



Can POCIS be used in Water Framework Directive (2000/60/EC) monitoring networks? A study focusing on pesticides in a French agricultural watershed



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HIGHLIGHTS

- Limitations in the use of the POCIS in regulatory programmes were evaluated.
- We determined that the POCIS data uncertainty is about 138%.
- We showed that POCIS is well-suited for investigative and operational monitoring.
- We showed that POCIS offers a gain in representativeness compared to spot samples.
- We proposed an innovative procedure for using POCIS for surveillance monitoring.

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ABSTRACT

In this study, the main current limitations in the application of the Polar Organic Chemical Integrative Sampler (POCIS) in regulatory monitoring programmes were evaluated. POCIS were exposed from March to December by successive periods of 14 days in the River Trec (Lot et Garonne, France) and analysed for 34 pesticides. The study of the uncertainty related to the POCIS data was performed and we concluded that it might be up to 138%, which is higher than European Union requirements but this issue was adequately counterbalanced by the gain of temporal representativeness. Comparison with data from the official monitoring programme from the French Water Agency showed that the POCIS is already suitable for both operational and investigative monitoring. The sampled fraction issue, and then compliance with Environmental Quality Standards, was also addressed. It was confirmed that POCIS samples only the dissolved fraction of dimethenamid and showed that for compounds like atrazine, desethylatrazine and metolachlor, the POCIS concentration is equivalent to the whole water concentration. For dimethenamid, which exhibited a tendency to adsorb on suspended matter, a method was suggested to assess the raw water concentration from the POCIS measure. Finally, an innovative procedure for using passive sampler data for compliance checks in the framework of surveillance monitoring is proposed.

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1. Introduction

The Water Framework Directive (WFD) 2000/60/EC implemented in 2000 by the European Union (EU) established a common framework for monitoring water quality and obliged member states to reach good ecological and chemical status for all water bodies by 2015 (EU, 2000),

with extended deadlines set for 2021 and 2027. In this context, 45 molecules including 20 pesticides were listed as priority compounds and environmental quality standards (EQS) were determined (EU, 2013). The WFD specifies three types of controls, all of which may be part of monitoring programmes implemented at the river catchment scale (for continental surface waters), depending on water quality status. Surveillance monitoring is designed to assess long-term changes in water quality and provide information for the implementation of other monitoring programmes. This type of control includes at least twelve water samples per year (taken once a month) and analysed for priority compounds and river-catchment specific compounds (discharged in significant quantities into the water body). The

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concentrations measured are compared with EQS to determine the chemical status of the water body. If good status is not achieved, then operational monitoring must be implemented, with the major objective of providing an overview of water quality and evaluating the effectiveness of remediation strategies. The operational programme requires at least four water samples per year (taken every three months), analysed for the chemicals responsible for the deterioration of water quality. Investigative monitoring is established prior to operational monitoring in order to identify contamination sources and select the most relevant parameters to analyse. It can also be implemented to assess the magnitude and impact of accidental pollution.

The implementation of the WFD requires an efficient monitoring network, based on reliable sampling and analytical techniques. Nowadays, grab sampling followed by extraction of analytes and chromatographic analysis (Herrero-Hernandez et al., 2013; Masia et al., 2013) is the most widespread strategy because (i) of its simplicity of implementation and (ii) it is the only method authorised for the three types of controls (surveillance, operational, investigative). However, grab sampling has numerous drawbacks which have been highlighted in the literature for several years (Allan et al., 2006a). The crux of the issue lies in the lack of temporal representativeness of this method. Indeed, very seasonal compounds such as pesticides may show high concentration peaks within short-term periods, and may therefore be completely missed with grab samples taken once a month. In such cases, Guidance Document No. 19 of the European Commission (2008) advises increasing the sampling frequency, especially during spring when the risk of contamination rises because of heavy rainfalls occurring just after pesticide applications. However, increasing the sampling frequency implies additional costs so this recommendation is scarcely applied. Another point of the grab sampling strategy subjected to criticism is the analytical performance, especially sensitivity. Some hydrophobic compounds that tend to accumulate in biota have a very low EQS. For example, trifluralin and endosulfan have EQSs of about 0.03 and 0.005 $\mu\text{g L}^{-1}$, respectively (expressed as annual average concentration (AA-EQS)). These low concentrations are sometimes difficult to reach with the usual sampling and analytical methods.

To overcome some of the problems associated with grab sampling, an alternative strategy could be the use of passive samplers. Theory and modelling about passive samplers have been largely described elsewhere (Alvarez et al., 2004; Huckins et al., 1993; Stuer-Lauridsen, 2005; Vrana et al., 2005). Passive samplers can be exposed for several hours to several weeks in the studied aquatic environment, resulting in the accumulation and pre-concentration of analytes inside the receiving phase. Analysis of analyte amount trapped in the receiving phase allows calculation of the time-weighted average concentration (TWAC) in the aquatic environment of exposure if the sampling rate constants (R_s) of the analytes are known. Several passive samplers have been developed over the past twenty years, including, for example, Semi-permeable Membrane Devices (SPMD) or Chemcatcher® for hydrophobic compounds or Diffusive Gradient in Thin Films (DGT) for trace metals and metalloids (Davison and Zhang, 1994; Huckins et al., 1993; Kingston et al., 2000; Zhang and Davison, 1995). The Polar Organic Chemical Integrative Sampler (POCIS), dedicated to polar neutral compounds was developed more recently (Alvarez et al., 2004). The characteristics of passive samplers (*in situ* pre-concentration step and TWAC) offer the possibility of detecting compounds at lower concentrations than in grab samples, and reduce the risk of missing potential contamination peaks. These features could be very useful in improving the reliability of data collected in WFD monitoring networks. However, some drawbacks restrain the extended use of passive samplers in regulatory programmes. The main difficulty is the influence of environmental conditions on the R_s value, a key parameter in calculating the TWAC. As the extent of this influence is not clearly known, it is difficult to determine the uncertainty associated with passive sampler data, as required in the EU (2009). The second major difficulty concerns the measured fraction of contaminant. Indeed, EQS values are established

for the whole water sample analysis, which includes both the dissolved and suspended particulate matter-adsorbed parts of molecules. It is admitted that passive samplers measure only the truly dissolved (or labile for DGT) part of compounds, which implies that data obtained from such samplers cannot be used for compliance checks. However, to our knowledge, this assumption has never been verified, at least for the POCIS. Moreover, Allan et al. (2009) recently proposed a novel approach permitting estimation of the whole water concentration from the TWAC obtained with samplers, thanks to a correction factor including organic carbon- and dissolved organic carbon-water partition coefficients (K_{OC} and K_{DOC} , respectively). This manipulation could make it possible to compare passive sampler data with EQS.

This contribution discusses the possible application of POCIS data in the regulatory monitoring programme for pesticides. It focuses on one of the main requirements of the WFD, *i.e.* determination of uncertainty, a key factor for all monitoring programmes. It is assumed that if this parameter is known, POCIS data could be used to complement or replace grab water samples in the context of operational and investigative monitoring. This is evaluated by comparing POCIS and institutional data collected in a French agricultural watershed. Since surveillance monitoring involves comparison with EQS established for raw water, there is a need to determine what fraction of pesticides is sampled by the POCIS. Finally, a schematic procedure for using POCIS data for compliance checking purposes is proposed.

2. Materials and methods

2.1. Field work and monitoring programmes

2.1.1. Study area in France

The River Trec is located in South-Western France (44°28'2.08"N; 0°13'18.06"E, Lot-et-Garonne) and runs through 25.6 km, draining a catchment of about 200 km² before joining the Garonne River after the city of Marmande. The sampling site was located right after the confluence point with the Canaule River (Fig. 1). The area is mostly molasse land, with moderate slopes (less than 10%). The climate is characterised as Atlantic oceanic with Mediterranean influences. Winter is generally mild with temperatures in January of about 5 °C. Rainfalls in spring are very irregular whereas periods of drought are common in summer (Fig. S1). 60% of the Trec catchment is dedicated to agricultural activities, not only cereal crops (maize and wheat) and oleaginous plants (sunflower and rape), but also arboriculture and vegetable crops. These types of crops make the use of herbicides such as metolachlor, acetochlor or dimethenamid by farmers very common in this area. Physico-chemical parameters such as water temperature and pH were measured throughout the exposure of the sampling devices and are available in Table S2.

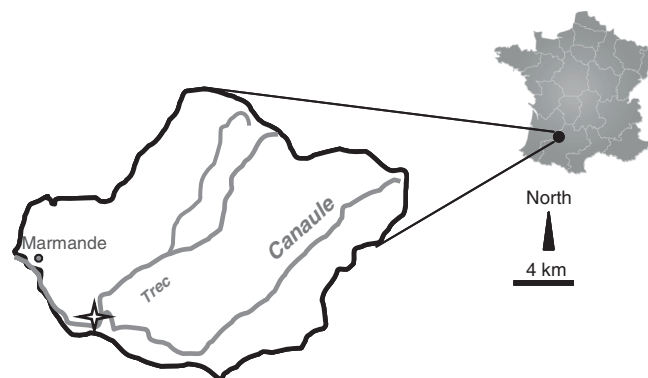


Fig. 1. Geographic location of the sampling station (star on the map) in the River Trec, Lot-et-Garonne, France.

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