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Monitoring of trace element in groundwater by DGT

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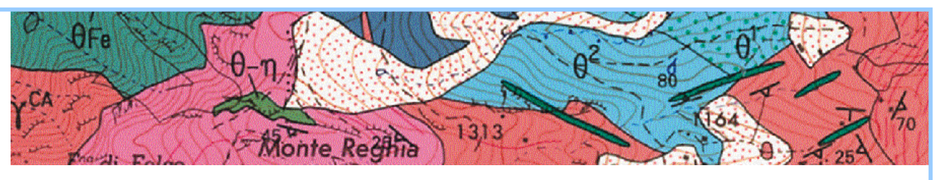
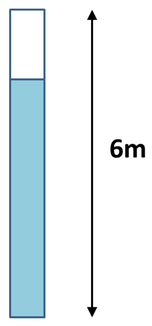


Applicability of DGT to groundwater monitoring of trace elements

The aim of this work is to evaluate the advantages and limits of DGT (passive sampling technology) for groundwater monitoring of trace elements. Four campaigns of measurements were conducted in order to estimate some characteristics of DGT in groundwater context and to compare concentrations in water estimated by passive sampling with those obtained by classical sampling. Classical Chelex DGT were used with some application of DGT with different diffusive gel thickness.

Deployment strategy

- Piezometric level : 1,4m
- Spot sampling : before and after purging (depth : 3m)
- Passive sampling DGT : triplicate at a depth of 3m (except campaign 1 : 2 and 4,5m)
- Diffusive gel thickness : 1,18mm except campaign 3 (triplicate with 0,76, 1,18 and 1,95 mm



Diffusive boundary layer estimation

Low flow of water is responsible in some environmental context for the formation of a diffusive boundary layer (DBL) at the surface of DGT. Underground water can be seen as a potential context in which this DBL should not be neglected for DGT concentration calculation. The DBL specific to this site was estimating by using three types of DGT of different diffusive gel thickness Δg during campaign 3.
Data were treated according to Kent W. Warnken, Anal. Chem. (2006). For different trace metal, curves 1/M=f(Δg) were plotted, with M the amount of metal fixed on DGT. The DBL thickness is then given by

$$\delta = \frac{b}{m}\left(\frac{D_W}{D_{gel}}\right)$$

With b and m, y intercept and slope of the curve and Dw and Dgel, diffusion coefficients in water and gel.

Diffusive boundary layer thickness estimation (mm)									
Al	Cr	Mn	Fe	Ni	Co	Cu	Zn	Cd	Pb
0.9	0.8	0.6	5	1.0	0.7	1.0	1.3	1.6	0.6

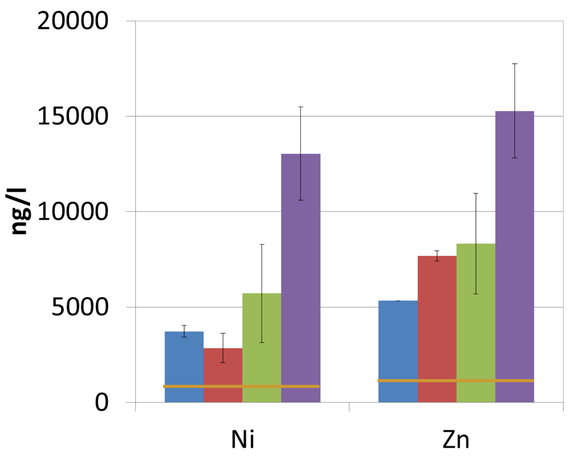
Fe result was considered abnormal and was rejected. As a mean result, thickness was estimated to around 1 mm. These results seem to indicate that for this site, DBL could not be neglected in the treatment of DGT results.

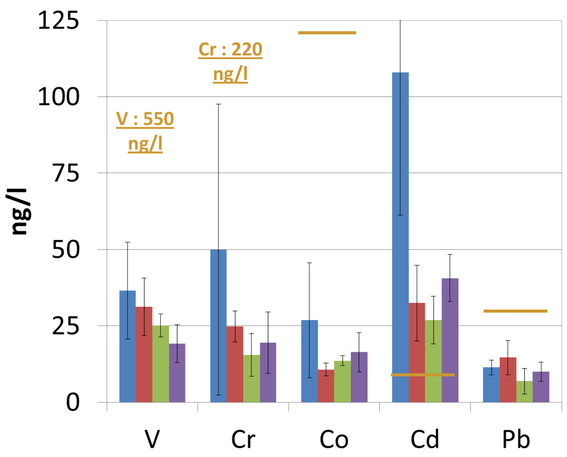
$$C_{DGT} = \frac{M\left(\frac{\Delta g}{D_{gel}} + \frac{\delta}{D_W}\right)}{At}$$

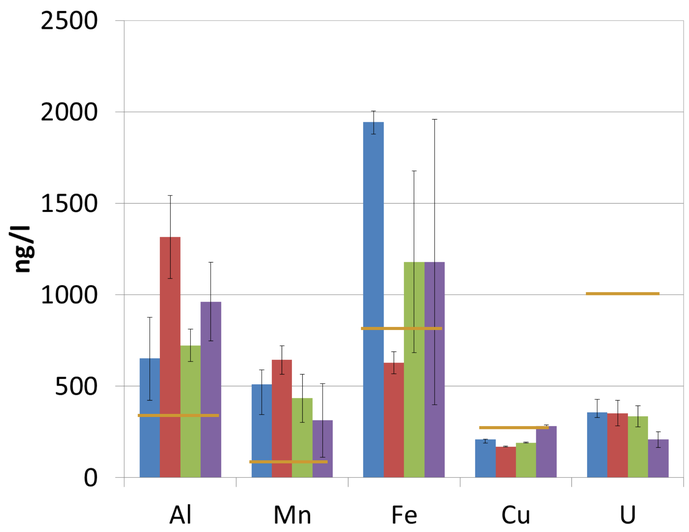
Multiplicative factor estimated compared to classical DGT calculation (DBL neglected) is around 1,5-1,8.
This point is important regarding accuracy of DGT resuts but, if confirmed, this is rather a limitation for the use of DGT in extended monitoring except if DBL thickness is at the end relatively constant in underground context.

Monitoring results

The following elements were monitored in each campaign : Al, Cr, Mn, Fe, Ni, Co, Cu, Zn, Cd, Pb, U. Four campaigns were conducted over a period of 4 months. For each campaign, time of deployment was around 14 days. The site was not selected because of high concentrations of metals. It was chosen because of the presence of different types of inorganic and organic pollutants for deployment of various passive samplers. Metals concentrations are then sometimes low. Classical spot sampling was applied at the beginning and at the end of each DGT deployment.







Results are given for the 4 campaigns (blue, red, green and purple). Confidence interval are 2 times standard deviation of DGT triplicates. Brown line and brown digits are mean value of spot sampling results after purging (these results were rather stable so mean result is presented)

Interpretation of monitoring results

These data show very contrasted results regarding the element which is considered and also regarding the difference for this element between spot sampling results before and after purging of the piezometer (classical underground water sampling usually includes a purge of the piezometer to get representative water).

- **V, Cr, Co, Pb, U and Cu** : small differences before and after purging. DGT results seems representative of concentration in the water body. The ratios DGT/spot sampling are variable between around 10% for V, Cr, Co to around 70-80% for Cu (around 30% for Pb and U). The ratio is certainly dependant on the speciation of the element in solution (oxyanions forms for example) and/or of the non suitable value of the applied diffusion coefficient (issue from bibliography) in the context of underground water.
- **Al, Mn, Fe, Ni, Zn, Cd** : small or important differences between spot sampling before and after purging are observed. Then DGT results seem more representative of water concentration in the piezometer than in the water body. For example at the end of campaign 4, Ni concentration before and after purging was 12 and 1 µg/l respectively (11,3 and 0,8 µg/l for Zn - 39 and 4 ng/l for Cd). It is important to note that this piezometer is very small and could be influenced by leaching of surface water.

Conclusion

Deployment of DGT in underground water allows the sampling at a define depth (interesting characteristic in some hydrogeological studies). However, quantitative interpretation of DGT results in this context seems difficult due to, the apparently non negligible diffusive bound layer, to the complex speciation of element and/or of question related to the fitness of classical diffusion coefficient. Another key point is the representativity of the water which is locally sampled in the piezometer compared to the water body. The absence of purging during DGT deployment could be a difficulty for some elements impacted by local contamination. Another experiment in deeper piezometer indicates that this phenomenon seems amplified here by the small depth of the piezometer.

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