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An evaluation of integrative passive samplers for measuring organic and inorganic chemicals in 15 springs in the Jura (Chlorokarst project)

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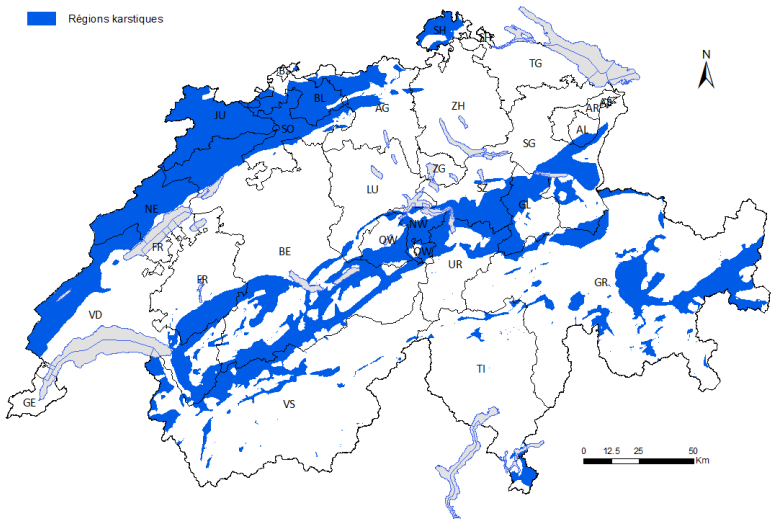
1. Context : many contaminated sites are located in karst in Switzerland

- 4’427 sites potentially contaminated with chlorinated hydrocarbons (CHCs) in karst in Switzerland (16.7%)
- Among them : 3’555 sites in the Jurassic Arc (13.4%)

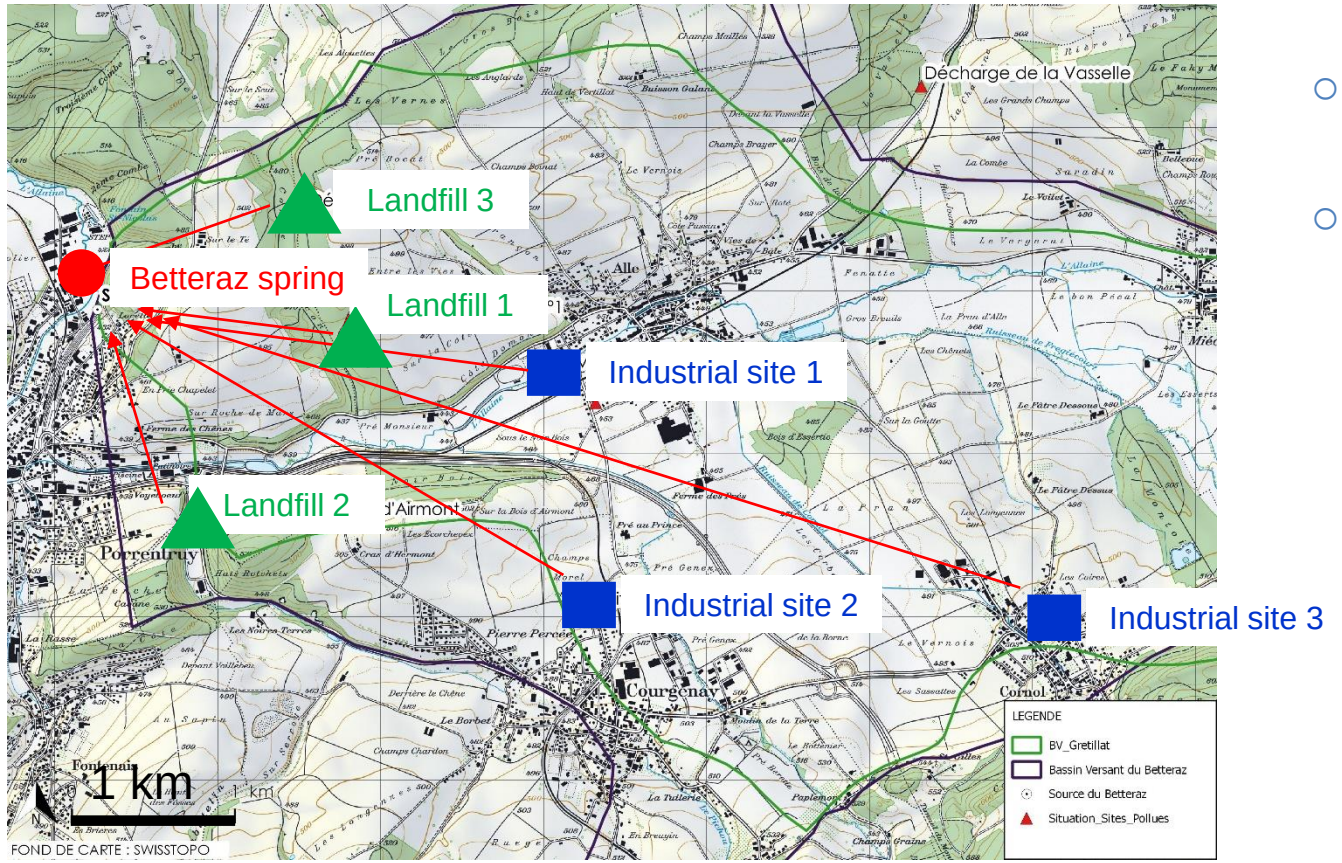


Karst : 24.5% of Swiss surface

26’502 sites potentially contaminated with CHCs

1. Context : difficult to assess the impact of contaminated sites on karst

- Springs are the easier groundwater monitoring points, but :



- They are usually located at large distances from the industrial sites or landfills
- Concentrations in springs **are low due to a strong dilution effect**

1. Context : difficult to assess the impact of contaminated sites on karst

- Springs are the easier groundwater monitoring points, but :
  - Concentrations in springs **fluctuate highly and rapidly**

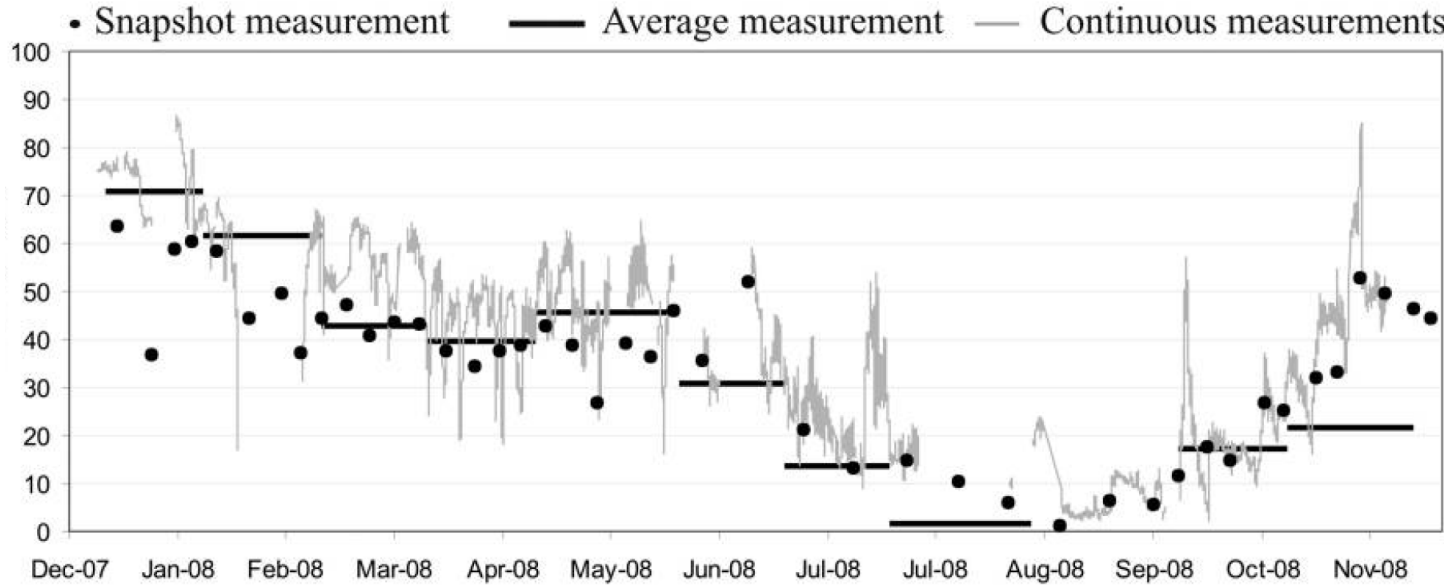
- Standard **snapshot** water samples : **inefficient**
- **Automatic** water samplers : **costs** of the device and repeated laboratory analyzes **prohibitive**
- Continuous or semi-continuous **in situ monitoring** of total CHCs concentrations : **in development**, no currently commercialized device

(P. Girod, 2014)

Time series of PCE and TCE concentrations in Betteraz spring (Jura) over 1 year

1. Context : specific investigation tools are required

- Integrative passive samplers
  - Samplers that allow to measure **time-integrated average concentrations** of contaminants in water
  - **No energy** (pumping) required to accumulate the contaminants in the sorbents constitutive of the samplers
  - Contaminant mass flux generated by a concentration gradient or a pressure gradient (**passive**)
  - **Inexpensive** devices are currently commercialized for measuring a large spectrum of organic and inorganic substances.



(J. Rozemeijer et al, 2010)

2. Goals : test of integrative passive samplers in springs

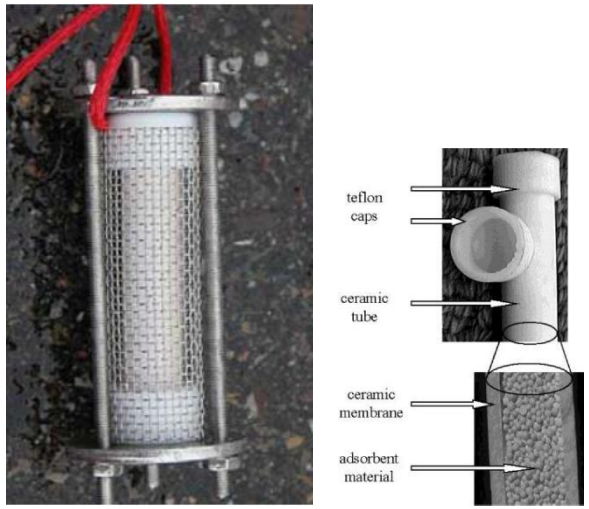
- Selection criteria of the samplers

  - Accumulate chlorinated hydrocarbons (CHCs) in priority
  - Long exposure periods : 2 to 3 months
  - Detection of low, but also high concentrations
  - Possible equipment of springs in various configurations
  - Resistant to water flow conditions in karst
  - Commercialized devices (no need to homemade production)

3. Materials : 3 integrative passive samplers were tested

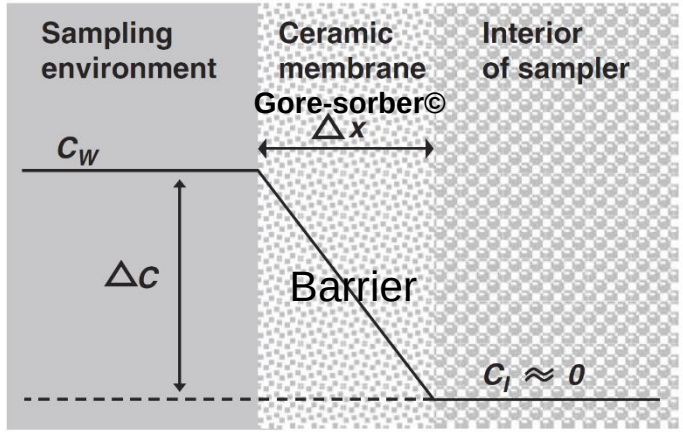
- Two diffusion passive samplers : Ceramic dosimeter and TIPS

Ceramic dosimeter



TIPS

Mass transfer by diffusion (Fick's first law)



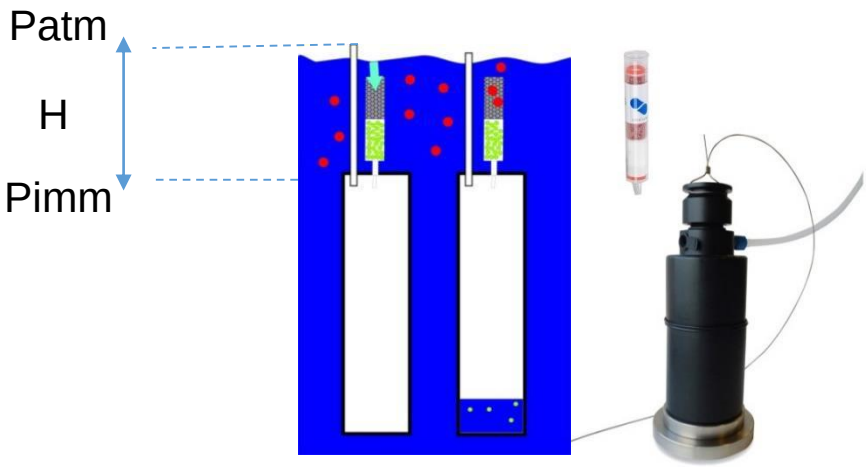
(H. Weiss et al., 2007)

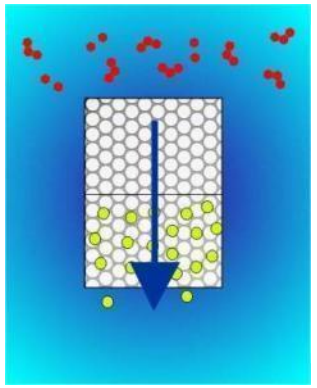
Concentration C_i in the sampler increases pseudo-linearly with time t : $C_i(t) = C_w \cdot k_1 \cdot t$

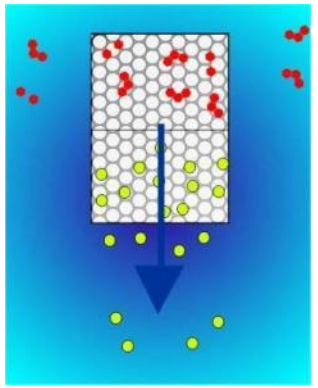
C_w : concentration in water
k_1 : sorption constant rate

3. Materials : 3 integrative passive samplers were tested

- One advection passive sampler : Sorbicell







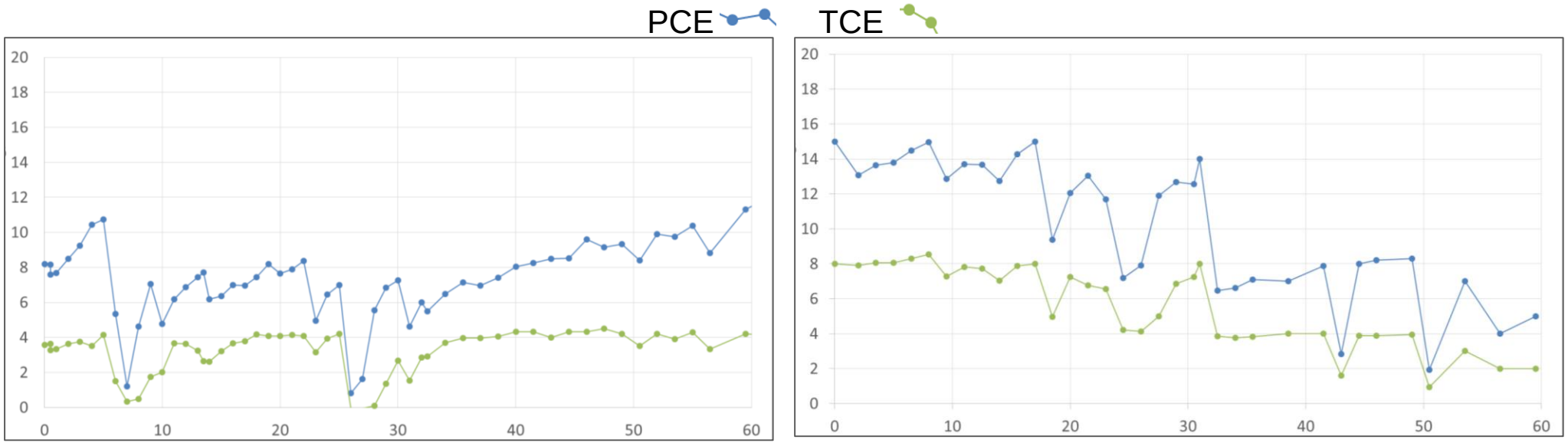
Water velocity in the cartridge : $u = -\frac{K}{\mu}\Delta(p + \rho g z)$

(H. De Jonge et al., 2011)

- The gradient of the hydrostatic pressure generates a flux in the cartridge
- Solid phase in the cartridge adsorbs the CHCs
- Dissolution of tracer salt is proportional to the water volume
- Concentration is computed from the mass of adsorbed CHCs and the quantity of dissolved salt.

4. First series of tests : compare the 3 samplers in the Betteraz spring

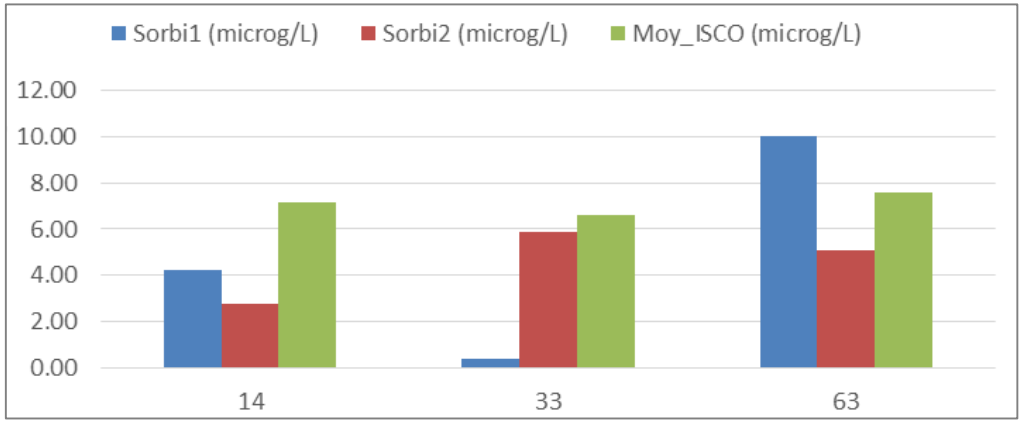
- Experimental protocol
  - Perchlorethylene (PCE) and Trichlorethylene (TCE) concentrations were measured with an automatic water sampler during the passive samplers exposure periods
  - The time-averaged concentrations of these data over the exposure period provide a reference to assess the validity of the concentrations measured with the 3 types of samplers.



4. First series of tests : compare the 3 samplers in the Betteraz spring

- Key results
  - The concentrations measured with the Sorbicell are consistent with the ISCO reference concentrations
  - TIPS under-estimate the reference concentrations, but can be used as sentinels
  - The ceramic dosimeters are not able to detect such low concentrations of CHCs.

Sorbicells



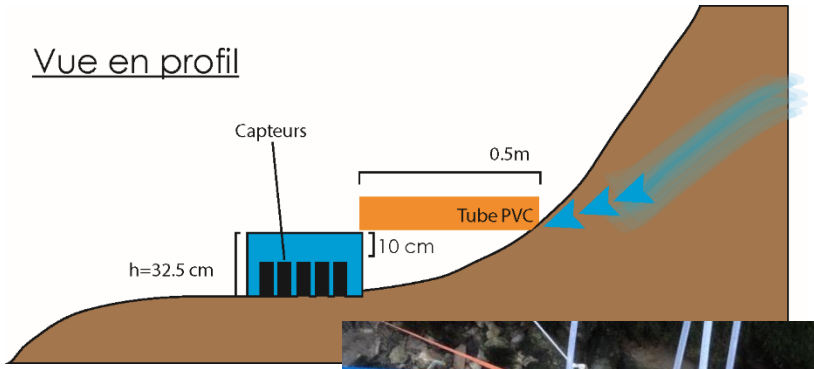
Exposure period in days

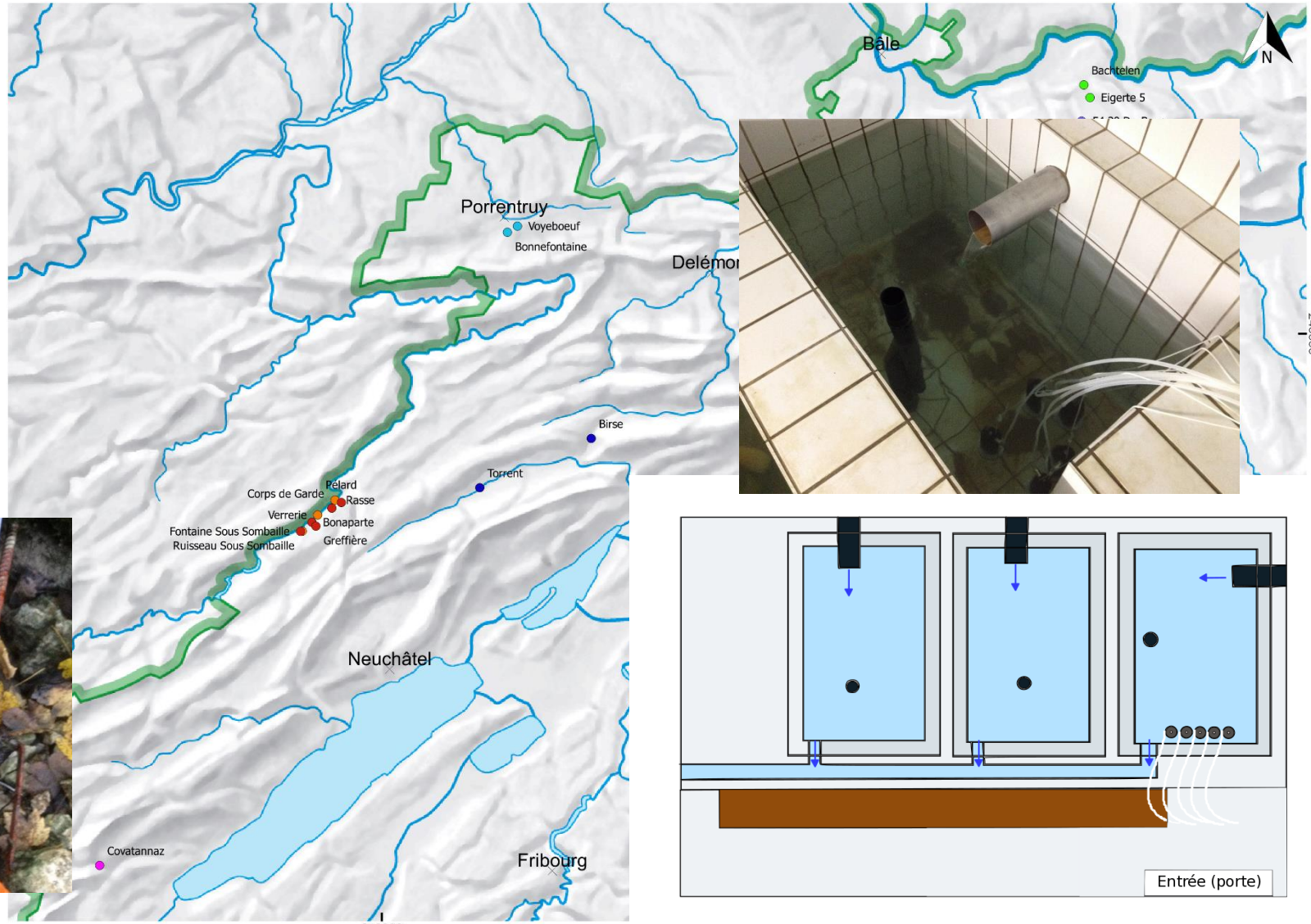
TIPS

Ceramic dosimeters

5. Second series of tests : Sorbicells in ~15 springs of the Jurassic region

- Various configurations
- Springs may be connected to contaminated sites
- Analyzes of various organic and inorganic compounds





5. Second series of tests : Sorbicells in ~15 springs of the Jurassic region

- Experimental protocol
  - 2 exposure periods : June – October and October – December 2016 (low flow conditions)
  - During each period in each spring :
    - 4 VOC cartridges for analyzing organic compounds (CHC, BTEX, PAH, phenolic compounds, PCB, MTBE)
    - 1 CAN cartridge for analyzing inorganic compounds (heavy metals, major elements)
    - 1 snapshot sample collected in the spring after 1 month
    - Volume of percolation water deduced from salt dissolution (laboratory) and measured in the field

5. Second series of tests : Sorbicells in ~15 springs of the Jurassic region

- Results : Sorbicell are able to measure very low concentrations
  - Detection of chlorinated hydrocarbons in 2 springs out of the ~15 equipped with integrative passive samplers, at very low concentrations.
  - Detection of metals in all the springs at low to very low concentrations, close to the limits of quantification (LOQ).
  - Concentrations measured with passive samplers are consistent with those measured with standard punctual water samples.
  - Sorbicell are able to measure concentrations, even in springs with discontinuous flow conditions, where snapshot samples can not be collected.

CHCs measured in the Covatannaz spring

In microg/L	Passive samplers		Snapshot samples	
	June-Oct.	Oct.-Dec.	June-Oct.	Oct.-Dec.
PER	< 0.4	< 0.5	0.5	0.8
TRI	0.4	0.68	1.1	1.5
1,2-DCE	0.35	0.40	0.9	1.9
1,1,1trichloréthane	< 0.2	< 0.3	< 0.1	0.2

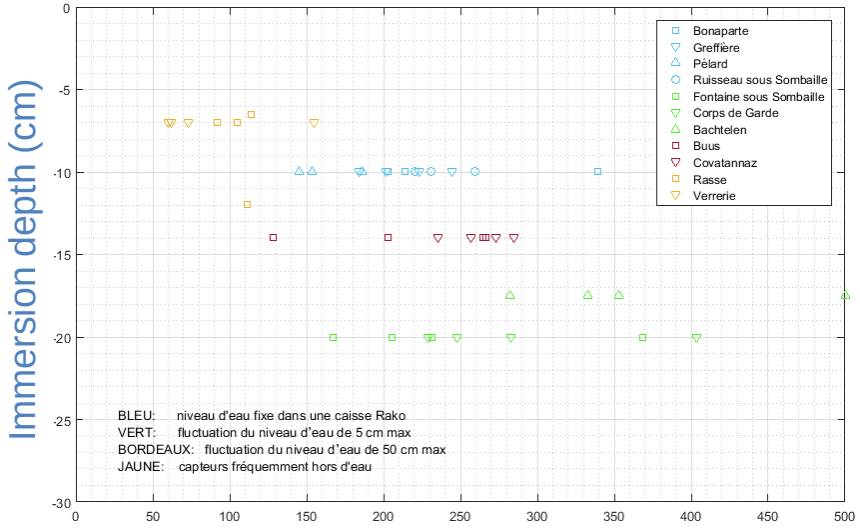
Metals measured in the Covatannaz spring

In microg/L	Passive samplers		Snapshot samples	
	June-Oct.	Oct.-Dec.	June-Oct.	Oct.-Dec.
Arsenic	< 0.2	< 0.6	< 1	< 1
Copper	0.7	2.2	< 2	< 2
Nickel	< 0.2	0.78	< 5	< 5
Lead	0.16	0.84	< 10	< 1
Tin	6.9	< 3	< 10	< 10
Zinc	**130**	**780**	**< 5**	**< 5**

5. Second series of tests : Sorbicells in ~15 springs of the Jurassic region

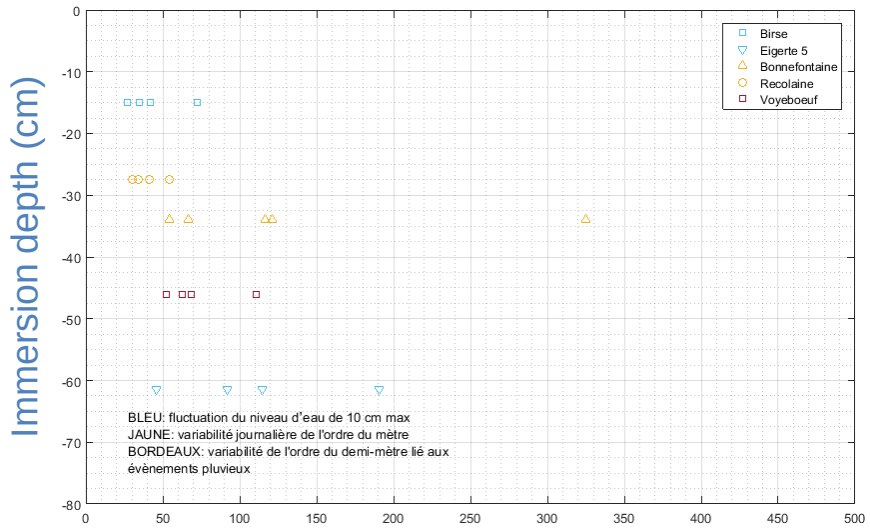
- Results : optimal exposure conditions of VOC Sorbicell samplers in springs (organic compounds)
  - Use of **Container** to collect water from spring with a ~constant immersion depth
  - Percolation volume of **~300 – 400 mL** over the exposure period (avoid < 50 mL) to insure acceptable low LOQs
  - The volume of percolation is smaller during the second month of exposure
  - Choose **immersion depth** and **permeability type** of the cartridges according to the above experimental graphs

Low permeability (VOC 101)



Volume of percolation (mL) /month

Intermediate permeability (VOC 102)



Volume of percolation (mL) /month

5. Second series of tests : Sorbicells in ~15 springs of the Jurassic region

- Results : optimal exposure conditions of CAN Sorbicell samplers (inorganic compounds)
  - The volumes of percolation are higher with the CAN than with the VOC of same reference (permeability of CAN 101 > VOC 101).
  - CAN 102 at ~30-40 cm depth allow a percolation volume of 200 – 400 mL.

- Anomalous concentrations in Zinc (and Tin) are found in the analyzes performed with Sorbicell for metals (CAN), but not in the snapshot samples.
- Additional laboratory test with “deionized tap water” showed that these metals may come from the constitutive elements of the passive samplers (filters in the cartridges, metallic parts of the reservoirs,…).
- Further investigations ongoing by Sorbisense

Metals measured in the Covatannaz spring

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6. Conclusions

Sorbicell integrative passive samplers prove to be efficient to measure :

- time-average pollutant concentrations in karst springs over long exposure periods (~2 months)
- very low concentrations of organic and inorganic compounds
- and to cope with variable and discontinuous flow which is difficult with standard sampling

Installation requires proper selection of :

- immersion depth and permeability level to control percolation volume → low limit of quantification

The Swiss federal office of the environment is thinking of recommending the use of Sorbicells to monitor karst springs, in the frameworks of the Contaminated sites ordinance.

7. Acknowledgements : our warmest thanks to

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