Environmental forensics in groundwater coupling passive sampling and high resolution mass spectrometry for screening
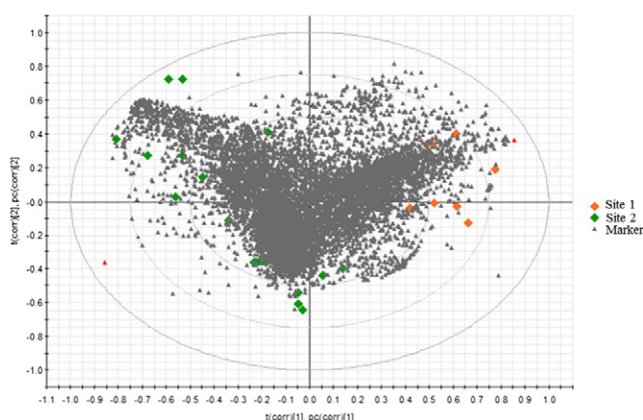
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HIGHLIGHTS

- Advantages of POCIS for environmental screening
- Implementation of data processing for environmental forensics
- Identification of unexpected compounds in environmental samples
- Highlighting of molecular fingerprints as a function of pollution sources

GRAPHICAL ABSTRACT

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One of the difficulties encountered when monitoring groundwater quality is low and fluctuating concentration levels and complex mixtures of micropollutants, including emerging substances or transformation products. Combining passive sampling techniques with analysis by high resolution mass spectrometry (HRMS) should improve environmental metrology. Passive samplers accumulate compounds during exposure, which improves the detection of organic compounds and integrates pollution fluctuations. The Polar Organic Chemical Integrative Sampler (POCIS) were used in this study to sequester polar to semi-polar compounds. The methodology described here improves our knowledge of environmental pollution by highlighting and identifying pertinent compounds to be monitored in groundwater.

The advantage of combining these two approaches is demonstrated on two different sites impacted by agricultural and/or urban pollution sources where groundwater was sampled for several months. Grab and passive sampling were done and analyzed by liquid chromatography coupled to a hybrid quadrupole time-of-flight mass spectrometer (LC–QTOF). Various data processing approaches were used (target, suspect and non-target screening). Target screening was based on research from compounds listed in a homemade database and suspect screening used a database compiled using literature data. The non-target screening was done using statistical tools such as principal components analysis (PCA) with direct connections between original chromatograms and ion intensity. Trend plots were used to highlight relevant compounds for their identification.

The advantage of using POCIS to improve screening of polar organic compounds was demonstrated. Compounds undetected in water samples were detected with these tools. The subsequent data processing identified sentinel molecules, molecular clusters as compounds never revealed in these sampling sites, and molecular fingerprints.

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Samples were compared and multidimensional visualization of chemical patterns such as molecular fingerprints and recurrent or specific markers of each site were given.

1. Introduction

Many micropollutants in the aquatic environment come from human and animal sources such as wastewater treatment plants, septic tanks, landfills, sewers, livestock and agricultural activities, etc. (Focazio et al., 2008; Mueller et al., 2011). More than 10,000 chemicals are registered under the European Union's REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) regulation (Directive REACH 2006/1907) and these can reach aquatic systems. These chemicals represent a wide range of physico-chemical properties and have different impacts in term of toxicity and potential harm. Only some of them are regulated in Europe for water pollution assessments by the Water Framework Directive (Directive 2000/60/EC). A text dealing specifically with groundwater protection from pollution and deterioration was written in 2006 (Directive 2006/118/EC) and revised in 2014 (Directive 2014/80/EU). In addition to these regulated compounds, others such as pharmaceutical compounds (PhACs), pesticides, personal care products (PCPs), endocrine disrupting compounds, surfactants, perfluorinated compounds, and industrial agents, which are known as emerging contaminants, are also detected in environmental samples (Bletsou et al., 2015; Lopez et al., 2015). Furthermore, regulated and non-regulated compounds can be degraded by various biotic and abiotic processes to form transformation products (TPs) that might be more persistent and toxic than their parent compounds and should be taken into consideration in environmental risk assessments (Escher and Fenner, 2011).

One challenge facing the scientific community is how to improve environmental monitoring. Whereas triple quadrupole analyzers currently enable us to seek only a pre-defined list of compounds in samples, new methodologies such as high resolution mass spectrometry (HRMS) enable comprehensive screening. Coupled with high pressure liquid chromatography (HPLC), HRMS makes it possible to detect, in one injection of a sample, several thousand compounds without preselection. Nevertheless, the physico-chemical properties range of organic compounds detected or identified with this technique is limited by sample pretreatment, chromatographic or ionization conditions. All of the detectable information is recorded and enables an a posteriori data search. HRMS is an analytical technique which allows identifying compounds and provides a level of confidence on target and non-target screening based on mass accuracy (Hug et al., 2014; Martinez Bueno et al., 2012). The quadrupole time-of-flight (QTOF) analyzer can be used in environmental analysis both for identifying TPs (Boix et al., 2014; Durand et al., 2006; Ibanez et al., 2006; Jelic et al., 2013) and for screening (Ferrer and Thurman, 2012; Guibal et al., 2015; Hernandez et al., 2015; Ibanez et al., 2005; Leendert et al., 2015).

The second constraint with regard to micropollutants is that they are present in the environment in mixtures at sub-ppb concentrations and at variable times and locations. Water samples are usually collected by spot sampling, which provides merely a snapshot of contamination at a given time and place. Better knowledge of these variables or of episodic pollution requires a multiplication of sample collection in time and space. To overcome these limitations passive sampling devices are able to provide time weighted average (TWA) concentrations, which are averaged concentrations over the exposure time of this type of tool (Vrana et al., 2005). They simplify sampling and decrease the conventional limit of detection (LOD) of the sampled compound. Polar Organic Chemical Integrative Samplers (POCIS) can be used for polar compounds such as pesticides, PhACs and steroids. These integrative passive samplers can remain in the aqueous medium for over two months (Vrana et al., 2005). Numerous compounds such as Polycyclic Aromatic Hydrocarbons (Tapie et al., 2011), pesticides (Alvarez et al., 2004; Berho et al., 2013; Guibal et al., 2015; Ibrahim et al., 2013a;

Mazzella et al., 2007), alkylphenols (Arditsoglou and Voutsa, 2008; Harman et al., 2009; Li et al., 2010), PhACs (Bartelt-Hunt et al., 2009; Martínez Bueno et al., 2009; Metcalfe et al., 2011; Togola and Budzinski, 2007), and perfluorinated compounds (Kovarova et al., 2012) have been detected with POCIS in various aquatic systems.

Using POCIS to improve conventional LOD coupled with LC–HRMS should improve the screening of micropollutants in aquatic samples. To our knowledge, only the published work of Guibal and co-workers deals with the combination of passive sampler and LC–HRMS (Guibal et al., 2015). Our study used POCIS to screen polar organic compounds in environmental samples, implemented a workflow for HRMS data processing, and applied it to two groundwater sites.

2. Materials and methods

2.1. Chemicals and reagents

Analytical standards (purity >98%) were purchased from Cluzeau Info Labo (CIL, Sainte-Foy-La Grande, France), TechLab (Metz, France), Sigma-Aldrich (Saint-Quentin Fallavier, France), and LGC standard (Molsheim, France).

The acetonitrile and methanol (HPLC grade) used for extraction were purchased from Fisher Chemical (Ilkirch, France). Ultrapure water was produced using a Millipore Direct-Ultrapure Water System. Oasis® HLB (divinylbenzene/N-vinylpyrrolidone copolymer) extraction cartridges (500 mg, 6 cm^3, 60 μm) were purchased from Waters Corporation (Guyancourt, France). Empty polypropylene SPE tubes with polyethylene frits were supplied by Supelco (Saint-Quentin Fallavier, France). The POCIS were purchased from Exposmeter SA (Tavelsjö, Sweden). Their pharmaceutical configuration consists of two 0.1-μm PolyEther Sulfone (PES) membranes containing OASIS® HLB sorbent.

The solvents used for the HPLC–HRMS analysis included acetonitrile and water (UPLC/MS grade) purchased from Biosolve (Dieuze, France), and formic acid (99%, LC/MS grade) purchased from Avantor (Deventer, the Netherlands). The lock mass used as an internal reference in the mass spectrometer's ionization source, Leucine Enkephalin (LeuEnk), was purchased from Waters Corporation and the calibrant for the mass spectrometer, sodium formate, was prepared with sodium hydroxide, purchased from Sigma Aldrich.

2.2. Sampling sites

Groundwater was sampled at two sites in France over a period of several months in 2014. Grab and passive sampling were done at the same time.

Site 1 is an alluvial aquifer impacted by diffuse agricultural pollution and urban effluents. Six successive one-month sampling campaigns were done from July to December 2014. A grab sample was collected at the beginning and end of each POCIS sampling campaign (7 samples). The POCISs were done in triplicate (18 samples).

Site 2 is an alluvial aquifer impacted only by diffuse agricultural pollution. Groundwater was sampled every 15 days from January to December 2014. A grab sample was collected at the beginning and the end of each 15-day POCIS sampling campaign (24 samples). The POCISs were done in triplicate (72 samples).

In order to compare results from these two sites, we took into account the same number of samples (n = 6 for water samples and n = 18 for POCIS). Both sites have comparable conditions concerning water velocity (both in alluvial plain). Temperature and pH were stable during exposure: 13.4 ± 2.3 °C and 7.2 ± 0.2 in site 1 and 12.8 ± 1.7 °C and 7.0 ± 0.2 in site 2.