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Combination of passive and grab sampling strategies improves the assessment of pesticide occurrence and contamination levels in a large-scale watershed

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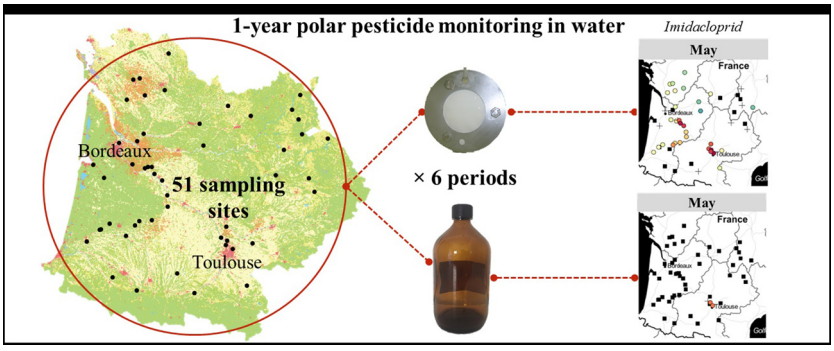
HIGHLIGHTS

- POCIS and grab samples were used for polar pesticide monitoring in freshwater.
- Large amount of data collected required specific graphical and map processing.
- Better temporal representativeness of monthly contamination levels with POCIS.
- Seasonal trends linked to pesticide application periods and land use are shown.
- Combining sampling strategies gives a more reliable overview of pesticide pressure.

GRAPHICAL ABSTRACT



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ABSTRACT

Fifty-one monitoring stations from the Water Framework Directive network (2000/60/CE) were selected in the Adour-Garonne basin (117,650 km^2, SW France). These stations were characterized by a diversity of land use, implying different water pesticide contamination profiles. In each, Polar Organic Chemical Integrative Sampler (POCIS) deployment (14 days) and grab water samples (1 per period) were performed 6 times in 2016 in order to obtain contamination levels (29 pesticides monitored). The large amount of data collected during this 1-year monitoring required specific graphical and map processing to compare the information provided by POCIS and grab samples. Graphical projections demonstrated that with POCIS the number of quantified pesticides and the quantification frequencies were higher than with grab samples. Additionally, projections showed that POCIS provided better temporal representativeness of monthly contamination levels. Indeed, the POCIS data showed seasonal trends which were directly linked with the use of each pesticide (application period) and the land use of each sampling site, that was not visible with the grab samples data. Map projections of the measured concentrations, using a common scale for the two sampling strategies, clearly showed the strengths of the POCIS deployment and the link between measured contamination levels, quantified pesticides and land use. Finally, this study shows that the combination of grab sample data (magnitude of contamination peaks) and POCIS data (average concentration over a given period) provided more complete and reliable knowledge of the contamination levels in the Basin than either method alone.

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1. Introduction

The use of pesticides in agricultural and non-agricultural contexts since the 1950s has brought considerable progress in food resource management and the quality of human and animal life. Nevertheless, during or after their use, pesticides are transferred from their application areas to environmental compartments (Loos et al., 2009), including freshwater. Monitoring programs are used to evaluate these contamination levels, as well as to monitor the effect of policies to reduce pesticide impact. Currently, the conventional method for freshwater analysis is grab sampling several times per year; favoured because of its simplicity. Despite practical benefits, a common criticism of grab sampling is that it provides concentrations with a lack of temporal representativeness, since it corresponds to a snapshot of freshwater quality at a point in time (Allan et al., 2006; Novic et al., 2017; Ort et al., 2010). Consequently, short-duration fluctuations (*e.g.* flood events, intensive runoff, punctual discharges, *etc.*) could be missed with low frequency grab sampling, resulting in only a partial picture of water quality.

To overcome these issues, the use of passive samplers has recently been considered as a suitable alternative. This sampling strategy consists of immersing a sampler in the water for a fixed period (Huckins et al., 1993; Petty et al., 1995; Vrana et al., 2005). With these samplers, contaminants in water are continuously integrated and an *in situ* pre-concentration of contaminant occurs. Thus, these passive sampling strategies provide a time-weighted average concentration (TWAC) with integration of contamination peaks (Mazzella et al., 2008; Novic et al., 2017), and low quantification limits (QL - Lissalde et al., 2011; Poulier et al., 2015). Moreover, due to the *in situ* pre-concentration of target compounds, these passive samplers can improve the QL obtained with the grab samples. Indeed, depending on the analytical methods and devices used, QL from laboratories enrolled in monitoring networks are currently about 0.01 μg L^{-1} for pesticides. If such QL are consistent with regularity thresholds (*e.g.* Environmental Quality Standard (EQS)) for atrazine is about 0.6 μg L^{-1} in the Water Framework Directive (WFD, 2000/60/CE, EU, 2000), or 0.1 μg L^{-1} for tap water (French Public Health Code, 2007), more stringent QL are required to detect and quantify compounds which are present at an ultra-trace level. Thus, this information would allow making the link between pesticide uses and their impact on water quality.

In this field study, the Polar Organic Chemical Integrative Sampler (POCIS), which is widely used for the sampling of polar organic chemicals ($0 < \log K_{ow} < 4$) including polar pesticides, (Alvarez et al., 2004; Mazzella et al., 2007) was used. Several studies performed at the watershed scale with this sampler compared its use for assessing water quality with grab sampling (Criquet et al., 2017; Guibal et al., 2017; Lissalde et al., 2014; Poulier et al., 2015) and all these studies demonstrated that with POCIS the number of quantified contaminants and the quantification frequencies were increased in comparison with grab sampling. Moreover, Poulier et al. (2014) demonstrated that POCIS could be used in addition to grab samples in regulatory monitoring programs because their integrative capacity allows the added value of temporal representativeness. A study performed in 100 small streams across the Midwest (USA) in summer 2013, demonstrated that POCIS revealed complex mixtures of pesticides at low levels of concentration and a correlation between pesticides and land use (Van Metre et al., 2016). Thus, the relationship between land use and water body contamination by pesticides have been demonstrated, but other trends, such as annual seasonal variability associated with pesticide contamination levels, have not.

In this context, a large-scale monitoring was performed during 6 periods in 2016. Fifty-one monitoring stations from the Water Framework Directive network (EU, 2000) were selected in the Adour-Garonne basin (117,650 km^2, SW France) which are characterized by a diversity of land use implying different pesticide contamination profiles. The large amount of data collected with POCIS and grab samples during this 1-year monitoring required the application of specific graphical and map methodologies. The aim of this data processing was to compare and contrast the information from POCIS and grab samples for the measurement of polar pesticide concentrations in water and to demonstrate links between pesticide use and freshwater contamination.

2. Materials and methods

2.1. Large-scale study area in France

The Adour-Garonne Basin in southwest France covers an area of 117,650 km^2 (Fig. 1). It is composed of two mountain ranges (the Pyrenees and the Massif Central), of 116,817 km of rivers and of a coastline strip of 650 km. This basin has a population of *c.a.* 7,000,000 with pronounced rural character (30% of the population), 35 cities with >20,000 inhabitants each (28% of the population) and two metropolises (Toulouse and Bordeaux) with *c.a.* 750,000 inhabitants each. The majority of the basin benefits from a mild and humid oceanic climate characteristic of the Atlantic influence (Southwest). The east is influenced by the continental climate and the southeast by the Mediterranean. Rainfalls are quite marked near the ocean and even abundant locally (Basque Country) and on the relief (>1400 mm $year^{-1}$), in comparison with relatively low rainfall in the central part and the southeast (600 to 700 mm $year^{-1}$). For this study, 51 sampling sites from the Water Framework Directive network (EU, 2000) were selected based on their agrochemical pressures and land use. The sampling sites are shown in Fig. 1 and their characteristics (*e.g.* principal percentage of land use, spatial coordinates) are available in the supporting information (Table S1).

2.2. Studied compounds

The studied compounds were chosen based on those analysed in the context of the monitoring network of the Adour-Garonne French Water Agency. Then, they were selected only if they could be sampled by the POCIS device (neutral and moderately polar compounds - $0 < \log K_{ow} < 4$) and if they were analysed by all the laboratories involved in this study (see Sections 2.5.1 and 2.5.2). The 29 selected compounds included different chemical families (triazine, urea, *etc.*) and biological activities (herbicides, fungicides, insecticides and metabolites) and are listed in Table 1. Of the 29, 13 were banned as agricultural pesticides several years ago, however, because of their persistence in environmental compartments, their possible illegal use and their current use as biocides (*e.g.* diuron), they were nonetheless investigated here. In addition, these banned compounds are still being investigated in the context of the WFD and are listed as priority substances.

2.3. Reagents and standards

The solvents (methanol, acetonitrile and ethyl acetate – HPLC grade) were obtained from Biosolve (Biosolve SARL, Dieuze, France). Ammonium acetate was purchased from Fluka (Sigma Aldrich, Schnelldorf, Germany). Ultrapure water (UPW, resistivity >18 MΩ) was produced by a Synergy UV system from Millipore (Billerica, MA, USA). Analytical standards (listed in Table 1) and internal standards (atrazine-*d5*, carbofuran-*d3*, DEA-*d6*, diuron-*d6*, methomyl-*d3*, metolachlor-*d6*, pirimicarb-*d6* and tebuconazole-*d6*) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) with purity higher than 95.5%. Individual stock solutions were prepared in acetonitrile (100 mg L^{-1}) and stored at −18 °C for no more than six months. A working solution containing each analytical standard was prepared by dilution of the individual stock solutions in acetonitrile (1 mg L^{-1}) and also stored at −18 °C for six months maximum.