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### ► To cite this version:

A. Dabrin, M. Chappedelaine, A. Larrose, L. Dherret, F. Barbier Bessueille, et al.. Seasonal inorganic arsenic speciation in surface waters of a small vineyard watershed assessed by passive sampling method. DGT conférence, Sep 2015, San Sebastian, Spain. pp.1, 2015. hal-02601995

**HAL Id: hal-02601995**

**<https://hal.inrae.fr/hal-02601995>**

Submitted on 16 May 2020

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# Seasonal inorganic arsenic speciation in surface waters of a small vineyard watershed assessed by passive sampling method

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## 1 Context

Ardières and Morcille watersheds (Fig.1) display high concentrations of arsenic (As) with a strong seasonal variation of concentrations, reaching up to 20 µg/L during summer period (Fig. 2).

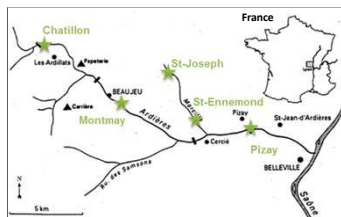


Fig 1. Mapping of Ardères-Morcille watersheds and sampling sites.

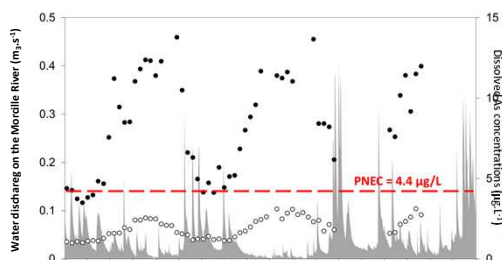
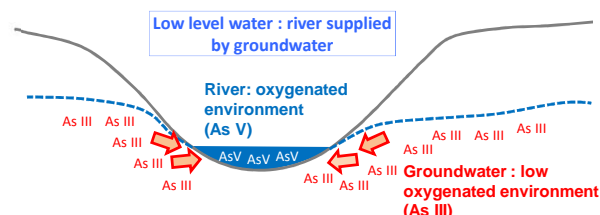


Fig 2. Water discharge of the Morcille River (m³.s⁻¹) and dissolved As concentrations (µg.L⁻¹) on upstream station (St Joseph, o) and on downstream station (St Ennemond, ●), during 2010-2012 period.

## As speciation in surface freshwaters

Hypothesis : inputs of As III from groundwater to the river are more pronounced during low level water

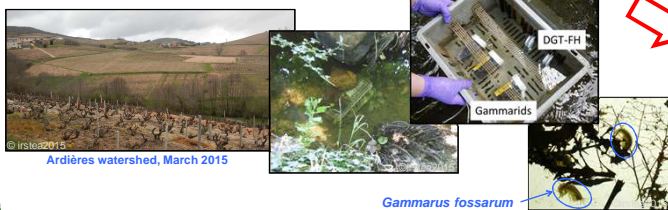


Relative toxicity of As for organisms

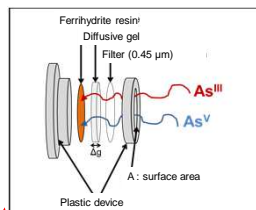
As III > As V

## 2 Aim of the project

To assess spatio-temporal variability of As III and As V contamination on Ardères and Morcille watersheds by passive sampling method.



## DGT-FH tool: Diffusive Gradient in Thin Film (Ferrihydrite resin)



Dissolved As labile concentration (As DGT) :

$$[As]_{DGT} = \frac{M \Delta g}{t A D}$$

M : mass of As trapped by the resin

Δg : thickness of the hydrogel + filter

t : exposure period

A : surface area of the tool

D : diffusive coefficient of As into the hydrogel

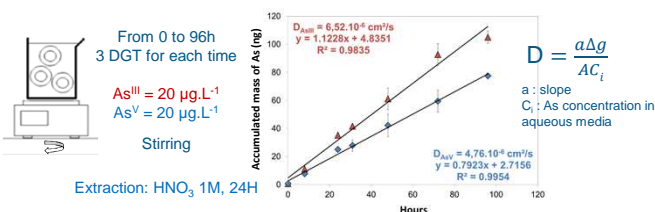
- Validate a method to measure As III and As V in surface waters, DGT eluates and biological matrix by HPLC-ICPMS
- Validate a method to extract As III and As V from DGT-FH
- Measure in situ As III and As V concentrations by DGT-FH during contrasted hydrological regime.
- Compare results with bioaccumulated As concentrations in a model organism (*Gammarus fossarum*)

## 3 Results

### Performance of the DGT-FH

#### Determination of diffusive coefficients: $D_{As^{III}}$ and $D_{As^V}$

Accumulation kinetics for As III and As V in the DGT-FH (n=3)



#### Extraction efficiency: As III and As V trapped by the ferrihydrite resins

##### Choice of the extractant:

N=6 resins	HCl, 1M, 1 hour		HNO <sub>3</sub> , 1M, 1 hour		NH <sub>2</sub> OH-HCl, 0.4M, 30 min	
	As <sup>III</sup>	As <sup>V</sup>	As <sup>III</sup>	As <sup>V</sup>	As <sup>III</sup>	As <sup>V</sup>
Amount of spiked As (ng)	68	924	68	924	68	924
As recovery (ng)	< LQ	593 - 770	< LQ - 16.6	154 - 200	18-23	190 - 219
RSD (%)	< LQ	9.3	45.2	10.7	9.3	5.4
As recovery (%)	0	73	0 - 17	19	31	22

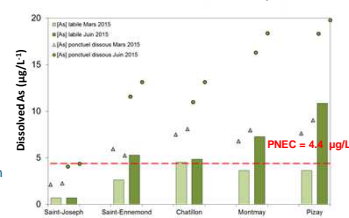
##### Improvement of extraction efficiency with NH<sub>2</sub>OH-HCl:

NH <sub>2</sub> OH-HCl	Test 1	Test 2	Test 3	
Concentrations	0.4 M	0.8 M	1 M	
Duration of extraction	from 30 min to 24h			No significative improvement of extraction efficiency

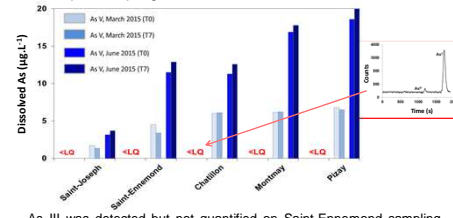
### In-situ measurements

#### Water column

Total dissolved As concentrations (<0.45 µm) and labile As concentrations measured by DGT-FH.



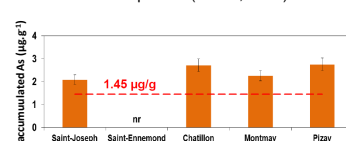
As III (●) and As V (●) concentrations (<0.45 µm) for spot sampling.



As III was detected but not quantified on Saint-Ennemond sampling site in June 2015.

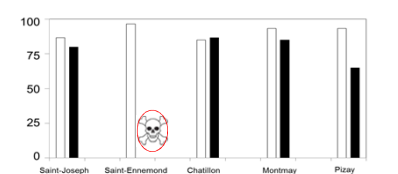
#### Biota: *Gammarus fossarum*

Bioaccumulation of total As in *gammarus fossarum* after 1 week of exposure (March, 2015).



Threshold value of contamination for bioaccumulation in *Gammarus fossarum* (Geffard et al., 2014)

Assessment of *gammarus fossarum* survival rate (%)



100 % of mortality on Saint-Ennemond site in June 2015  
No direct link with As contamination but global degradation of the environment

## 4 Perspectives

- To apply the more adapted extractant (NH<sub>2</sub>OH-HCl) on resins which were exposed in situ, allowing to decrease limit of quantification for As III
- To measure organic species of As in *gammarus fossarum*