In situ intercomparison exercise on “home-made” DGT for the monitoring of trace metals, mercury and arsenic in surface freshwaters

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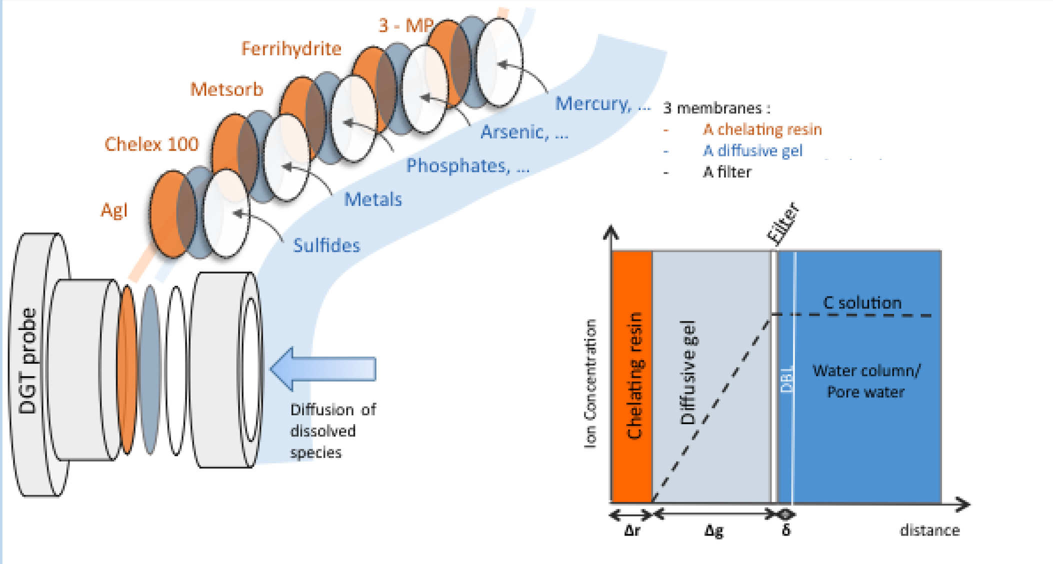
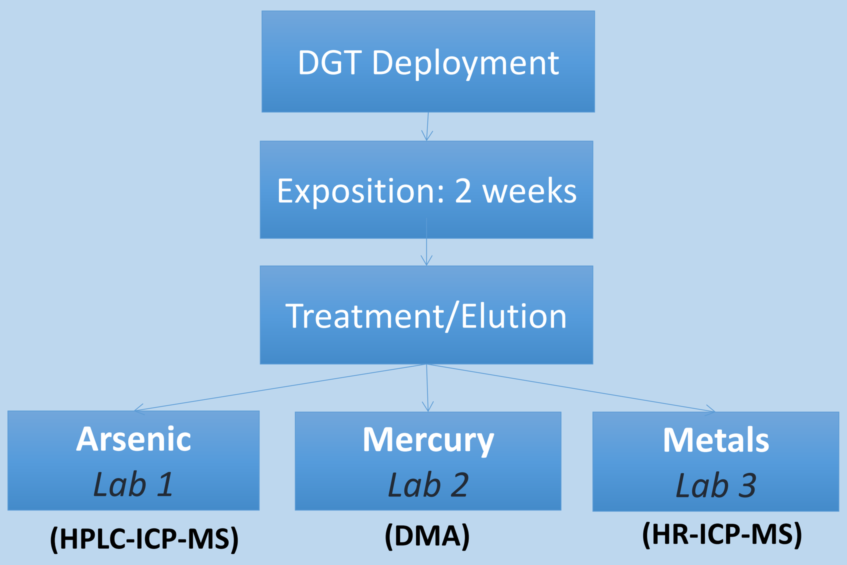
Most monitoring programs for surface waters within a legislative framework such as the Water Framework Directive (WFD) rely on conventional techniques such as spot or automated sampling to determine total dissolved concentration of a target substance. These sampling methods are generally time-consuming, do not take into account temporal variability and could induce samples contamination, loss of analyte or speciation modifications. The Diffusive Gradient in Thin films (DGT) technique is an alternative sampling method to assess a time-weighted average (TWA) metal concentration in surface waters, as it takes into account metal variations during the period of exposure. This tool coupled with different resins adapted to different kind of substances is commercially available but several laboratories are now developing their home-made DGTs. As each laboratory prepares its home-made gel or resin in different working conditions by using different reagents (i.e. purity and/or supplier) and by using different methods to determine diffusive coefficient, the comparison of results obtained with these tools could be not relevant. To answer this question, the objective of our study was to compare commercial and "home-made" DGT performances for cationic metals (Cd, Pb, Cu, Zn), arsenic and total mercury during an *in situ* intercomparison exercise in Deûle River.

Strategy and DGT method



Different kinds of chelating resins using in DGT method. In our study, Chelex 100 , 3-MP, spheron thiol and ferrihydrite chelating resins were used.



		Deployment of "home-made" DGT				Deployment of commercial DGT (from Lancaster)				Deployment Time
		Diffusive Gel	Resin	Number of prepared DGT	Team which will participate	Diffusive Gel	Resin	Number of bought DGT	Team which will participate	
Cationic	Cu, Cd, Pb, Zn, Ni, Fe, Mn, Co, Cr	polyacrylamide	Chelex	6 DGT (triplicat + 3 blanks)	Labs 1, 2, 3	polyacrylamide	Chelex	6 DGT (triplicat + 3 blanks)	furnished Lab 2	2 weeks
Hg speciation	Total Hg	agarose	3-mercapto	6 DGT (triplicat + 3 blanks)	Labs 1, 2, 3	polyacrylamide	spheron thiol	12 DGT (2 triplicat + 6 blanks)	furnished Lab 2	
	Hg(II) and MeHg	agarose	3-mercapto	6 DGT (triplicat + 3 blanks)	Labs 1, 2, 3	polyacrylamide	spheron thiol	12 DGT (2 triplicat + 6 blanks)	furnished Lab 2	
As		polyacrylamide	3-mercapto	6 DGT (triplicat + 3 blanks)	Labs 1, 2, 3	polyacrylamide	ferrihydrite	6 DGT (triplicat + 3 blanks)	furnished Lab 2	

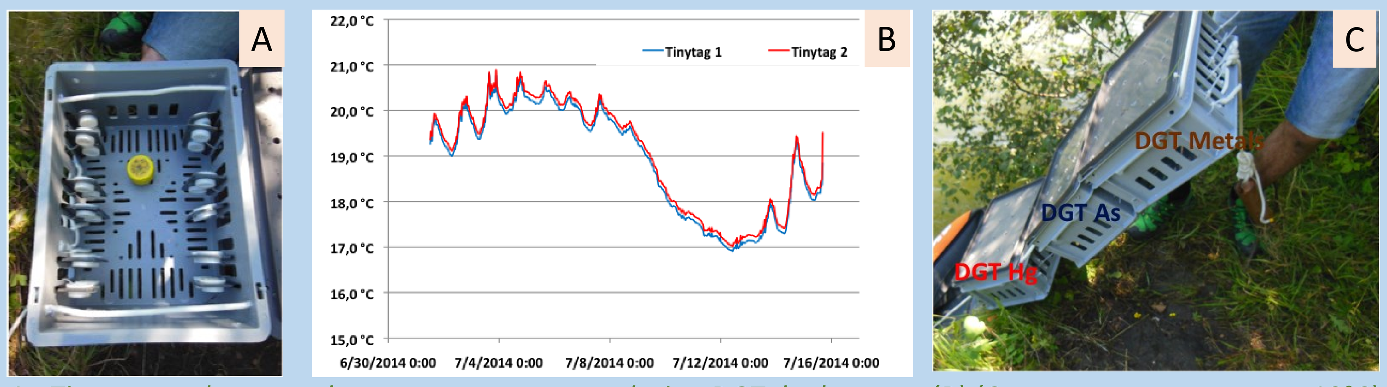
Analysis of arsenic, total mercury and cationic DGTs performed respectively by Lab 1, 2 and 3. Note that comparison is done between manufacturing of « home-made » chelating resin+diffusive gel and do not into account treatment + analysis with specific apparatus.

Sampling site

DGT exposition in Deûle river (North of France) near Douai Town. Station situated near Metaeurop, former which has strongly impacted this site until 2003 by metal discharges.

parameter	unit	01/07/2014	15/07/2014
DOC	mg/L	2,45	2,5
NO_3^-	mg/L	30	27
PO_4^{3-}	mg/L	0,3	0,63
HCO_3^-	mg/L	305	291
Cl^-	mg/L	45	39
SO_4^{2-}	mg/L	59	54
Ca^{2+}	mg/L	124	111
Mg^{2+}	mg/L	7,4	6,7
Na^+	mg/L	24	22,5
K^+	mg/L	5,3	5,2

Major parameters measured in the sampling site from the beginning to the end of DGT exposition



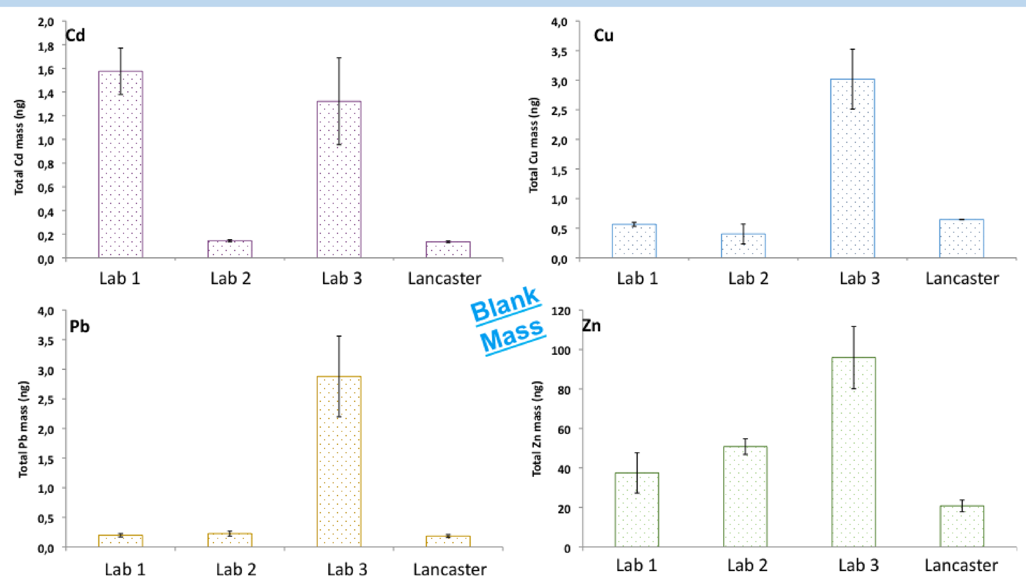
A : Tinytag used to record average temperature during DGT deployment (B) (C: average temperature : 19°C)

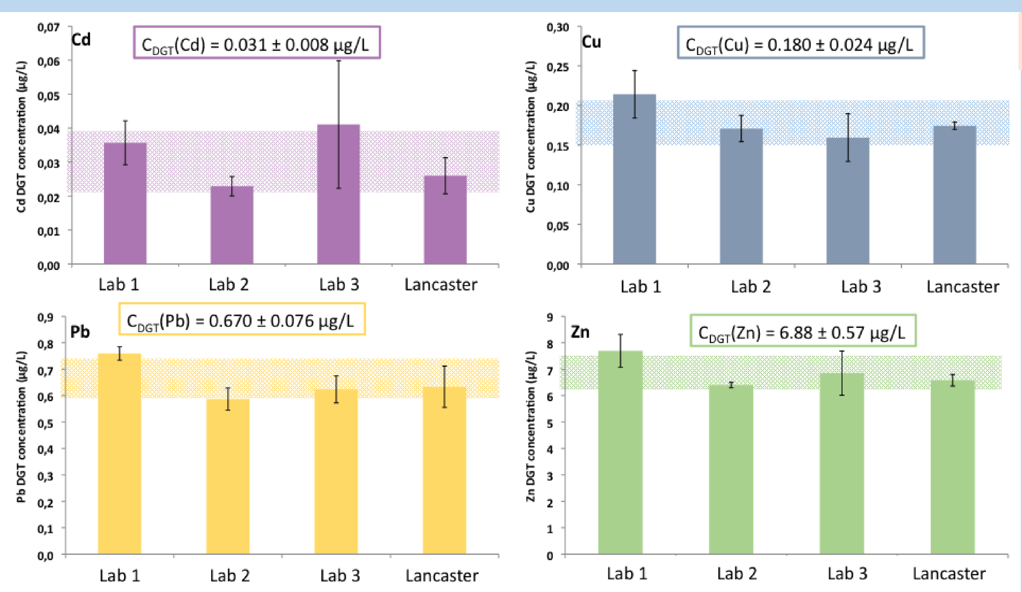
Results and dicusssion

Metals

A

Team	Δg (diffusive gel) mm	D reference	Thickness filter (mm)	Filter nature
Lab 1	0.80	DGT Research	0.135	Cellulose acetate
Lab 2	0.80	DGT Research	0.18	nitrocellulose
Lab 3	0.80	DGT Research	0.135	cellulose acetate
Lancaster	0.78	DGT Research	0.18	nitrocellulose



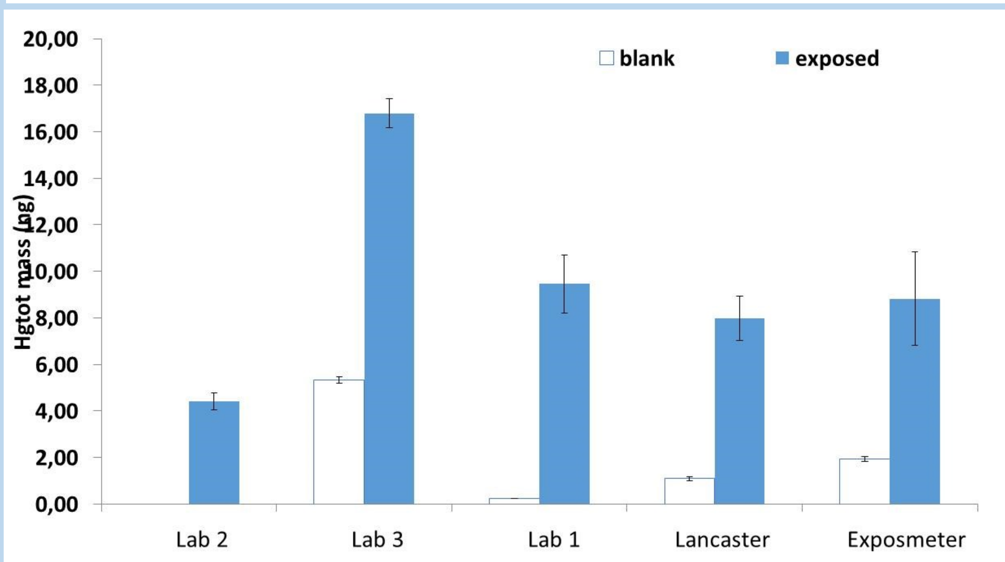


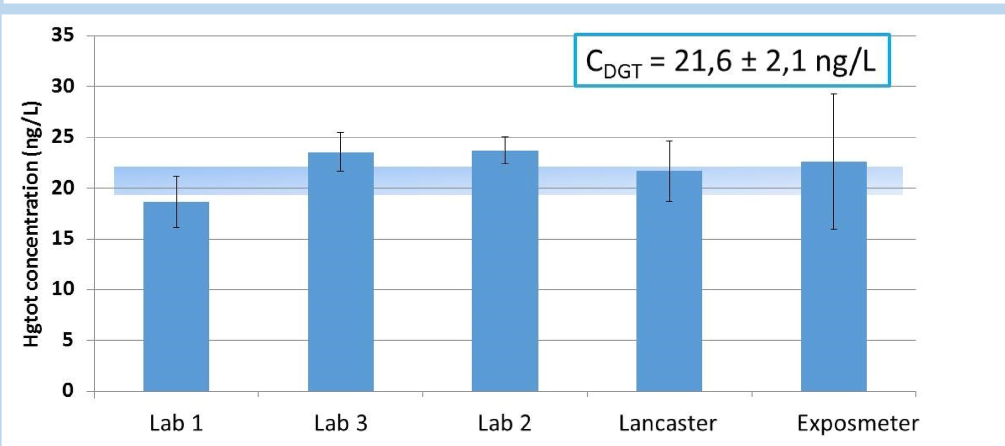
→ Same diffusive gel thickness for all DGTs : ~0.8 mm (A)
→ Same diffusion coefficient (Lancaster) (A)
→No difference between mass and concentration variations
→Metal concentration from home-made DGT close to commercial DGT (B)

Total mercury

A

	Team	Δg (diffusive gel) mm	D T=18,965° C cm²/s	D reference	Thickness filter (mm)	Filter nature
3-MP	Lab 1	0.50	$8.16\ 10^{-6}$	Kinetic exp.	0.135	Cellulose acetate
	Lab 2	0.60	$3.57\ 10^{-6}$	Kinetic exp.	0.18	Cellulose nitrate
	Lab 3	0.60	$9.31\ 10^{-6}$	Kinetic exp.	0.135	Cellulose acetate
spheron thiol	Lancaster	0.76	$7.4\ 10^{-6}$	Docekalova and Divis, 2005	0.135	Cellulose nitrate
	Exposmeter	0.80	$7.4\ 10^{-6}$	Docekalova and Divis, 2005	0.135	Cellulose acetate



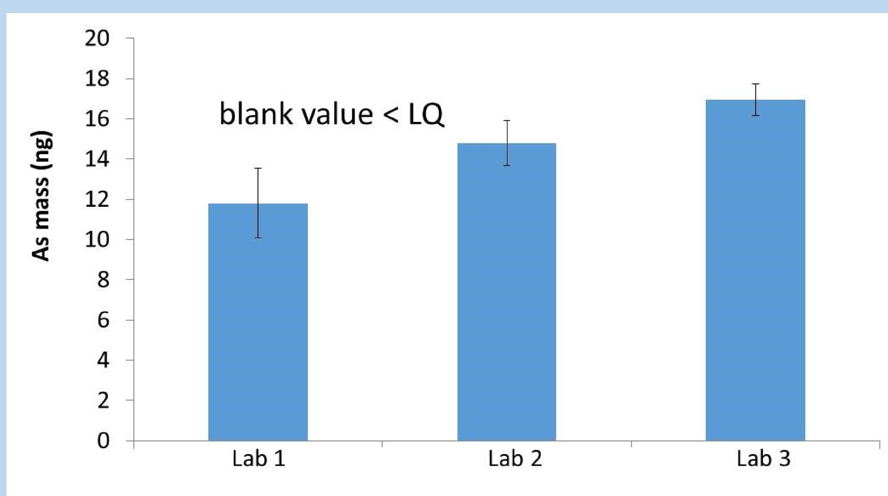


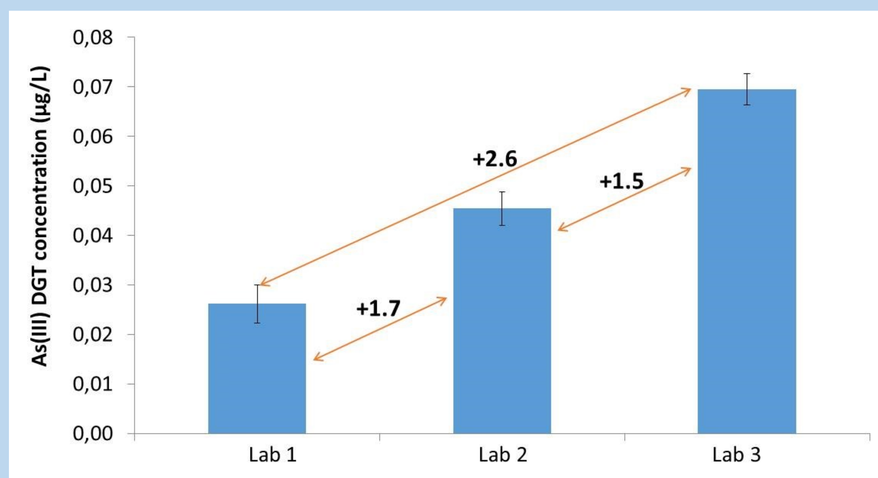
→Blank values (B) shown differences imputed to clean room conditions (lab 3 : polarographic environment)
→Same concentration range (C) for all results
→Different levels of Hg accumulation on 3-MP resin for each lab (B) due to « home-made » DGT used
→Calculation of Hg concentration using experimental diffusive coefficient (A)

Arsenic

A

	Team	Δg (diffusive gel) mm	D (T=18,965 °C) cm²/s	D reference	Thickness filter (mm)	Filter nature
3M	Lab 1	0.50	$7.45\ 10^{-6}$	Bennett et al., 2011	0.135	Cellulose acetate
	Lab 2	0.70	$7.45\ 10^{-6}$	Bennett et al., 2011	0.18	nitrocellulose
	Lab 3	0.86	$6.09\ 10^{-6}$	Kinetic exp.	0.135	cellulose acetate
ferrhydrite	Lancaster	0.78	$3.45\ 10^{-6}$	???	0.18	nitrocellulose





→Blank values < LQ (B)
→All arsenic concentrations determined from DGT method are differents (C)
→Need to characterize own diffusion coefficients for each « home-made » DGT used (A)

Conclusion

→Intercomparison exercise has shown a good fit between the different concentrations of trace metals and total mercury sampled by "home-made" DGT.
→Results have clearly indicated that diffusion coefficients have to be determined for each "home-made" DGT (chelating resin+diffusive gel+filter) in order to achieve the best suitable results.
→Working conditions from clean lab to polarographic laboratory (using mercury drop electrode) impact blank results

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