An innovative and comprehensive study to identify relevant emerging contaminants in French surface waters

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1. Introduction

The Water Framework Directive (WFD) requires Member States to establish national lists of substances to be monitored at river basin level. Despite these provisions, it is widely recognised by the scientific community that several substances of emerging concern are currently overlooked and as a result they are not adequately monitored by national authorities. As part of the implementation of the National Action Plan on Micropollutants in the Aquatic Environment, the French Ministry of Ecology decided to implement an innovative and comprehensive approach to improve national monitoring programmes under the WFD. This includes the setting up of a watch list of substances to be investigated at the national level in order to acquire missing information about the level of exposure of emerging contaminants in the aquatic environment and allow regular updating of the list of River Basin-Specific Pollutants to be regularly monitored. As part of this action plan a large national screening study took place in 2012 in France.

2. R&D approach

INERIS was charged with the design and technical implementation of this project for surface water. Sampling was carried out by local laboratoties contracted by the agencies according to AQUAREF's (National Reference Laboratory for Aquatic Environment) technical specifications and a unique courier was selected for transport of samples to the laboratories. Four academic laboratories were selected for chemical analyses. A common data reporting template was developed as well as a national database specific for this study.

3. Substances prioritisation

For the selection and prioritisation of the watch list compounds the National Expert Group for prioritisation of substances (CEP) decided to adopt the criteria of the NORMAN methodology for prioritisation of emerging substances [1]. Unlike other prioritisation methods, which aim simply to rank all candidate substances against one single prioritisation objective, the NORMAN method combines the ranking process with a prior allocation of the substances into action categories, which allows substances to be managed on the basis of the level of available information, thereby avoiding the exclusion of substances for which there are limited data. That methodology uses a decision tree that first classifies chemicals into six categories, on the basis of the existing knowledge gaps and the actions to be taken by the research community and the public authorities to fill them. The priority within each category is then ranked on the basis of specific indicators, which allows a score to be calculated. The watch list was derived from one of those six categories. About 2400 compounds were considered as potential candidate substances. An exhaustive assessment of the level of adequacy of the existing monitoring data (11 million datasets), both in terms of relevant matrix and compatibility between the limit of quantification of the existing data and the environmental protection thresholds (PNEC) (i.e. LOQ <PNEC) was performed as part of the selection of the watch list compounds. As a result of the prioritisation process a total of 170 molecules were assigned were selected, of which more than 100 were never measured in river basin monitoring programmes .

4. Sampling site selection criteria and tools deploied

For surface water three campaigns were performed on water matrix and one in sediments at about 159 sampling points. Two types of surface water bodies were investigated: rivers (140 sites) and lakes (19 sites). The choice of sites was made on the basis of previous investigation results and the following target criteria:

at least 20% reference sites, and 16% sites where conditions for good ecological status are not achieved. The remaing 64% were chosen on the basis of land use: urban sites; sites for agricultural activities or breeding; and industrial areas. Grab sampling was applied on all sites. In addition, passive samplers (POCIS) were deploied in 20 rivers in order to allow the implementation of bioassays.

5. Analytical methods, QA/QC issues and biological complementary tests

As regards target chemical analysis a national analytical working group (including nine French research laboratories) was set up to assess the analytical feasibility for the candidate priority pollutants and to define harmonised QA/QC protocols for the analysis of the selected compounds. Only methods with an LOQ below the PNEC value were accepted. The analytical work for a given group of compounds was performed by one single laboratory selected based on its proven capability to analyse this compound in order to ensure data comparability. 170 substances were finally selected for chemical analysis in water and sediment (Table 1).

Table 1: Number of substances by use category

Use category	Example of substances	Sediment	Water
Antioxydants	4-sec-Butyl-2,6-di-tert-butylphenol, 2,6-di-tert-butyl-4-phenylphenol	4	2
Flame retardants	Tetrabromobisphenol A, BDE-209	11	0
Gazoline additive	Organolead metabolites	3	3
Industrial chemicals	3,4 dichloroaniline, Decahydronaphtalene	6	4
PAH & metabolites	Not regulated HAP	20	1
Personal care products	Triclosan, Parabens and UV screening agents	3	5
Pesticides/Biocides and metabolites	Carbendazim, Prochloraz, Pendimethalin, Permethrin, Piperonyl-Butoxide	44	50
Pharmaceuticals	Amiodarone, Diosgenin, Clotrimazole	28	22
Plasticisers	Phtalathes and bisphenol A	5	5
Polyfluoro- substances (PFASs)	Carboxylates, sulfonates, sulfonamides and sulfonamide acetic acids	6	6
Surfactants	Nonyl-, octylphenol derivatives	4	2
Total		134	100

Besides target chemical screening, effect-based biological tools were applied on 20 selected sites in order i) to characterise site contamination profiles by endocrine active and dioxin-like chemicals in both water (POCIS) and sediments by using a panel of *in vitro* and *in vivo* bioassays and ii) to assess impacts in wild population of fish using biochemical biomarkers.

6. Conclusions

An innovative approach for identification of relevant emerging contaminants in French waters and revision of nationally monitored substances, was launched in 2011. The benefits of the approach are:

- A unique prioritisation scheme (NORMAN Network) applied at French national level for substance and site selection;
- Information on occurrence, source and variability for 170 substances (50 000 robust analytical data items) collected in different areas (urban, agricultural, industrial, no-anthropogenic pressure);
- An efficient method for data collection, validation and exploitation thanks to a unique data collection template and an exhaustive set of metadata (easy access to full dataset for water managers 4 months after last sampling);
- Application of effect-based tools to classify 20 sites of various quality; relationship with chemical monitoring data is under evaluation.

The results contributed to the selection of substances to be integrated in the national river basins monitoring programmes. This exercise will be repeated on a regular basis in line with the 6-year cycle under the WFD.

7. References

[1] Dulio V. and van der Ohe P.C. (2013) NORMAN Prioritisation framework for emerging substances, published by : NORMAN Association - *ISBN : 978-2-9545254-0-2*, 70p.

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