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Marine monitoring campaign in France and French overseas departments: more than 10 000 datasets from grab and passive sampling

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1. Introduction

A screening study of emerging contaminants was carried out in 2012 in coastal waters in both metropolitan France and overseas departments (Martinique, Guadeloupe, Reunion, Mayotte and French Guiana) as part of the National Action Plan against pollution of the aquatic environment, which requires the regular updating of the lists of substances to be included in monitoring programmes. The Action Plan stresses the need to set up a watch list of substances to be investigated at the national level in order to acquire missing information about the level of exposure to emerging contaminants in the aquatic environment and allow identification of substances for which specific actions need to be implemented. The Ministry of Ecology appointed ONEMA as principal contractor and INERIS as project leader. One of the main objectives of this screening study was to gain knowledge of the occurrence of substances of "emerging" concern in the marine environment. Different data were collected, such as the presence/absence of each investigated compound and the level of concentration observed in the aquatic environment (water and sediment). Moreover, the performance of different sampling techniques was assessed.

2. Materials and methods

For the selection and prioritisation of the compounds to be included in this screening study, the CEP (National Expert Group on Prioritisation) decided to adopt the main criteria defined in the NORMAN methodology (Dulio & von der Ohe, 2013, ISBN : 978-2-9545254-0-2). The substances monitored in this campaign included 157 substances from a large range of contaminants (PAHs & degradation products, alkyl perfluorinated compounds, plasticisers, pharmaceuticals, pesticides, antioxidants, petrol additives and industrial products). Passive sampling techniques and direct extraction techniques were tested through the implementation of *in situ* systems integrators – POCIS (Polar Organic Chemical Integrative Sampler) – and extraction by SBSE (Stir Bar Sorptive Extraction) directly in the water samples. Sediment samples were also collected (Figure 1, sampling stages on Guadeloupe Island).



Figure 1: Sediment sampling (a); POCIS sampling (b) and SBSE sampling (c) (photo: PARETO Ecoconsult)

One sampling campaign was conducted for a total of 42 sites selected throughout metropolitan and overseas departments. Passive samplers were deployed by the IFREMER's operators in April-August 2012 for 3 weeks. After field exposure, they were frozen, and then sent to the laboratory for analysis. The POCIS's phase was eluted by a mixture of DCM/MeOH. Pharmaceuticals were analysed by LC/MS/MS and pesticides by GC/MS and LC/MS/MS.

3. Results

Overall, 1054 analyses were carried out on POCIS membranes and only 64 measurements exceeded the limit of detection (LD). As regards analyses from SBSE extraction, 304 results above LD were observed out of 12 726 analyses. For sediments, 237 data out of 1536 analyses were above the limit of quantification (LQ). Out of the 157 different substances investigated, 68 were detected at least once in water or sediment. For the sediment matrix, 47 substances were quantified. In France, the 15 substances that were quantified at higher frequencies (> 50 %, one out of 2 sites) were also quantified in sediments. These are the congeners of PAHs (11 substances), organotins (2 substances), diethyl lead and BDE 209. In overseas departments, the 22 substances that were quantified at higher frequencies (> 50 %, one out of 2 sites) were measured in sediments. These are congeners of PAHs (13 substances), alkylphenols (3 substances: the mono and diethoxylate nonylphenol and the 4-ter butylphenol), organotins (2 substances), products of metabolism of the insecticide DDT (2 products), diethyl lead and BDE 209. Nine substances were detected in both water and sediment, both in Metropolitan France and in overseas departments (Table 1).

Table 1: List of substances detected in water and sediment

Substance	***Water (sampling followed by SBSE)***	***Water (POCIS sampling)***	***Sediment***
benzy butyl phthalate	X	_	X
bisphenol A	X	_	X
benzo(e)pyrene	X	_	X
coronene	X	_	X
triphenylene	X	_	X
dibenzothiophene	X	_	X
chlordecone	X	_	X
NP1EO	_	x	X
NP2EO	_	x	X

Substances quantified at higher frequency are those measured in the sediments. PNEC exceedance is recorded for 4 substances in water (imidacloprid, chlordecone, phosphamidon, 3 pesticides and triclosan) and for 11 substances in sediment (among them, chlordecone, BPA and diethyl/triethyl lead). The distribution of data by use or nature of the substance shows that, in both Metropolitan France and overseas departments, plasticisers and pesticides predominate in raw water, while PAHs dominate in sediments.

4. Conclusions

This study contributes to increased knowledge of emerging pollutants in French waters and to the wider considerations for updating the list of relevant substances to be included in the new monitoring programmes to be established. Triplicate sampling of water at the same site followed by SBSE extraction displayed a high results variability, which limits the exploitation of the quantified results. Neverthless, the testing of *in situ* systems integrators – POCIS – and extraction by SBSE bars has proven the added value of these two complementary techniques for monitoring hydrophobic and hydrophilic compounds in marine water. Finally, analyses of sediment allowed a more complete assessment of the quality of the waterbodies.

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