



HAL
open science

Comparison of two experimental systems for the calibration of passive SBSE (Stir Bar Sorptive Extraction) for 16 pesticides in water

C. Guillemain, A. Assoumani, Marina Coquery, C. Margoum

► **To cite this version:**

C. Guillemain, A. Assoumani, Marina Coquery, C. Margoum. Comparison of two experimental systems for the calibration of passive SBSE (Stir Bar Sorptive Extraction) for 16 pesticides in water. 16th International Conference on Chemistry and the Environment, Jun 2017, Oslo, Norway. pp.1, 2017. hal-02606446

HAL Id: hal-02606446

<https://hal.inrae.fr/hal-02606446>

Submitted on 16 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Comparison of two experimental systems for the calibration of passive SBSE (Stir Bar Sorptive Extraction) for 16 pesticides in water

C. Guillemain, A. Assoumani, M. Coquery, C. Margoum

FRESHWATER SYSTEMS, ECOLOGY AND POLLUTIONS RESEARCH UNIT – Irstea, Lyon – Villeurbanne Center - France

Contact : celine.guillemain@irstea.fr, christelle.margoum@irstea.fr

INTRODUCTION

Several types of passive samplers have been developed for the time-integrative monitoring of organic contaminants in the aquatic environment. We recently demonstrated that the passive SBSE (p-SBSE) is a suitable passive sampling technique for pesticide monitoring in rivers located in agricultural watersheds^[1,2]. The determination of time-weighted average concentrations (TWAC) in surface waters requires a previous calibration of the passive sampler under controlled conditions that enables the determination of sampling rates (R_s)^[3]. Many laboratory calibration systems have been described in the literature, but we could not find any comparative study of these experimental systems for a same passive sampler and same tested compounds.

OBJECTIVES

The aim of this study was to compare the performances of two different laboratory systems for the calibration of passive p-SBSE for 16 pesticides in water. We focus our discussion on the comparison of main operational conditions, cost and easy of use.

LABORATORY CALIBRATIONS

Material and Method

Calibration parameters:

Exposure duration: 7 days
Exposure temperature: 20°C

Passive sampler – p-SBSE:

Gerstel SBSE Twister® I = 20 mm, df = 1.0 mm

Pesticides:

16 pesticides with a range of
Log Kow from 2.3 to 5.1



F: Fungicide, H: Herbicide, I: Insecticide
Log Kow: Octanol-water partition coefficient

Molecule	Abbreviation	Use	Log Kow
Simazine	SMZ	H	2.3
Azoxystrobin	AZS	F	2.5
Chlorothalonil	CTU	H	2.5
Isoproturon	IPU	H	2.5
Norfurazon	NFZ	H	2.5
Atrazine	ATZ	H	2.7
Dimethomorph	DMM	F	2.7
Linuron	LNJ	H	3.0
Metolachlor	MTC	H	3.1
Tebuconazole	TBZ	F	3.7
Chlorfenvinphos	CFV	I	3.8
Chlorpyrifos Methyl	CPM	I	4.0
Acetochlor	ATC	H	4.1
Diflufenican	DFP	H	4.2
Chlorpyrifos Ethyl	CPE	I	4.7
Flufenoxuron	FFX	I	5.1

Pesticide analysis:

- Liquid desorption of p-SBSE
- UHPLC-MS-MS analysis
- Limits of quantification from 0.01 to 4 µg per sampler



Liquid desorption: 200 µL of
Acetonitrile / Methanol (50/50 : v/v)
in ultrasonic bath



Quantification by UHPLC-MS/MS
Nexera Shimadzu, API 4000 AB Sciex

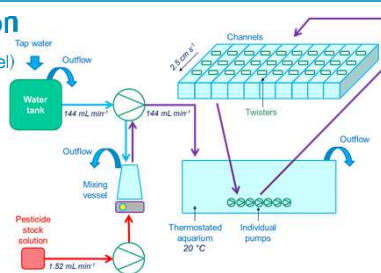
Continuous Flow Calibration

- 15 glass channels (3L of tap water per channel)
- Up to 45 p-SBSE (3 per channel)

- Flow velocity: 2.5 cm.s⁻¹

- Nominal concentration of pesticides:
0.05 to 40 µg.L⁻¹

Constant supply of contaminated water:
pesticide stock solution in acetone.



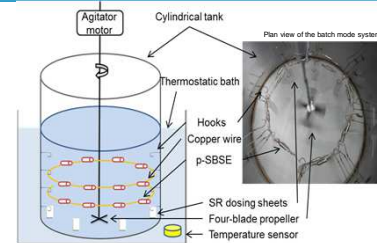
Batch Mode Calibration

- 1 stainless steel tank (30 L of tap water)
- 24 p-SBSE

- Flow velocity: 10 cm.s⁻¹

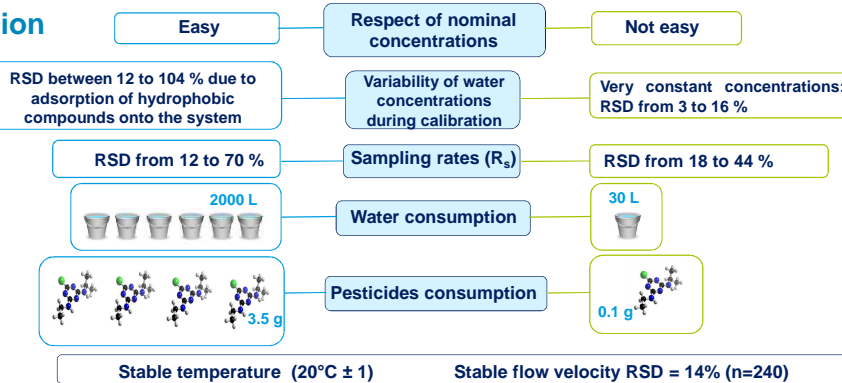
- Nominal concentration of pesticides:
0.5 to 200 µg.L⁻¹

Diffuse source of contamination:
previous step to spike 8 silicone rubber sheets with pesticides^[4]



RESULTS AND DISCUSSION

Continuous Flow Calibration

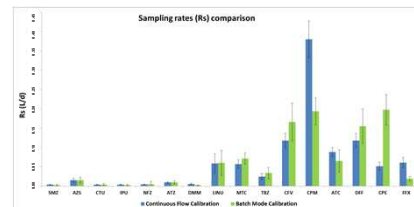


Batch Mode Calibration



Molecule	Nominal Concentration (µg/L)	Mean measured concentration (µg/L)	RSD (%)	n=10
Simazine (SMZ)	0.2	0.3	13	
Azoxystrobin (AZS)	4	2.9	16	
Chlorothalonil (CTU)	4	4.2	14	
Isoproturon (IPU)	8	8.1	12	
Norfurazon (NFZ)	16	14.3	21	
Atrazine (ATZ)	1	0.9	13	
Dimethomorph (DMM)	4	2.7	19	
Linuron (LNJ)	8	3.8	25	
Metolachlor (MTC)	0.4	0.2	24	
Tebuconazole (TBZ)	5	3.2	18	
Chlorfenvinphos (CFV)	8	2.8	34	
Chlorpyrifos Methyl (CPM)	16	0.3	104	
Acetochlor (ATC)	20	7.7	27	
Diflufenican (DFP)	4	0.2	69	
Chlorpyrifos Ethyl (CPE)	4	0.2	21	
Flufenoxuron (FFX)	40	10.5	74	

In accordance with the theory regarding the effect of flow velocity on R_s :
- For hydrophilic compounds, calculated R_s were similar with both systems, although the different flow velocities.
- For hydrophobic compounds, the R_s values obtained with the batch mode calibration system were greater for most compounds, which is in accordance with the difference in flow velocity between the two systems. Opposite results were observed for FFX and CPM, which could be explained by the unstable concentrations of these two compounds in the continuous flow calibration system (RSD = 74 and 104 % respectively).



Nominal Concentration (µg/L)	Mean measured concentration (µg/L)	RSD (%)	n=12	Molecule
0.2	0.3	13		Simazine (SMZ)
10	0.5	11		Azoxystrobin (AZS)
10	0.6	14		Chlorothalonil (CTU)
20	0.9	16		Isoproturon (IPU)
40	1.0	11		Norfurazon (NFZ)
2.5	0.1	16		Atrazine (ATZ)
10	0.4	14		Dimethomorph (DMM)
20	7.3	15		Linuron (LNJ)
1	0.7	10		Metolachlor (MTC)
12.5	2.9	11		Tebuconazole (TBZ)
20	12.1	3		Chlorfenvinphos (CFV)
40	47.5	12		Chlorpyrifos Methyl (CPM)
100	56.2	9		Acetochlor (ATC)
10	2.8	3		Diflufenican (DFP)
10	0.8	3		Chlorpyrifos Ethyl (CPE)
200	12.9	1		Flufenoxuron (FFX)

PERFORMANCE COMPARISON

Continuous Flow Calibration:

- ☺ Hydrodynamic conditions representative of *in situ* conditions in rivers
- ☺ Easy to reach the nominal concentrations
- ☺ High consumption of water and pesticides
- ☺ Numerous immersed pumps needed
- ☺ Poor stability of contaminant concentrations
- ☺ Poorer repeatability of calculated R_s

Batch Mode Calibration:

- ☺ Limited consumption of water and pesticides
- ☺ Easy to use
- ☺ Stable contaminant concentrations
- ☺ Previous step for spiking silicone sheets
- ☺ Not easy to reach the nominal concentrations

CONCLUSIONS

Both calibration modes enabled to obtain sorption profiles for 16 pesticides on passive SBSE that were used for the determination of R_s . Despite the step of preliminary silicone sheets spiking, the batch mode calibration system is easier to use, limits the consumption of both water and pesticides, and stable contaminant concentrations in water can be maintained easily for obtaining more precise R_s .

ACKNOWLEDGEMENT

The authors thank the French Agency for Biodiversity (AFB) for financial support. This work was realized within the framework of AQUAREF program.

REFERENCES

- [1] A. Assoumani, M. Coquery, L. Liger, N. Mazzella, C. Margoum, Environ Sci Pollut Res 22:3997-4008 (2015).
- [2] A. Assoumani, C. Margoum, S. Chataing, C. Guillemain, M. Coquery, J. Chrom A 1333 (2014).
- [3] B. Vrana, G. Mills, I. Allan, E. Dominiak, K. Svensson, J. Knutsson, G. Morrison, R. Greenwood, TrAC-Trends Anal. Chem. 24, 845 (2005).
- [4] TP. Rusina, F. Smedes, M. Koblikova, J. Klanova, Environ Sci. Technol. 44:362-367 (2010).