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POCIS for pesticide monitoring in groundwaters: from “low flow” lab calibration to in situ monitoring

1. Introduction

Since few decades, polar organic chemical integrative sampler (POCIS) has been successfully applied to the measurement of a wide range of polar organic contaminants including pesticides. Passive sampling offering time integrated sampling that compensates for fluctuations in concentrations and lower detection limits compared to standard water sampling [1]. Applications have been deployed in surface waters [2, 3] or wastewaters [4] after obtaining sampling rate (Rs) by laboratory calibrations. POCIS sampling rates are affected by environmental factors such as water flow rates, that is particularly significant for groundwaters, characterized by low water flow conditions [5, 6].

To develop a better understanding of the relationship between water flow and POCIS accumulation, an experimental system has been implemented to obtain sampling rates for POCIS on representative groundwater hydraulic conditions. In parallel, monitoring campaigns have been undertaken during one year to obtain in situ sampling rate values.

Both approaches are evaluated and compared to improve quantitative performances of POCIS for groundwater monitoring.

2. Materials and methods

2.1. Pilot experiment

The experimental system was composed of three open parallel columns with an ascendant water circulation and automatic injection system for spiking experiments. 3 different water flows were tested: 1m.day⁻¹; 2m.day⁻¹ and 4m.day⁻¹. POCIS were deployed in triplicates for different durations: 3, 7, 10, 14, 18, 21, 28 and 35 days. Natural water was spiked with a mix of 60 pesticides (see table1) at 500 ng.L⁻¹ with continuous spiked water renewal. Physico-chemical parameters (Temperature, pH, Conductivity, Turbidity) were on line measured during all the experiment, as well as water circulation thanks to the entrance water flow measurement.

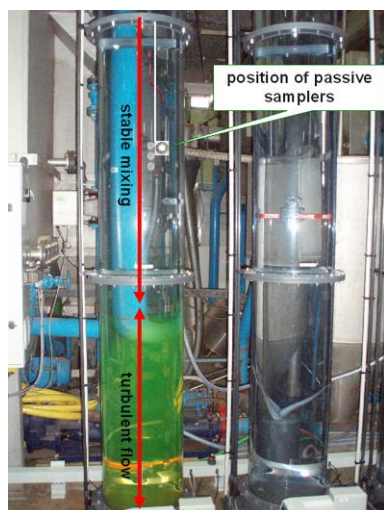


Figure 1: Design of the pilot

ACETOCHLORE	SIMAZINE	IMAZAMETHABENZ METHYL
ALACHLORE	TERBUTHYLAZINE	ISOXABEN
AMETRYNE	TERBUTRYNE	METALAXYL
ATRAZINE	DIMETHENAMIDE	METAMITRONE
CHLORTOLURON	FLUZILAZOLE	METCONAZOLE
CYANAZINE	TEBUCONAZOLE	METHABENZTHIAZURO
DESETHYLATRAZINE	TETRACONAZOLE	METOBROMURON
DESETHYLTERBUTYLAZINE	AZACONAZOLE	METOXURON
DESMETRYNE	AZOXYSTROBINE	METRIBUZINE
DEISOPROPYLATRAZINE	BITERTANOL	MONOLINURON
DIURON	BOSCALIDE	MONURON
HEXAZINON	CHLOROXURON	NAPROPAMIDE
ISOPROTURON	CYPROCONAZOLE	NEBURON
ISOPROTURON-1CH3	CYPRODINIL	PENCONAZOLE
ISOPROTURON-2CH3	DIFENOCONAZOLE	PROCHLORAZE
LINURON	DIMETHENAMIDE	PROPANIL
METAZACHLORE	EPOXICONAZOLE	PROPICONAZOLE
METOLACHLORE	FENPROIIMORPHE	PROSULFOCARBE
PROMETRYNE	FLUZILAZOLE	TEBUCONAZOLE
PROPAZINE	HEXAACONAZOLE	TETRAACONAZOLE
PROPYZAMIDE	IMAZALIL	TRIFLOXYSTROBINE
SEBUTYLAZINE		

Table 1 : Targeted compounds

2.2. Monitoring campaigns

Two sampling stations have been selected with contrasted agricultural pressures, located in alluvial plains and already identified as polluted by pesticides. Monitoring was undertaken during 6 months for each station. POCIS (in triplicates) were exposed during 15 days and spot sampling were done at each POCIS retrieval. Same pesticides (see Table 1) were monitored, as well as major elements, pH and water temperature.

3. Results and discussion

3.1. Pilot experiment results

The set of sampling rates obtained in different conditions gives some information about the impact of water flow on the ability of POCIS to accumulate compounds of interest. Relationship between sampling rates and flow can be done and applied to environmental monitoring.

3.2. Monitoring campaign

Several targeted compounds have been detected, including withdrawn pesticides (triazines, ...) but also still used ones, parents compounds (fungicides, ureas ...) and transformation products. For some of them (triazines), the contamination level was constant, allowing determining in-situ sampling rates.

3.3. Comparison of the different approaches.

Comparison of in-situ and low-flow / high-flow in lab calibrations allows to better estimate the impact of water circulation on POCIS accumulation.

4. Conclusions

This work compares 3 approaches for POCIS calibrations to determine impact of flow on POCIS accumulation in groundwater context. By this way, lab calibration, that is easiest to implement, could be used and corrected to better fit with environmental condition, allowing the use of passive sampler for a semi-quantitative approach.

5. References

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