VOLATILE ORGANIC COMPOUNDS EMISSIONS FROM CATTLE SLURRY ON AN AGRICULTURAL SOIL

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Introduction

Volatile organic compounds (VOC) are essential drivers of atmospheric chemistry and precursors of pollutants constituting a threat for human health and the environment : ozone and secondary organic aerosols. 90% of VOC are biogenic (BVOC), and are not exhaustively quantified. In particular, managed ecosystems are the largest potential emitter of BVOC. It is estimated that 55% of the emissions come from forest, 27% from agriculture and 18% from other land use. Current estimates however do not account satisfactorily for emissions linked with agricultural practices due to a lack of data and in particular emissions following slurry application.

Objectives

Measurements of VOC emissions from cattle slurry applied on a silt loam soil in laboratory

Estimation VOC flux

Identification of chemical families VOC

Evaluation of impact cattle slurry on soil

Material and Methods

Experiment device

We simulated a spreading slurry under controled conditions.

The samples deposited over a aluminium tray are introduced in a glass tube in which cleaned air was flowed through at a controlled flow rate (cf characterics on table.

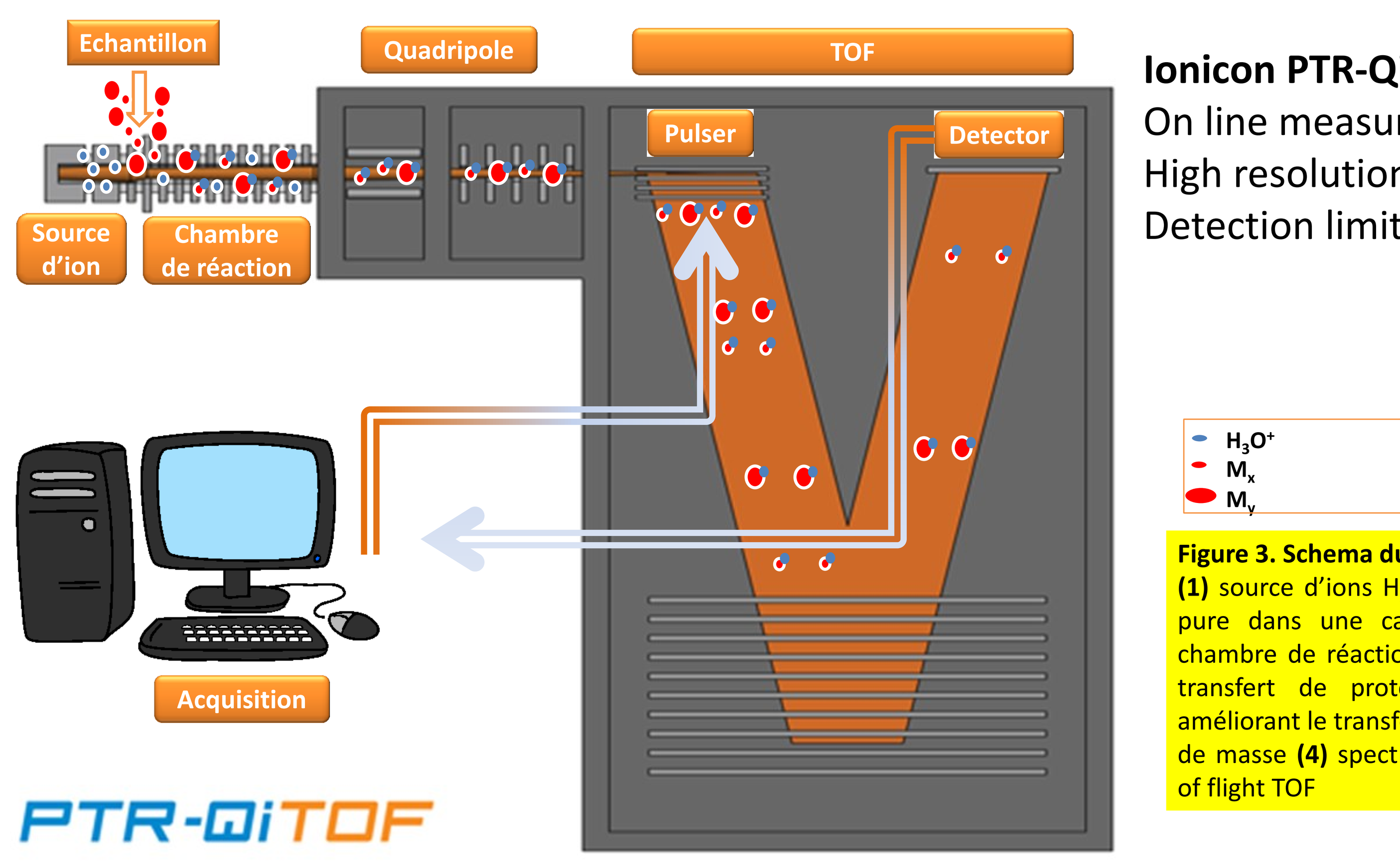
The outgoing air was sampled with an Ionicon PTR-QiTOF-MS (Proton Transfer Reaction - Quadrupole Ion Time of Flight Mass Spectrometry).

VOC emissions of system (blank), of soil sample and of soil mixed with slurry were measured.

Material and Methods characteristics		
SOIL (top 15cm)	**SLURRY**	**Glass Chamber**
silt loam	Cattle origin	Lengh : 40cm
clay : 18.9%	C/N : 8.7	Diameter :
silt : 71.3%	Organic Matter : 6.7%	Zero Air flow : 200 mlmin^{-1}
Humidity : 22%	Humidity : 91%	Exchange area : 100 cm²
Organic content : 20 gCkg^{-1}	Total carbone : 34 g kg^{-1}	Soil Mass :
pH in water : 7.6		Slurry Proportion :
Bulk density : 1.3 kg dm^{-3}		

COV measurement by PTR-QiTof-MS

Using an high-resolution PTR-QiTOF-MS (Proton Transfer Reaction - Quadrupole Ion Time of Flight Mass Spectrometry, Ionicon) coupled with a fast GC (Gas Chromatography).



Ionicon PTR-QiTOF-MS

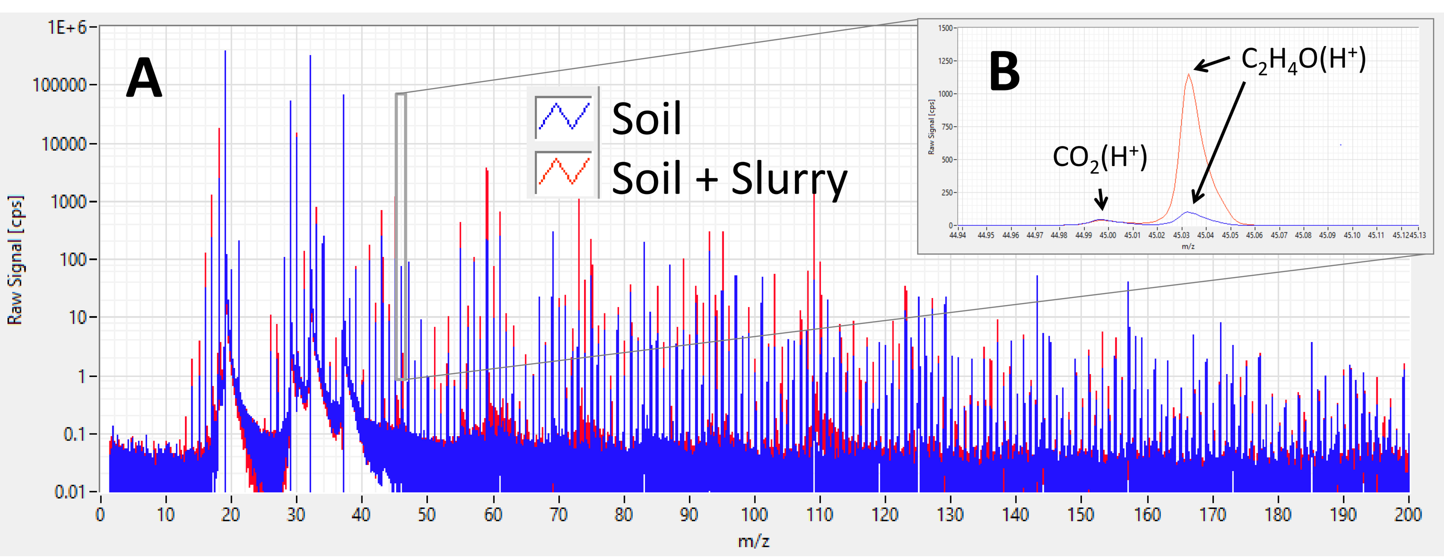
On line measurements

High resolution

Detection limit < 10pptv

Figure 3. Schema du PTR-MS-Qi-TOF. **(1)** source d'ions H_3O^+ produits par injection d'eau pure dans une cathode creuse à décharge **(2)** chambre de réaction (drift-tube) où la réaction de transfert de proton s'effectue, **(3)** quadripôle améliorant le transfert des ions vers le spectromètre de masse **(4)** spectromètre de masse de type time of flight TOF

Results

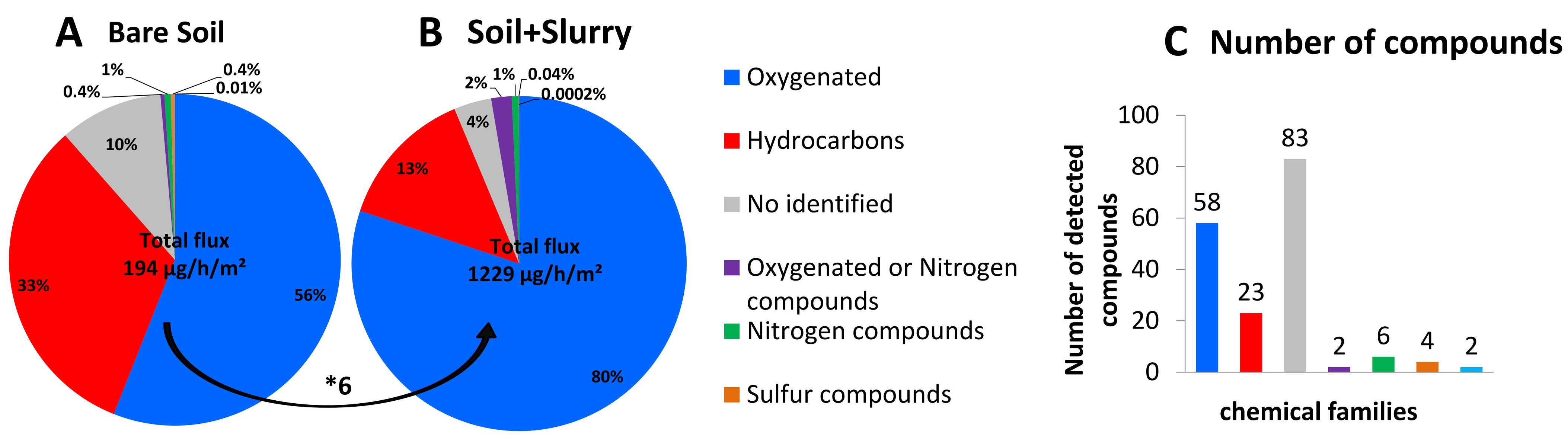


(A) PTR-MS spectra of soil and soil + slurry.

Plot of ion count rate (in Logarithmic scale) versus m/z (mass number / charge number of each ion). Only the low mass region is displayed (total range measured m/z 0-500)

(B) Zoom on 2 compounds separation at m/z 45

VOC Flux and Classification by chemical families



Flux contribution by chemical families in bare soil (A) and soil+slurry (B)

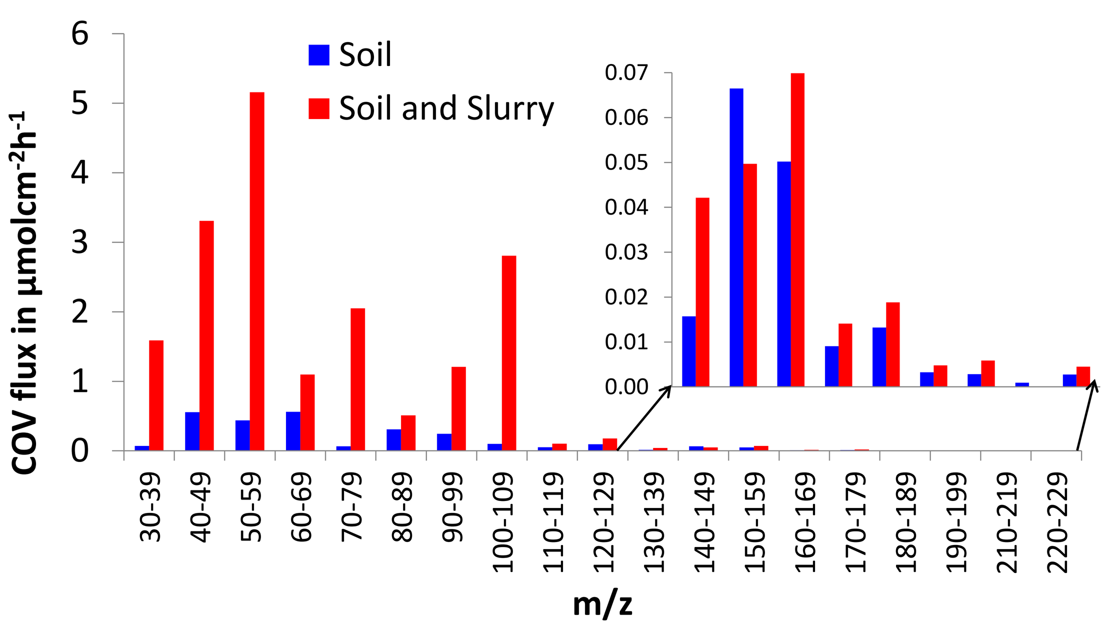
- ✓ COV emissions is 6 times higher in soil with slurry than soil alone.
- ✓ Oxygenated compounds and hydrocarbons are the predominant contributor emissions (>80%).
- ✓ Nitrogen, sulfur and chlorinated compounds are emitted in very low quantities

Number of potential detected compounds per chemical families (C)

i.e.: In fig B, the 54 oxygenated compounds = 79% from total flux

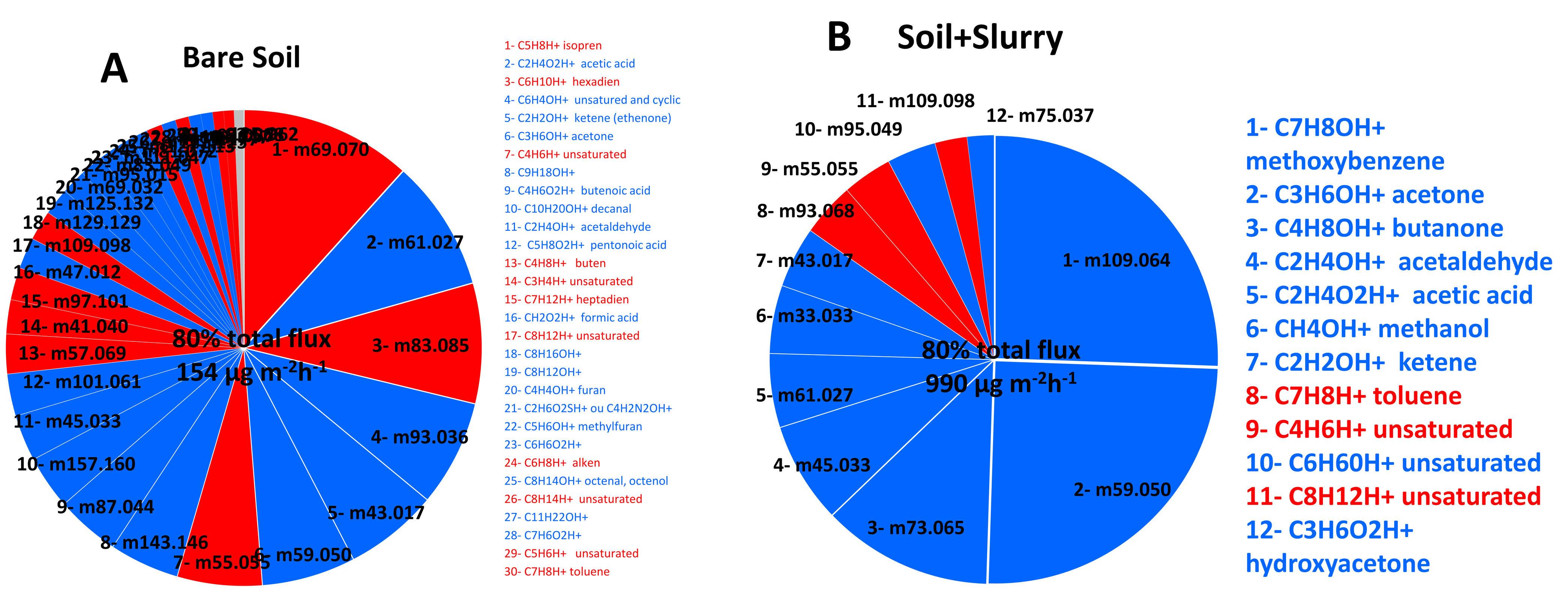
- ✓ The contribution to the total flux of each unidentified compound is negligible on soil+slurry
- ✓ …

VOC classification by mass ranges



COV flux of bare soil and soil+slurry categorized by mass ranges

- ✓ Soil+slurry emitted higher COV fluxes than bare soil
- ✓ Most VOCs are below 110 uma



Fractional contribution to 80% total flux of m/z ions species in bare soil (A) and soil+slurry (B), brut formulea and their potentially contributing compounds.

- ✓ The emissions profile of 2 samples are completely different .
- ✓ 12 compounds represents 80% total flux in soil+slurry, 32 for bare soil.
- ✓ Methoxybenzene and acetone seem to be predominant in soil+slurry, isopropen, acetic acid, cetone and unsatured compounds in bare soil.
- ✓ The slurry is a physical,chemical or biological barrier for few compounds emitted by soil and not by soil+slurry (isopren, hexadien, butanoic acid, formic acid, furan)

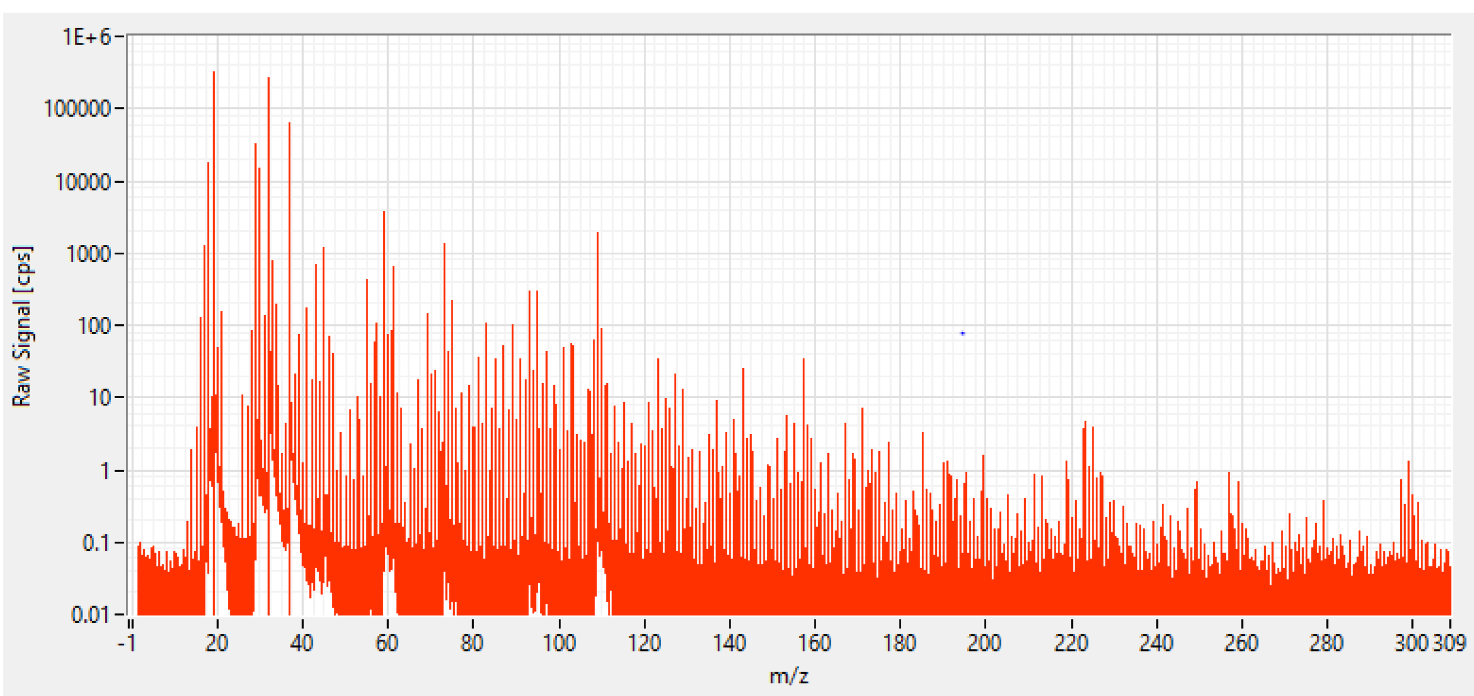
Conclusion

Contribution par rapport emission biblio?

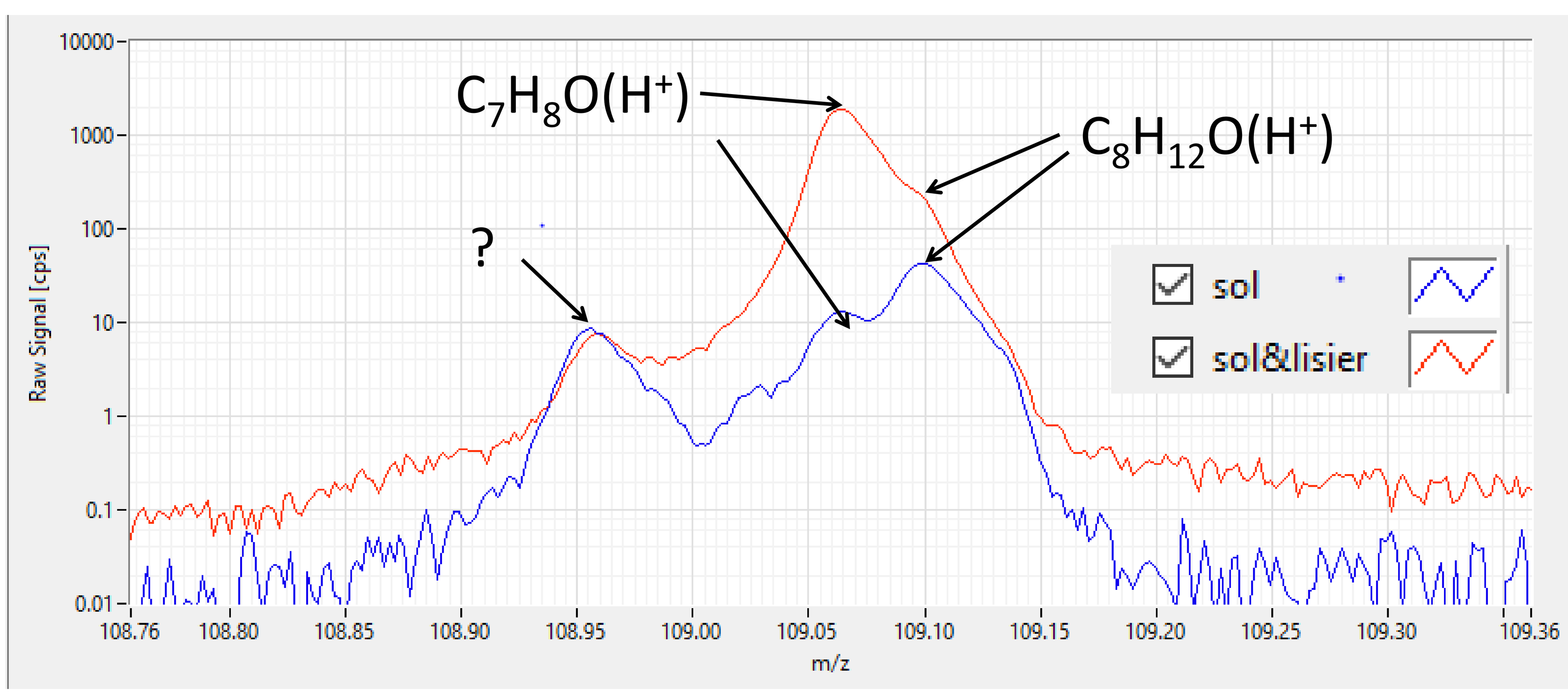
Perspectives

- Improve and confirm C OV identification and quantification by using µGC (Gas chromatography) and other ionization modes
- study temporal emissions
- Apply to the study to :
  . the emissions from other residual organic products (husbandry, agro-industry and urban), quantification and specificities
  . the effects of meteorological conditions, soil conditions and agricultural practices: application rate and technique

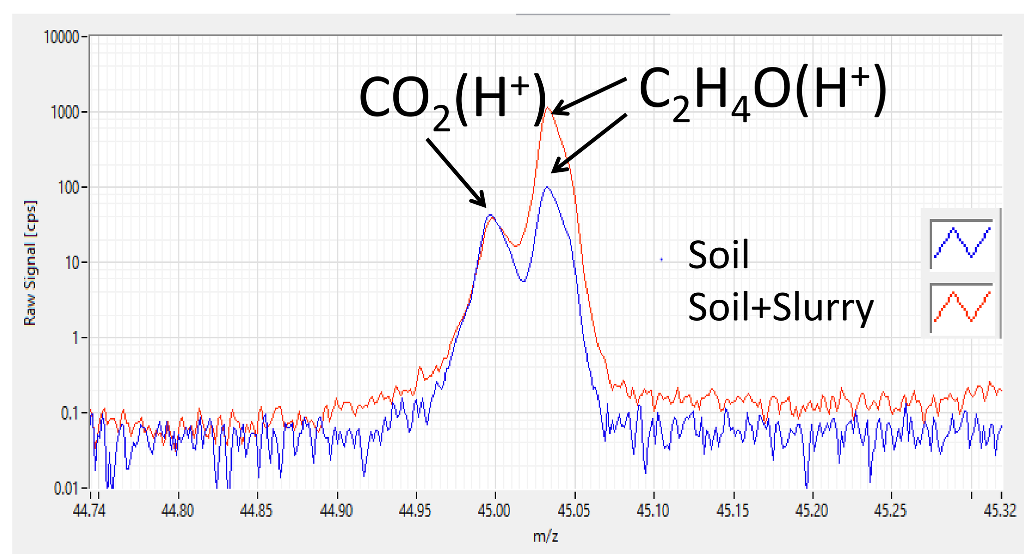
Acknowledgements : The PTR-MS is a service of the national research infrastructure **ANAEE-France** (Analysis and Experimentation on Ecosystems - France)



Raw Signal [cps]
m/z



C7H8O(H+)
C8H12O(H+)
?
sol
sol&lisier
Raw Signal [cps]
m/z



CO2(H+)
C2H4O(H+)
Soil
Soil+Slurry
Raw Signal [cps]
m/z

INTRODUCTION / CONTEXTE cf lefe Raluca et CoV3ER BL et PAPIER icos BL
Impact environnementaux et sanitaires des COV
Formation d'O3 troposphérique & concentration de gaz à effet de serre dans l'atmosphère
Les composés organiques volatils (COV) sont des composants clé en chimie atmosphérique. Ils participent à des réactions photochimiques dans la basse atmosphère et jouent ainsi un rôle majeur dans le cycle de l'ozone troposphérique et la formation d'aérosols organiques secondaires. A l'échelle globale, ces COV sont à 10% d'origine anthropique et à 90% d'origine biotique.

+ cf 3B manure manageùent July 2015

Mat et Meth :

Results

Calculer les COV en flux
Unités : mlc / g / carbone / azote?

Graphes :

- FLUX les plus abondants : 1 histogramme ou 3 camemberts
  - Sol
  - Lisier
  - sol+Lisier
  - 3 replicats? Afficher varaibilite

  Est-ce les mêmes COV ?

  Montrer :
  - puits : disparition (depot / adsorption / dissolution
  - sources : apparition

  - classement par masses :
  - classement par fonction chimique :

    HC saturé / insaturé : alcane alcène alcyne
    oxygéné : alcool cetone aldehyde acide ether ester
    Azoté :

Figures mat et met

Schema dispositif

Schema ptrms

Spectre

Séparation GC?

Figures results

Spectre
Zoom sur 2 masses proches INTEGRATION
Séparation GC?
Identification : mode H3O+ ::NO

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Conclusion perspectives