First measurements of VOC fluxes by eddy covariance with a PTR-QI-TOF-MS on a wheat barley field at anthesis at the FR-GRI ICOS site

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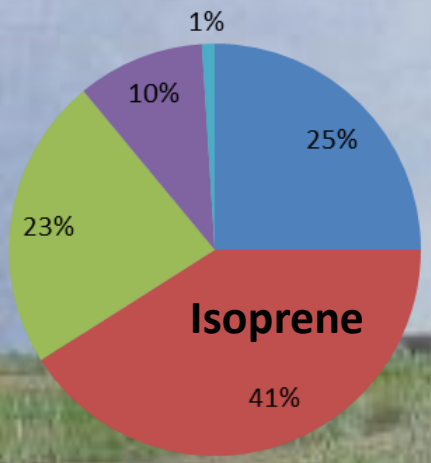
Overview

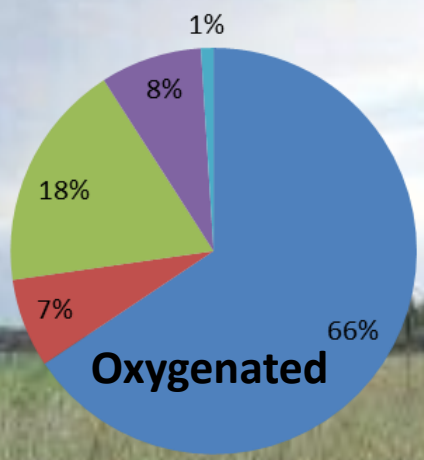
- Context
- Material and methods
- Eddy covariance fluxes
- Conclusions
- Next steps

Context

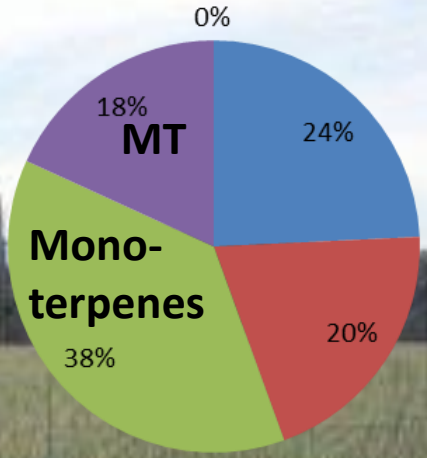
- Volatile organic compounds (VOC) as an atmospheric pollutant
  - VOC are precursors of ozone and secondary organic aerosols
  - 80% of COV are from biological sources
  - In Europe: **55% forest**, 27% agriculture, 18% grasslands



Forest



Crops



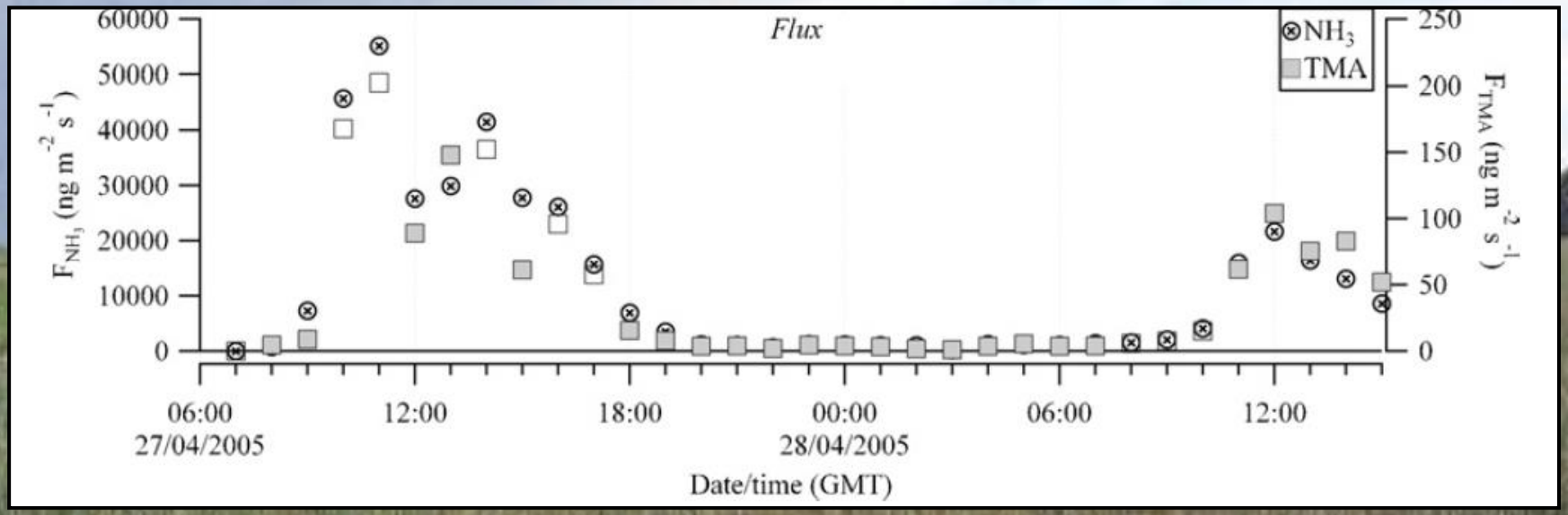
Other land use

{Karl, 2009 #14761}

Context

- Emissions by agriculture are not well documented
  - Which compounds and seasonality ?
  - Manure and farmyard applications ?
  - Litter decomposition and residue incorporation ?
  - Emissions by farms, storage ?

Trimethylamine emissions following slurry spreading ~ 0.5% of NH_3 losses



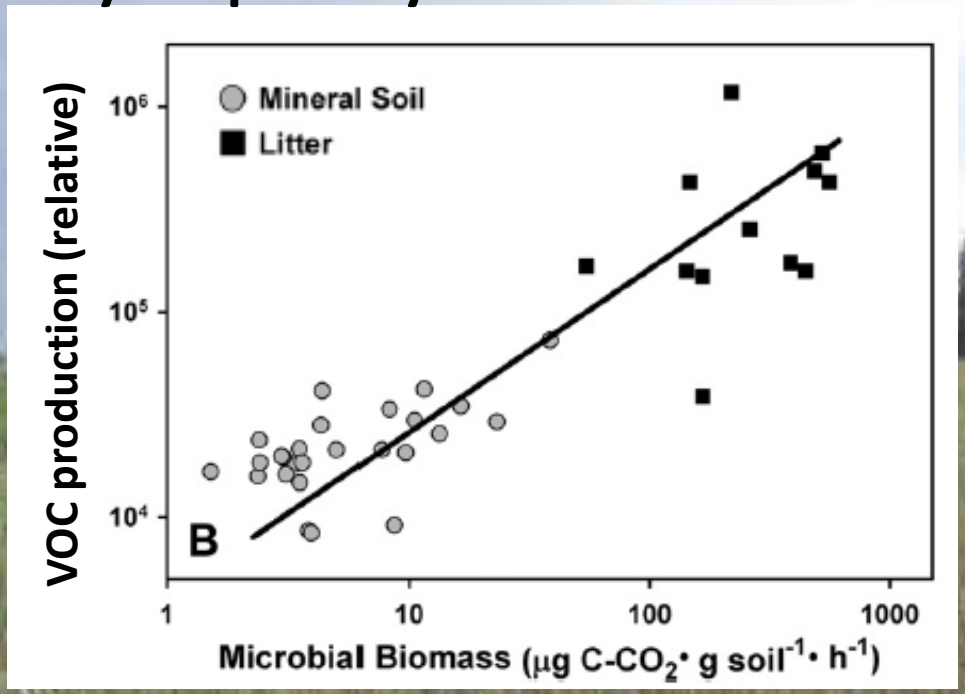
{Twigg, 2011 #5391}

Context

- VOC may be a **proxy** to better understand microbial processes

  (Sugar and fatty acid degradation, alcoholic fermentation, aminoacid biosynthesis, sulphur reduction)

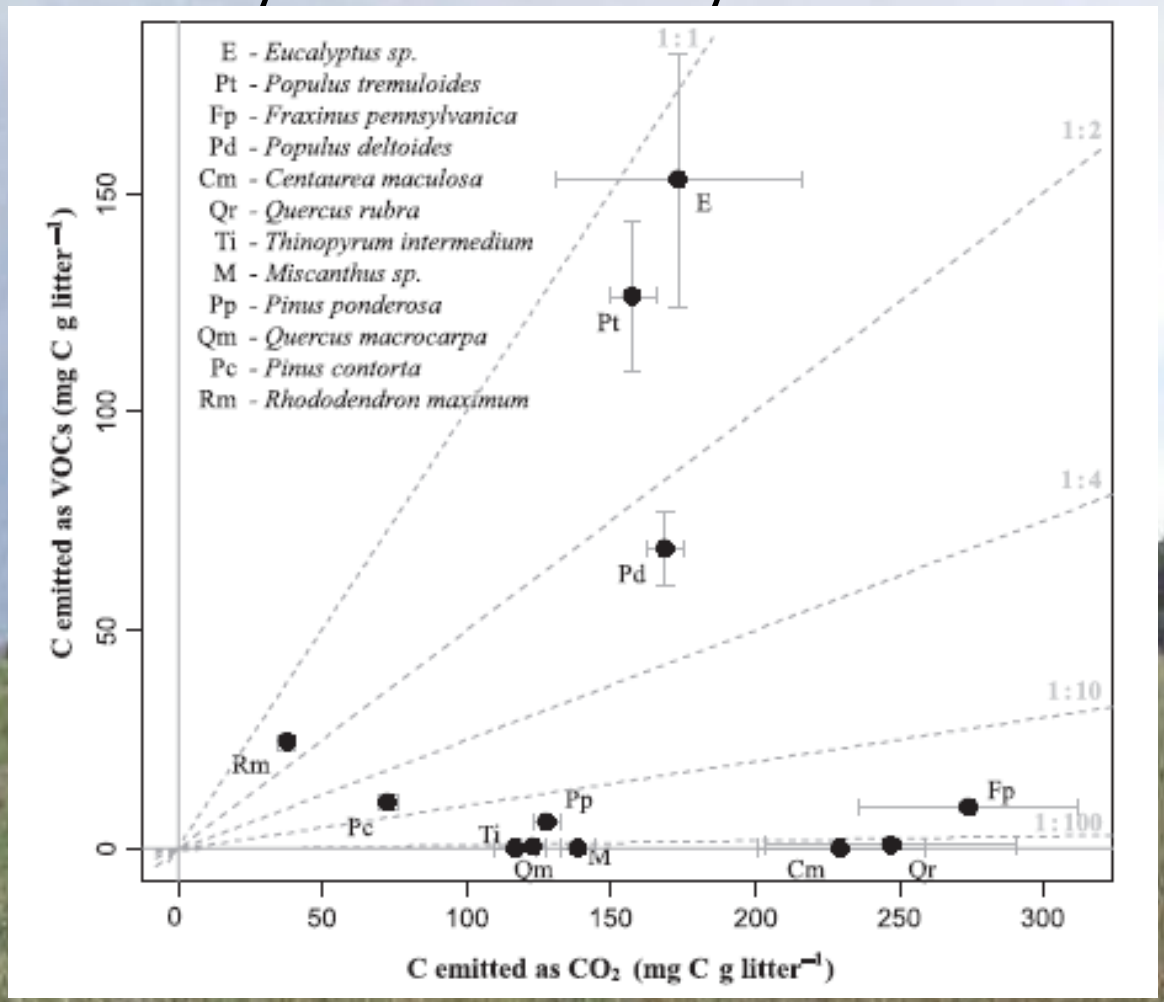
A proxy to quantify the microbial biomass ?



{Leff, 2008 #7407}

Context

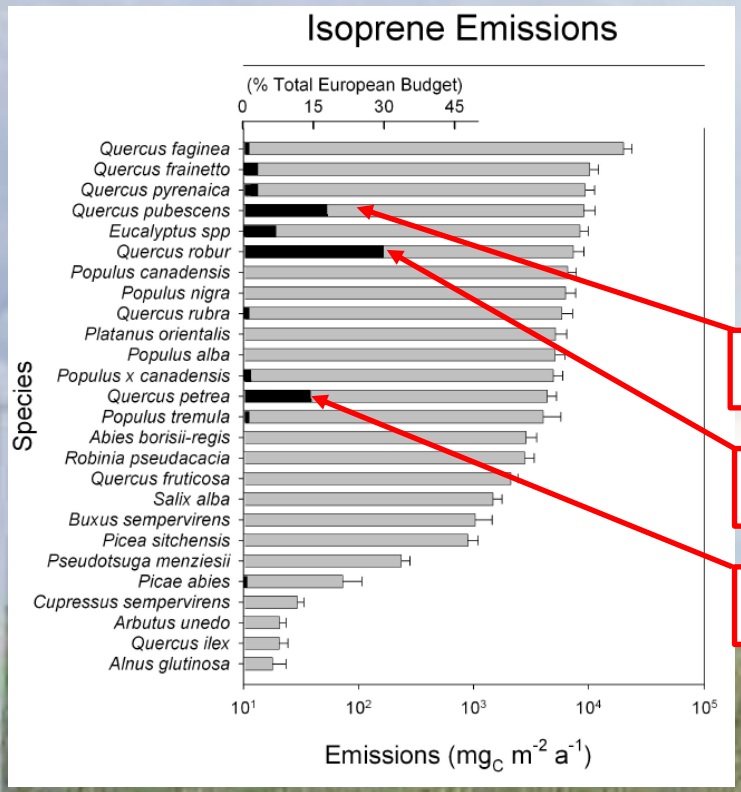
Carbon losses by VOC in litter may be of same order as CO_2



{Gray, 2012 #7449}

Context

- Existing VOC emissions databases are weak



Quercus pubescens

Quercus robur

Quercus petraea

~60 % of Total European Isoprene Budget	**– 4 refs**
	– 3 refs
	– 1 refs

{Keenan, 2009 #5483}

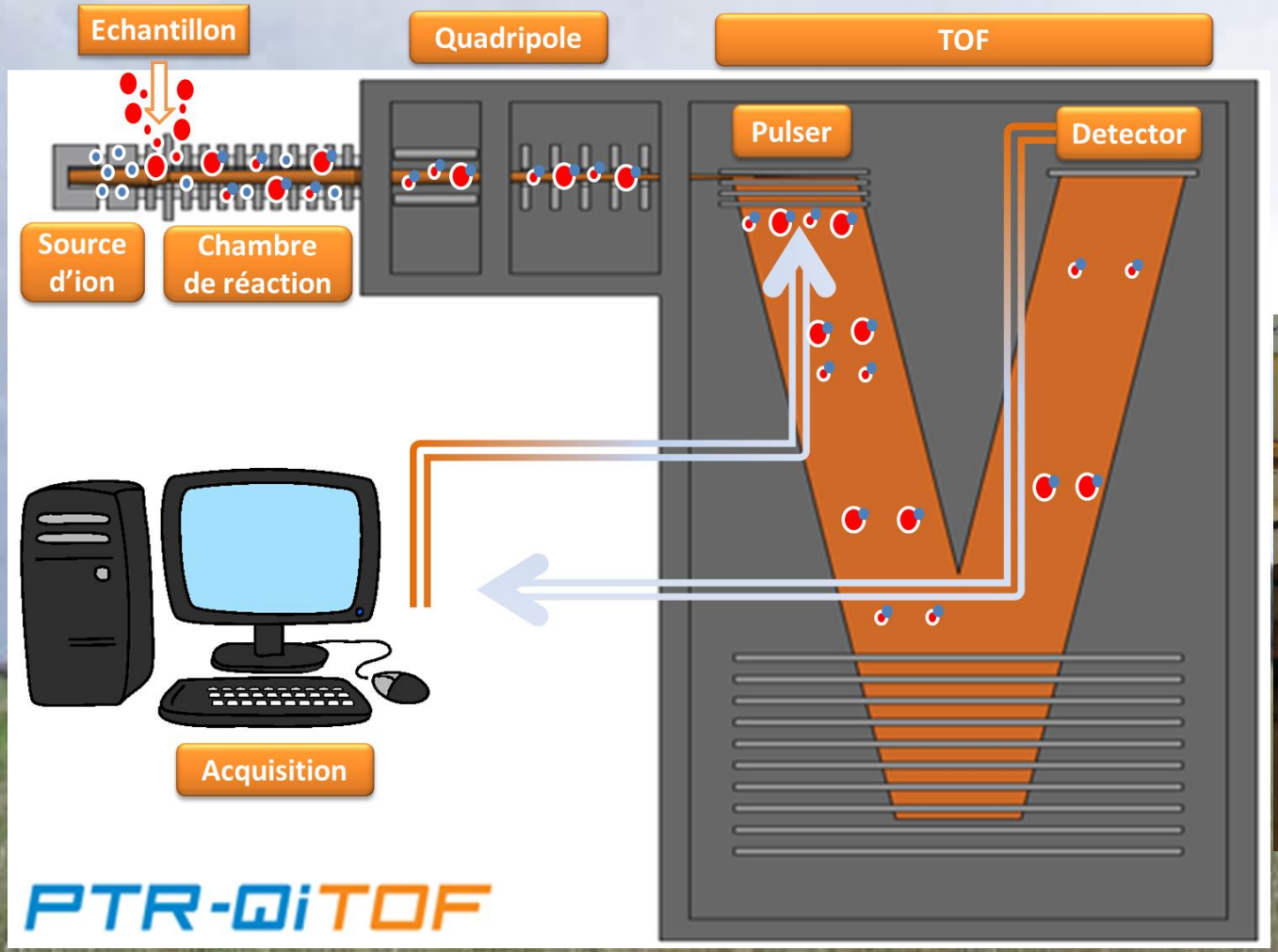
Objectives of the COV³ER project

- To measure the VOC fluxes
  - Over representative crops and forest ecosystems in France
  - Over slurry and farmyard applied in the field
- To use direct measurement techniques
  - At the canopy scale (Eddy covariance)
  - At the plant, branch and litter scale (dynamic chambers)
- To demonstrate the capability of the ANAEE-France PTRMS service

COV³ER

COV biogéniques : Emissions par les Ecosystèmes gERés

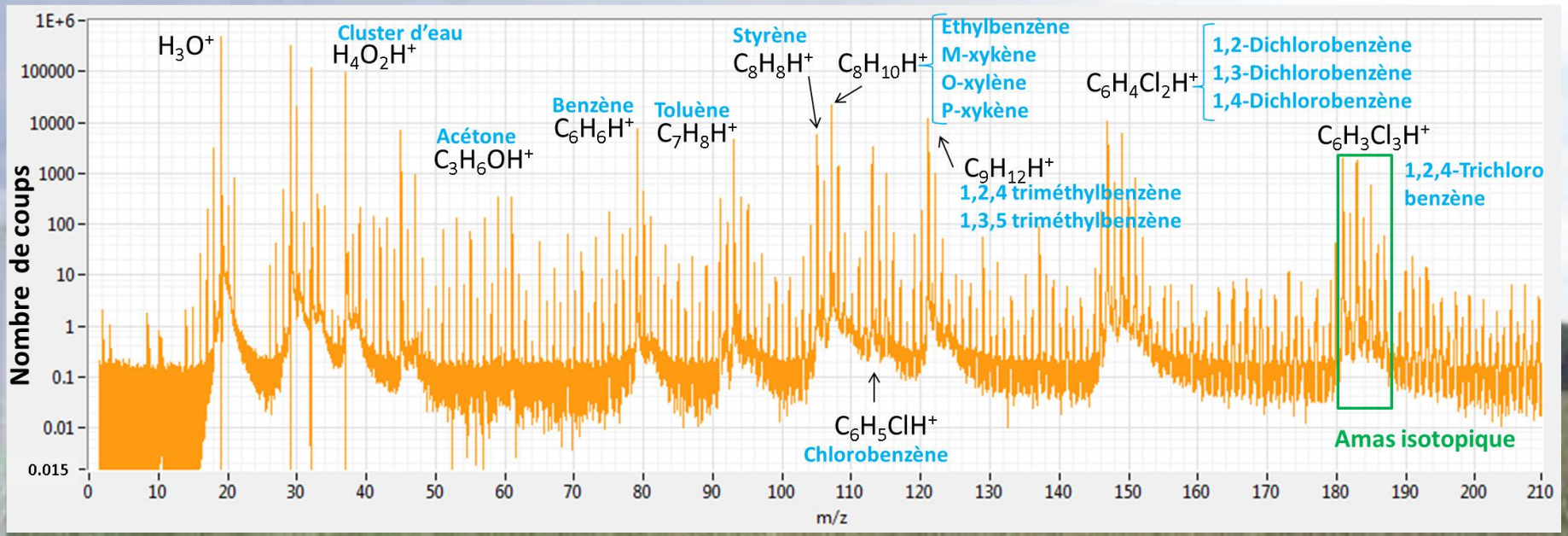
Material and methods: the PTR-TOF



Lafouge et al. (2015)

Material and methods: the PTR-TOF

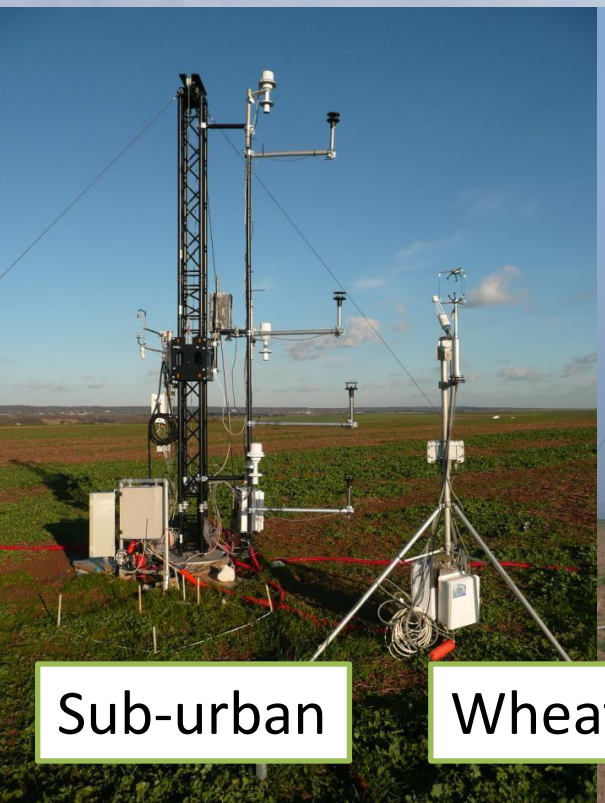
Example of mass spectra from a standard with 14 compounds at 110 ppb



Lafouge et al. (2015)

Fr-Gri: crop site

Soil type : luvisol (loamy clay) ***(25%Cl, 70% Si, 5% Sa)***



Sub-urban

Wheat, maize, oilseed rape

Cow and sheep farm

Loubet et al. (2016)

Material and method

- 1 June - 20 July 2016 (Wheat @ maturity towards senescence)
- Fongicides applied the 4 June
- ICOS measurements (met, soil, CO_2/H_2O)
- Additional measurements
  - QCL N_2O/CH_4/H_2O eddy covariance fluxes, O_3, NOx, NMHC (LSCE), OH reactivity (LSCE)
- PTR-TOF-MS measurements
  - VOC concentrations and VOC fluxes by Eddy covariance
  - VOC profile in the canopy
  - Plant and soil chambers VOC an OH reactivity on wheat
- Photosynthesis, PAR, Temperature profiles

Plant chamber

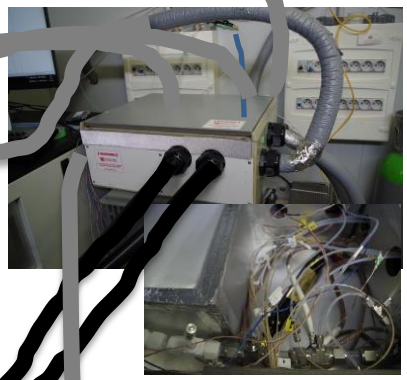
Profile

PTR-TOF-MS online
Eddy covariance,
in-canopy profile
plant and soil chamber

Sonic and sampling head

Soil chamber

60°C heated Manifold

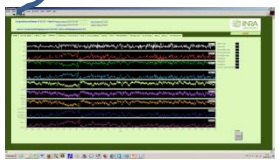


60°C heated & insulated tube

PTR-TOF-MS

HTTP acquisition

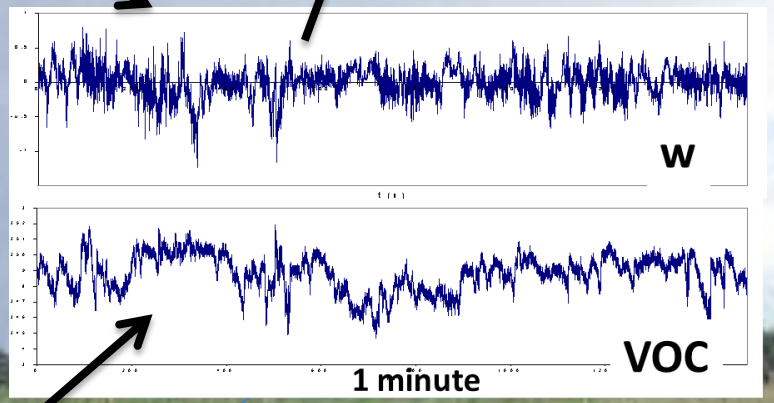
Labview program
Online flux calculations
PTR automation
4G connection

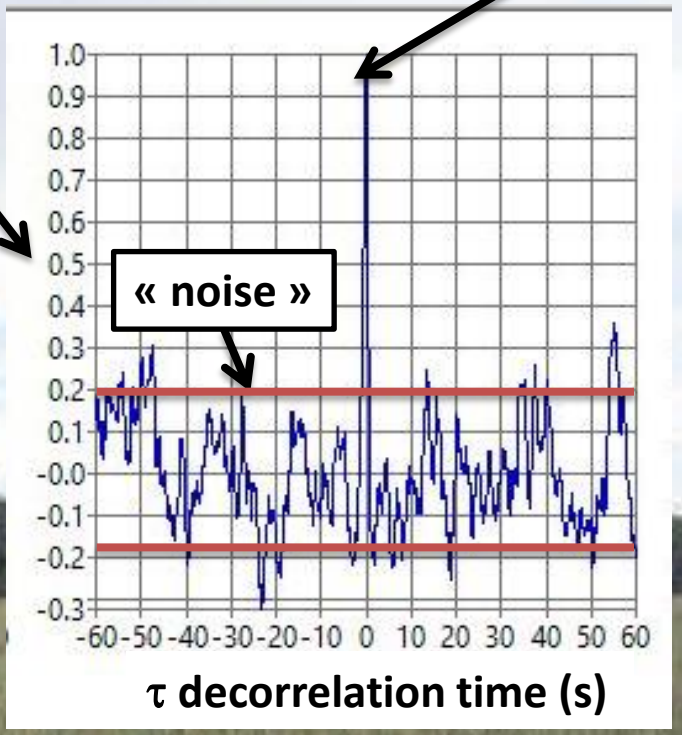


Pump with flowmeter
60 L min^{-1}

The principle of Eddy covariance

$$F_c = \max\left(\overline{w'(t-\tau).c'(t)}\right)$$



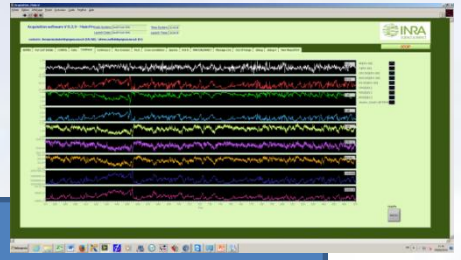


Covariance function

Material and method: acquisition

Mass table

100 Gb switch



TOFF computer

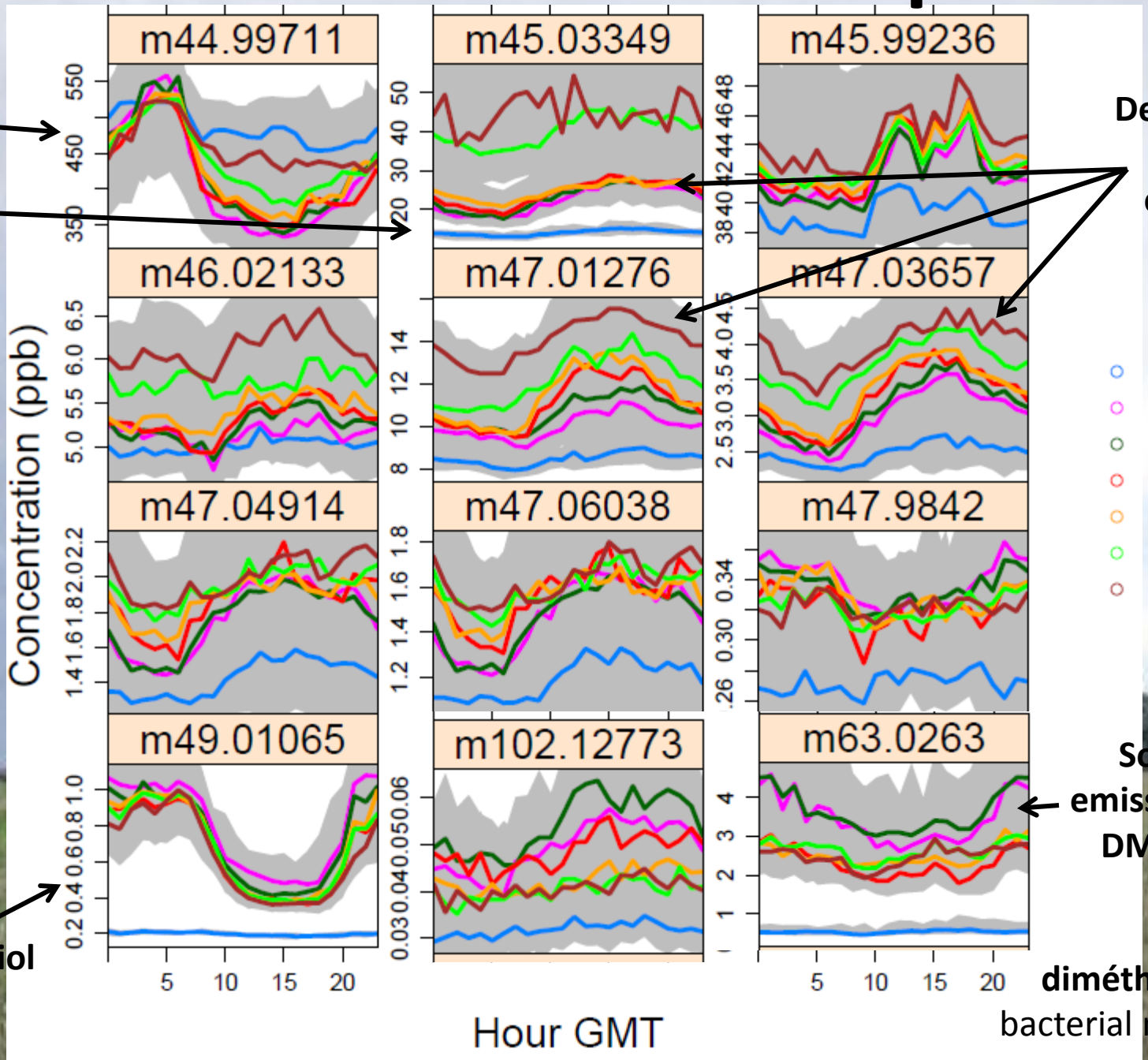
Acquisition computer

what	Start time (min)	End time (min)	Length (min)
Eddy cov.	0	20	20
Profile 5	20	20.5	0.5
Profile 4	20.5	21	0.5
Profile 3	21	21.5	0.5
Profile 2	21.5	22	0.5
Profile 1	22	22.5	0.5
Profile 1	22.5	23	0.5
Profile 2	23	23.5	0.5
Profile 3	23.5	24	0.5
Profile 4	24	24.5	0.5
Profile 5	24.5	25	0.5
Chamber in	25	26	1
Chamber out	26	27	1

- Mass calibration every 5 min
- Peak integration
- Variables sharing

- 10 Hz acquisition
- MS Peak data acquisition
- Online flux calculation
- 5 min avearged spectra

Results: VOC concentrations profiles



CO2

Acetal-dehyde

Decreasing within canopy

Filtered air
0.05
0.25
0.50
0.75
1.0
2.7

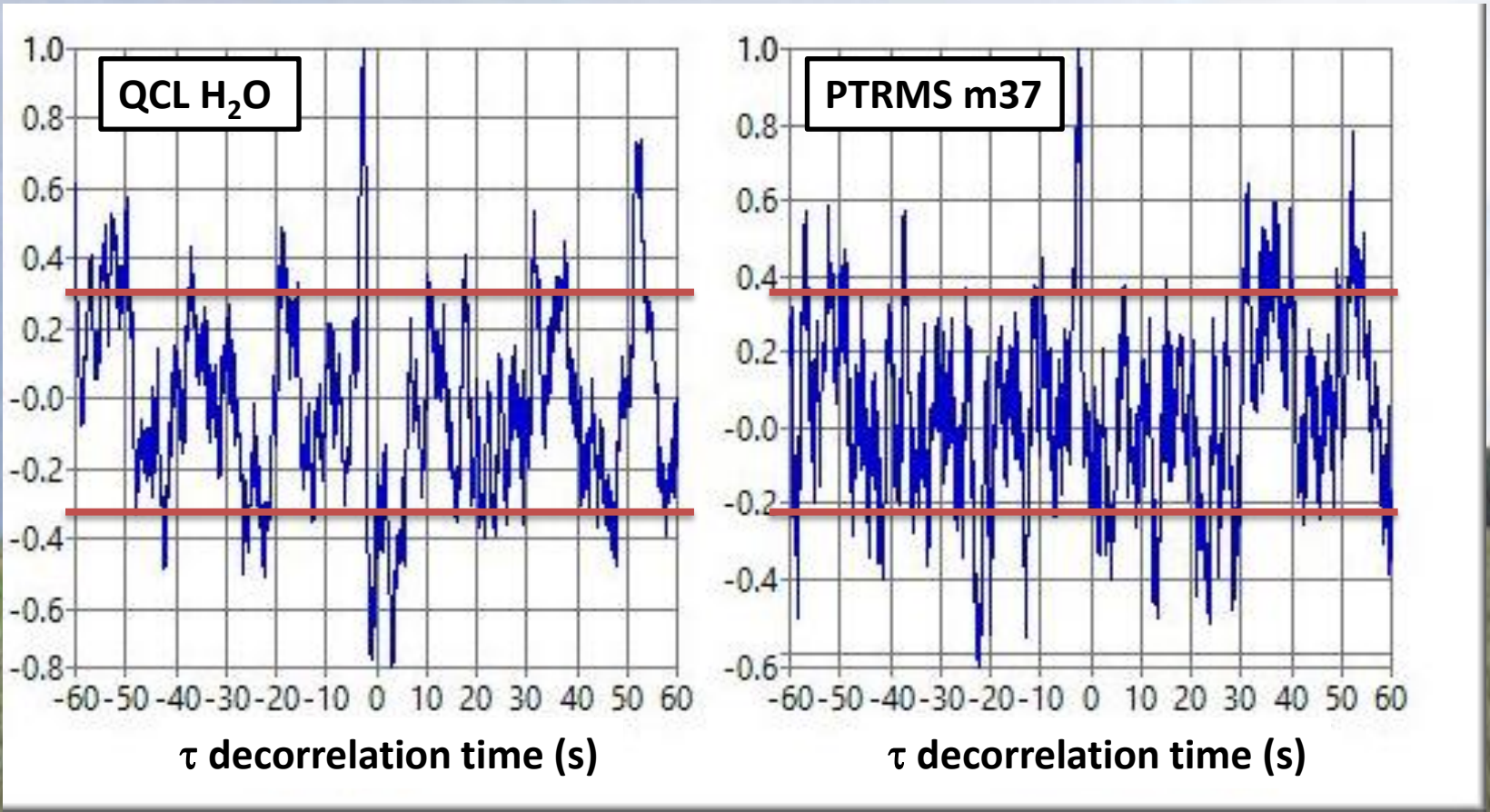
Soil emissions DMS?

Methanethiol

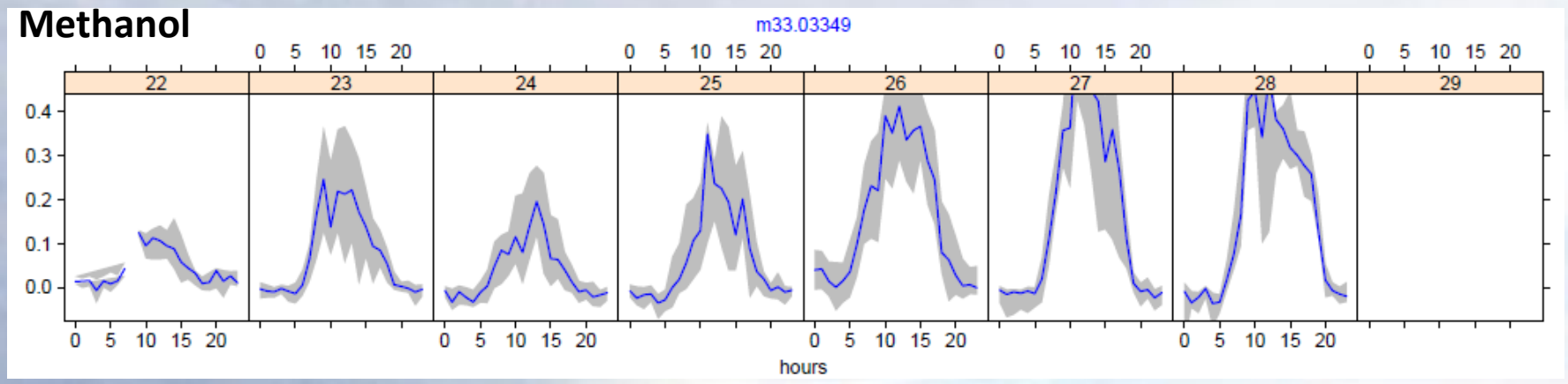
diméthylsulfure
bacterial metabolism

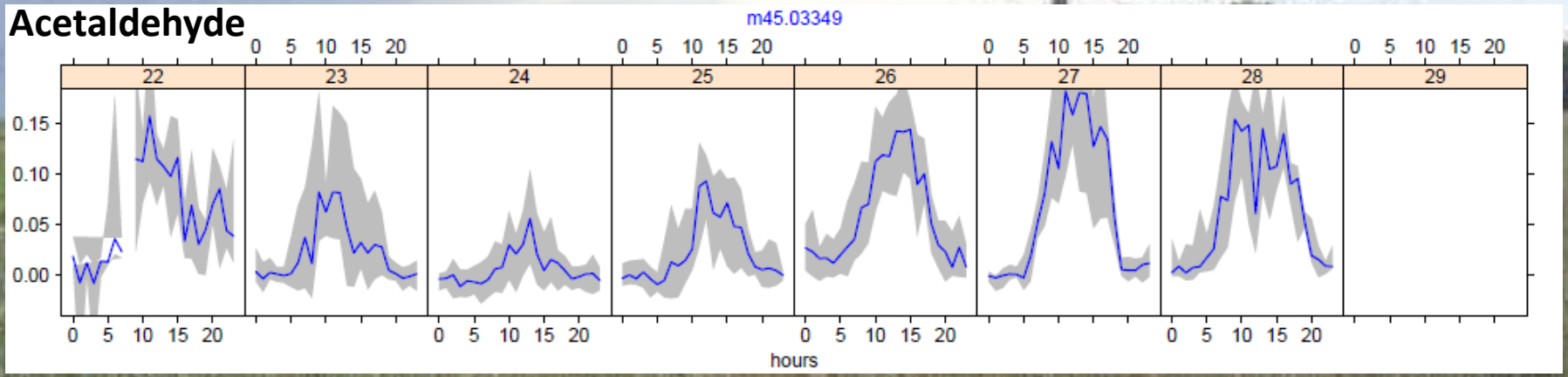
Results: Eddy covariance method

Lag time was very stable on mass 37 (water cluster) ~ 2 seconds



Results: Some compounds emitted

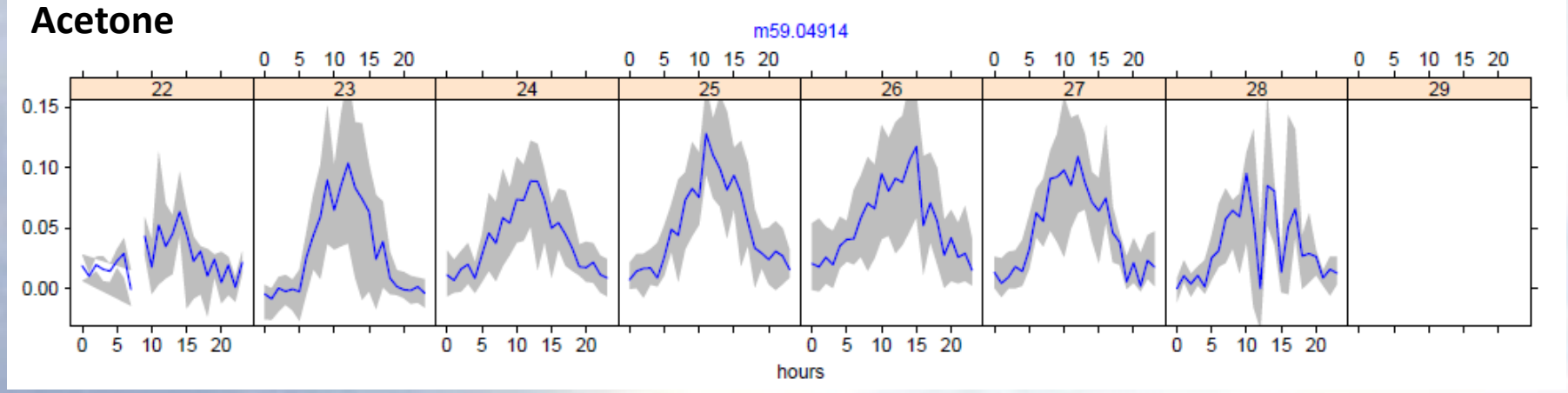




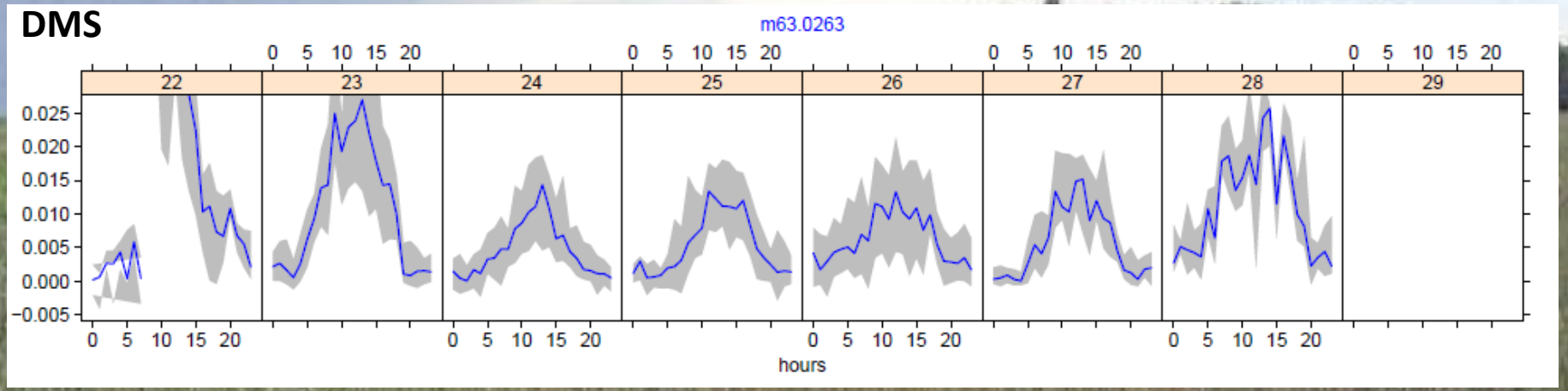
ppb m s^{-1}

Results: Some compounds emitted

Acetone

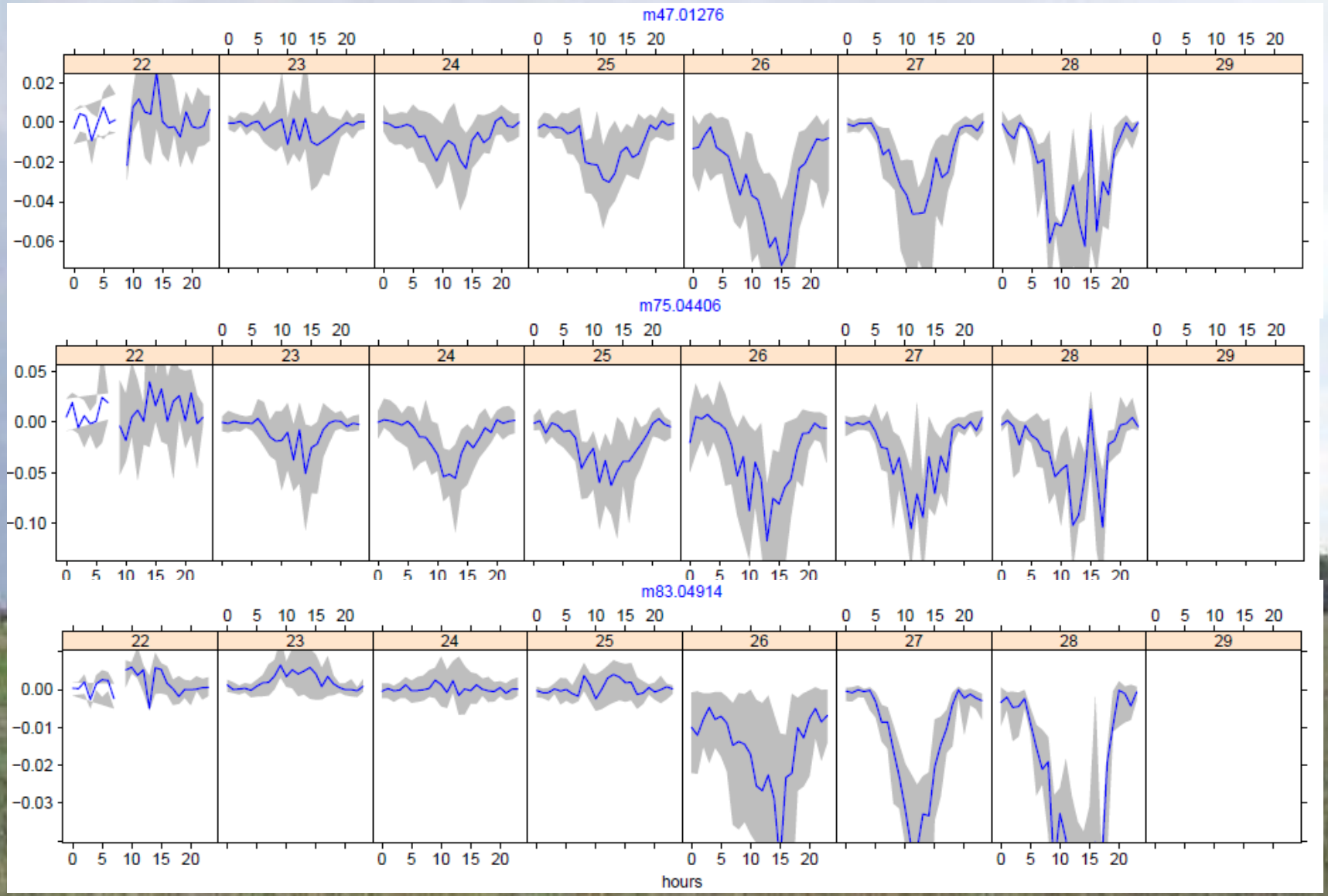


DMS

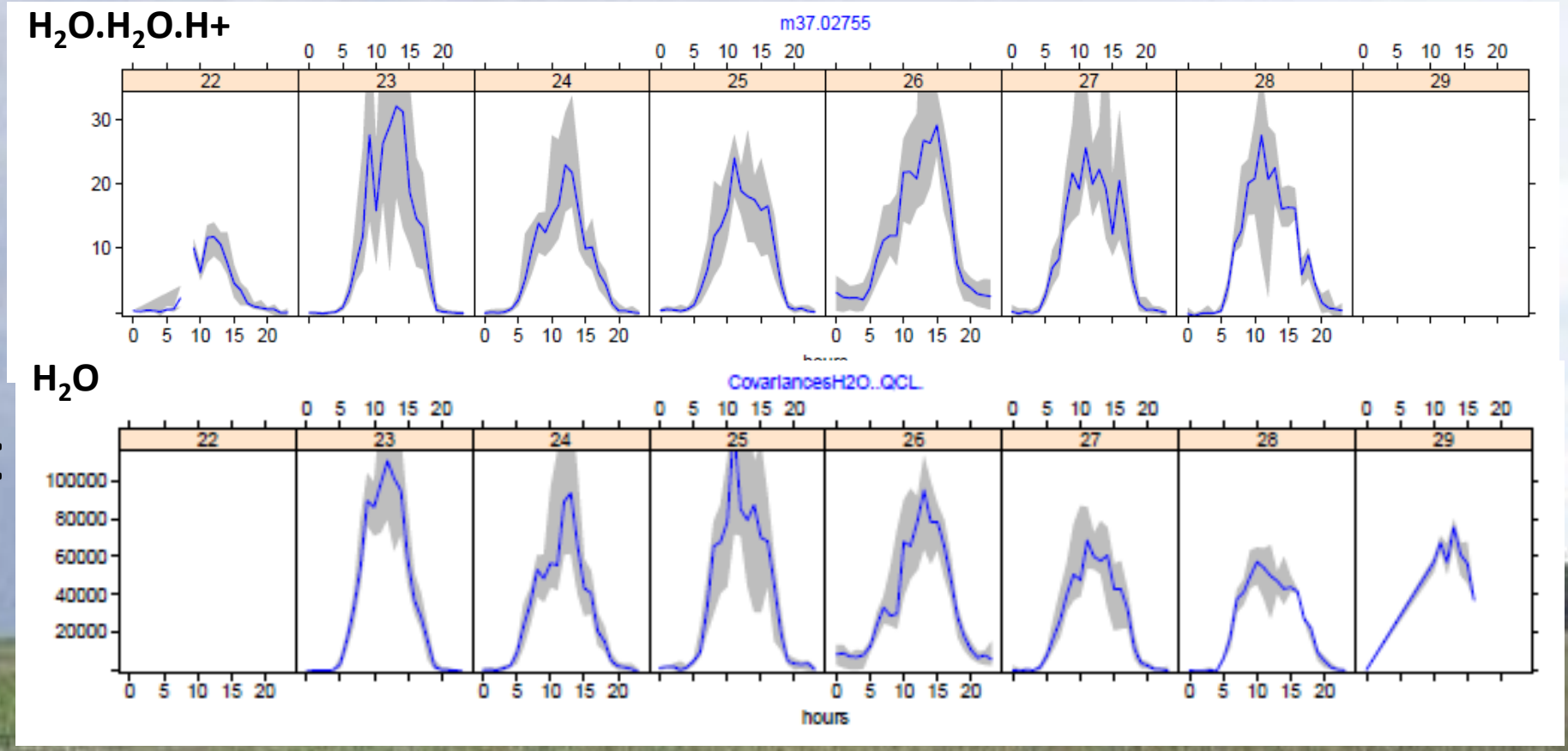


ppb m s^{-1}

Results: Some compounds depositing

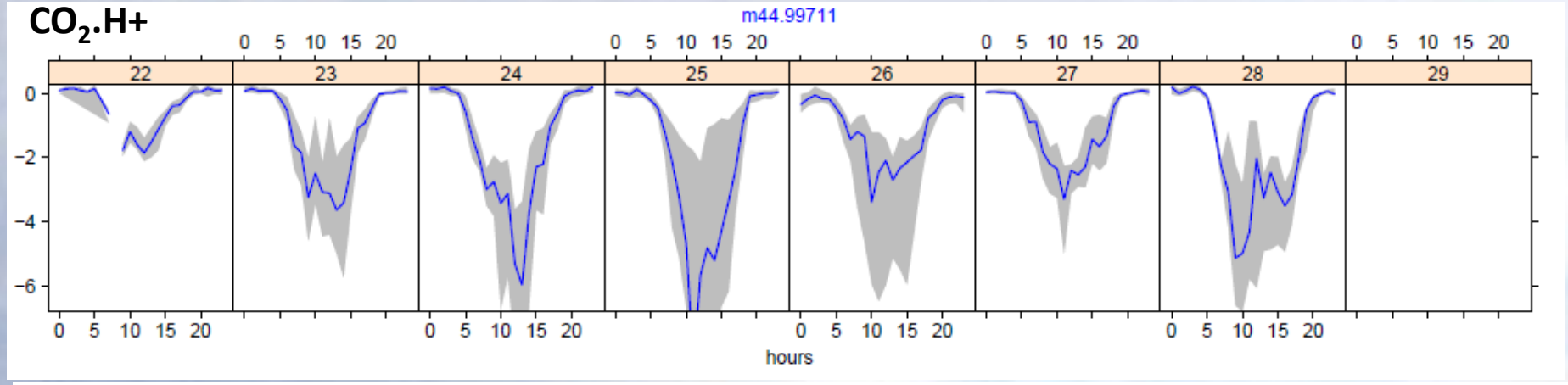


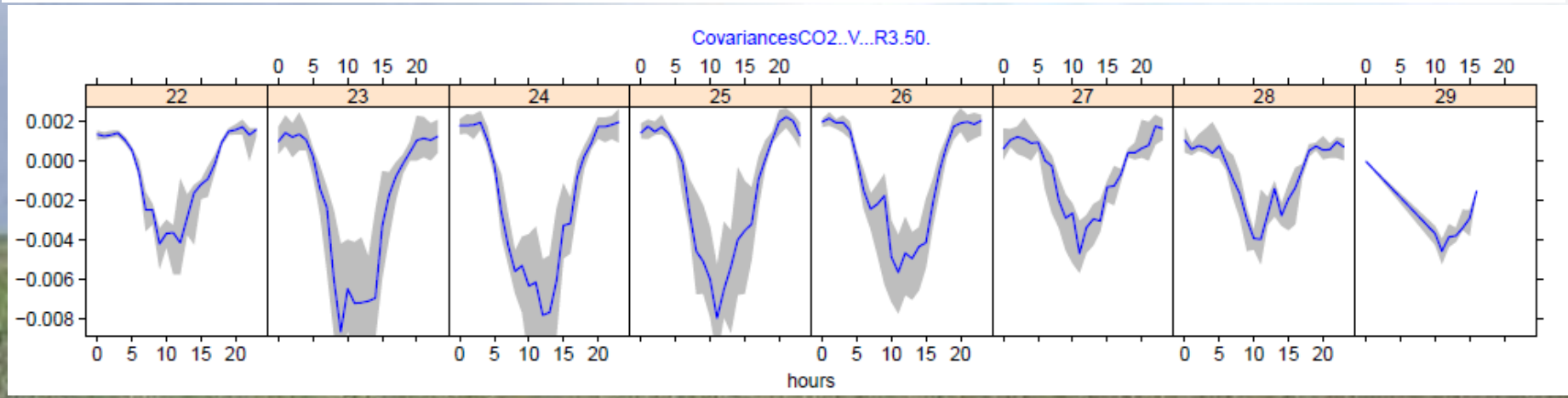
Results: control with H_2O and CO_2



Calibration of the reaction rate as function of conditions

Results: control with H_2O and CO_2

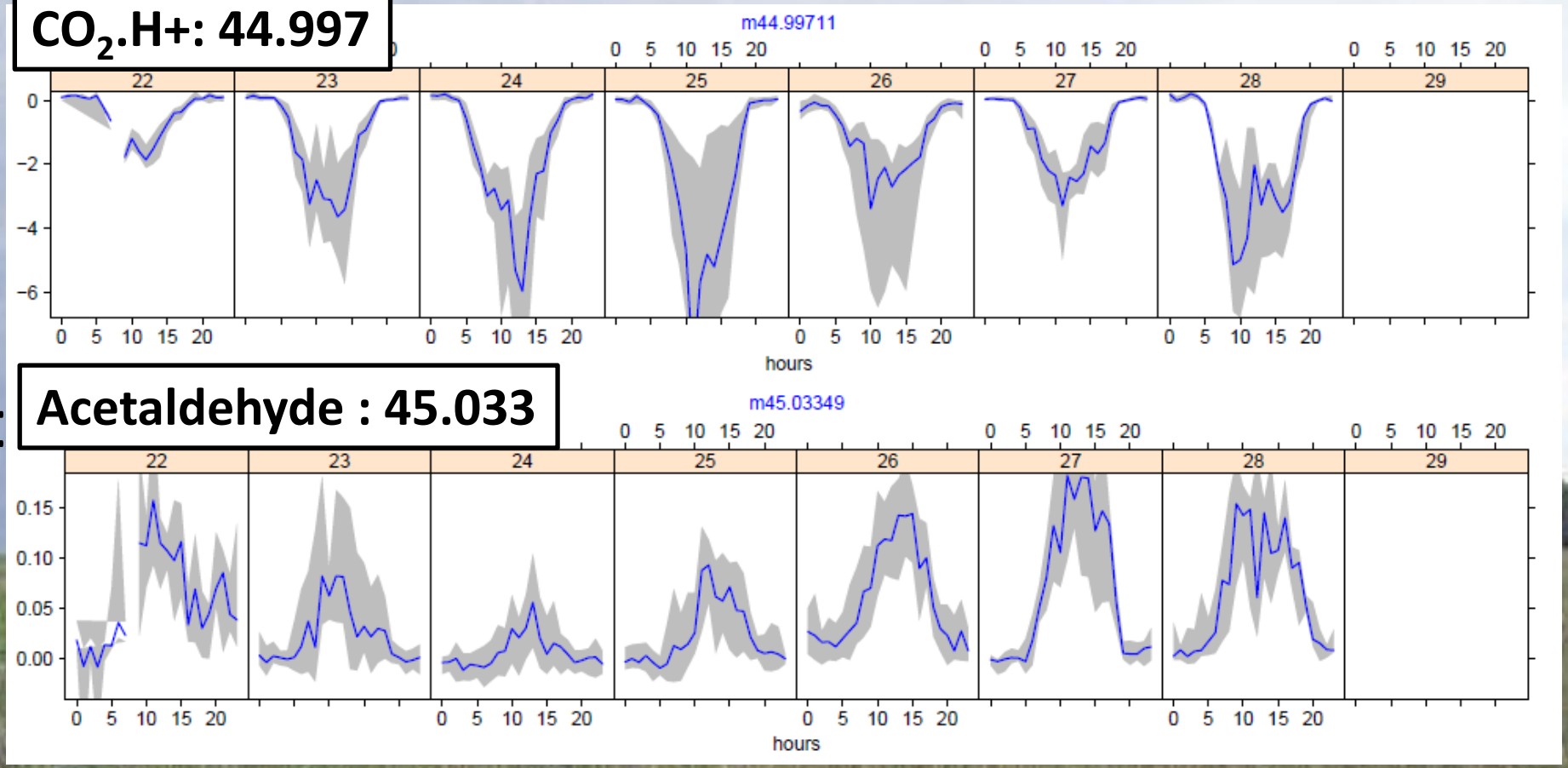




Calibration of the reaction rate

Results: Is mass resolution correct?

CO_2.H+: 44.997



Acetaldehyde : 45.033

Results: VOC spectra

Which compounds were emitted by the wheat?

ketones	aldehydes	alcohols	alkenes	dienes	acids
acetone	acetaldehyde	methanol	propene	isoprene + MBO	octenoic acid or hexenyl acetate
butanone MEK	Formaldehyde		pentene	hexadiene or C6 green leaf volatiles	acid acetique
Ethyl vinyl ketone (pentenone) or pentenal or cyclopentanone			heptene	ISOPOOH (unsaturated hydroperoxides from isoprene oxidation)	butenoic acid
pentanal/pentanone or methyl butenol (MBO) or pentenol			hexene	thymol or cymenol	
MVK+MAKR					

N compounds	Aromatic compounds	S compounds
pyridine	Methoxybenzene	DMS
propylamine or trimethylamine	aromatic C8 ethylbenzene	
Acetonitrile	benzene	

Conclusions

- Eddy covariance was set up in Fr-Gri with new PTR-TOF-MS
- The method was successful for measuring both emissions and depositions of VOC
- Emissions of methanol, acetaldehyde, acetone, DMS
- Some compounds were deposited
- Bi-directional fluxes were observed
- $CO_2.H^+$ was measured although CO_2 should not be protonated.

Next steps

Analyze the data further

- Validate lag time for all masses
- Identify each compounds (GC)
- Calculate total carbon fluxes

Improve Calibration

- ppt range zeroing
- Document transmission of the instrument for most masses

Prepare next experiments

- Grignon (oilseed rape : april 2017)
- Oak forest (Barbeau 2017), green oak (Puechabon 2018)
- Seasonal dynamic chamber measurements in Grignon 2017-2018

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Thanks!

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