AQUAREF intercomparison passive sampling exercise: monitoring of pesticides in surface water

C Berho[1], N. Mazzella[2], D. Munaron[3], B. Lepot[4], H. Budzinski[5], C. Gonzalez[6] , A. Gravell[7], R. Gunold[8], E. Peinerud[9], F. Smedes[10], B. Vrana[11], **C. Miège[12]***

1 **BRGM**, Laboratories Division, 3 av. Claude Guillemin, 45060 Orléans, France. **2 Irstea**, UR REBX, 50 Avenue de Verdun, Gazinet, 33612 Cestas Cedex, France, **3 Ifremer**, LERLR, avenue Jean Monnet, BP 171, 34203 Sète Cedex, France, **4 INERIS** F-60550 Verneuil-en-Halatte, France, **5 UMR 5805 EPOC – OASU, Equipe LPTC**, Univ. Bordeaux 1, F-33405 Talence CEDEX, France, 6 Ecole des Mines d'Alès, 7 Environment Agency NLS, 8 UFZ, 9 ALS Scandinavia AB, 10 Deltares, 11 Water research institute, 12 **Irstea**, UR MALY, 5 rue de la Doua, CS70077, 69626 VILLEURBANNE Cedex, France

*: corresponding author (cecile.miege@irstea.fr)

1 Objective of the AQUAREF intercomparison passive sampling exercise

Passive samplers (PSs) can be valuable tools as complementary method in monitoring water quality in the context of the WFD. Nevertheless, there is still a lack of quality assurance and control (QA/QC) procedures that demonstrate the reliability and the comparability of results obtained by passive sampling. The objective was **to assess the potential function and the efficiency of PSs for monitoring pesticides in surface and coastal waters in the context of the WFD.**

2 Description of the trials

• **2 TRIALS OF 14 DAYS DURATION AT TWO SITES**

Coastal water	**Etang de Thau** (Hérault) April/May 2010	
Surface Water	**Fleuve Charente Site de Beillant** (Charente maritime) May/June 2010	

• **PARTICIPANTS**: 12 expert laboratories i.e IRSTEA Lyon, IRSTEA Bordeaux, BRGM, IFREMER, ALS Scandinavia AB, Ecole des Mines d'Alès, Environment Agency NLS, INERIS , EPOC-LPTC, UFZ, Water research institute, Deltares

• **MOLECULES**: 9 pesticides (acetochlor, S-metolachlor, alachlor, atrazine, diuron, isoproturon, simazine and DEA, DIA). Some laboratories analysed less than the 9 pesticides.

• **QA/QC PROCEDURE:** Exposure of PS in triplicate & Field blanks ; Analysis of a reference solution (QC) to identify the outliers ; More information available : C. Miège et al, Trends Anal. Chem., 2012,36, 128-143

• **TYPES of PASSIVE SAMPLERS (PS) DEPLOYED IN TRIPLICATES:** POCIS (pharmaceutical & pesticide configuration), polar Chemcatcher with SDB XC or C18 phases, silicon rod, speedisk hydrophilic DVB. 17 PS deployed at Beillant and 12 at Thau. To be noted that 50% of the passive samplers were POCIS pharmaceutical configuration.

• **PESTICIDE CONCENTRATION IN WATER:** analysis of pesticides in spot water samples (5 samples/site) collected at regular intervals during the campaigns by 2 laboratories Irstea of Bordeaux (Beillant) and EPOC-LPTC of Bordeaux (Thau)

Average concentration (n=5) in spot samples during campaigns (ng/L)	Thau (dissolved fraction)	Beillant (dissolved fraction)
Acetochlor	< LOQ	< 10
Alachlor	< LOQ	< 10
Atrazine	0.37+/-0.10	< 10
DEA	< LOQ	49.2+/- 18.7
DIA	< LOQ	13.3+/- 4.3
Diuron	2.41+/- 0.34	< 20
Isoproturon	0.05+/- 0.02	< 10
Metolachlor	1.73+/- 0.84	18.3-/+4.2
Simazine	0.73+/- 0.24	< 10

3 Example of Results

• **DESCRIPTION OF ACCUMULATION in POCIS and TWA concentration (BEILLANT)**
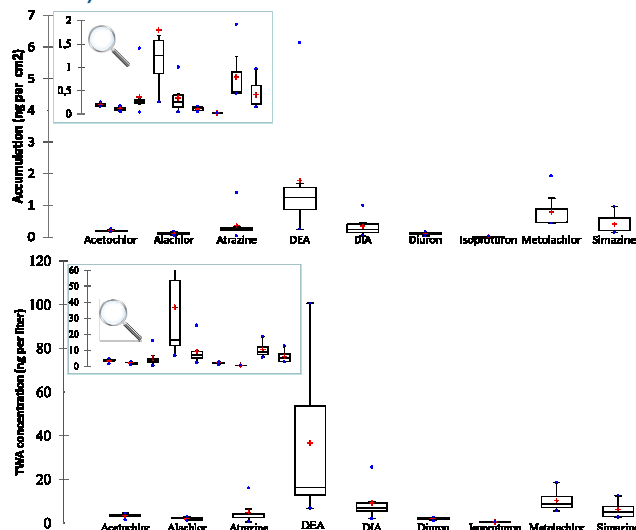
-> **Similar accumulation** roughly between 0 and 2 ng/cm²; -> Similar descriptive statistics are observed for acetochlor, alachlor diuron and simazine. -> For atrazine, DEA, DIA, maximum value was measured by the same laboratory.

-> Similar results are observed for TWA concentration : no additional dispersion induced by the calculation step for the estimation of the TWA concentration.

• **PESTICIDE FINGERPRINTS IN THE VARIOUS PASSIVE SAMPLERS COMPARED WITH THOSE IN GRAB SAMPLES (BEILLANT)** *for laboratories that analysed all the 9 pesticides (n=4)*
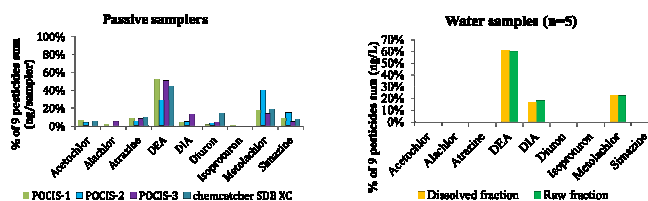
-> **PS point out 6 to 9 molecules** whereas spot sampling points out 3 molecules only ; -> **Similar fingerprints between POCIS and chemcatcher** although DIA, alachlor, isoproturon are not quantified on the chemcatcher -> **Similar fingerprints between POCIS and dissolved water fraction**: the more abundant molecules are DEA, metolachlor and DIA.

• **MEAN AND VARIABILITY OF TWA CONCENTRATIONS OF PESTICIDES AND COMPARISON WITH WATER CONCENTRATION**

□Outlier (Grubbs tests on PS data); ●Outlier (Cochran tests on QC data)

-> Satisfying variability in the determination of pesticide water concentration
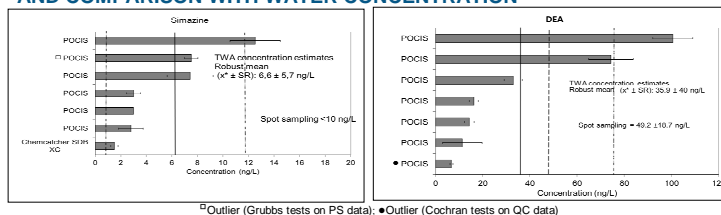
4 Conclusion

Few participants & delivered results at Thau did not allow data statistic treatment. At Beillant, PS pointed out the presence of molecules that were not detected by spot (or grab) sampling approach. A satisfactory estimation of mean TWA concentrations by comparison with average spot sampling concentration was observed. Statistical data treatments are limited because of too few passive samplers deployed (except for POCIS pharmaceutical configuration) and the fact that all molecules were not analysed by laboratories. To identify the sources of TWA concentrations variability, more quality controls tools should have been implemented.