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).

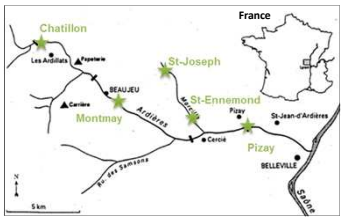


Fig 1. Mapping of Ardières-Morcille watersheds and sampling sites.

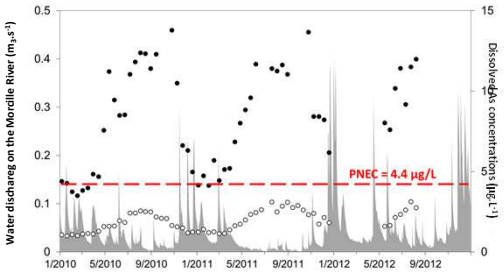
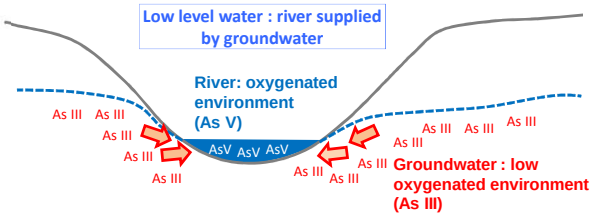


Fig 2. Water discharge of the Morcille River ($m^3.s^{-1}$) and dissolved As concentrations ($\mu g.L^{-1}$) on upstream station (St Joseph, o) and on downstream station (St Ennemond, ●), during 2010-2012 period.

As speciation in surface freswaters

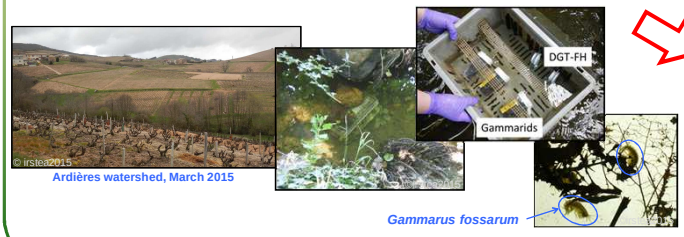
Hypothesis : inputs of As III from groundwater to the river are more pronounced during low level water



Relative toxicity of As for organisms
As III > As V

2 Aim of the project

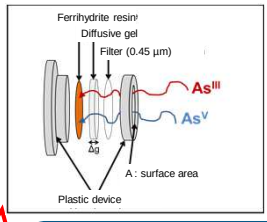
To assess spatio-temporal variability of As III and As V contamination on Ardières and Morcille watersheds by passive sampling method.



Ardières watershed, March 2015

Gammarus fossarum

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

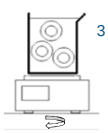
- Validate a method to measure As III and As V in surface waters, DGT eluates and biological matrix by HPLC-ICPMS
- Validate a method to extract As III and As V from DGT-FH
- Measure in situ As III and As V concentrations by DGT-FH during contrasted hydrological regime.
- Compare results with bioaccumulated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

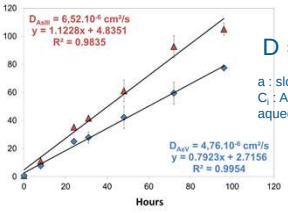


From 0 to 96h
3 DGT for each time

As^{III} = 20 µg.L^{-1}
As^{V} = 20 µg.L^{-1}

Stirring

Extraction: HNO_3 1M, 24H



$$D = \frac{a \Delta g}{AC_i}$$

a : slope
C_i : As concentration in aqueous media

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

Choice of the extractant:

N=6 resins	HCl, 1M, 1 hour		HNO_3, 1M, 1 hour		NH_2OH-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 NH_2OH-HCl:

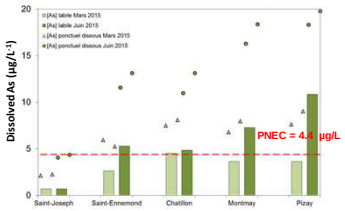
NH_2OH-HCl	Test 1	Test 2	Test 3
Concentrations	0.4 M	0.8 M	1 M
Duration of extraction	from 30 min to 24h		

No significative improvement of extraction efficiency

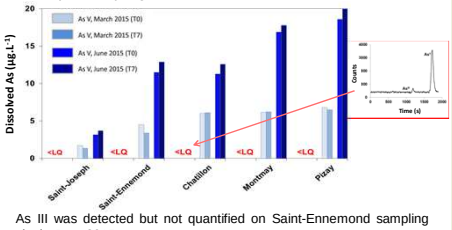
In-situ measurements

Water column

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



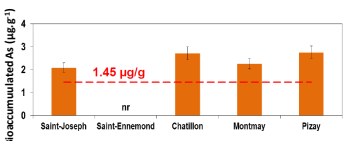
As III (■) and As V (■) concentrations (<0.45 µm) for spot sampling.



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

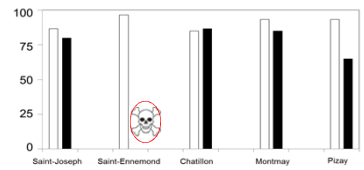
Biota: Gammarus fossarum

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



Treshold 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_2OH-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***

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Reference: *O. Geffard et al. (2014) Rapport de synthèse de l'étude pilote: déploiement de l'outil gammare encagé au niveau national, résultats pour les métaux ciblés. Rapport Irstea-ONEMA, 60p.*