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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).

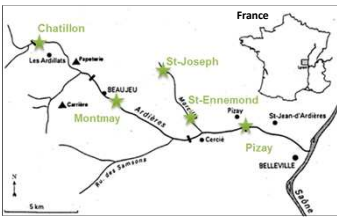


Fig 1. Mapping of Ardères-Morcille watersheds and sampling sites.

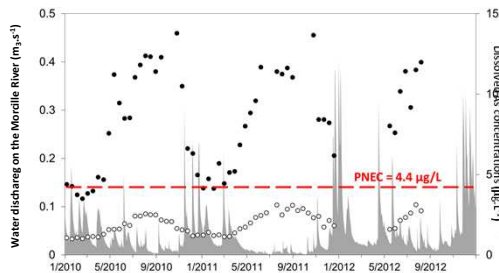
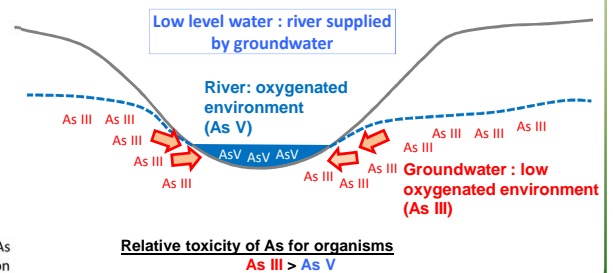


Fig 2. Water discharge of the Morcille River (m³.s⁻¹) and dissolved As concentrations (µg.L⁻¹) on upstream station (St Joseph, o) and on downstream station (St Ennemond, ●), during 2010-2012 period.

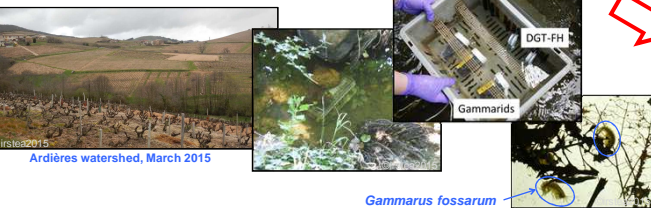
As speciation in surface freshwaters

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

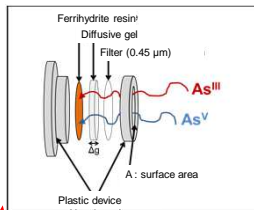


2 Aim of the project

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 (Ferrhydrite 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

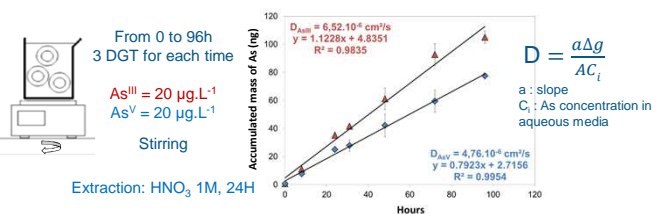
- Validate a method to measure As III and As V in surface waters, DGT eluates and biological matrix by HPLC-ICPMS
- Validate a method to extract As III and As V from DGT-FH
- Measure in situ As III and As V concentrations by DGT-FH during contrasted hydrological regime.
- Compare results with bioaccumulated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

3 Results

Performance of the DGT-FH

Determination of diffusive coefficients: D_{AsIII} and D_{AsV}

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



Extraction efficiency: As III and As V trapped by the ferrhydrite resins

Choice of the extractant:

N=6 resins	HCl, 1M, 1 hour		HNO ₃ , 1M, 1 hour		NH ₂ OH-HCl, 0.4M, 30 min	
	As ^{III}	As ^V	As ^{III}	As ^V	As ^{III}	As ^V
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 NH₂OH-HCl:

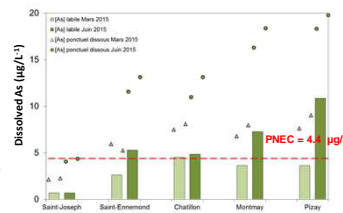
NH ₂ OH-HCl	Test 1	Test 2	Test 3
Concentrations	0.4 M	0.8 M	1 M
Duration of extraction	from 30 min to 24h		

No significative improvement of extraction efficiency

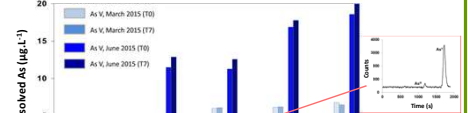
In-situ measurements

Water column

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



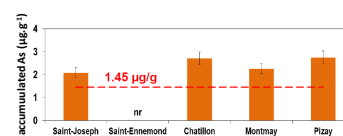
As III (red) and As V (blue) concentrations (<0.45 µm) for spot sampling.



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

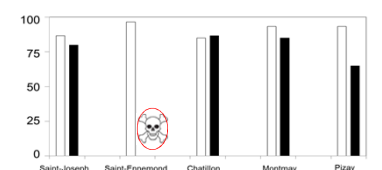
Biota: Gammarus fossarum

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 (NH₂OH-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*