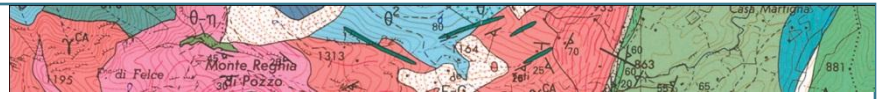

Passive samplers such as PDB, DGT and POCIS for monitoring groundwater quality : A field trial

C. Berho, A. Togola, J-P. Ghestem

AQUAREF

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Context of the work

> Groundwater is characterised by

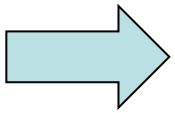
- Low water flow
- Sampling using a well
- Well purged before groundwater sampling (representativity of sample)

> Few applications of passive samplers in groundwater by comparison with surface waters

- Some publications on the use of equilibrium passive samplers in groundwater (Passive Diffusive bags PDB) (USGS works)

- Only few publications (Gustavson et al., 2000, Vrana et al., 2005) about integrative passive sampling in groundwater :
  - SPMD only
  - It is more likely that SPMD uptake is limited by groundwater flow.

- More recently, preliminary tests of PDB, ceramic dosimeters, Sorbicells in groundwater in polluted sites (INERIS, METROCAP project, May 2011)



Applicability of such tools in groundwater ?

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Objectives

- **To perform preliminary tests to study of the applicability of passive sampling in groundwater**
  - Comparison between passive sampling and classical sampling in a groundwater
  - Demonstration of the advantages and drawbacks of passive samplers on a case study

- **Study done in 2010 under Aquaref programme (report available on the web site of AQUAREF)**

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The study site : criteria of choice & description

> Choice criteria

- Presence of several types of pollutants which can be targeted by available passive samplers
- Concentrations at environnemental levels
- Difficulties to find a site which has multi pollutant's

> Site selected : A drinking water supply site presently closed

- Presence of volatile organic compounds and polar pesticides & metals at low concentrations
- Well : 6m of depth and 80 mm of diameter

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Selected compounds & passive samplers

> Types of compounds

- Polar pesticides – 60 compounds
- Pharmaceuticals -15 compounds
- VOC – 54 compounds
- Metals – 11 compounds

> Types of Passive samplers

- POCIS (Polar Organic Compound Integrative Sampler)
- PDB (Passive Diffusive Bag)
- DGT (Diffusive Gradient in Thin film)

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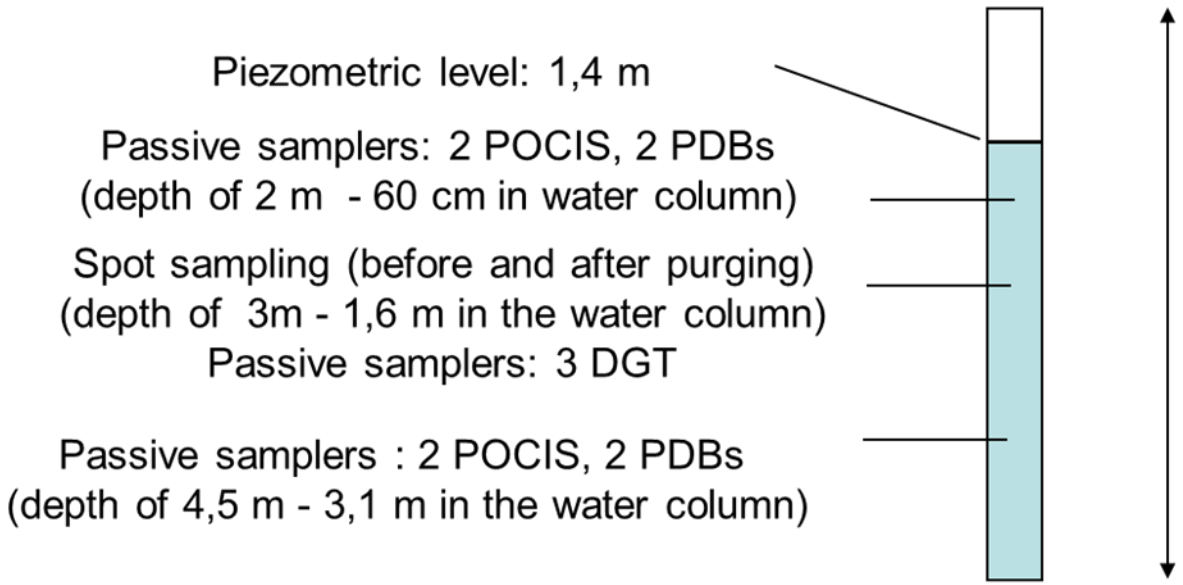
General methodology of sampling

- 4 campaigns of about 15-20 days duration
- Classical sampling with a twister pump at 3m before and after purging (3* volume of the well)
- Measurement of physico chemical parameters before and after purging
- Deployment of passive samplers in replicates on a plastic chain at 2 depths



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Passive Diffusive Bags (PDB) / VOC sampling

- LDPE bag with desionised water (Exposmeter)
- Equilibrium passive sampler
- At the end of exposure, transfert of water in flasks
- Analysis of VOC by ITEX/GC/MS
- Comparison with classical sampling (before and after purging) at the retrieval of PDB.

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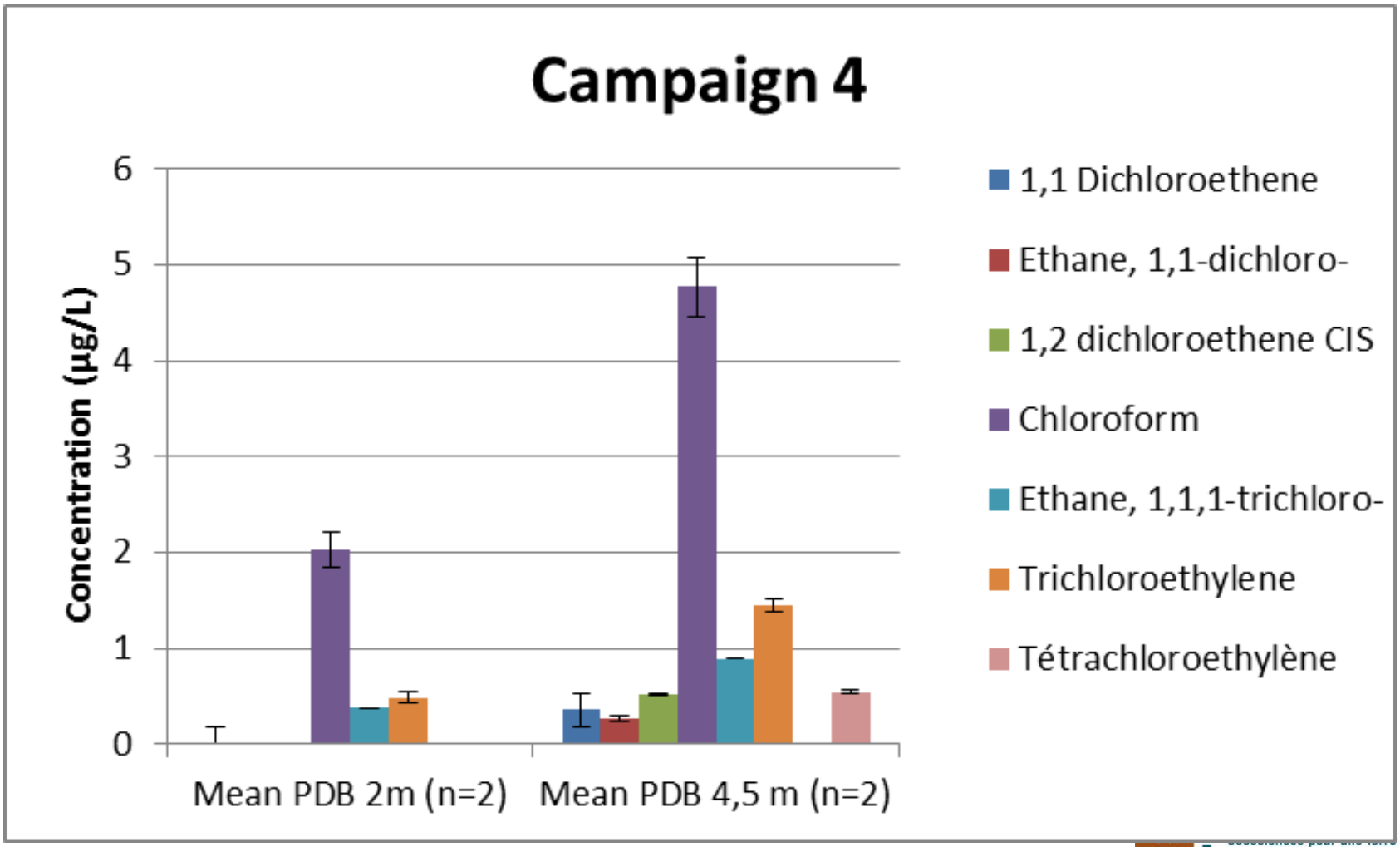
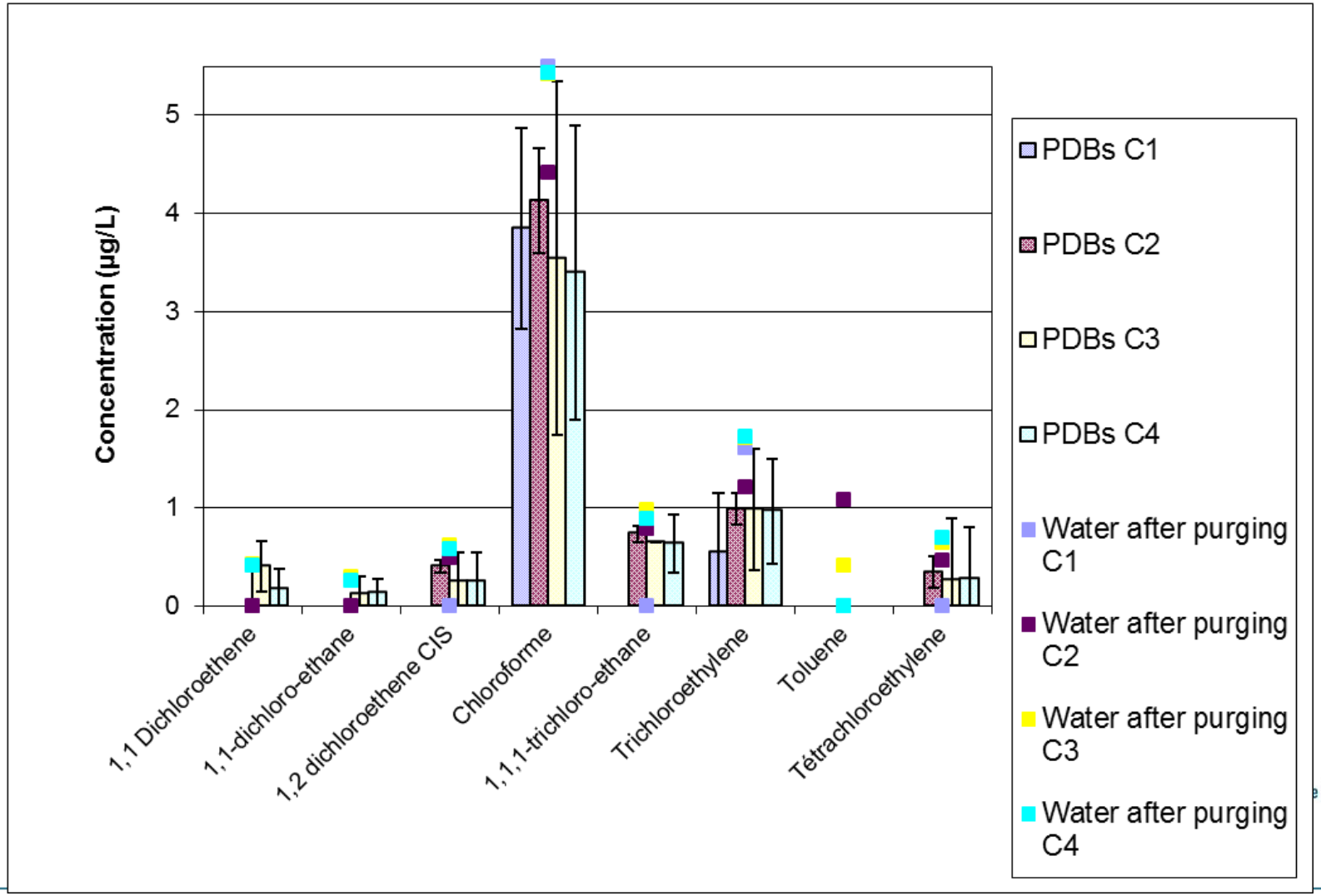
Example of PDB concentrations at two depths



Comparison between PDB and classical sampling (4 campaigns : C1 C2 C3 C4 ; after purging)



PDB > Conclusion

- **Detection of 7 molecules of the 54 which were analysed at low concentrations (<6 µg/L)**
- **Slight stratification in the piezometer, probably due a vertical distribution of compounds in the water column (stratification in accordance with volatility)**
- **PDB results in good agreement with classical sampling results (before or after purging)**

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POCIS - Polar organic compound integrative sampler

- **POCIS with phase in OASIS HLB (Exposmeter) for groundwater**
- **Elution with methanol followed by HPLC/MS/MS analysis**
- **TWAC estimation : TWAC = m/(Rst)**

TWAC : Time Weight Average Concentration
m : accumulated mass
Rs : Sampling rate from littérature (L/d/g of Pocis)
t : time duration (days)

- **Comparison with the average concentration in water samples during the campaign**

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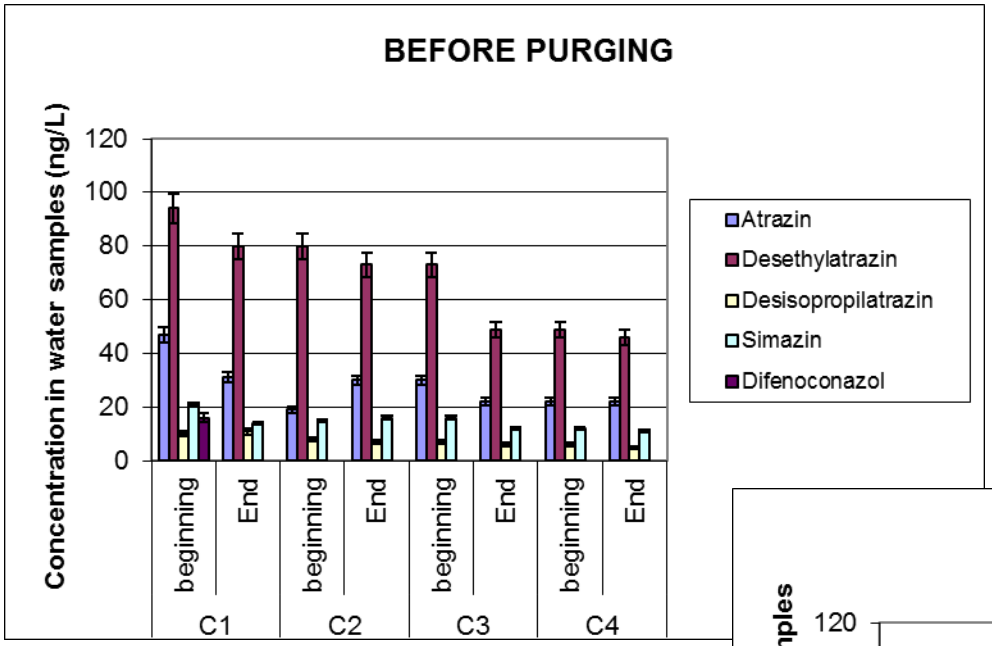
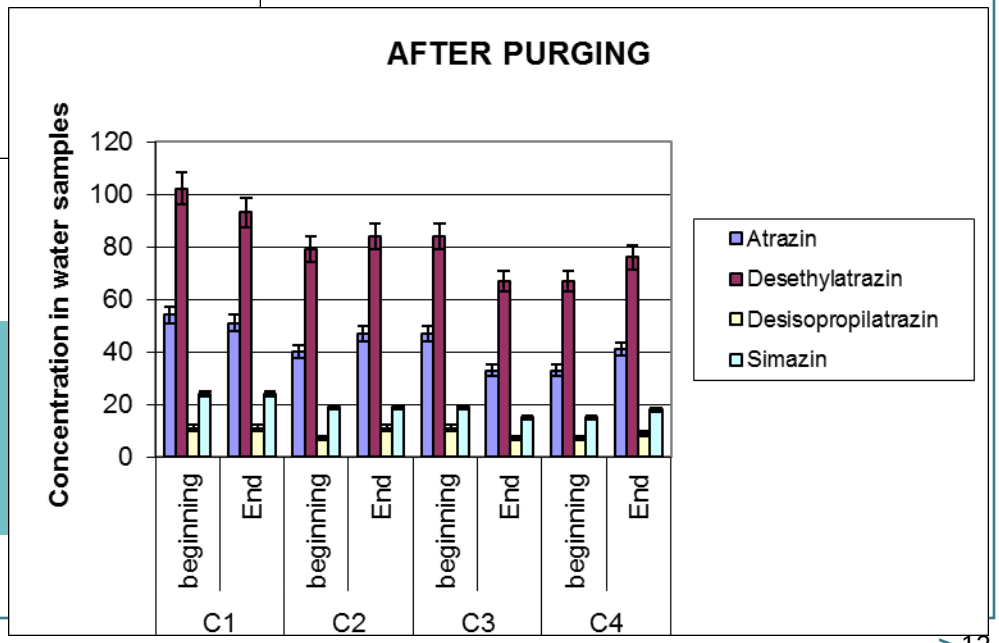
Pesticide concentrations in water samples over the 4 campaigns

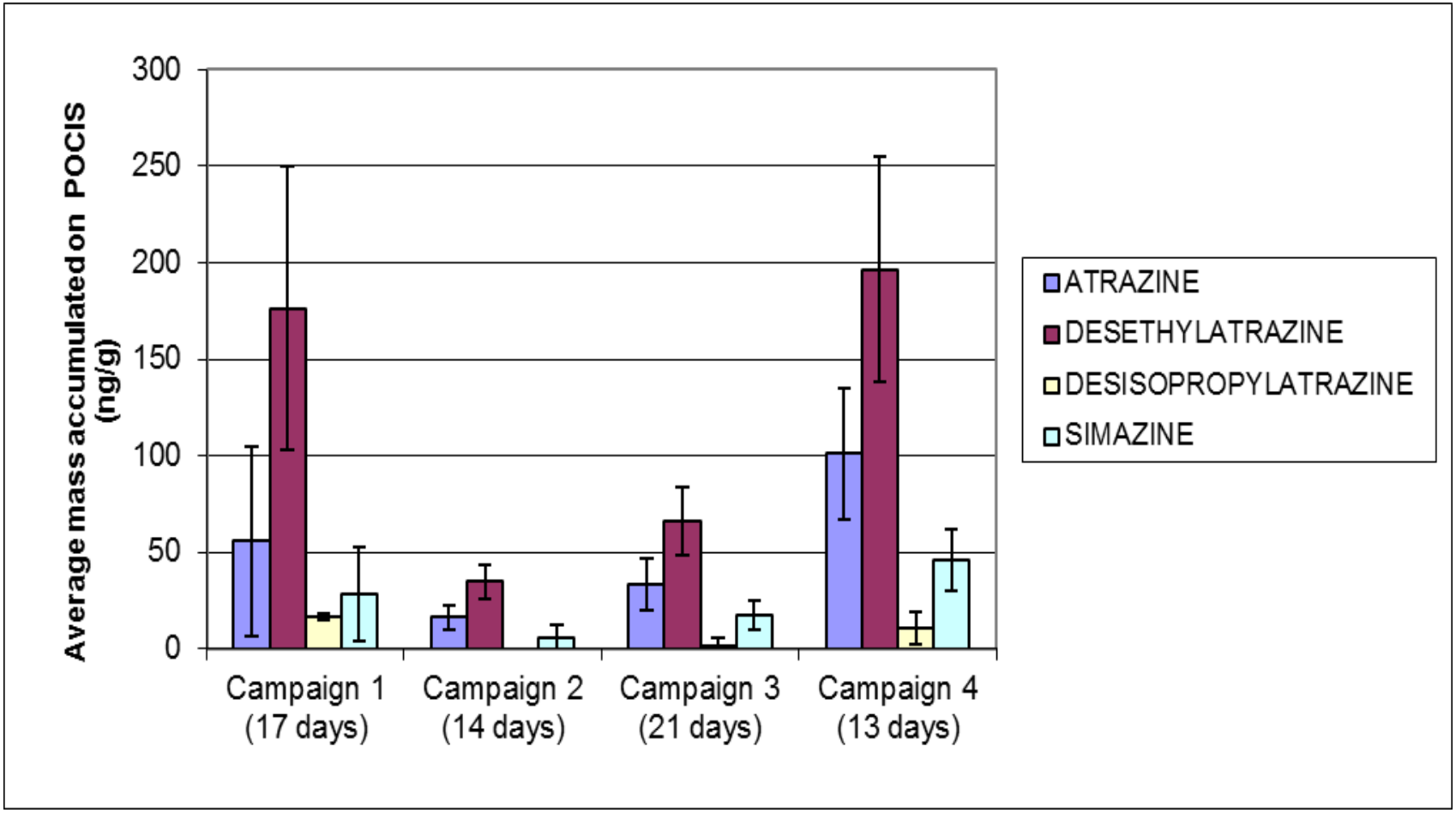


Before and after purging concentrations of the same order (except for atrazine (C2) and DEA (C3, C4)



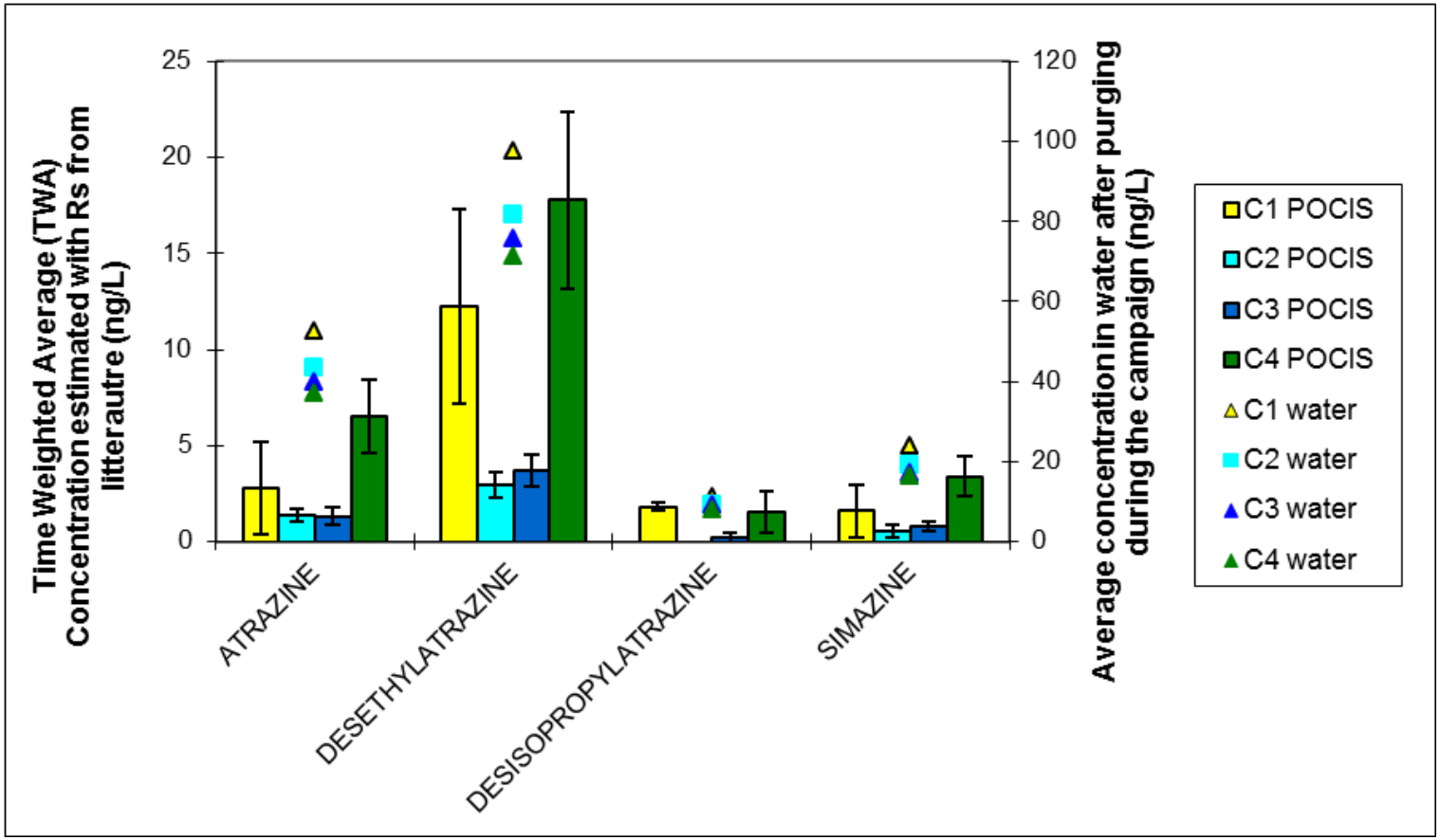
Slight variation of concentrations in groundwater

POCIS/pesticides : accumulated mass (ng/g) during the 4 campaigns



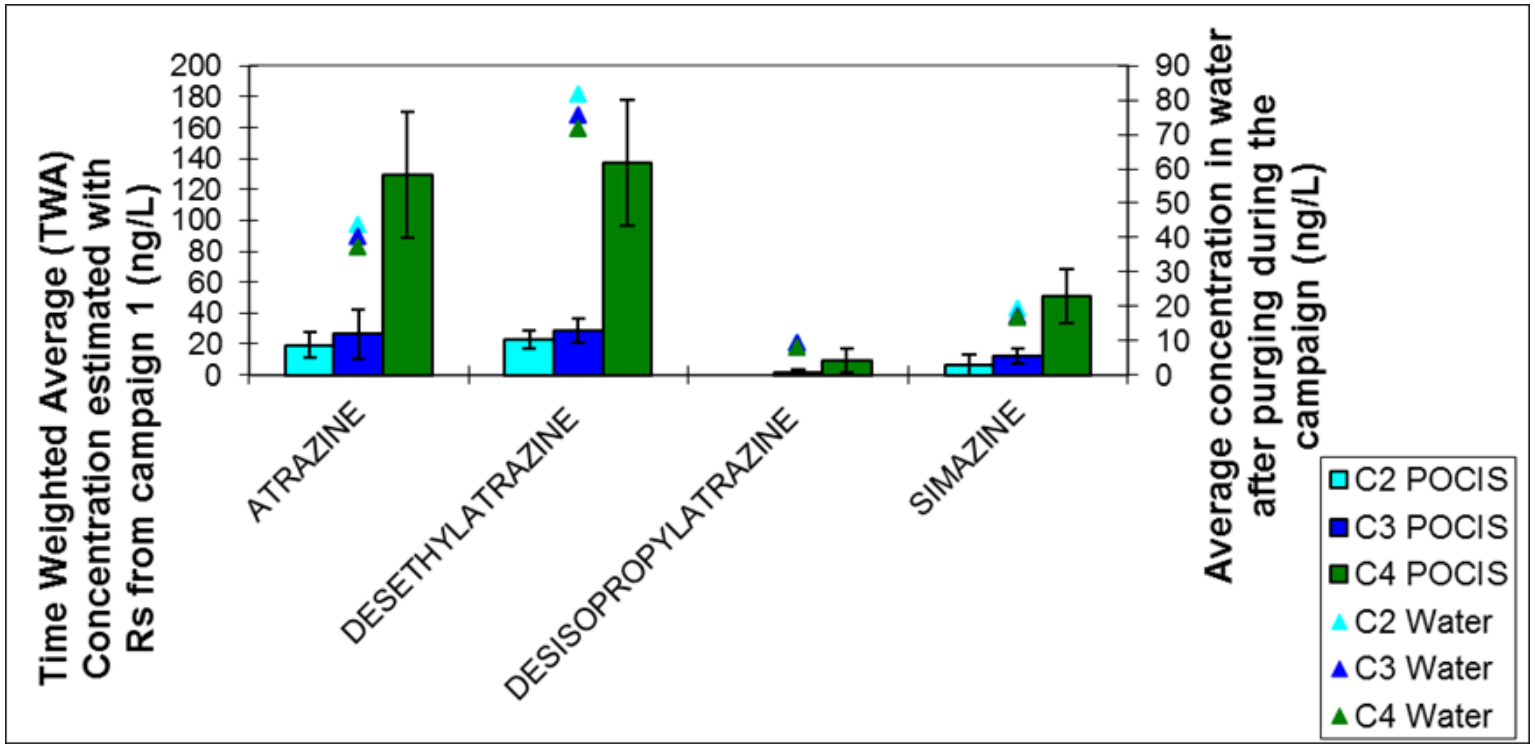
No « logical results » between time duration and accumulated mass, variation of water flow ??

TWAC (with Rs from litterature) vs spot sampling analysis



Factor of 4 to 50 between TWAC and Water concentration
Rs found in littérature are not applicable to this site

TWAC (Rs from campaign 1) vs spot sampling analysis



Factor of 2-3 between TWAC and water concentration
As accumulation is not reproducible from a campaign to another, POCIS does not allow to follow the pesticide concentrations in groundwater

Pharmaceuticals : qualitative information (screening)

Classical sampling Passive sampling

Pharmaceuticals	Water Campaigns 1,2,3,4	POCIS campaign 1	POCIS campaign 2	POCIS campaign 3	POCIS campaign 4
FENOFIBRIC ACID				+	
CARBAMAZEPINE		+	+	+	+
BROMAZEPAM			+	+	+
SULFAMETHOXAZOLE			+	+	+
LORAZEPAM				+	+
DICLOFENAC					+
OXAZEPAM					+

Detection of compounds not detected by classical sampling

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POCIS >Conclusion

> Qualitative information

- screening of pesticides and pharmaceuticals
- Improvement of the screening performance in comparison with classical approach

> Quantitative information

- Sampling rate from litterature are not applicable to this site
  - Accumulation from a campaign to another is not reproducible
  - Is water flow sufficient to ensure a constant concentration at the surface of POCIS ?
  - Is water flow constant over the 4 campaigns ? (probably not due to the starting of the drinking water supply unit)

> Others results more promising in other sites

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DGT –Diffusive Gradient in Thin film

- **Classical DGT used except for one campaign for which 3 types of DGT used with different thickness, 0.76, 1.18 et 1.95 mm (DGT Research)**
- **Estimation of the diffusion boundary layer according the publication (Kent W. Warnken et al., 2006)**
- **Elution by HNO3 followed by ICP/MS analysis**
- **Estimation of the TWAC in water :**

C_{DGT} : Time weight average metal concentration
M : mass accumulated
Δg : gel thickness
δ : gel thickness
D_{gel} , D_w : Diffusion coefficients
t : time duration
A : Area

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

- **Comparison with the average concentration in metals in water samples during the campaign**

Metal concentrations in water samples & influence of purging

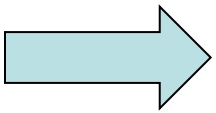
concentration (ng/L)			Ni	Co	Cu	Zn	Cd	Pb	U
Campaign 1	beginning	before purging	1159	129	947	7559	39	44	997
		after purging	839	124	635	1726	6	16	999
	end	before purging	1640	130	445	4305	55	33	1093
		after purging	877	123	280	1627	20	50	1107
Campaign 2	beginning	before purging	1480	135	435	2020	33	25	965
		after purging	1025	150	260	1070	8	10	985
	end	before purging	3017	140	583	5720	23	20	980
		after purging	900	130	280	1653	6	20	1037
Campaign 3	beginning	before purging	3017	140	583	5720	23	20	980
		after purging	900	130	280	1653	6	20	1037
	end	before purging	2787	130	403	4973	18	67	1043
		after purging	843	120	243	1063	6	50	1067
Campaign 4	beginning	before purging	2787	130	403	4973	18	67	1043
		after purging	843	120	243	1063	6	50	1067
	end	before purging	12270	137	757	11350	39	23	997
		after purging	1063	140	230	807	4	17	1013

Low concentrations of metals in groundwater
Ni, Zn : High Influence of purging
Co, U : Concentrations are constant - No influence of purging
Pb, Cu, Cd : Concentrations are constant over the 4 campaigns- low influence of purging

Estimation of the diffusive boundary layer

- **Low flow in comparison with surface water**
- **The DBL was calculated according Kent W. Warnken et al., 2006 by using DGT with several gel thickness**
- **<u>Rough</u> estimation of the DBL :**

Al	Cr	Mn	Ni	Co	Cu	Zn	Cd	Pb
0,9	0,8	0,6	1	0,7	1	1,3	1,6	0,6



δ = 1 mm

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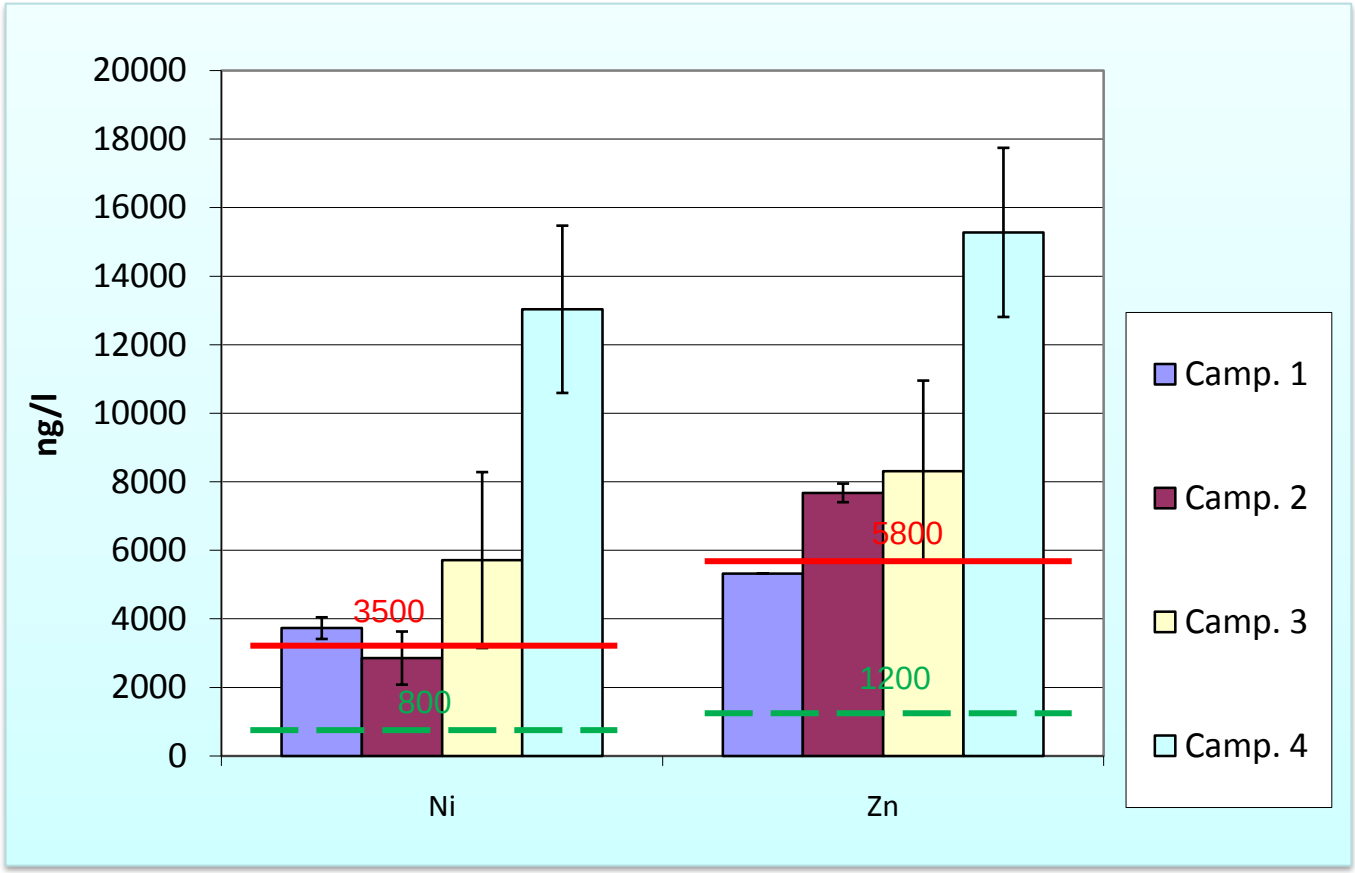
TWAC vs spot sampling analysis

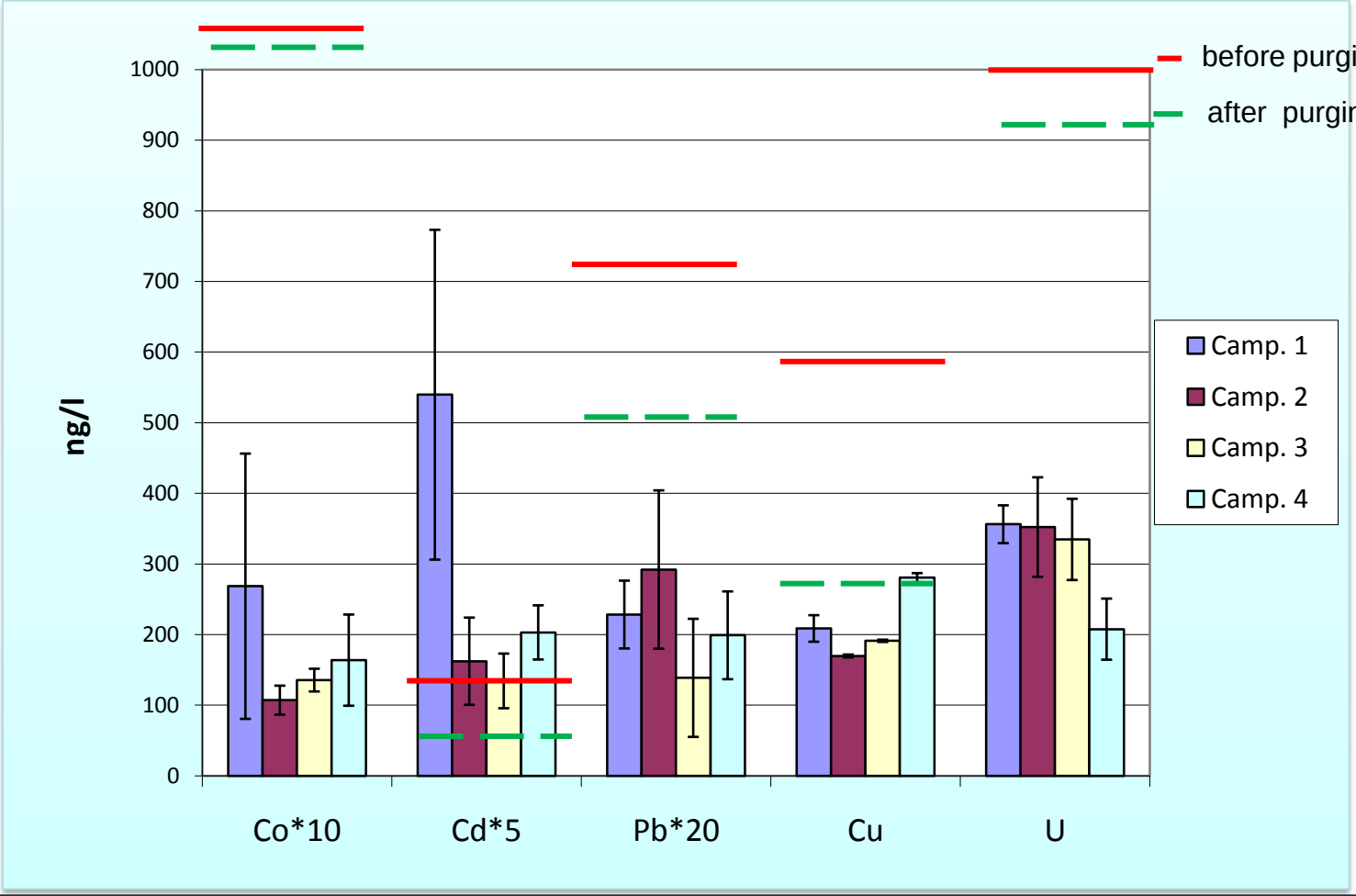
Average concentration in water samples over the 4 campaigns before purging

Average concentration in water samples over the 4 campaigns after purging



Ni, Zn : overestimation of water concentration probably due to the water quality before purging

TWAC vs spot sampling analysis



Good reproducibility from a campaign to another
Co, Pb, U : probable influence of the speciation
Cd : little overestimation, influence of the water quality before purging
Cu : influence of the water quality before purging

DGT conclusions

- **The DBL does not seem to be negligible for this site**
  - Need to get more data in other sites
- **Representativity of water in the well & local pollution**
  - all the more so as the well was not very deep (influence of runoff ??)
  - Depends on the elements
- **Speciation : is there any interest to know the « bioavailable fraction » in groundwater ?**

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Conclusion on this case study : applicability of passive sampling in groundwater

> Limits which are identified

- Representativity of water in the well & local pollution especially for metals all the more so as the well was not very deep
- Pollution by the deployment system
- Variation of the water flow & direction of the flow ?

> Qualitative tool

- Screening of molecules
- Deployment at several depths to estimate vertical variability

> Quantitative tool

- PDB powerful tool
- Influence of the water flow especially for POCIS

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Perspectives : Applicability of passive samplers in groundwater

- **Need to investigate the applicability on other sites**

- **Identification of conditions (water flow) for which passive sampling is applicable for quantitative information**

- **Acquisition of specific sampling rates**
  - Use of PRC : difficult in groundwater used for drinking water supply
  - Experimental calibration system representative of groundwater → ORIGAMI PROJECT (ANR 2012-2015)
  - In situ calibration : need of « model groundwater site »

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