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Quality survey of natural mineral water and spring water sold in France: Monitoring of hormones, pharmaceuticals, pesticides, perfluoroalkyl substances, phthalates, and alkylphenols at the ultra-trace level

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HIGHLIGHTS

- 40 French bottled waters representing 70% of the market volume were analyzed.
- Ng/L-level LOQs were reached using 12 analytical procedures with 49 methodologies.
- None of the 172 pharmaceuticals, 11 hormones and 11 phthalates was quantified.
- 330 compounds were investigated, 19 were quantified and 11 samples were positive.

GRAPHICAL ABSTRACT

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ABSTRACT

The aim of the present study, one of the most complete ever performed in France, was to carry out an extensive survey on the potential presence of a large amount of emerging contaminants in 40 French bottled waters, including parent compounds and metabolites. The studied samples represented 70% of the French bottled water market in volume. Six classes of compounds were investigated, most of them being unregulated in bottled waters: pesticides and their transformation products (118), pharmaceutical substances (172), hormones (11), alkylphenols (APs) (8), phthalates (11) and perfluoroalkyl substances (PFAS) (10). One of the objectives of this work was to achieve low and reliable limits of quantification (LOQs) (87% of the LOQs were below 10 ng/L) using advanced analytical technologies and reliable sample preparation methodologies, including stringent quality controls. Among the 14,000 analyses performed, 99.7% of the results were below the LOQs. None of the hormones, pharmaceutical substances and phthalates were quantified. Nineteen compounds out of the 330 investigated were quantified in 11 samples. Eleven were pesticides including 7 metabolites, 6 were PFAS and 2 were APs. As regards pesticides, their sum was at least twice lower than the quality standards applicable for bottled waters in France. The presence of a majority of pesticide metabolites suggested a former use in the recharge areas of the exploited aquifers. The quantification of a few unregulated emerging compounds at the nano-trace level, such as PFAS, raised the issue of their potential sources, including long-range atmospheric transport and

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deposition. This study confirmed that the groundwater aquifers exploited for bottling were well-preserved from chemicals, as compared to less geologically protected groundwaters, and also underlined the need to pursue the protection policies implemented in recharge areas in order to limit the anthropogenic pressure.

1. Introduction

In 2014, bottled water consumption worldwide reached 282.8 billion liters, representing a 6.9% increase since 2009 (Rodwan, 2015). France is the sixth leading country in Europe, with a consumption of 118 L per capita (EFBW, 2014). Packaged spring waters (SPW) or natural mineral waters (NMW) are clearly distinguishable from ordinary drinking water by their protected groundwater origin and by the fact they are not submitted to any treatment aiming at removing contaminants of human origin nor to any disinfection (Codex Standard 108-1981, 2008; Codex Standard 227-2001; Directive 2009/54/EC). Indeed, the exploited groundwaters in France for NMW or SPW bottling benefit from a natural geological protection, characterized by the absence of direct relationships with surface waters and by the long transit time from infiltration to abstraction (several years to several decades (Blavoux et al., 2013)), but also from physical protection in boreholes and spring areas. In addition, French bottlers are applying long-term protection policies on their watersheds, by (1) setting partnerships with local actors, in order to limit the impact of the local anthropogenic activities such as agriculture, weeding along the roads and railways, wastewater collection and treatment, and forestry (Beley et al., 2016; Lachassagne et al., 2011, 2014), (2) banning some chemicals such as pesticides and fertilizers, and raising the local awareness on good practices regarding gardening and biological pest figthing, (3) protecting and restoring wetlands, and (4) expanding protected areas with the acquisition of lands. As for NMW, the CODEX Standard 108-1981 (2008) only defines 4 classes of organic substances to be lower than the quantification limits (LOQs): surface active agents, pesticides and polychlorobiphenyls, mineral oils and polynuclear aromatic hydrocarbons. In France, the Decree of 12/28/2010, set standards in NMWs for pesticides and their metabolites, whose sum has to be below 100 ng/L, without establishing a strict list of compounds and of their related metabolites to be monitored. In Europe, the maximum concentration for water intended for human consumption and SPW is 100 ng/L for individual pesticides and their related metabolites (except aldrin, dieldrin, heptachlor and heptachlorepoxyde for which it is 30 ng/L, this limit also standing for NMW) and 500 ng/L for their sum (Directive 1998/83/EC).

Pesticides are now subject to long-term monitoring in Europe aiming at better understanding their sources and pathways to aquifers with the implementation of the EU Water Framework Directive (Directive 2013/39/UE). According to the annual monitoring of water resources performed by the French water agencies (CGDD, 2011), in 2013, the two most frequently detected compounds are glyphosate (39%) and its main metabolite aminomethylphosphonic acid (AMPA) (56%) in surface water, which is related to its use. In addition, some prohibited parent compounds are still frequently detected in surface and groundwaters with only atrazine being detected in both matrices. Moreover, metabolites are quantified to a greater extent in groundwaters than in surface waters, the first five being atrazine-related ones: desethyl-atrazine (DEA, 47%), deisopropyl-desethyl-atrazine (DEDIA, 27%), atrazine (23%), deisopropyl-atrazine (DIA, 13%) and 2-hydroxy-atrazine (2OH-At, 12%). Considering the fact that their low rate degradation mechanisms and long residence times encourage long-term contamination, it is therefore crucial that both currently used and prohibited compounds as well as their metabolites should be monitored (Kolpin et al., 2009; Postigo and Barceló, 2015). In fact, compounds such as atrazine and its metabolites are still quantified decade after their banishment (Kolpin et al., 2000). In this study, a specific focus on transformation product analysis was made, especially for the class of pesticides.

Due to their potential risk for the environment, perfluorooctanesulfonic acid (PFOS), 4-nonylphenol (4-NP), 4-octylphenol (4-t-OP) and di(2-ethylhexyl)phthalate (DEHP) were added to the list of 45 priority substances in surface waters by the European Decree 2013/39/UE stating the environmental quality standards of 0.65 ng/L, 300 ng/L, 100 ng/L and 1300 ng/L respectively. The commission's implementing decision 2015/495/EC added several compounds to the watch list such as hormones (17α-ethinylestradiol, estrone and 17β-estradiol), pesticides (e.g. imidaclopride) and pharmaceuticals including diclofenac, which is one of the most widely used and persistent pharmaceutical substance in Europe with a chronic toxicity for marine and freshwater organisms. Alkylphenols (APs) and their related degradation products, perfluoroalkyl substances (PFAS), phthalates, hormones and pharmaceuticals, all suffering from a lack of data regarding their occurrence and potential toxicity in water intended for human consumption, have been recently studied by the French Food Safety Agency (ANSES, 2011; Boiteux et al., 2012; Colin et al., 2014). These studies tend to highlight higher levels of contamination in raw surface waters than in raw groundwater used to produce water intended for human consumption, regardless of the considered class of compounds. Indeed, groundwaters are subject to contamination by emerging contaminants from point and diffuse sources, such as contaminated surface waters, manure application on soils, atmospheric depositions and the treatments of cultures with pesticides (Lapworth et al., 2015) despite their possibly high potential of attenuation through natural processes (Jurado et al., 2012; Lapworth et al., 2012; Luo et al., 2014; Meffe and de Bustamante, 2014; Stuart et al., 2012).

The survey of such compounds is of critical importance for the bottled water industry to assess: i) the actual occurrence of trace emerging contaminants in the marketed bottled waters, ii) the effectiveness of the natural protection of the aquifers (hydrogeological settings) and (iii) the effectiveness of the long-term protection policies adopted by the French bottlers. Some other studies focused on the occurrence of emerging contaminants in bottled waters, but either targeting a specific class in a large panel of samples such as PFAS (Schwanz et al., 2016), or considering different types of compounds (e.g. APs and phthalates) in fewer samples (Amiridou and Voutsa, 2011). In a previous study, 120 compounds including hormones, pharmaceuticals, APs and phthalates were specifically investigated in two French NMW (Dévier et al., 2013) leading to an absence of quantification despite the low LOQs ranging from 1 to 150 ng/L. This result confirms the good hydrogeological context of these two exploited aquifers and the effectiveness of the protection measures.

To our knowledge, this is the first study aiming at providing such an extensive survey on the potential presence of emerging contaminants (pharmaceuticals, hormones, pesticides, phthalates, APs and PFAS) in 40 brands of bottled NMW or SPW sold in France, corresponding to 70% of the French bottled water market in volume. For such aqueous matrices, investigating at the expected low ng/L level is essential, but may represent a real challenge (Capdeville and Budzinski, 2011). The emphasis put on analytical methodologies, including the use of a wide range of quality assurance and quality control procedures (QAQC) will be extensively discussed below.

2. Materials and methods

2.1. Water resources context of the analyzed bottled waters

25 samples of NMW and 15 samples of SPW were analyzed in this study (Table S3). They mostly originate from continental France, at the

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