

Suspect screening of emerging pollutants in groundwater and runoff water using passive sampling coupled with high resolution mass spectrometry

Suspect screening des polluants émergents dans les eaux souterraines et de ruissellement par échantillonnage passif couplé à la spectrométrie de masse haute résolution

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RÉSUMÉ

Les écosystèmes souterrains sont de plus en plus utilisés pour le développement des sociétés modernes. Il est donc nécessaire d'évaluer avec précision la présence de polluants émergents tels que des pesticides et pharmaceutiques dans les eaux souterraines. La pollution des eaux de ruissellement doit également être évaluée car en zone urbaine, les bassins d'infiltration utilisés pour la prévention des inondations peuvent être une source de contamination des écosystèmes souterrains. Dans ce contexte et dans le cadre du projet ANR FROG, une évaluation de la contamination des eaux souterraines et de ruissellement par les pesticides et les pharmaceutiques a été réalisée en décembre 2017, lors d'un épisode pluvieux, dans cinq bassins d'infiltration autour de Lyon (France). Des échantillonneurs passifs ont été exposés *in-situ* pendant 10 jours. Les analyses ont été effectuées par chromatographie liquide couplée à la spectrométrie de masse haute résolution (HPLC-QToF-MS) et le traitement des données a été effectué par suspect screening. Finalement, 101 composés ont été suspectés dont 40 confirmés. Le nombre de détections des pesticides est plus élevé dans les eaux souterraines que dans les eaux de ruissellement, contrairement aux pharmaceutiques. En termes de fréquence de détection, les eaux souterraines impactées par l'infiltration des eaux de ruissellement ne sont pas significativement plus contaminées que les eaux souterraines non impactées par l'infiltration.

ABSTRACT

There is a need to evaluate precisely the occurrence of emerging pollutants such as pesticides and pharmaceuticals in groundwater as underground ecosystems are increasingly used for the development of modern societies. Runoff water pollution has also to be characterized as stormwater infiltration basins used in urban area for flood prevention are a possible source of groundwater contamination. In this context, related to the FROG ANR project, a characterization of groundwater and runoff water contamination by pesticides and pharmaceuticals was carried out during a rain event in five stormwater infiltration sites around Lyon (France) in December 2017. Passive samplers were exposed 10 days *in-situ* and analysis was performed by liquid chromatography coupled to quadrupole time of flight mass spectrometry (HPLC-QToF-MS) with a suspect screening approach for data processing. As a result, a total of 101 compounds were suspected including 40 confirmed compounds. It was found that pesticides were mainly detected in groundwater unlike pharmaceuticals which were more often found in runoff water. In terms of detection frequency, groundwater impacted by infiltration were not significantly more contaminated than non-impacted groundwater.

MOTS CLÉS

Emerging pollutants, groundwater, passive sampling, runoff water, suspect screening

1 INTRODUCTION

Underground ecosystem goods and services are increasingly being used for the development and well-being of modern societies. Indeed, groundwater is more and more extracted for drinking water supply in order to adapt to global population growth (Danielopol et al., 2004). However, as a result of human activities, a wide range of organic contaminants are detected in groundwater ecosystems (Kurwadkar, 2017; Loos et al., 2010; Vulliet and Cren-Olivé, 2011). Pesticides were found at the level of hundreds of ng/L, as well as pharmaceuticals. Atrazine, desethyl atrazine, DEET, carbamazepine and sulfamethoxazole were among the most detected compounds in groundwater.

One potential source of groundwater contamination is associated with urban stormwater management practices based on infiltration basins (Fischer et al., 2003). These practices are very efficient for flood prevention in urban areas. The soil and unsaturated zone of infiltration basins are also recognized as efficient filters to trap pollutants present in stormwater runoff such as heavy metals, preventing the pollution transfer to groundwater. Nevertheless, little is known about the impact of infiltration practices on groundwater contamination by organic pollutants. Thus, there is an urgent need to determine precisely the occurrence of organic contaminants such as pesticides and pharmaceuticals in groundwater and runoff water.

Many analytical methods have been developed for the determination of polar organic contaminants in water, in particular high performance liquid chromatography (HPLC) coupled with a triple quadrupole mass spectrometer (QqQ) (Lissalde et al., 2011; Petrie et al., 2016). However, this technique has some limitations as only a pre-defined list of compounds can be analyzed. To circumvent these limitations, high resolution mass spectrometry (HRMS) allows the detection of a large number of compounds without preselection and enables comprehensive screening. Moreover, HRMS coupled with the suspect screening approach is a useful tool as it allows a more comprehensive analysis than with target screening while being less time consuming than non-target screening.

Another challenge concerning organic contaminants in groundwater impacted by infiltration practices is that they occur at ppb concentrations and at variable times. In most studies, grab sampling is the chosen sampling method but it only provides a snapshot of contamination at a given time and the question of measurement representativeness remains. Passive sampling devices such as polar organic chemical integrative sampler (POCIS) and Empore™ disks (ED)-based passive samplers are able to overcome these limitations and to provide a more representative assessment of groundwater contamination. To the best of our knowledge, only two studies have been reported on the combination of POCIS and HPLC-HRMS for the assessment of groundwater contamination (Guibal et al., 2015; Soulier et al., 2016).

This work is the first to report a strategy that combines ED passive samplers with HPLC-HRMS analysis for suspect screening of emerging pollutants in groundwater. The aims of the present study were to: i) assess the applicability of ED passive samplers coupled with HPLC-HRMS analysis to evaluate groundwater contamination; ii) provide a qualitative overview of the occurrence of pesticides and pharmaceuticals in groundwater and runoff water with a suspect screening approach. For this purpose, we used liquid chromatography coupled to quadrupole time of flight mass spectrometry (QToF-MS) for the screening of 30 groundwater and runoff water from five stormwater infiltration sites around Lyon.

2 MATERIAL AND METHODS

2.1 Field exposure

ED-based passive samplers were exposed in five stormwater infiltration sites located in the eastern of Lyon metropolitan area, France. Each stormwater infiltration site consisted in a settling and an infiltration basin that collected stormwater from residential, commercial, agricultural and/or industrial areas. Each stormwater infiltration site is equipped with piezometers located upstream and downstream of the infiltration basin. The upstream piezometer was used for sampling groundwater not impacted by stormwater infiltration whereas the downstream piezometer allows the sampling of impacted groundwater. Additionally, runoff water collection tanks were placed at the entrance of infiltration basins. In December 2017, during a rain event, three passive samplers were deployed during 10 days on each site: one in the upstream piezometer, one in the downstream piezometer and one in the runoff water collection tank.

2.2 Passive sampler processing and HPLC-QToF-MS analysis

Briefly, SDB-XC and SDB-RPS Empore™ extraction disks (ED) (47 mm diameter, 12 µm particle size, 3M) were conditioned by soaking in methanol then in pure water before being placed on supports. Supports had dimensions adapted to a piezometer and were composed of cylindrical stainless steel cages in which ED were placed and stuck behind a second stainless steel grid. Four SDB-XC disks and four SDB-RPS disks were placed per support. After deployment, organic chemicals sampled by ED were extracted in 10 mL acetone then 10 mL methanol, 10 min each. The acetone and methanol fractions were pooled together and reduced to dryness under nitrogen flow. Finally, samples were reconstituted in 500 µL of water/methanol (90/10, v/v) prior to analysis.

Analysis was performed with an Ultimate 3000 UHPLC system (Thermo Scientific®) equipped with a binary pump and reverse-phase analytical column, coupled to a QToF mass spectrometer (Maxis Plus, Bruker Daltonics®) operating in positive and negative mode. The MS/MS experiments were conducted using three different acquisition modes: broadband collision induced dissociation mode (bbCID, data independent analysis) for the suspect screening, the Auto-MS/MS mode (data dependent analysis) to confirm the suspected molecules and a specific selected mass by daughter scan mode method for compounds that were not fragmented with Auto-MS/MS mode. Target Analysis for Screening and Quantitation (TASQ)® 1.4 (Bruker Daltonics®), a software including two databases of about 2,500 pesticides and pharmaceuticals, was used for data processing.

3 RESULTS AND DISCUSSION

3.1 Suspect screening

Confrontation with databases consisted of a comparison of experimental data acquired throughout sample analysis, with theoretical data. All precursor and product ions were evaluated on three main criteria: retention time, *m/z* and isotope pattern. Additionally, the detection of at least one product ion for each precursor was mandatory. Deviations between experimental and theoretical data were calculated and scored according to tolerance thresholds previously set for each of the three criteria. In total, 101 compounds were suspected. In order to reach the level one of identification described by Schymanski et al. (2014), confirmation by injection of a reference standard was carried out for 43 compounds. Finally, 40 compounds were confirmed (Fig. 1.) and only 3 compounds were excluded because of insufficient matching with the reference standard.

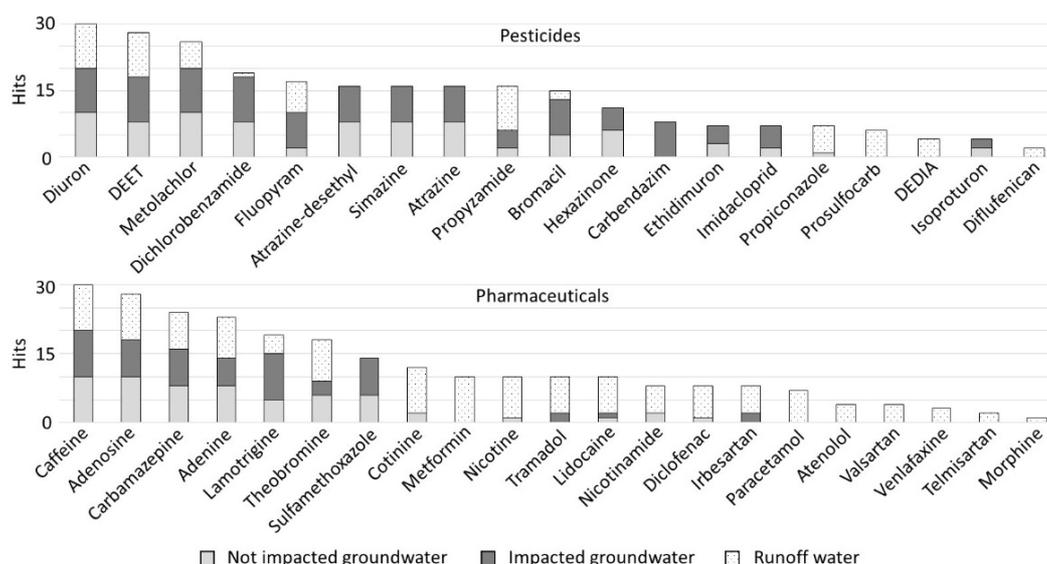


Fig. 1. Hits of confirmed pesticides and pharmaceuticals in impacted and not impacted groundwater and runoff water, all stormwater infiltration sites and the two extraction disks combined.

3.2 Passive sampler water quality monitoring

The application of passive sampling in combination with the suspect screening allowed the confirmation

of 30 compounds in groundwater, corresponding to 16 pesticides and 14 pharmaceuticals. In runoff water, 31 compounds were confirmed with 11 pesticides and 20 pharmaceuticals.

Globally, pesticides were mainly found in groundwater unlike pharmaceuticals which were more detected in runoff water (Fig. 1). Therefore, the presence of pesticides in groundwater could not be explained exclusively by the infiltration of runoff water. Several pesticides have probably reached and contaminated groundwater since many years. Indeed, the detection of pesticides like atrazine which has been banned from use since a few years comforts this hypothesis. In the case of pharmaceuticals, our results suggest that they were transported by runoff water. However, pharmaceuticals found in runoff water are not necessarily found in impacted groundwater. When comparing the frequency of detection, impacted groundwater do not seem to be more contaminated than not impacted groundwater. This suggests a low transfer from the infiltration basin to the groundwater. However, in order to conclude on the role of the soil and vadose zone on the dynamics of pollutants, a quantification would be necessary.

4 CONCLUSION

This work showed that ED passive samplers in combination with high resolution mass spectrometry analysis and suspect screening processing workflow can be very useful to characterize the occurrence of pesticides and pharmaceuticals in groundwater in a simple way. Passive samplers allowed the detection of contaminants generally found at very low concentrations in water as compounds were accumulated on the extraction disks. As a result, 101 suspects were detected in the five stormwater infiltration sites, including 40 confirmed compounds. It was found that pesticides were mainly detected in groundwater whereas pharmaceuticals were more often found in runoff water. To better understand the mechanisms involved in the migration of contaminants through the soil, a supplementary field exposure with a semi-quantitative approach will be undertaken.

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