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

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# *In situ* intercomparison exercise on "Home-made" DGT for the monitoring of trace metals, mercury and arsenic in surface water

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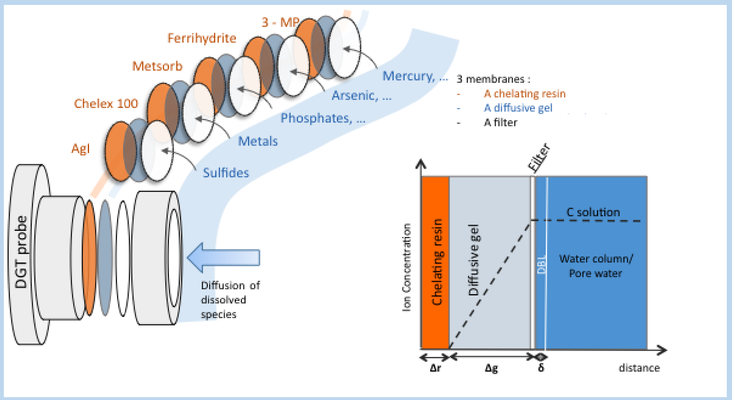
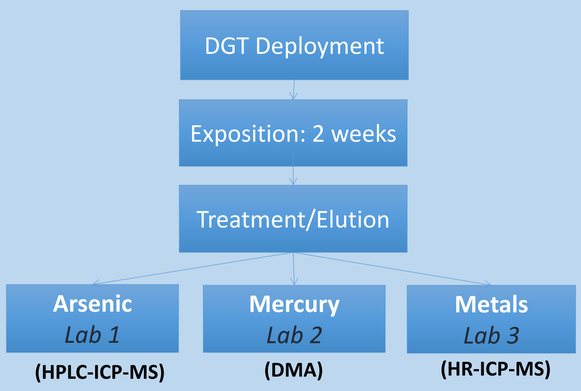
Most monitoring programs for surface waters within a legislative framework such as the Water Framework Directive (WFD) rely on conventional techniques such as spot or automated sampling to determine total dissolved concentration of a target substance. These sampling methods are generally time-consuming, 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 | |

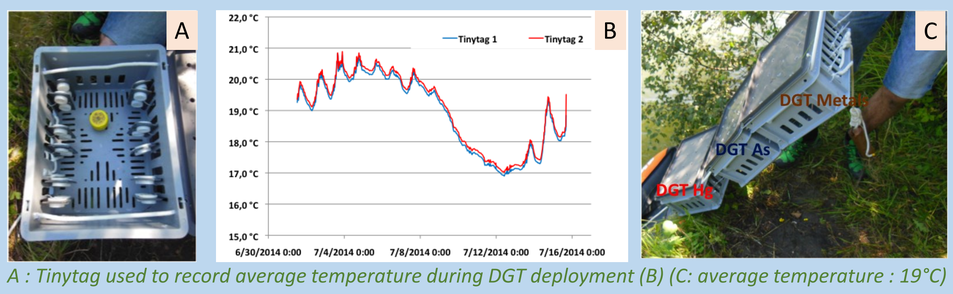
*Analysis of arsenic, total mercury and cationic DGTs performed respectively by Lab 1, 2 and 3. Note that comparison is done between manufacturing of « home-made » chelating resin+diffusive gel and do not into account treatment + analysis with specific apparatus.*

## 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*



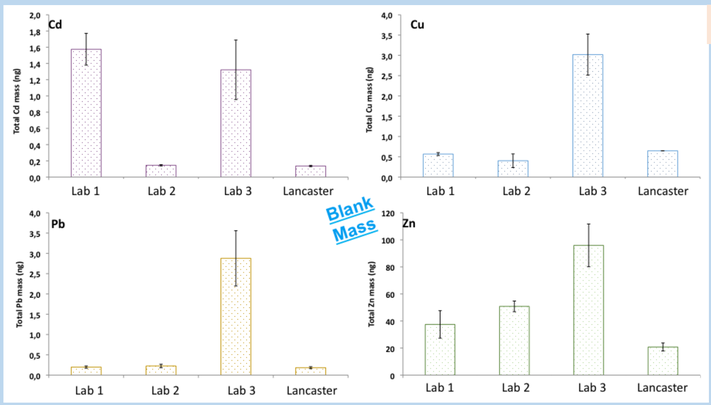

*A : Tinytag used to record average temperature during DGT deployment (B) (C: average temperature : 19°C)*

## Results and dicusssion

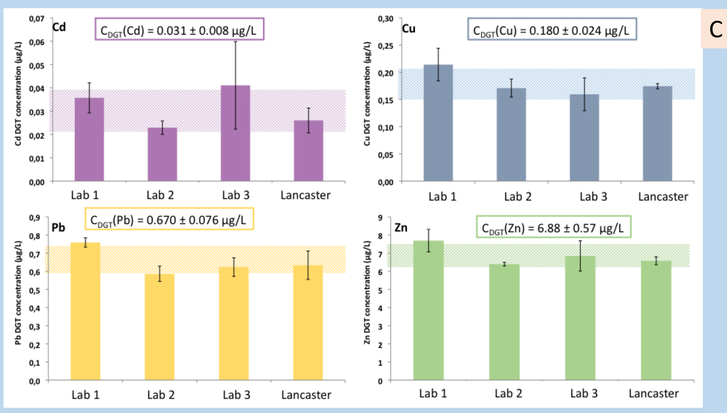
### Metals

| | Team | Δg (diffusive gel) mm | D reference | Thickness filter (mm) | Filter nature |
|---|---|---|---|---|---|
| A | 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 |

B




C

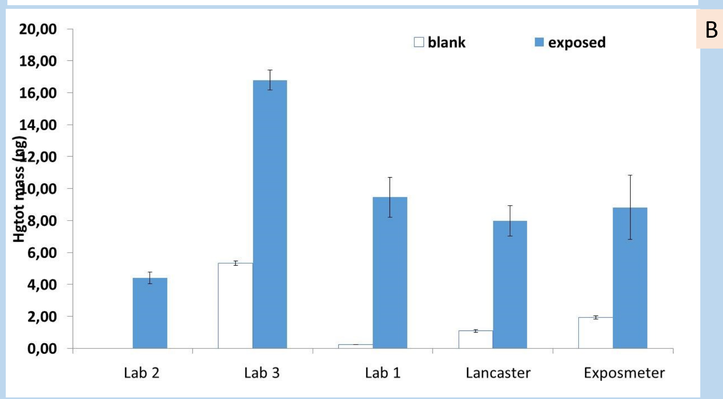



→ Same diffusive gel thickness for all DGTs : ~0.8 mm (A)
→ Same diffusion coefficient (Lancaster) (A)
→No difference between mass and concentration variations
→Metal concentration from home-made DGT close to commercial DGT (B)

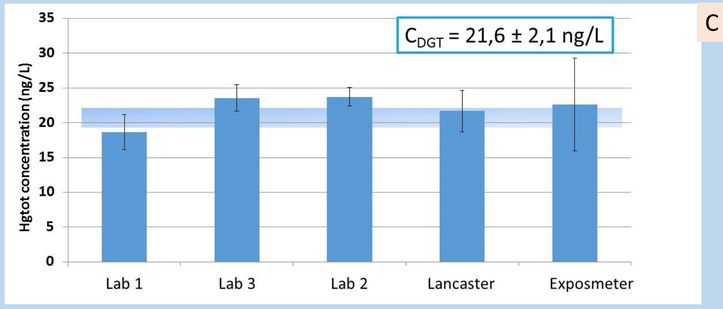
### Total mercury

| | Team | Δg (diffusive gel) mm | D T=18,965° C cm²/s | D reference | Thickness filter (mm) | Filter nature |
|---|---|---|---|---|---|---|
| A | Lab 1 | 0.50 | $8.16\ 10^{-6}$ | Kinetic exp. | 0.135 | Cellulose acetate |
| 3-MP | 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 |

B




C

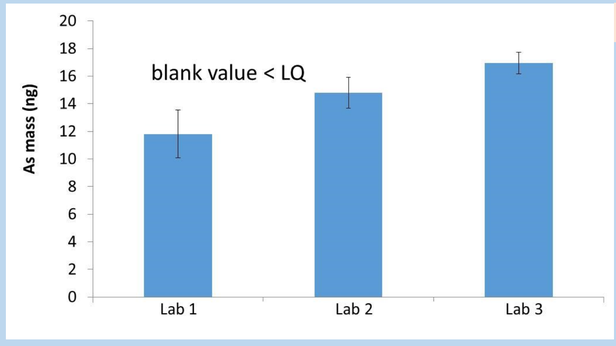



→Blank values (B) shown differences imputed to clean room conditions (lab 3 : polarographic environment)
→Same concentration range (C) for all results
→Different levels of Hg accumulation on 3-MP resin for each lab (B) due to « home-made » DGT used
→Calculation of Hg concentration using experimental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

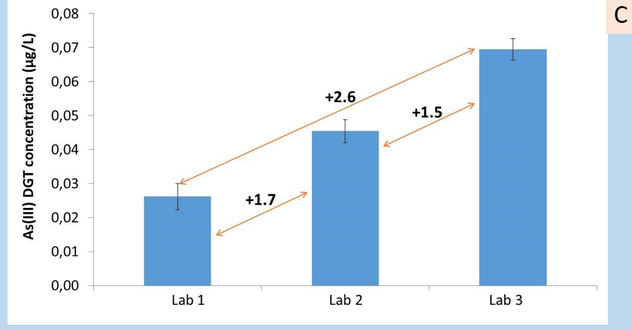
### Arsenic

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

B




C




→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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