

High resolution infrared spectroscopy applied for measurements of trace gas emissions from various land surfaces to atmosphere: Performances and applications to monitor the dynamic of biodegradation of gasoline BTEX in contaminated aquifers.

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LE STUDIUM Conference - Water micropollutants: from detection to removal,
Orléans, Nov. 26 to 28



Instrumentation : The high resolution laser infrared spectrometer (SPIRIT) Performances

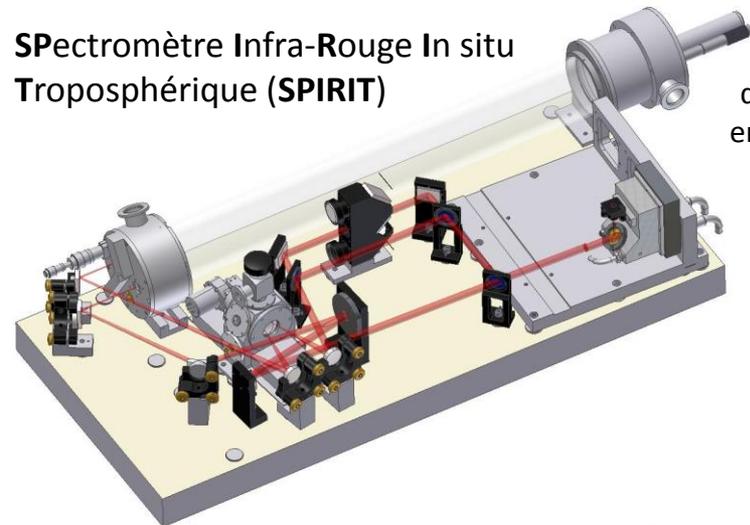
Patented non resonant multi-pass optical cell (Robert, 2007) => 3 spherical mirrors

- > Length path varying from 32 to 224 m thanks to the rotation of one half of a broad band spherical mirror
- > High versatility as regard the type and the concentration range of species to be measured : GHG (CO_2 , CH_4 , N_2O)

Quantum Cascade Laser (QCL) : Continuous Wave (CW) Distributive FeedBack (DFB) operating near Room Temperature (RT) in the Mid IR region

- > High power and high spectral resolution : $10^{-4} \text{ cm}^{-1} \Rightarrow$ **no overlap between molecules (ro-vibrational spectrum) ;**

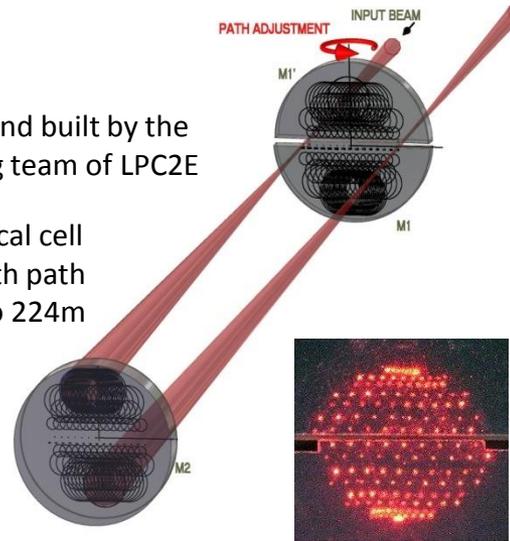
Spectromètre Infra-Rouge In situ
Troposphérique (**S**PIRIT)



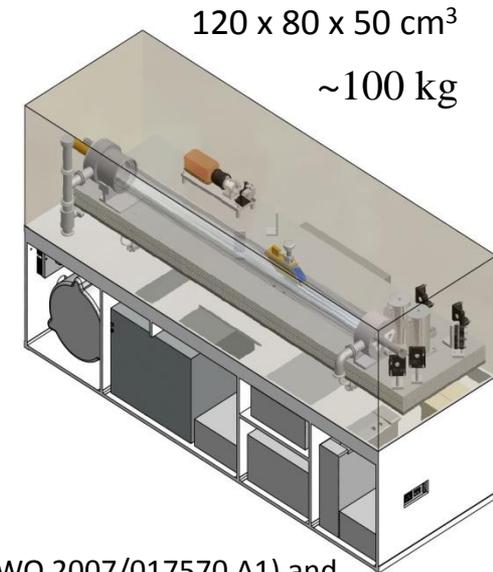
Schematics of the SPIRIT instrument : the path of the laser beam is symbolized by a red ray

designed and built by the
engineering team of LPC2E

Optical cell
length path
32 to 224m



- Multipass cell: International Patent (WO 2007/017570 A1) and
Applied Optics, 2007, 46, 5408.



120 x 80 x 50 cm³
~100 kg

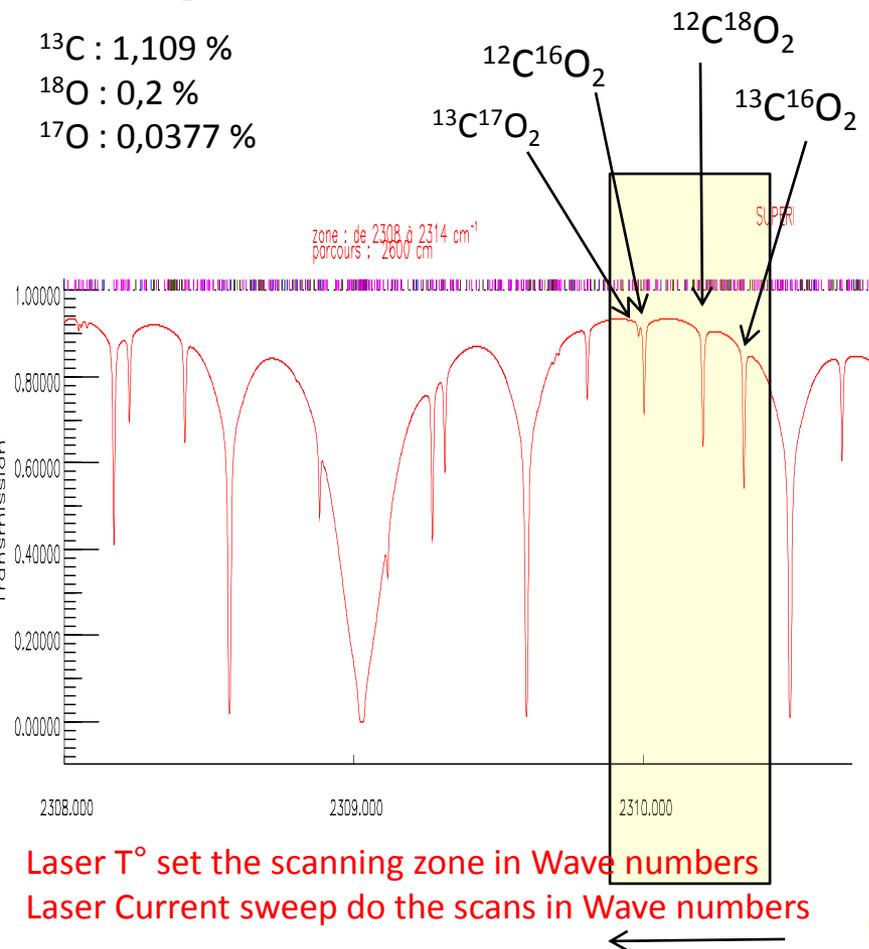
Mixing ratio precision and accuracy : 0.2% at 0.7 Hz at 400 ppm CO_2 and 2 ppm CH_4 ; 0.3% at 0.7 Hz at 320 ppb N_2O

$\delta^{13}\text{C}/^{12}\text{C}$ of CO_2 precision (< 0.1 ‰) and accuracy (< 0.3‰), reached by temperature regulation of the optical cell system (0.05°C) and derived from 3-15 min integration times (300-1000 ppm) in dynamic closed chamber in the field (*Keeling plot*)

Instrumentation : SPIRIT spectrum resolution and $\delta^{13}\text{C}/^{12}\text{C}$ precision

CO₂ Spectrum (26 meters at 30 hPa)

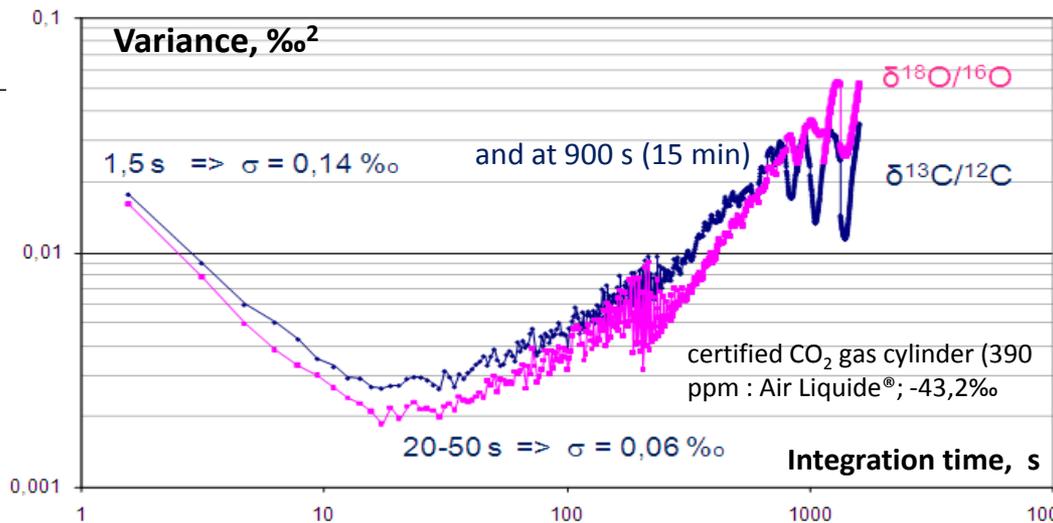
¹³C : 1,109 %
¹⁸O : 0,2 %
¹⁷O : 0,0377 %



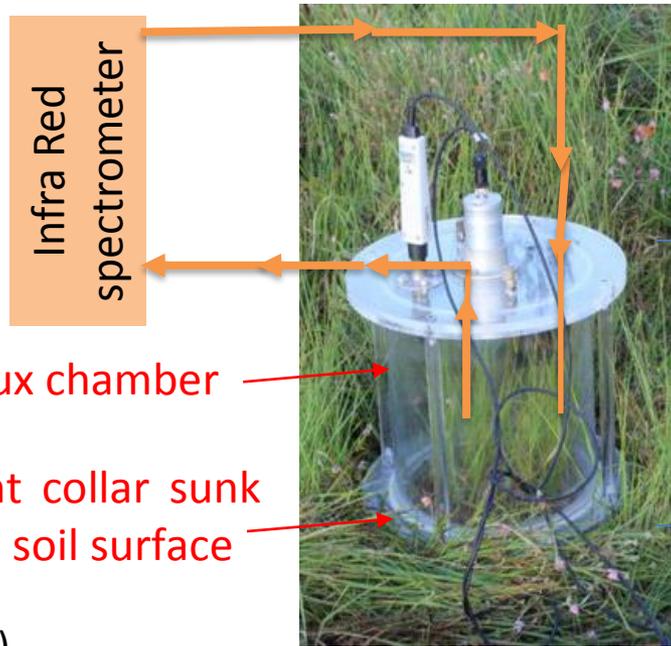
Laser T° set the scanning zone in Wave numbers
 Laser Current sweep do the scans in Wave numbers

SPIRIT's laser emission Scan
 2310,6 -> 2309,7 cm⁻¹

Obtained from the laser current emission scan (55-85mA at -18°C)
 Resolution: 10⁻³ cm⁻¹



Methodology : Flux of CO₂ derived from the dynamic closed chamber method

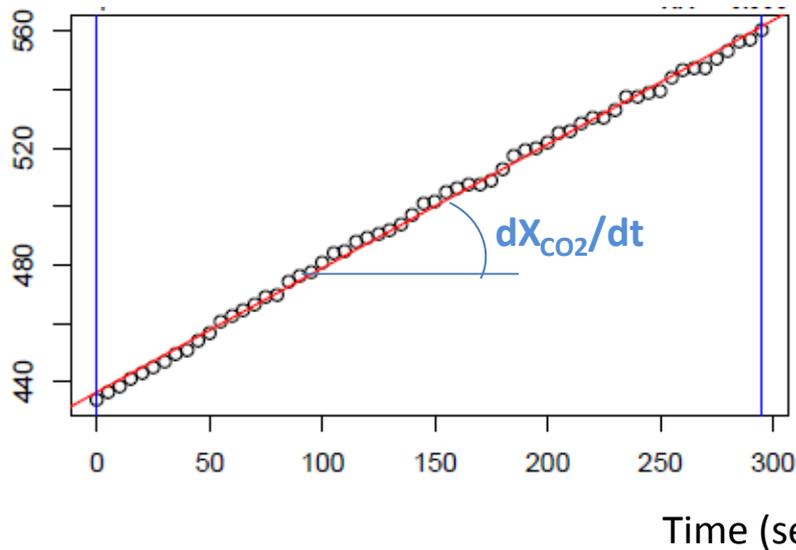


F^S : Flux from ground to atmosphere, given per surface unit
 > 0 if release to atmosphere

$$F^S_{CO_2} = h \cdot dC_{CO_2} / dt$$

(molecules m⁻² s⁻¹):

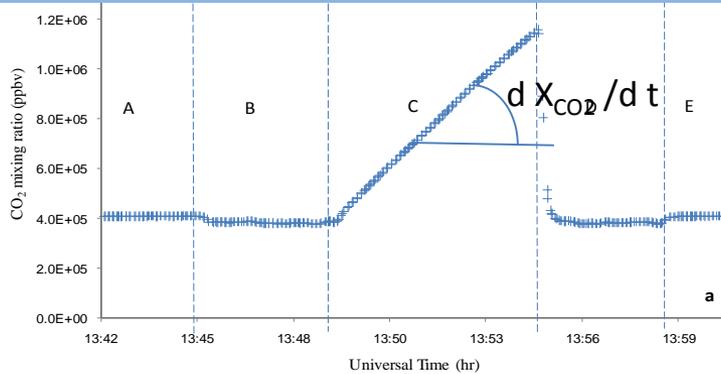
[CO₂] (ppm)



$$F^S_{CO_2} = \frac{P}{k_B \cdot T} \cdot h \cdot \frac{d X_{CO_2}}{d t}$$

- P : pressure in the chamber (Pa),
- k_B : Boltzmann constant
- T : absolute temperature (K),
- h : mean height of the chamber above soil surface (m)
- X_{CO_2} : volume mixing ratio of CO₂ (unit-less),

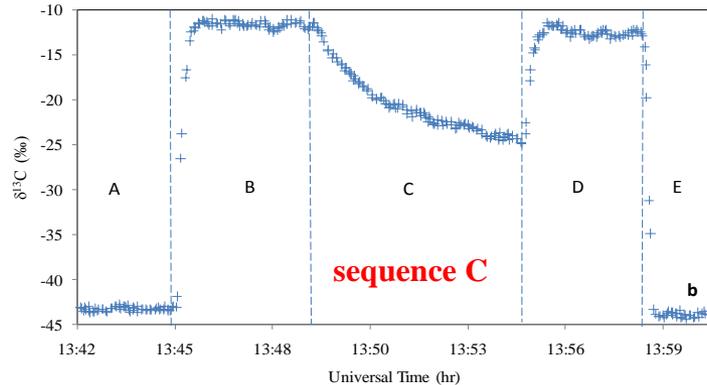
Methodology : $\delta^{13}\text{C}/^{12}\text{C}$ of CO_2 derived from the dynamic closed chamber method, using the Keeling plot approach



$$F_{\text{CO}_2} = (P \cdot h / k_b \cdot T) \cdot dX_{\text{CO}_2} / dt$$

→ **CO₂ mixing ratio versus Universal Time**

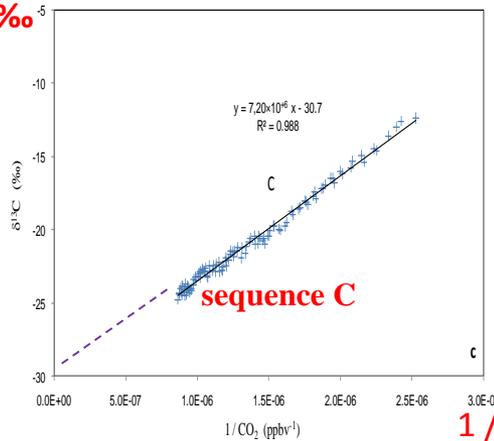
→ **Flux Plot**



- Sequences A (calibration) and E (drift analysis): calibration with standard cylinder (CO_2 406 ppmv; $\delta^{13}\text{C}$ -43.20‰ VPDB);
 - Sequences B and D: ambient air analysis;
 - Sequence C: flux measurement from collar.
- (collar number 16 at 13:49 UT on 2 August 2014)

→ **$\delta^{13}\text{C}$ of CO_2 versus Universal Time (UT)**

$\delta^{13}\text{C}/^{12}\text{C}$ of CO_2 ; ‰



$$\delta^{13}\text{C}_{\text{sample}} = \left(R^{13}\text{C}/^{12}\text{C}_{\text{sample}} / R^{13}\text{C}/^{12}\text{C}_{\text{Standard}} - 1 \right) * 1000$$

Standard : Vienna-Pee-Dee-Belemnite (VPDB) Craig, H. (1954).

The origin intercept gives the $\delta^{13}\text{C}/^{12}\text{C}$ signature of the CO_2 emitted

→ **$\delta^{13}\text{C}$ versus $1/\text{CO}_2$ during sequence C**

→ **Keeling Plot**

Hydrocarbon (BTEX) C balance in contaminated aquifers from fuel tanks leaks in gasoline station, during stimulated aerobic bio-treatment

(without extraction of soil matter)

Objectives : develop and certify non-invasive/destructive methods :

- geophysics (soil electric resistivity, capacity)
- ground surface analysis of CO₂ emissions (flux , $\delta^{13}\text{C}/^{12}\text{C}$ determination)

for monitoring *in situ* biodegradation of hydrocarbons in order to optimize soil bio-treatment.

Objective: Assess the dynamic of biodegradation of remaining hydrocarbon substrates (BTEX mainly) by monitoring the CO₂ $\delta^{13}\text{C}$ released at ground surface from BTEX biodegradation

Funded by the French National Agency for Research : **ANR ECOTECH BIOPHY 2010 : Optimization of BIO processes for the decontamination of hydrocarbon-contaminated groundwater by geoPHYsic monitoring and online gas analysis** , “ Programme Production Durable et Technologies de l'Environnement ”



Agence de l'Environnement
et de la Maîtrise de l'Énergie

**PROGRAMME PRODUCTION
DURABLE ET TECHNOLOGIES DE
L'ENVIRONNEMENT**

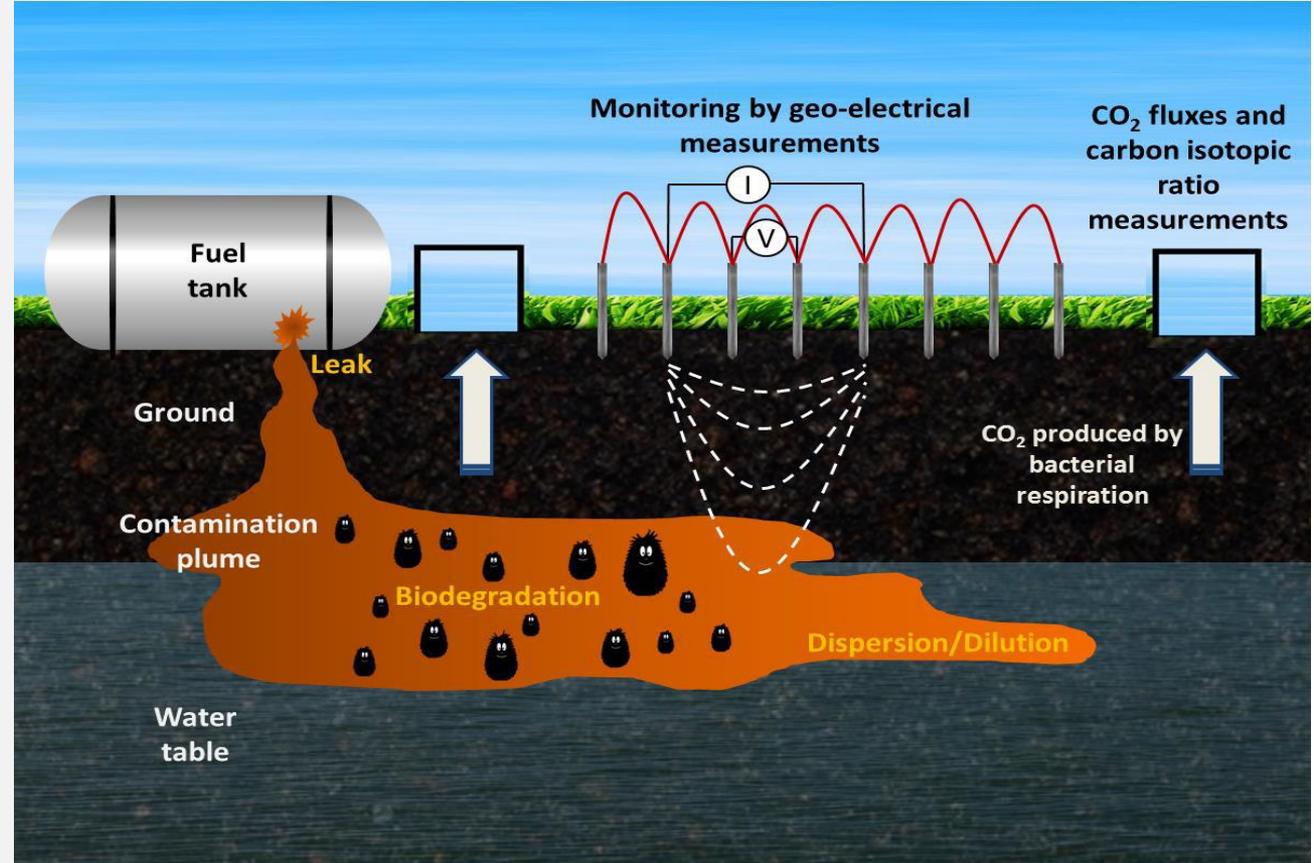
ECOTECH

Édition 2010



The hydrocarbon polluted site : Bio-decontamination monitoring

Pictures showing the geophysical methods (Electrical Resistivity and Induced Polarization) combined with gas analyzes with SPIRIT IR spectrometer (CO₂ flux with ¹³C/¹²C isotopic ratio determination) used on a BTEX polluted site from spill of gasoline fuel tank to monitor stimulated aerobic biodegradation .

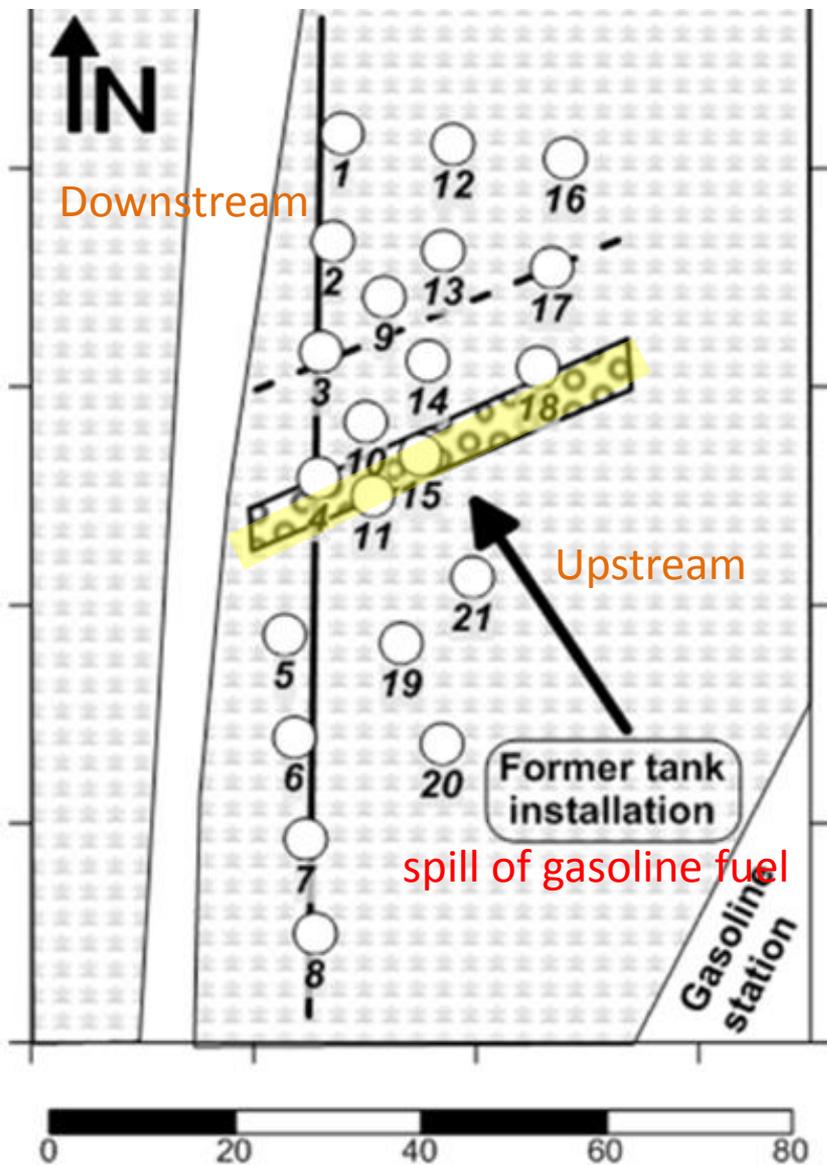


Gaz analysis

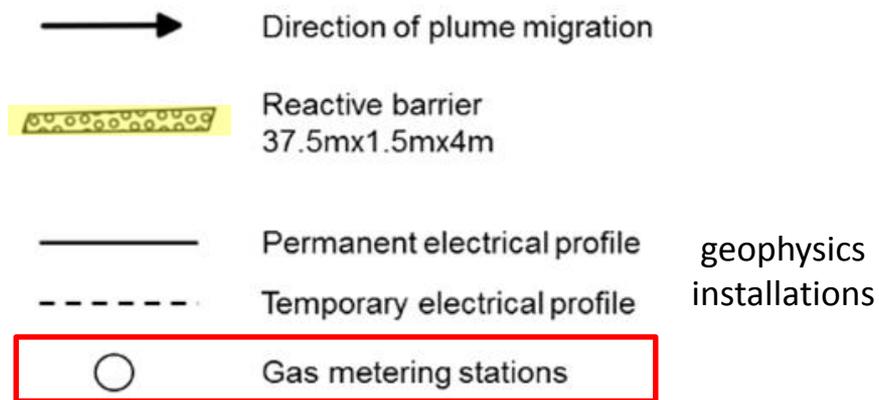


Geophysics analysis

The hydrocarbon polluted site : Bio-decontamination monitoring

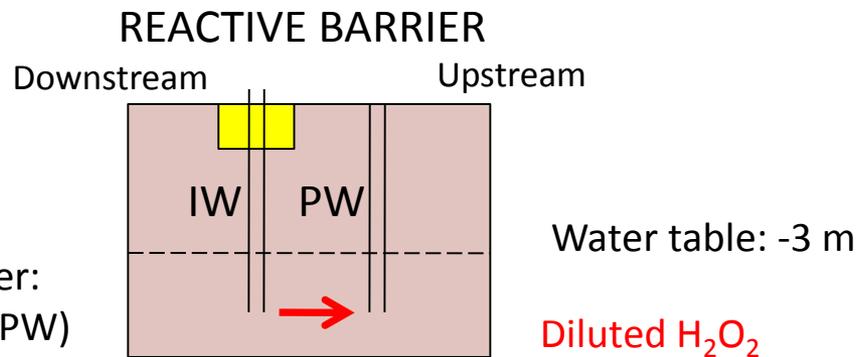


Biodegradation stimulation started on March 27, 2014 : A trench has been dug to set a reactive barrier to supply oxygen (from liquid water injection enriched in H₂O₂) to the water table to stimulate aerobic metabolic bioprocesses.

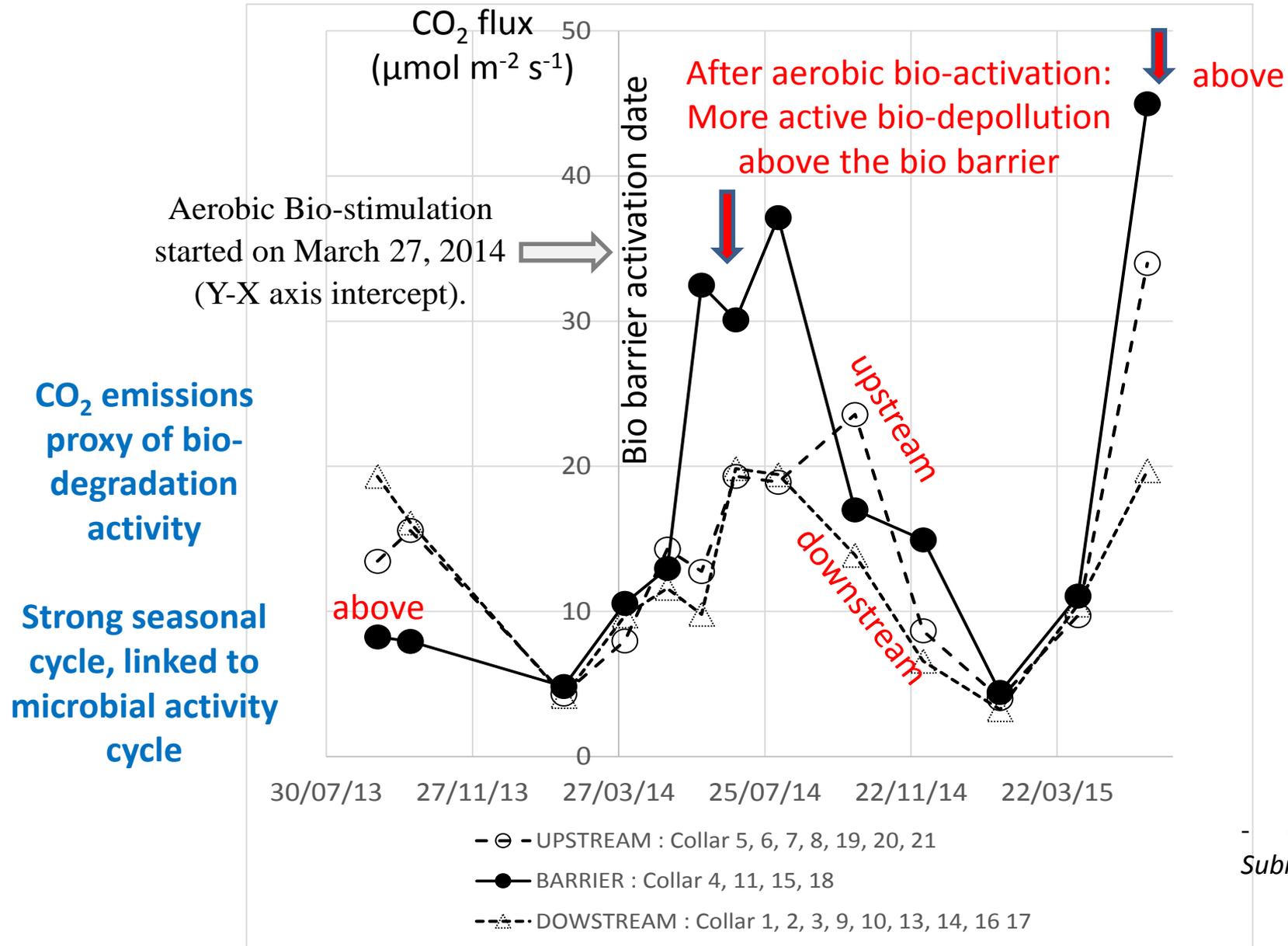


CO₂ flux with $\delta^{13}\text{C}$ determination
 -> **Bacterial respiration from underground hydrocarbon aerobic biodegradation measured above 21 collars sunk 15 cm below the soil surface (for ground respiration removal)**

4 m depth wells, along the reactive barrier:
 Injection wells (IW) Pumping wells (PW)



RESULTS : CO₂ average flux (μmol m⁻² s⁻¹) along the pollution plume versus time, showing the effect of the bioactive barrier



RESULTS : Average changes of CO₂ fluxes over a one year lapse time, showing the effect of the bioactive barrier

average and mean deviation of the ratio “year +1 flux” to “year flux ”

	Sep 14 / Sep 13	Oct 14 / Oct 13	Feb 15 / Feb 14	Apr 15 / Apr 14	Jun 15 / Jun 14
UPSTREAM	1.6 ± 0.2	1.9 ± 0.6	1.7 ± 0.5	1.6 ± 0.2	N/A
BARRIER	3.9 ± 1.1	2.6 ± 0.7	3.5 ± 0.8	1.4 ± 0.3	2.0 ± 0.6
DOWSTREAM	1.0 ± 0.1	1.2 ± 0.2	2.1 ± 0.4	1.2 ± 0.2	2.4 ± 0.3
Status	after relative to before bio-activation			after bio-activation	

Highest Ratio of average flux (or flux rise) above the bio-reactive barrier, **when calculated after bio-activation relative to before bio-activation.**

Late effect of the bioactive barrier is also observed downstream the pollution plume, more than one year after aerobic bio-stimulation where **the ratio of average flux in 2015 (2.1, 1.2, 2.4) reached higher values than in 2014 (1.0 and 1.2).**

RESULTS : $\delta^{13}\text{C}$ values of CO_2 emission at ground surface (up panel) and of some BTEX (benzene + toluene) in aquifer (down panel), reported along the axis of the pollution plume.

CO_2 $\delta^{13}\text{C}$ emitted at soil surface follow the same trend of BTEX $\delta^{13}\text{C}$ as representative hydrocarbons, with some fractionation factor

$\uparrow \text{CO}_2 \delta^{13}\text{C}$ and $\uparrow \text{BTEX} \delta^{13}\text{C}$
from upstream to downstream
the pollution plume

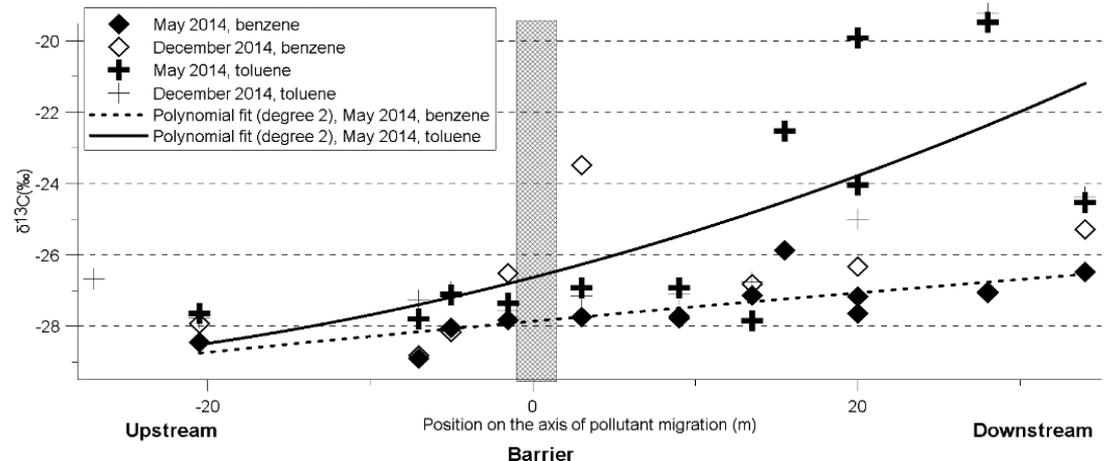
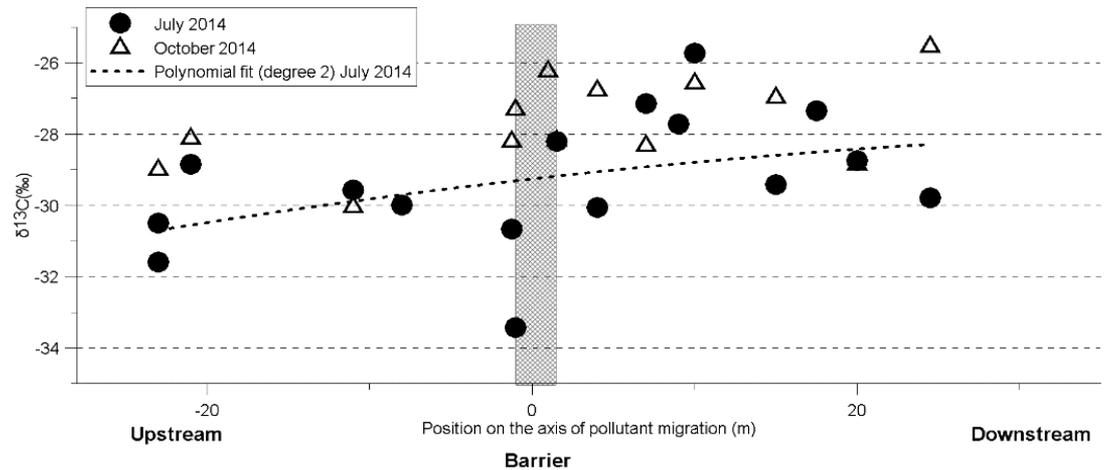
$\text{CO}_2 \delta^{13}\text{C} - \text{BTEX} \delta^{13}\text{C} = \sim -3 \text{ ‰}$

$\sim \epsilon = -3 \text{ ‰}$ or $\alpha = 0.997$

(for BTEX hydrocarbon substrate)

Cause : during the migration of the pollution plume ^{12}C from BTEX is easier catalysed from microorganisms and released as CO_2

- Guimbaud et al., JES 2016



Rayleigh equation, applied for the HC substrate S_x at spot X (no migration):

$$R_{S,t1}^X / R_{S,t0}^X = (C_{S,t1}^X / C_{S,t0}^X)^{(\alpha-1)}$$

$$R_{P,t1}^X / R_{P,t0}^X = (C_{S,t1}^X / C_{S,t0}^X)^{(\alpha-1)}$$

S : Hydrocarbon substrate (BTEX mainly); P : CO_2 produced from biodegradation of S .

$\alpha = R_p/R_s$: Kintic fractionation factor alpha from biodegradation of S to P

$R_{S,t}^X$ and $R_{P,t}^X$: Isotopic ratio $^{13}\text{C}/^{12}\text{C}$ of S and of released CO_2 P at ground surface

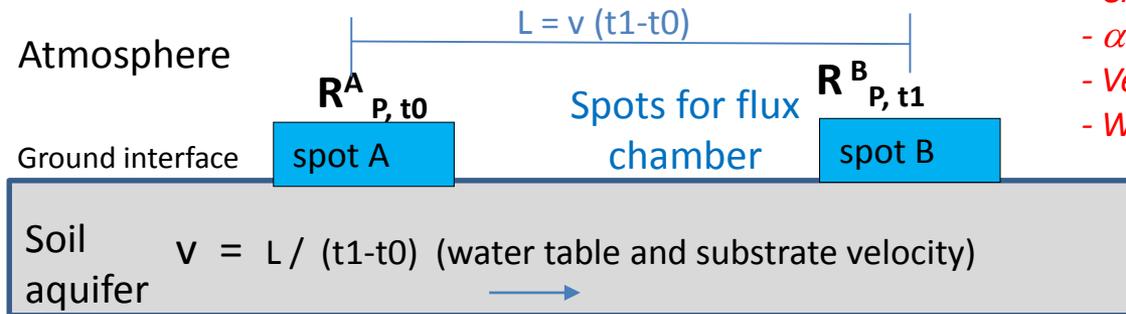
$C_{S,t}^X$: Hydrocarbon substrate S concentration at spot X along the migration axis at time t.

Rayleigh equation applied for the CO_2 biodegratation product P released at ground surface, in a pollution plume, where S migrate from spot A, at t_0 , to spot B at t_1 along the stream of the pollution plume

$$R_{P,t1}^B / R_{P,t0}^A = (C_{S,t1}^B / C_{S,t0}^A)^{(\alpha-1)}$$

Hypothesis

- Closed system for the HC substrate
- α known and constant with time and space,
- Vertical diffusion FF negligible relative to α
- Water table velocity known



Percentage of biodegradation of the residual substrate S from Rayleigh equation obtained from the release Biodegradation product CO_2 only:

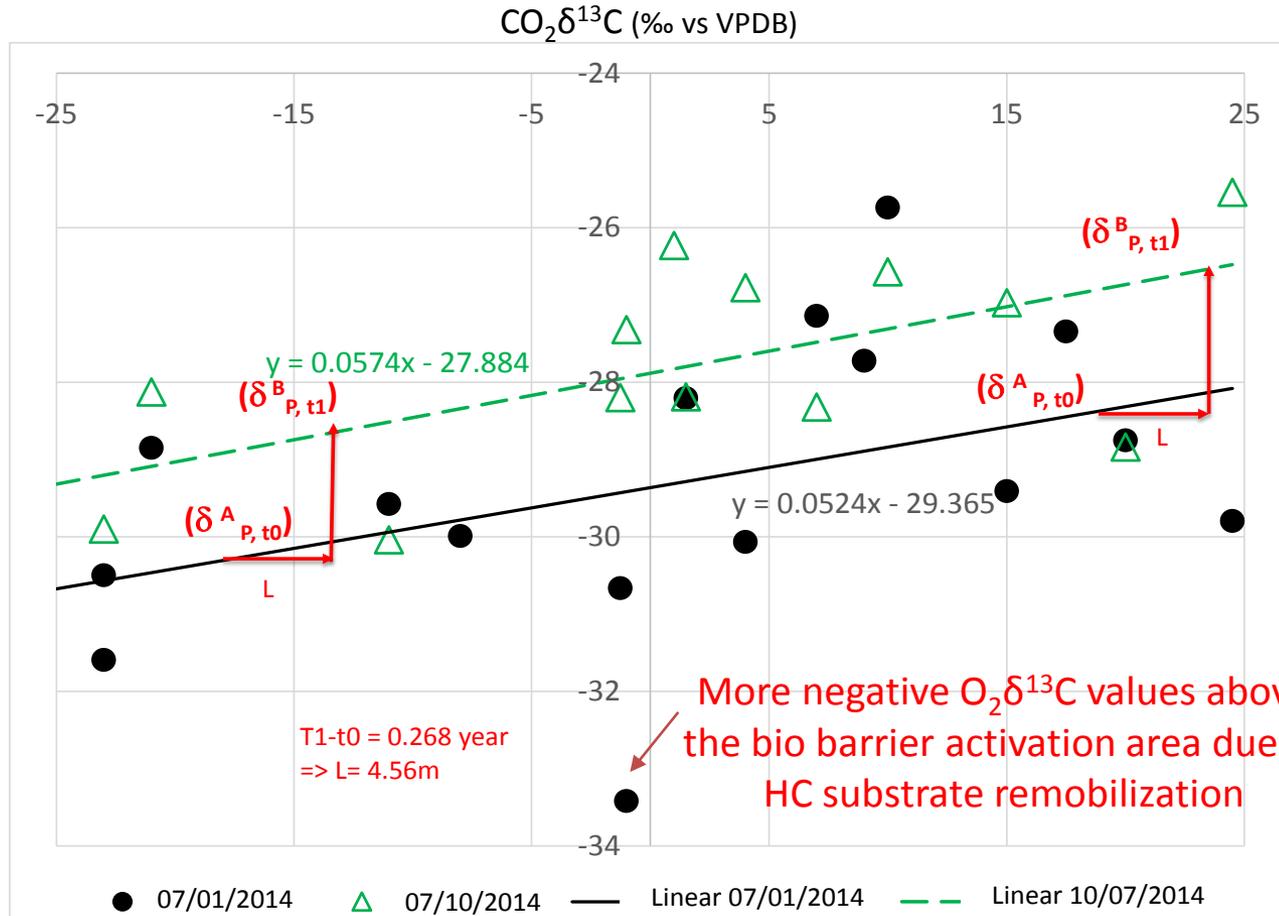
$$S f_{t_1-t_0} [\%] = (1 - (R_{P,t_1}^B / R_{P,t_0}^A)^{1/(\alpha-1)}) \times 100$$

RESULTS : $\delta^{13}\text{C}/^{12}\text{C}$ of CO_2 (‰ versus VPDB) as a function of pollution plume coordinate (m)

a) July, October, 2014, showing the use of Rayleigh parameters to assess the kinetic of S (BTEX mainly) biodegradation

Coordinate axis of the pollution plume (m)

linear assumption of the trend



The 0 coordinates (Y-X axis intercept) is where the front line of the bio-depollution barrier is installed; Negative coordinates are located upstream the flow of the pollution plume. Aerobic bio-stimulation started on March 27, 2014.

July 1 and October 7, 2014 data set, showing the overall rise of $\text{CO}_2\delta^{13}\text{C}$ values over time for that period, and the use of Rayleigh parameters (according to Eq. 12) to assess the dynamic of hydrocarbons biodegradation between this two consecutive measurement campaigns. From the period of July 1 to October 7, hydrocarbon substrates migrate with a time lapse $t1-t0 = 0.268$ year corresponding to a migration distance L of 4.56 meters. $\delta^B_{P, t1}$ values are derived from $\delta^A_{P, t0}$ values, with the shift of 4.56 meters downstream, using the fitted linear functions.

RESULTS : Kinetic decomposition rate (% molar fraction loss per month) of underground hydrocarbon substrates

calculated from $\delta^{13}\text{C}$ of CO_2 changes over time (Rayleigh equations), assuming fractionation $\epsilon = -3 \text{ ‰}$ or $\alpha = 0.997$ (from BTEX or representative petroleum hydrocarbon substrates, biodegraded into CO_2 (g))

	% loss per month	From 10/09/2013 to 01/07/2014	From 01/07/2014 to 07/10/2014	From 07/10/2014 to 02/12/2014	From 02/12/2014 to 03/02/2015	From 03/02/2015 to 08/04/2015	From 08/04/2015 to 04/06/15
UPSTREAM	-10 m	8.3	13.7	7.4	8.1	3.2	6.5
	- 3 m	9.4	13.9	4.6	6.8	4.3	5.3
DOWNSTREAM	+ 3 m	10.2	14.1	2.0	5.7	5.2	4.1
	+ 10 m	11.2	14.3	-1.1	4.3	6.3	2.8
	Average	9.8	14.0	3.2	6.2	4.8	4.7

The 0 coordinates (Y-X axis intercept) is where the front line of the bio-depollution barrier is installed Negative coordinates are located upstream the flow of the pollution plume. Aerobic Bio-stimulation started on March 27, 2014.

-BR $f_t = 9.8\%/month$ averaged from September 2013 to end of June 2014.

-Significant seasonal variation

BR $f_{t_{MAX}} = 14\%/month$ in summer 2014; BR $f_{t_{MIN}} = 5\%/month$ in winter and spring 2015

in agreement with stimulation factors of biodegradation efficiency (temperature increase, oxygenation of the biofilm when water table is lowering in summer)

-No significant increase after aerobic bio stimulation, downstream the depollution barrier relative to upstream with the timescale of the experiments (14 months).

Effectiveness demonstrated to monitor HC biodegradation to improve soil bio-treatment :

- by emission of CO₂ at soil surface : flux and $\delta^{13}\text{C}$ (Guimbaud *et al.*, 2016, and in prep):

-> Hydrocarbon BTEX $\delta^{13}\text{C}$ map correlation (BTEX) of the aquifer and gaseous CO₂ emitted on the surface, from upstream to downstream of the pollution control plume and the bioactive barrier

=> **Ability to extract a bio-depollution rate from Rayleigh eq. based on CO₂ degradation products only** <-> in agreement to CO₂ fluxes seasonal variation and to literature review data

- by geophysical measurement (2D tomography), which shows that an active depollution of a contaminated site with hydrocarbons is characterized by a zone (Noel *et al.*, 2016 a,b):

- of high conductivity (or low resistivity) due to the formation of conductive metabolites (ions in solution) resulting from the biodegradation of hydrocarbons

Technique : Electrical Resistivity Tomography (ERT)

- of high chargeability due to the presence of many bacteria behaving like induced dipoles and often present in the form of biofilms

Technique : Time Domain Induced Polarization (DIP)

CONCLUSION

Major advances of the application of the *Rayleigh* equation to the CO₂ biodegradation product released at ground surface compared to conventional methods of underground water or soil HC substrate analysis

Economic impact:

Reduction of the costs to follow-up or study depollution process compared to existing conventional methods using isotopic analysis of pollutants in subsoils by excavation

No boreholes, land manipulations, underground sampling are needed

Prospective:

Improve the accuracy of *in situ* biodegradation kinetic of hydrocarbons in contaminated aquifers, by providing best accurate values of ϵ fractionation factor for representative hydrocarbons pollutants on laboratory well characterize soil macrocosms, such as the experimental platforms PIVOTS-PRIME (joint Region Centre - Europe funded project ARD2020) under construction at BRGM and Labex Voltaire) .

Publications

Guimbaud C. et al., A new approach to quantify kinetic in situ biodegradation of hydrocarbons in a contaminated aquifer by CO₂ monitoring at ground surface with isotopic ¹³C/¹²C characterization, In prep to “Environmental Science: Processes & Impacts”.

Guimbaud et al., A quantum cascade laser infrared spectrometer for CO₂ stable isotope analysis: field implementation at a hydrocarbon contaminated site under bio-remediation; *Journal of Environmental Sciences*, 40, 60-74, 2016.

Noel et al., Combining geoelectrical measurements and CO₂ analyses to monitor the enhanced bioremediation of hydrocarbon-contaminated soils: a field implementation; *Applied and Environmental Soil Science*, Article ID 1480976, 2016a.

Noel et al., Suitable real time monitoring of the aerobic biodegradation of toluene in contaminated sand by Spectral Induced Polarization measurements and CO₂ analyses, *Near Surface Geophysics*, 14 (3), 263-273, 2016b.

Gogo, S. et al., In situ quantification of CH₄ bubbling events from a peat soil using a new infrared laser spectrometer, *Journal of Soils and Sediments*, 11, 545-551, 2011.

Acknowledgments

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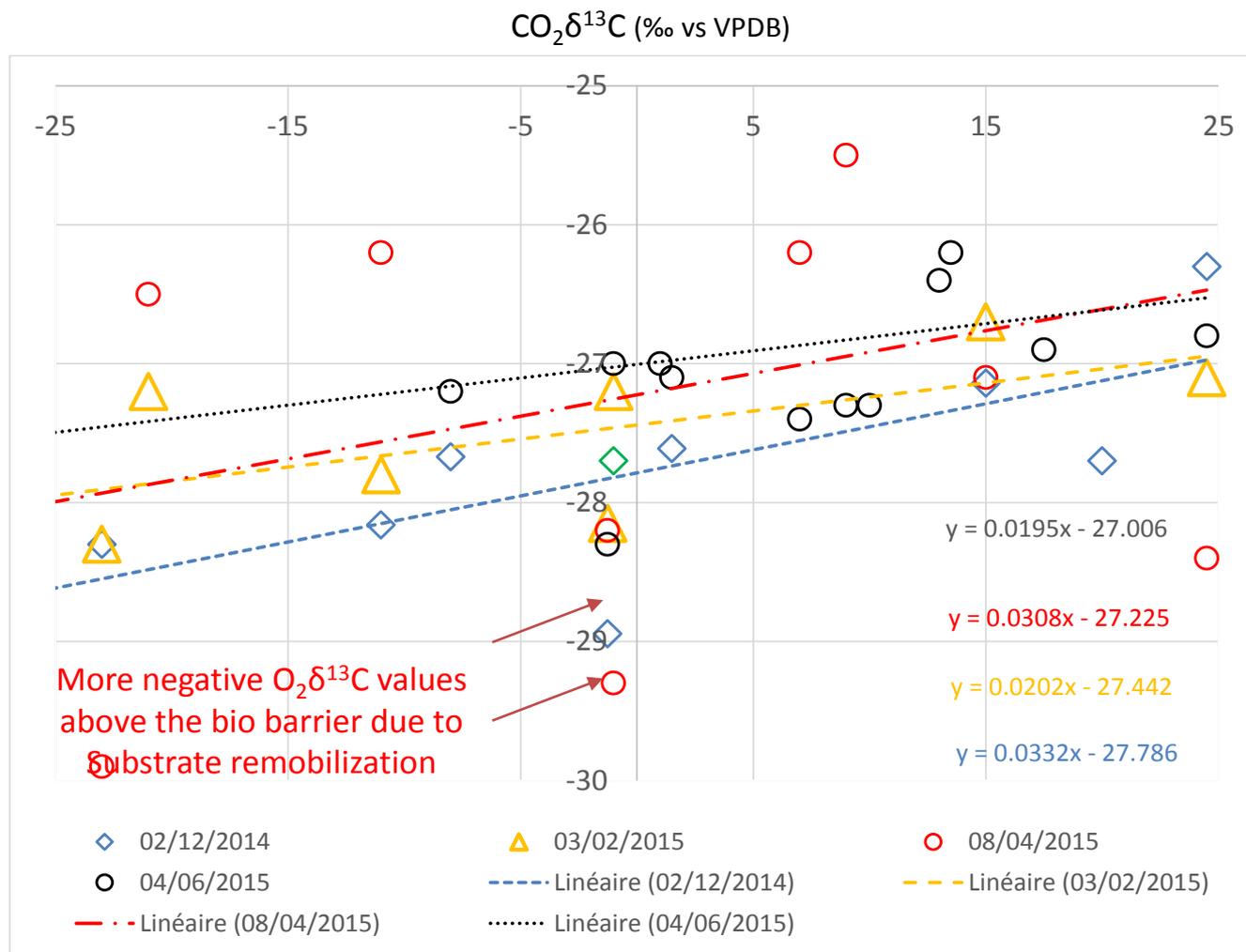
Durabilité de la Ressource
en Eau Associée aux
Milieux

Thanks for your attention

Additional materials

b) December 2014; February, April and June 2015, showing the rise of $\delta^{13}\text{C}/^{12}\text{C}$ of CO_2 over time

Coordinate axis of the pollution plume (m)



The 0 coordinates (Y-X axis intercept) is where the front line of the bio-depollution barrier is installed. Negative coordinates are located upstream the flow of the pollution plume. Aerobic bio-stimulation started on March 27, 2014.

Natural or bio-stimulated depollution dynamic of contaminated soil aquifers by gasoline hydrocarbons can be monitored by CO₂ fluxes and quantified by CO₂δ¹³C analysis emitted at ground surface from underground hydrocarbons bio-degradation.

-> The seasonal variation for the % of biodegradation rate per month (BR ft) from Rayleigh eq. (slide 15) agrees with CO₂ flux measurements (Slide 9)

-Due to low CO₂δ¹³C spatial resolution, the linear fit used to calculate (BR ft) from Rayleigh eq. at the scale of the polluted site suppresses the quantification of the bio-depollution efficiency just above the depollution barrier

-> Despite CO₂δ¹³C low spatial and temporal resolutions that do not cover the upstream zone affected by the a bio-stimulation in the scale of 1 year, a CO₂ flux increase (Slide 9) and a CO₂δ¹³C decrease (Slides 13 and 14) above the bio-depollution barrier is observed after installation and activation of the bio-barrier.

-> **Bio-degradation decay (BR f_t value) of substrate hydrocarbons may be underestimated above and downstream the reactive after the barrier construction and bio-activation, due to possible remobilization of fresh unreacted contaminants from the lower to upper level of the saturated zone of the aquifer.**

-BTEX conc. increases upstream, above and downstream the reactive barrier (not shown).

-Decrease, or no increase, of BR ft downstream the barrier, after bio-activation.

Bio-stimulated depollution dynamic is harder to asses due to disturbance of the pollution plume by the installation and activation of bio barrier