

intersol'2017

Congrès-Exposition International sur les Sols, les Sédiments et l'Eau
International Conference-Exhibition on Soils, Sediments and Water

On site Characterization of media contaminated with volatile compounds: total content and first estimation of the mobility

Valérie Laperche, Valérie Guérin, Benjamin Girardeau¹, Bruno Dubéarnès², Martin Gaboriau, Philippe Tresca³ et Coralie Monferran⁴

1: BRGM; 2 : EauGéo; 3 : TESORA; 4 : FONDISBIORITECH
Mardi 14 septembre 2016

ADEME



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



TESORA eau géo



Géosciences pour une Terre durable

brgm

Aim

The CISTTEM project is part of an approach to "Improve and consolidate methods of site diagnosis and characterization of pollution sources" in order to "Improve the evaluation of transfers ".

- Validate the on-site use of the HAPSITE for the measurement of volatile organic compounds on polluted site
- Approach mobility as close to field conditions as possible.

Plan

- > Methodology used
- > Presentation of the tested device
- > Results in terms of on-site analysis
- > Proposals for mobility estimation protocols
- > Conclusions and perspectives

Methodology used

1. Tests of 3 devices (gas chromatography):

- AccuSense® from SEER Technology, Inc.,
- TRIDION™ -9 from TORION,
- HAPSITE ER® from INFICON.

2. Selection criteria:

- Ease of use,
- Mode of injection,
- Capacity (identification, semi-quantification).

3. Approche de la mobilité:

- Identification of protocols,
- On site tests.

Presentation of the selected tool : HAPSITE

- > GC / MS (Gas Chromatography Coupled to a Mass Spectrometer)
- > Independent device: can be used Without PC, standalone / power and gas
- > Start-up time: 45 min (Heater of the instrument + operation tests)
- > Battery life
 - Autonomy: 2-3 hours
 - Charging time: 14-20 h
- > Direct analysis of the gases in air, ie the air in the headspace of a vial containing a liquid or solid sample (previously heated or not).



	Analysis	Analysis + exploitation
Nb of analysis per hour	3-4	1
Nb of analysis per day	20-25	6-7

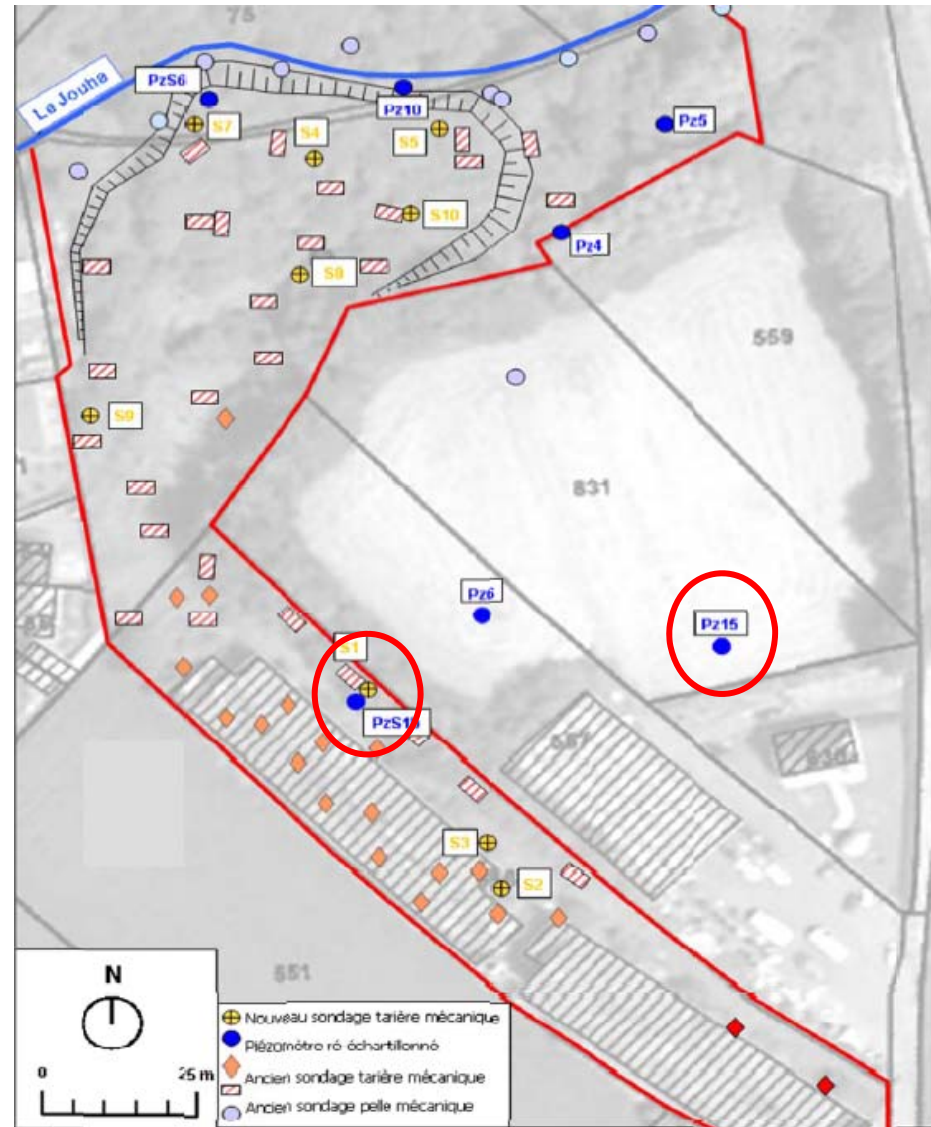
brgm

On site tests

> Sniffing / head of well

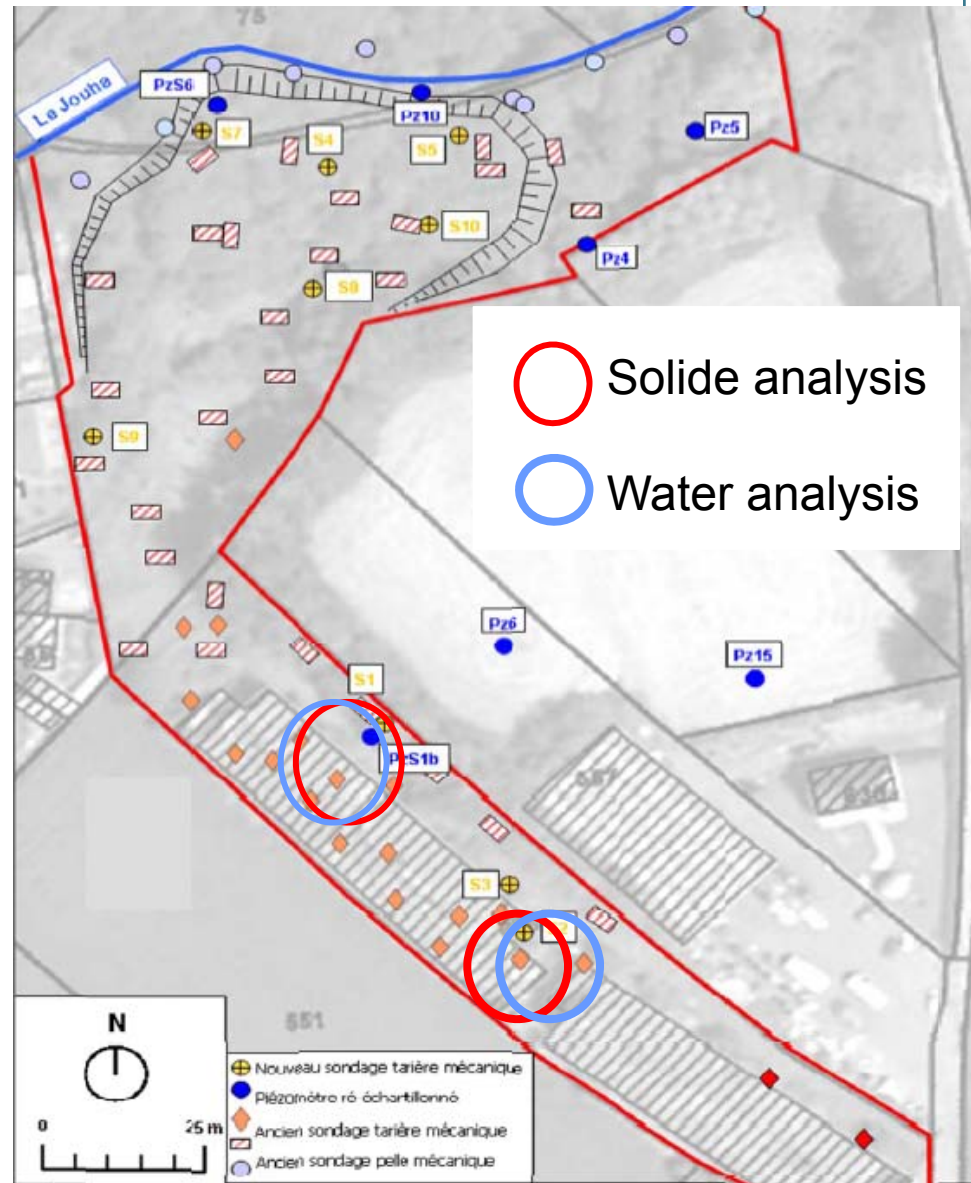


> Groundwater sampling



On site tests

> Drilling



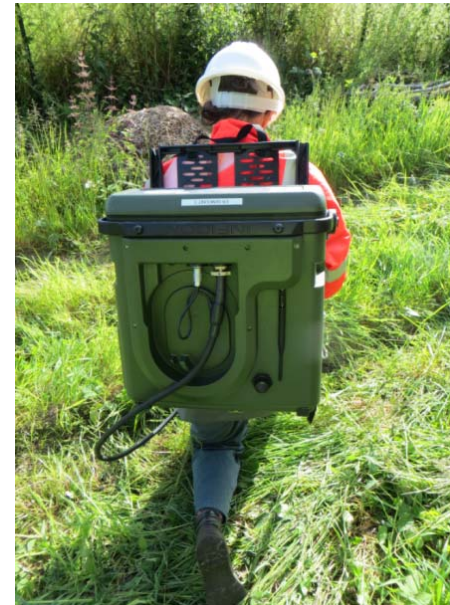
Feedback on on-site use

> The +

- Simple to use in everyday use even for non-chemists,
- Possibility of portability for measurements at the head of well.

> The –

- Battery life,
- Additional accessories are required for low temperatures.



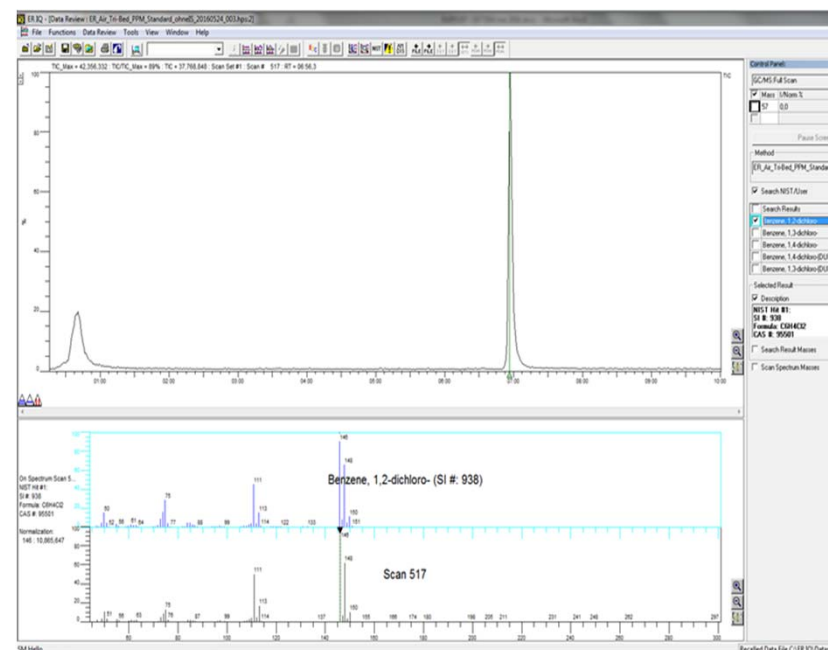
Results in terms of on-site analysis

> Qualification for 29 targeted compounds

- 1 PAH
- HVOC
- BETX
- Hydrocarbons

> NIST library included

Note: m and p xylenes are not differentiable and are analyzed as a sum. Same for m and p ethyltoluene.



1,1 dichloroethene	benzene	isopropyl benzene	1,2 dichlorobenzene
1,1 dichloroethene	trichloroethylene	m + p ethylToluene	1,2,4 trichlorobenzene
Dichloromethane	toluene	1,3,5 trimethylbenzene	naphthalene
trans 1,2 dichloroethene	tetrachloroethylene	o ethylToluene	1,2,3 Trichlorobenzene
cis 1,2 dichloroethene	ethylbenzene	1,3,5 trimethylbenzene	Dodecane
chloroforme	m + p xylene	1,2,4 trimethylbenzene	
1,2 dichloroethane	styrene	1,4 dichlorobenzene	
1,1,1 trichloroethane	o xylene	Decane	

Results in terms of on-site analysis

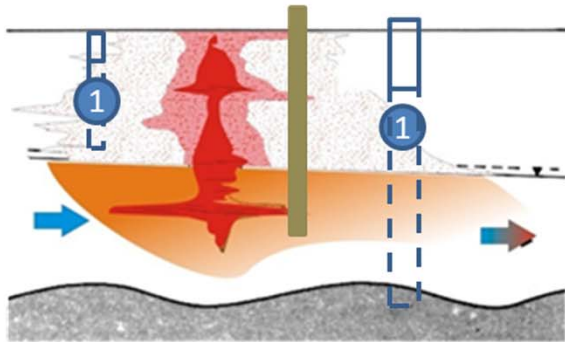
- > In the majority of cases a good match
- > **Detection of compounds not pre-selected in the analytical pack** (concentrations of the order of a few $\mu\text{g} / \text{L}$ or ppb):
 - Eg: during a campaign o-ethyltoluene and m + p ethyltoluene. These compounds were added following on-site analysis by HAPSITE.
- > **Some differences between compounds detected on site and in the laboratory:**
 - Presence of unidentified compounds at first analysis was confirmed on HAPSITE by studying the spectra in screening mode (expert mode).
 - Complementary work to better assess losses or false positives
 - Method of calculation of concentrations to be improved

Approach for an initial estimation of mobility

- > Gas analysis (well or cuttings):
Gives an image of the gas contamination in unsaturated zone (ZNS).
- > Water analysis:
 - Groundwater sampling (superficial part) gives an estimate of the risk of degassing in the unsaturated zone,
 - Water samples taken at several levels give an image of the possible heterogeneity of the contamination of saturated zone,
 - By heating the water samples we enhanced volatilization of low volatile compounds. This allows :
 - To be in increasing conditions for the estimation of the degassing potential in ZNS,
 - To approach the spectrum of compounds detected by laboratory methods.
- > Soil analysis:
 - Analysis of soil at ambient temperature gives a potential for degassing in ZNS,
 - A simplified test of on-site water leaching makes it possible to estimate the risk of contamination of the water resource

Gas analyses

Accumulation of the Henry and Raoult's Laws



NB : making a preliminary measurement with a PID avoids the risks of fouling of the column

Direct analysis with the HAPSITE probe

First approach of risk due to degassing in UZ



Analysis head of water well

Analysis in gas well

Analysis by sniffing directly on cuttings

Injection of a known gas volume

40 mL nitrogen-filled flask

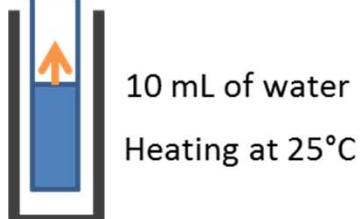
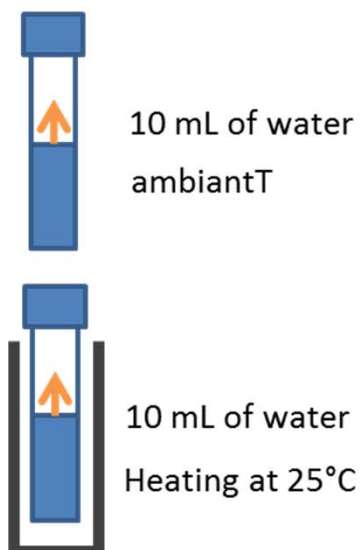
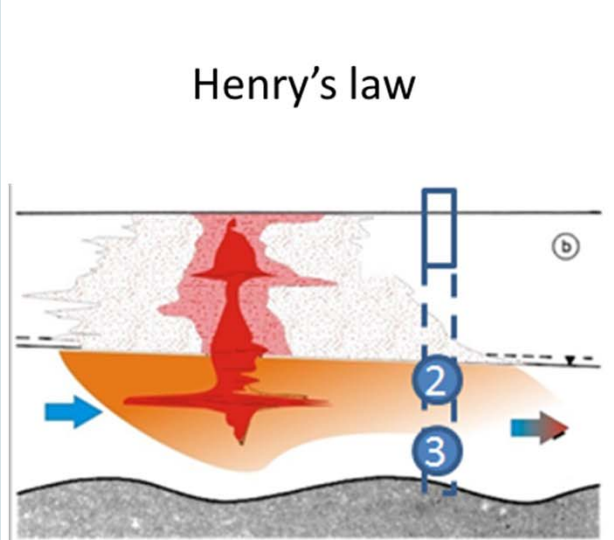
Dilution if necessary

u y m

Water analyses

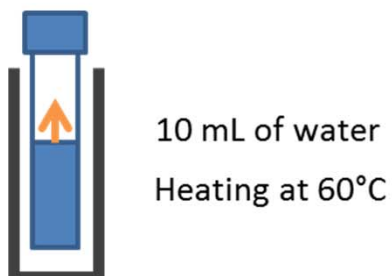
Indirect analysis with the HAPSITE probe – transfer in gas phase

Approach of the degassing risk from groundwater pollution



A maximising approach to mimic summer conditions

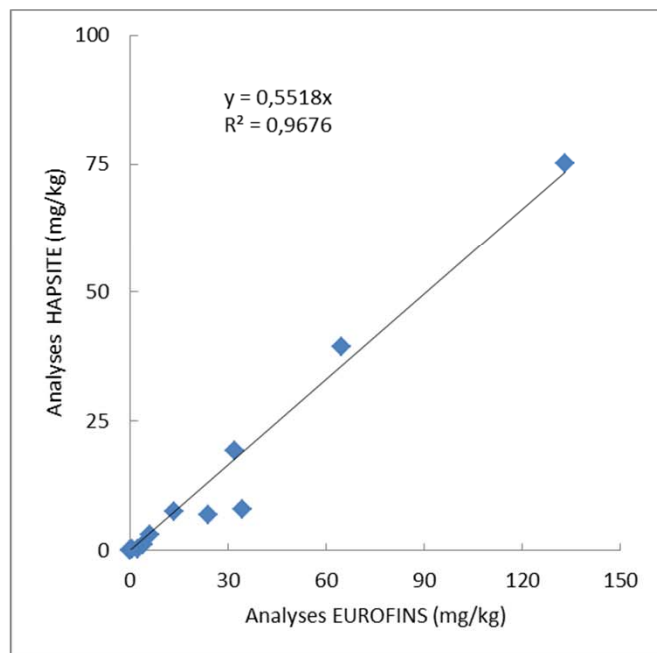
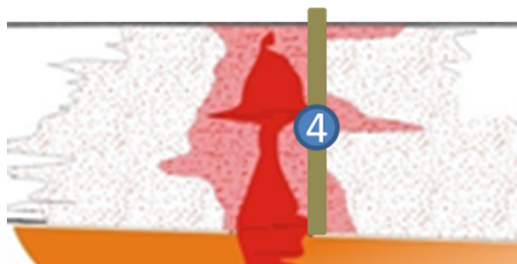
Approach to the concentration in water of volatile compounds



Heating makes it possible to get closer to the laboratory analyzes by forcing the passage in gas phase: makes it possible to detect more compounds than at ambient T

Soil analyses

Raoult's law



Indirect analysis with the HAPSITE probe – transfer in gas phase

Approach of the risk of degassing from UZ – Approach of the soil contamination



Ambiant T

Analyse of compounds in gas phase

x g of soil in variable volume

Approach of motility toward groundwater



T ambiante

100 mL of water

10 g of soil

Stir 3*2 min + 3*5 min pause



40 mL vial

10 mL of lixiviat



Conclusions et perspectives

- > The use of this portable GC has demonstrated:
 - its ability to obtain on-site an initial identification of compounds that are not included in the usual analytical packages.
 - Its ability to provide semi-quantitative analyses.
- This allows to adapt on site the analyses to be performed (case of an incomplete history of the site).
- > Regarding the estimation of the mobility, the first results are encouraging but it remains to consolidate the protocols to make them robust (usable and transferable to all soil types) and to develop routines for calculation.