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

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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® l = 20 mm, df = 1.0 mm

Pesticides:

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

Molecule	Abbreviation	Use	Log Kow
Simazine	SMZ	H	2.3
Azoxystrobin	AZS	H	2.5
Chlortoluron	CTU	H	2.5
Isoproturon	IPU	H	2.5
Norflurazon	NFZ	H	2.5
Atrazine	ATZ	H	2.7
Dimethomorph	DMM	F	2.7
Linuron	LINU	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	DFF	H	4.2
Chlorpyrifos Ethyl	CPE	I	4.7
Flufenoxuron	FFX	I	5.1

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

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

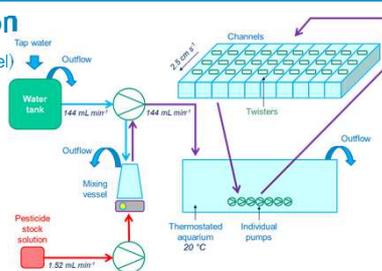Quantification by UHPLC-MS/MS
Nexera Shimadzu, API 4000 AB Sciex

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}

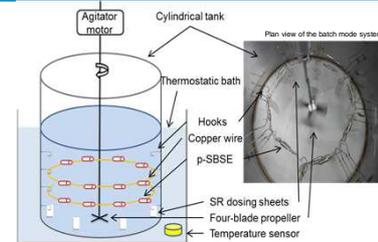**Constant supply of contaminated water: pesticide stock solution in acetone.**

Batch Mode Calibration

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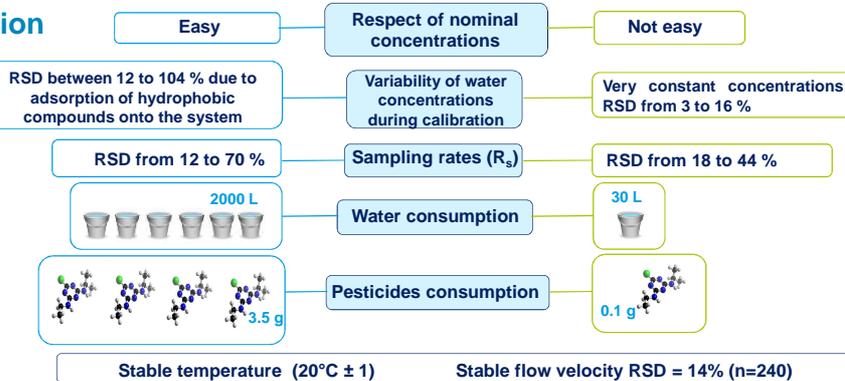- 24 p-SBSE

- 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
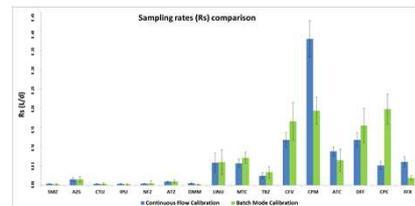
Continuous Flow Calibration

Batch Mode Calibration

	Continuous Flow		Batch Mode
Respect of nominal concentrations	Easy		Not easy
Variability of water concentrations during calibration	RSD between 12 to 104 % due to adsorption of hydrophobic compounds onto the system		Very constant concentrations: RSD from 3 to 16 %
Sampling rates (R_s)	RSD from 12 to 70 %		RSD from 18 to 44 %
Water consumption	2000 L		30 L
Pesticides consumption	3.5 g		0.1 g

Stable temperature (20°C ± 1)   Stable flow velocity RSD = 14% (n=240)

Molecule	Nominal Concentration (µg/L)	Mean measured concentrations (µg/L)	RSD (%) n=16
Simazine (SMZ)	0.2	0.3	13
Azoxystrobin (AZS)	4	2.9	16
Chlortoluron (CTU)	4	4.2	14
Isoproturon (IPU)	8	8.1	12
Norflurazon (NFZ)	16	14.3	21
Atrazine (ATZ)	1	0.9	13
Dimethomorph (DMM)	4	3.7	15
Linuron (LINU)	8	3.8	25
Metolachlor (MTC)	0.4	0.2	24
Tebuconazole (TBZ)	4	3.2	18
Chlorfenvinphos (CFV)	8	2.0	34
Chlorpyrifos Methyl (CPM)	16	0.3	104
Acetochlor (ATC)	20	7.7	27
Diflufenican (DFF)	4	0.2	60
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).

Sampling rates (Rs) comparison
■ Continuous Flow Calibration ■ Batch Mode Calibration

Molecule	Nominal Concentration (µg/L)	Mean measured concentrations (µg/L)	RSD (%) n=13
Simazine (SMZ)	0.5	0.02	13
Azoxystrobin (AZS)	10	0.5	11
Chlortoluron (CTU)	10	0.6	14
Isoproturon (IPU)	20	0.9	16
Norflurazon (NFZ)	40	1.0	11
Atrazine (ATZ)	2.5	0.1	16
Dimethomorph (DMM)	10	0.4	14
Linuron (LINU)	20	7.3	15
Metolachlor (MTC)	1	0.7	10
Tebuconazole (TBZ)	12.5	2.9	11
Chlorfenvinphos (CFV)	20	12.2	3
Chlorpyrifos Methyl (CPM)	40	47.5	12
Acetochlor (ATC)	100	58.2	9
Diflufenican (DFF)	10	2.8	3
Chlorpyrifos Ethyl (CPE)	10	0.8	3
Flufenoxuron (FFX)	200	12.0	1

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 immerged 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.

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