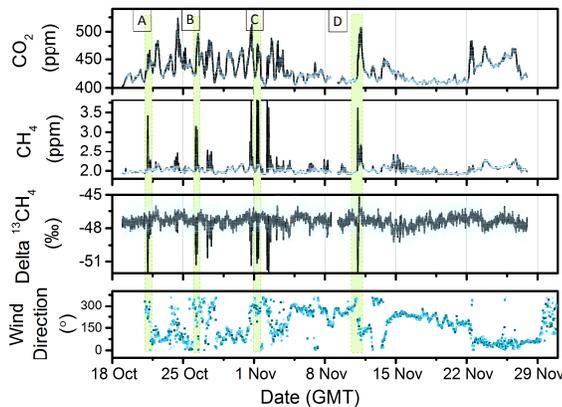


Fig.3. Data from Oct-Nov 2016.

CH<sub>4</sub> has sporadic peaks of up to 4 ppm corresponding to emissions by specific sources. The tendency of δ<sup>13</sup>CH<sub>4</sub> to lighter values during the dominant methane peaks and similar wind direction (green highlights in Fig. 3) suggests that there is one major source during Oct-Nov 2016.

Preliminary analysis of VOCs data did not show any specific correlation with methane for these events.

The isotopic composition of CH<sub>4</sub> for the four highlighted events in Fig. 3 were estimated using the Miller-Tans plot technique [3] in Fig. 4. Here the δ<sup>13</sup>CH<sub>4</sub>\*CH<sub>4</sub> values are plotted against CH<sub>4</sub> to calculate the isotopic signature of the CH<sub>4</sub> source in unstable background conditions.

The slopes of the regressions represent the CH<sub>4</sub> signature which indicate that these emissions are biogenic and likely to be related to animal ruminants or manure which are reported to have δ<sup>13</sup>CH<sub>4</sub> signatures of between -59‰-65‰ [4], however can vary widely depending on diet [5].

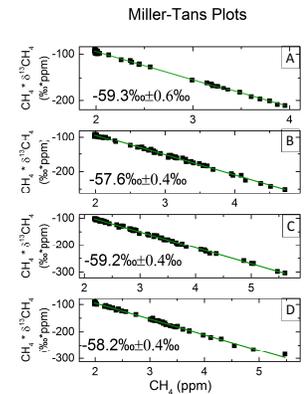


Fig.4. isotopic signatures of peaks highlighted in fig.3

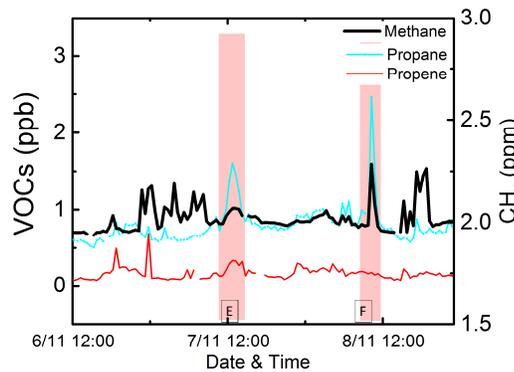


Fig.5. Methane, propane and propene during November 2016.

A preliminary comparison with Propane and Propene on November 7<sup>th</sup> suggests that there are a number of non-biogenic emissions. Two emission peaks were selected for further analysis and their isotopic fingerprints estimated in Fig. 6.

PTRMS data was compared with Methane for the peak E (Fig. 7.) as its source was unclear. A number of different molecules (alkenes, oxygenated as well as aromatics) seem to be well correlated suggesting the need for further investigation of the source.

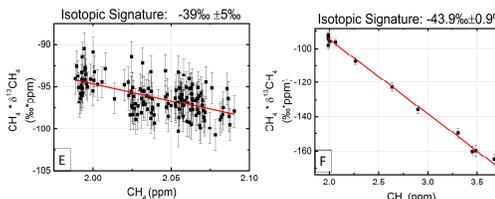


Fig.6. Isotopic signatures for the peaks highlighted in red in Fig. 5.

The isotopic signatures estimated by the Miller-Tans plots of the peaks highlighted in red in Fig.5 suggest that these particular emissions originate from fossil fuel sources. Peak F has strong correlation with propane (Fig.5) and ethane suggesting a natural gas source. The origin of peak E is still unknown as there are a number of VOCs correlated with CH<sub>4</sub> as shown in Fig.7.

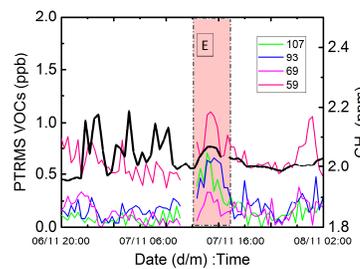


Fig.7. Covariations between methane and VOCs.

## 5. Conclusion and Perspectives

Methane and VOCs data are compared in this study to determine their source of emission from a site affected by various sources. Preliminary analysis show clear covariability when the source is anthropogenic. Further studies of samples collected at the sources will help determining the exact sources of ambient data.

## Acknowledgments

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