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Analysis and identification of pesticides and their transformation products in groundwater by High Resolution Mass Spectrometry

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SUMMARY:

Nowadays it is increasingly important for public policy to know what compounds are present in groundwater, which of them must be monitored and their fate. Thus, specific analytical methodology is required to identify these micropollutants, including emerging substances or transformation products (TPs) potentially present at low concentrations. To improve limit of detection, POCIS (Polar Organic Chemical Integrative Sampler) were used as passive samplers for the pre-concentration of polar compounds. High Resolution Mass Spectrometry (HRMS) offering the possibility of detecting a large number of contaminants without pre-selection of analytes due to its accurate-mass full-spectrum acquisition was also applied. The combination of these two techniques carried out on several groundwater sampled monthly confirms the advantage of i) improvement of organic chemical screening with POCIS and ii) identification of non-targeted organic compounds with HRMS technique. Several pesticides and some of their transformation products were detected for the first time in these sites.

Key words: High Resolution Mass Spectrometry, passive sampling, pesticides, transformation products

INTRODUCTION

The high resolution mass spectrometry (HRMS) has gained increasingly in importance for monitoring organic compounds. Indeed, its high resolving power, mass accuracy and the sensitive full spectrum acquisition are the key points to identify compounds (Schymanski et al., 2014). However, implementation of this technique to groundwater samples remains rare.

On the other hand, main difficulties of monitoring are related to low and fluctuating concentration levels and complex mixture of pollutants. Therefore there is a strong interest to use passive sampler. These tools allow accumulating compounds during exposure that improves trace detection and integrating pollution fluctuations (Vrana et al., 2005). The Polar Organic Chemical Integrative Sampler (POCIS) was employed to sampling polar and semi-polar compounds ($\log K_{ow} > 4$).

Using POCIS to improve limit of detection coupled with LC-HRMS should improve the screening of micropollutants in waters. This study used POCIS to screen polar compounds in groundwaters, and implemented a workflow for HRMS data processing.

MATERIALS AND METHODS

Different groundwater sites were investigated and sampled during several months. Grab and passive sampling were deployed and analyzed by HRMS. The HRMS analyzer was a hybrid Quadrupole- Time of flight coupled upstream with a liquid chromatography. To process data, different approaches were investigated and the level of confidence on the identification will be different (Schymanski et al., 2014). The first one is based on research of compounds listed on our homemade database (around 450 with experimental). For the no identified signals the second approach, suspect screening, was employed. This consists to compare accurate masses, isotopic pattern and fragmentation data of signals to external databases (from bibliography, online databases, etc.). Finally, as a third approach, for the non-attributed signals the non-

targeted screening was applied using statistical tools such as principal components analysis with direct connections between original chromatograms and ion intensity. Trend plots are used to highlight relevant compounds for their identification which is time consuming.

RESULTS AND DISCUSSION

More compounds were identified in POCIS extracts than grab samples attesting of the interest of passive samplers as storage tool. However some compounds which were at the limit of POCIS application ($\log K_{OW}$ near to 4) were not detected in the POCIS extract but were detected in grab samples. It is the case for example of beflubutamid, a hydrophobic herbicide ($\log K_{OW}$: 4.28).

Moreover, the data processing enabled us to identify organic compounds in groundwater by target and suspect screening. Most of identified compounds were pesticides and their TPs. Contrary to quantitative analysis method routinely used in laboratories no compounds are targeted before analysis that improves the number of detected compounds.

CONCLUSIONS

The environmental screening of organic compounds is improved by the use of POCIS device which acts as a preconcentrator tool. The combination of passive sampler and HRMS allows detecting and/ or identifying more known or unknown compounds than the coupling of passive sampler and conventional quantitative analysis.

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