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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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exception of one SPW from New Caledonia, and one from the Reunion Island, and two springs from France's neighborhood (a NMW - Beckerich/Ophélie - from Luxembourg, and a SPW from near Italy - Mont-Blanc). The sampled bottled waters are representative of French geological diversity, with springs from the Alps (3 NMW and 3 SPW), Pyrenees (3 NMW), Massif Central (9 NMW and 2 SPW), Vosges and Ardennes (2 NMW and 1 SPW). The others originate from the Parisian basin (6 NMW and 4 SPW), the northern (1 NMW and 1 SPW) and southern parts of France (1 NMW and 1 SPW), and Britany (1 SPW). As the geology (and consequently the hydrogeology) of France is very various, these bottled waters correspond to different kinds of aquifers. From the oldest (>300 Ma) with Primary fractured plutonic and metamorphic hard rock aquifers (13 NMW and 4 SPW), most of them being deep aquifers providing natural carbo-gaseous water, to a relative majority of Secondary, Tertiary and Quaternary glacial sedimentary aquifers (11 NMW and 9 SPW) and also recent (Tertiary and Quaternary) volcanic aquifers (1 NMW and 2 SPW). Not all sampled groundwaters were dated previously to this study, but from the known ages and the hydrogeological context, their age distributions range from several years to several tens of years, and even a few centuries. From a regulatory standpoint, NMW and SPW must have an effective geological protection and NMW must mandatory have stable physico-chemical parameters (temperature, major ions and trace elements, etc.). As a consequence, NMW and SPW have no direct relationships with surface water, and of course no alluvial nor karstic aquifers were sampled in this study.

Since each of these springs belongs to a different aquifer, it is beyond the scope of this study to describe the land use of each aquifer's watershed. Nevertheless, none of these watersheds were in a predominantly urban or industrial environment. At the exception of some quite small watersheds without significant anthropogenic surface activities, most of the watershed environments include a major part of forest and/or extensive agricultural land, with often a few secondary roads and some villages. As described in section 1, several French bottlers have applied long term protection policies on their watersheds.

### 2.2. Targeted compounds

The targeted compounds were chosen according to several criteria such as existing or missing data on aquatic matrices, the review of their use at the national scale (qualitative and quantitative), their physico-chemical properties (ability to leach and stability), ecotoxicological data and analytical capabilities. All those data were gathered using several external databases such as NORMAN-EMPODAT, TOXNET, PPDB and the INERIS web portals (e.g., the Chemicals Portal, SIRIS) and the selection process followed the NORMAN approach (Working group 1 Prioritisation of emerging substances (Dulio and Von der Ohe, 2013)). Internal data generated in other projects were also used to implement the list of target compounds. Regarding PFAS, 10 compounds with short to medium chain length ($C_4$–$C_{10}$) were investigated, including 7 perfluoroalkyl carboxylates (PFCAs) and 3 perfluoroalkyl sulfonic acids (PFSAs) (Table S1) due to their recurrent quantification in surface waters (Munoz et al., 2015).

A list of 330 compounds was established including parent molecules and transformation products (TPs) in order to take into account pathways of contamination whether punctual or diffuse and to increase the representativeness of the study (Table S1). These compounds belong to 6 classes, namely pesticides (118 including 19 TPs), hormones (11), pharmaceuticals (172 including 12 TPs), PFAS (10), APs (8), and phthalates (11). The specific focus on transformation product analysis was made possible depending on the availability of standards. Chemical standards as well as full details on solvents and consumables are indicated in the Supplementary information document (S2).

### 2.3. Sampling and sample preservation

Samples (Table S3) were provided, on a voluntary basis, by the members of the French Federation of Bottled Water, including NMW and SPW bottlers.

Sampling was directly performed at the end of the packaging lines, just after bottling, from July 2013 to September 2013. As a consequence of both technical and regulatory constraints, the bottling process was very similar from one bottler to another. The fillers are mostly made of stainless steel and the other pieces all comply with alimentary norms. The fillers are located in a room pressurized with filtered air, and groundwater is in contact with this filtered air for a few seconds only in this room during the filling of the bottle. In accordance with applicable regulation, both NMW and SPW are not disinfected; no chemicals are added to the water at any stage of the bottling process with the exception of carbon dioxide for sparkling waters. The bottling installation (from the well to the filler) is regularly cleaned in place and thoroughly rinsed before bottling. Samples were then transported in their original packaging (PET and glass) in coolers in the dark, with an additional wrapping of aluminum foil for PET bottles to avoid any contamination from external air, and then stored at −20 °C upon receipt in the laboratory until extraction and analysis.

### 2.4. Chemical analysis

Due to the high number of target compounds, a wide range of analytical methods were used: the 330 compounds were investigated using twelve analytical procedures presented in the analytical workflow in Table 1. Some consisted in coupling offline Solid Phase Extraction (SPE) to LC/MS/MS and others in coupling on-line techniques with GC/MS, GC/MS/MS and LC/MS/MS, in order to limit the loss of compounds and risk of contamination. Indeed, these techniques have proven their robustness and ability to achieve more reliable and lower LOQs for specific compounds by reducing manipulation steps as compared to offline techniques (Valsecchi et al., 2015).

#### 2.4.1. Analysis by offline SPE LC/MS/MS

The majority of compounds were analyzed using SPE followed by LC/MS/MS analysis. Most of them were analyzed according to procedures already detailed in Munoz et al. (2015) for PFAS (group 1, see Table S1), in Belles et al. (2013) for polar pesticides (group 2) and in Dévier et al. (2013) & Togola and Budzinski (2008) for polar pharmaceuticals (groups 3 and 4). APs ethoxylates' extraction (group 5) was adapted from Cailleaud et al. (2007) and their analysis was fully described in Dévier et al. (2013).

As for hormones (groups 6 and 7), the extraction procedure was adapted from Labadie and Budzinski (2005a, 2005b) while the analytical procedure by LC/MS/MS was adapted from Miège et al. (2009) and specifically developed for this study. The sample injection volume was set at 5 μL. The chromatographic separation was achieved using a Kinetex $C_{18}$ column (100 × 2.1 mm, particle size 1.7 μm). Gradient conditions and optimized detection parameters are described in Tables S4-1 and S5.

Four different LC/MS/MS systems were used to conduct all the analyses: (1) an Infinity 1290 chromatograph system coupled to an Agilent 6460 QQQ triple quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA, USA) for the analysis of group 2, or (2) to an Agilent 6490 QQQ triple quadrupole mass spectrometers (Agilent Technologies, Santa Clara, CA, USA) for the analyses of groups 1 and 7, (3) an Agilent 1200 Series Rapid Resolution Liquid Chromatography system coupled to an Agilent 6410 QQQ triple quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA, USA) for the analysis of group 3, and (4) an Acquity ultra performance liquid chromatography coupled to an Acquity Quattro Premier triple quadrupole mass spectrometer (Waters, Milford, MA, USA) for the analyses of groups 4, 5 and 6. All the

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**Table 1**
Analytical procedure for the analysis of hormones, pharmaceuticals, pesticides, APs, PFAS and phthalates.

| Class (number of compounds) | Analytical procedure | Groups[b] | Sources |
|---|---|---|---|
| Pharmaceuticals (172) | Offline SPE LC/MS/MS: 151 | 3, 4 | (Dévier et al., 2013; Togola and Budzinski, 2008) |
| | On-line SPE-LC/MS/MS: 17 | 9, 10, 11, 12, 13, 14 | Method development[a] |
| | Direct injection: 4 | 15, 16 | Method development[a] |
| Hormones (11) | Offline SPE LC/MS/MS | 6, 7 | Extraction fully described in (Labadie and Budzinski, 2005a, 2005b) without the purification step – Method development adapted from Miège et al., (2009)[a] |
| Pesticides (118) | Offline SPE LC/MS/MS: 74 | 2 | (Belles et al., 2013) |
| | SBSE GC/MS/MS: 35 | 18 | Method development[a] |
| | On-line SPME-GC/MS/MS: 6 | 17 | (Belles et al., 2013) |
| | On-Line SPE-LC/MS/MS: 3 | 8 | Method development[a] |
| PFAS (10) | Offline SPE LC/MS/MS | 1 | (Munoz et al., 2015) |
| APs ethoxylates (5) | Offline SPE LC/MS/MS | 5 | (Cailleaud et al., 2007; Dévier et al., 2013) |
| APs (3) | On-line SPME-GC/MS | 20 | Adapted from phthalates analysis fully described by Dévier et al. (2013) |
| Phthalates (11) | On-line SPME-GC/MS | 19 | (Dévier et al., 2013) |

[a] This method was specifically developed to achieve very low and reliable LOQs and to avoid any interference linked to the matrix.
[b] For more details, see Table S1. Compounds in each group were analyzed using distinct analytical methodologies in order to reach low LOQs.

correspondences between compounds/groups, quantification methods and internal standards (ISs) are fully detailed in Table S1.

*2.4.2. Analysis by on-line SPE-LC/MS/MS*

On-line SPE was used for the analysis of 3 pesticides, namely cyromazine, pymetrozine and foramsulfuron (group 8), and of 16 pharmaceuticals (groups 9 to 14). The analyses were performed on an Infinity 1290 chromatograph system coupled to an Agilent 6490 QQQ triple quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). On-Line SPE extractions were performed using a stand-alone module composed of an Agilent 1260 series quaternary pump and autosampler, as well as a six-way solenoid valve and a multi-cartridge support (up to 6 cartridges) (Agilent 1200 series), and directly connected to the LC/MS/MS system at the entrance of the column. Two on-line extraction cartridges were used: PLRP-S phase (15–20 μm, 2.1 × 12.5 mm) for groups 8 and 12 and an Oasis HLB phase (30 μm, 10 × 2 mm) for groups 9 to 14 excluding group 12. Data acquisition was performed in the multiple reactions monitoring (MRM) mode. Further details are given in Table S4-2.

Finally, 4 pharmaceuticals were analyzed by direct injection. In order to achieve reliable LOQs and due to erratic behaviors during the extraction phase, two methods were used: one for danofloxacine, maduramicine and narasin (group 15) and another one for 5-fluorouracil (group 16). Separation was achieved using a Kinetex (100 × 2.1 mm; particle size 1.7 μm) column at a flow of 0.5 mL/min. Solvents A and B were water and acetonitrile for both groups, with a specific addition of 0.02% of $NH_4OH$ for the analysis of group 16. The detailed protocol is presented in Table S4-3. In both cases, data acquisition was performed in the MRM mode.

*2.4.3. Analysis by SBSE-GC/MS/MS and on-line SPME coupled to GC/MS or GC/MS/MS*

SBSE and on-line SPME extraction were both performed using a MPS2XL Autosampler (Gerstel, Mülheim van der Ruhr, Germany) coupled to a GC/M/MS or a GC/MS.

35 hydrophobic pesticides (group 17) were extracted by Solid Bar Stir Extraction (SBSE) using a PDMS stir-bar (0.5 mm × 10 mm) (Gerstel, Mülheim van der Ruhr, Germany) immersed in 100 mL of sample. Sorption was performed at room temperature during 16 h under continuous agitation (800 rpm). The stir bar was then removed and analytes were thermodesorbed at 280 °C in the splitless mode during 5 min under helium. Analytes were then focalized at −50 °C on a second trap and re-desorbed at 280 °C, held 5 min, and analyzed by a gas chromatography system (Agilent 7890A, Palo Alto, CA, USA) equipped with a tandem mass spectrometer (Agilent 7000A, Palo Alto, CA, USA). Separation was performed on a HP5MS-UI column (size 30 m × 0.25 mm, 0.25 μm film thickness) using Helium 6.0 as carrier gas during 49 min (60 °C for 6 min - 25 °C/min to 150 °C - 3 °C/min to 200 °C – 8 °C/min to 300 °C (for 10 min)). The MSD was operated in the electron impact ionization mode (70 eV). The compounds were quantified using the MRM transition giving the most intense response. MRM transitions, dwell times and collision voltages are shown in Table S6.

On-line SPME coupled to GC/MSMS was used for 6 hydrophobic pesticides (group 9) (Belles et al., 2013) using a PDMS/DVB fiber (65 μm). Analyses were carried out on an Agilent 7890A gas chromatography system coupled to a tandem mass spectrometer (Agilent 7000A). On-line SPME coupled to GC/MS was used for phthalates (Dévier et al., 2013) with a PDMS/DVB fiber (65 μm) (group 10) and with a PA fiber (85 μm) for APs (group 11). Analyses were carried out on an Agilent Technologies 7890A gas chromatograph coupled to an Agilent Technologies MSD 5975C mass spectrometer (Palo Alto, CA, USA). The detailed protocol for the analysis of APs is given in the supplementary information document (S4-4).

*2.4.4. Quality assurance and quality control (QAQC)*

All analytical procedures were optimized to minimize laboratory background contamination, with specifically dedicated glassware, equipment, hoods, and rooms and very strict quality criteria to minimize the risk of false positive and false negative results. Before use, glassware was washed using a detergent, rinsed with Milli-Q water and baked at 450 °C overnight. All additions of matrix and standard solutions were controlled by gravimetry and each analysis was performed in triplicate. When samples were positive for targeted class of compounds, a second analysis was performed including a second extraction and injection in order to confirm or not the first quantification and avoids any false positives.

Two control points for analytical instruments were performed. Injection blanks were injected after each samples in order to prevent from memory effects (cross contamination). For ubiquitous compounds, several injection blanks were performed: three for phthalates and APs, two for pharmaceuticals and pesticides and one for hormones. A specific precaution was taken regarding the analysis of PFAS. In fact, in order to prevent contamination induced by the aqueous mobile phase, a Zorbax SB C18 column (2.1 × 30 mm; particle size of 3.5 μm) was installed between the pump head and the mixing chamber (Munoz et al., 2015). Standard solutions were injected at least each ten samples to monitor any drift in instrumental performance, and check the accuracy of the quantification throughout the analysis.

When considering the whole analytical procedure (extraction and analysis), two types of quality controls were performed for each batch: procedural blanks and control samples (reference water spiked with analytes and related ISs) undergoing the whole analytical procedure, in order to check background contamination and analytical

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performance (accuracy). NMW in glass bottles (Grande Source, Vittel) were used as reference waters in control samples in order to control matrix effects induced by the high mineral content of some bottled waters. For on-line SPME analysis of phthalates and APs, fiber blanks were performed before each sample and consisted in exposing the SPME fiber to an empty vial under the same conditions as the samples (Dévier et al., 2013).

Accuracy and LOQs were estimated for each batch of samples by analyzing control samples and procedural blank samples. For undetected compounds in procedural blanks, the LOQs were determined as the concentration with a signal to noise ratio of 10 in control samples. For compounds detected in the blanks, such as caffeine, salicylic acid, 4-NP and some phthalates (such as BBP, DEHP, DEP, DBP and DHP), the LOQs were estimated assuming at least a factor of three between the amount of analytes in the samples and in the procedural blanks (see Table S8). As for phthalates, an added precaution was to apply at least a factor of ten between the amount of analytes in the samples and in the related fiber blanks. The compounds were identified according to four criteria: retention time, two MRM transitions (or two ions when analyzed by on-line SPME-GC/MS) and their ratio with a relative standard uncertainty of 20%. Quantification was done relatively to isotopically marked compounds used as ISs (when available), except for phthalates where the transition giving the most intense response or having the highest S/N was used. For some compounds (see Table S1), quantification was performed using the standard addition method or using an external calibration when ISs were not available. This last method was used when the linear dynamic ranges obtained in the reference water and in the sample were similar. External calibration was also used for the quantification of phthalates, by spiking reference water with ISs in order to prevent internal phthalates contamination (Dévier et al., 2013). This type of calibration could be applied assuming the equivalence between model and IS response factors (equivalence verified at concentrations significantly higher than background contamination). Simultaneously, samples were spiked with ISs in order to check their recovery rates and to assess the quantification's accuracy.

Finally, participations in inter-comparison laboratory studies on pharmaceutical compounds and hormones contributed to achieve additional quality assurance (AFSSA, 2010; AQUAREF, 2012; Farré et al., 2008; Heath et al., 2010). Thanks to the numerous QAQC performed throughout the experimental procedure, environmentally relevant LOQs were achieved for all the investigated compounds. LOQs ranged from 0.5 ng/L for PFOS to 315 ng/L for bacitracin with 87% of the LOQs being lower than 10 ng/L (26% ≤ 1 ng/L) (Table S1). The most remarkable ones are the LOQs of phthalates ranging from 5 to 50 ng/L which are among the lowest ever reported in the literature (Bono-Blay et al., 2012; Lopez et al., 2015).

## 3. Results and discussion

### 3.1. Distribution of the studied emerging contaminants in bottled waters

In this study, 330 molecules were analyzed in 40 French bottled waters. 99.7% of the results were below LOQ (13,161 out of 13,200 data). The results are summarized in Fig. 1. Over the 40 bottled waters studied, at least one compound was found in 11 samples (Table 2). None of the investigated phthalates, pharmaceuticals or hormones were detected. 4 samples were positive for PFAS, 2 for APs and 9 for pesticides. All the samples are in conformity with the applicable regulations (Fig. 2).

19 distinct molecules were quantified at the sub-ng/L to ng/L levels: 11 pesticides, 6 PFAS and 2 APs. Concentrations and profiles of the 11 positive samples, arbitrarily identified as W1 to W11, are shown in Table 2 and Fig. 2. All the other samples were below the LOQs for each compound investigated. 4 positive samples out of the 11 showed simultaneous quantification of two classes of compounds: APs and pesticides in one sample and pesticides and PFAS for the other 3.

### 3.2. Pesticides

In this study, 118 pesticides and their related metabolites were investigated. It is the only investigated class of compounds to be regulated in SPW under european legislation, with threshold values of 100 ng/L for the individual substances (except 30 ng/L for aldrin, dieldrin, heptachlor and heptachlorepoxyde) and of 500 ng/L. for their sum (Directive 1998/83/EC, 1998), and under national legislations for NMW, with a threshold value of 100 ng/L for their sum (Decree of 12/28/2010). 11 molecules were quantified with levels in the range of 1 to 28 ng/L, corresponding to 9 samples (Table 2). The sum of pesticides and metabolites ranged from 1 to 44 ng/L (mean = 19 ng/L; median = 22 ng/L; n = 9), which is more than twice lower than the purity criteria set in France for NMW (i.e. 100 ng/L) and >10 times lower than the value set for SPW (i.e. 500 ng/L) (Fig.2). All the detected compounds were herbicides: 4 parent compounds (atrazine, simazine, diuron and hexazinone) and 7 metabolites (acetochlor ethane sulfonic acid (ESA), DEA, DIA, 2-OHAt, metolachlor ESA, metolachlor oxanilic acid (OXA) and desethyl-terbuthylazine). The most frequently detected compounds in the 40 bottled waters were DEA (12.5%) followed by atrazine, DIA and metolachlor ESA (10% each). The most abundant compounds were metolachlor ESA (mean = 17 ng/L, n = 4), followed by DEA (8.4 ng/L, n = 5), DIA (3.8 ng/L, n = 4) and atrazine (3.6 ng/L, n = 4) (Table 2). Parent compounds, namely metolachlor, acetochlor and terbuthylazine, were not detected.

To our knowledge, this is the first study on the screening of such a wide range of pesticides, including acetochlor and metolachlor, and their metabolites in French bottled water, at such low LOQs. The obtained results are rather consistent with the hydrogeological context: On the one hand, most of these 40 distinct aquifers have no significant anthropogenic activities on their watersheds, are well protected (geologically, and by protection policies), and mostly produce rather old waters. The ratio of 9 over 40 samples showing at least one quantification of a pesticide ratio is much lower than in vulnerable groundwater or in tap water (see occurrence data in Table S9), and also of course in surface water. On the other hand, detecting some pesticides at the nano-trace level would be expected as several of the aquifers' watersheds have a few percents to a few tens of percents of extensive agricultural land use, and/or may have been subjected to some herbicides used in the past in the villages (for instance in cemeteries, or near the houses) and along some roads or railways, before the implementation of protection policies.

Finally, in the 9 samples positive for pesticides in this study, metabolites were more frequently detected than the parent compounds (71% of the 28 quantifications). They were also most abundant, contributing from 57% to 100% of the total amount per sample, as shown in Fig. 3, except in W11 where only diuron was quantified at 3 ng/L.

This predominance of metabolites is a consequence of the long residence time of water in the aquifers. More specifically, in this study, atrazine was quantified in almost all samples containing its metabolites, whereas metolachlor ESA, OXA and acetochlor ESA were quantified without their parent compounds. In fact, atrazine and chloroacetamide herbicides are known to behave differently during their transfer to aquifers. As far as atrazine and its metabolites are concerned, all the long-term monitoring studies focusing on European groundwaters (Baran et al., 2008; Köck-Schulmeyer et al., 2014; Vonberg et al., 2014) converge towards the same trend: even years or decades after its ban, residual concentrations of atrazine are found in groundwaters, showing its persistence, high storage in soils and/or in the unsaturated zones and leaching during infiltration processes. Moreover, a slight decrease in atrazine and an increase in DEA over the years suggest that the percolation rate of atrazine (from soils and/or unsaturated zones towards the underlying groundwaters) becomes lower than the degradation rate in all hydrological compartments (soils, unsaturated and saturated zone of the aquifers). Therefore, metabolites can leach in larger amounts than the parent compound. As a consequence, the occurrence of

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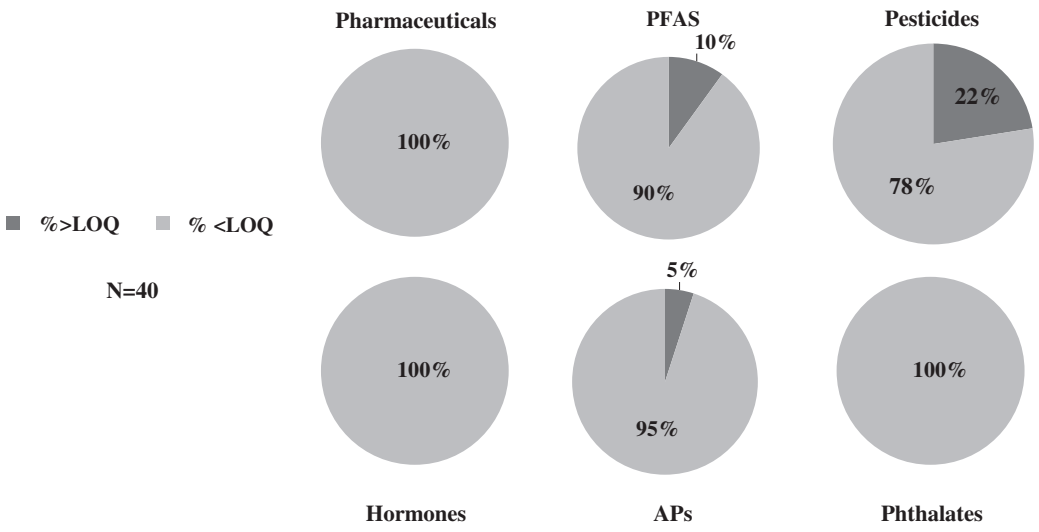


**Fig. 1.** Frequency of quantification or absence of quantification of the investigated compounds in the 40 bottled waters (N).

atrazine and its metabolites in this study seems to be related to former applications. When considering metolachlor, acetochlor and their related metabolites, their occurrence is still not well established in European groundwaters (Table S9). A single study by Baran and Gourcy (2013) has assessed that metolachlor and metolachlor ESA are more frequent and abundant than metolachlor OXA in groundwaters. Metolachlor, acetochlor and their metabolites were also investigated in groundwaters intended for human consumption in the United States and the results revealed a clearly opposed trend compared to atrazine, showing higher metabolite concentrations than those of the parent compounds regardless of the season (Hladik and Bouwer, 2008). Parent compounds metolachlor and acetochlor are then rarely quantified regardless of the application timing, due to their rapid degradation into metabolites. Consequently and contrary to atrazine, it cannot be fully claimed that the presence of metolachlor metabolites observed in this study is only linked to former applications, since s-metolachlor is still authorized (Commission, 2011) and can also generate ESA/OXA metabolites (Table 3).

Due to their banishment and depending on the mean transit time in such aquifers, it is expected to observe a concentration decrease of detected compounds in the upcoming years or decades. Nevertheless, despite the very low levels quantified, the presence of some very persistent and/or ancient herbicides or their metabolites, underlines the need to better prevent the use of non-biodegradable substances, especially for agriculture, and also to pursue and even reinforce the protection measures that are already in place.

### 3.3. Perfluoroalkyl substances (PFAS)

Six perfluoroalkyl substances (PFAS) were quantified in the 0.6–9.5 ng/L range in 4 distinct samples, with $\sum$PFAS not exceeding 20 ng/L (mean = 6.7 ng/L and median = 3.4 ng/L; n = 4) (Fig. 2). Detection frequencies of PFSAs in the 40 bottled water were as follows: PFOS (10%), PFHxS (5%) and PFBS (2.5%). Among the 7 PFCAs investigated, PFPA, PFHxA, PFNA and PFDA were never detected. PFBA, PFHpA and PFOA were quantified in one sample only (detection frequency of 2.5%) along with PFOS, PFHxS and PFBS. Among the 4 positive samples, 3 were contaminated by PFSAs only. This class contributed to 70% of the 10 PFAS quantifications (Table 2). The two $C_8$ perfluoroalkyl chain-lengths (PFOS and PFOA) were the most abundant compounds, with maximum concentrations of 3.7 ng/L and 9.5 ng/L respectively, representing 69% of the total concentration of the 4 positive samples. The molecular profile of the single sample containing both PFCAs and PFSAs ($\sum$PFAS = 19.3 ng/L) was as follows: PFOA (49%), PFOS (18%), PFHxS (13%), PFHpA (7.2%), PFBS (7.1%) and PFBA (5.5%).

**Table 2**
Distribution of quantified APs, PFAS and pesticides in the 11 positive samples of bottled water. All values are in ng·L$^{-1}$.

| | | Parent compounds | LOQ (ng/L) | W1 | W2 | W3 | W4 | W5 | W6 | W7 | W8 | W9 | W10 | W11 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| APs | 4-NP | – | 10 | – | – | – | – | – | – | – | – | – | 30.1 | – |
| | 4-t-OP | – | 2 | – | – | – | – | – | 2.2 | – | – | – | – | – |
| PFAS | PFBA | – | 1 | – | – | – | – | – | – | – | – | 1.1 | – | – |
| | PFBS | – | 1 | – | – | – | – | – | – | – | – | 1.4 | – | – |
| | PFHpA | – | 1 | – | – | – | – | – | – | – | – | 1.4 | – | – |
| | PFHxS | – | 1 | – | – | – | – | – | – | – | – | 2.5 | – | 2.0 |
| | PFOA | – | 1 | – | – | – | – | – | – | – | – | 9.5 | – | – |
| | PFOS | – | 0.5 | – | – | – | – | – | – | 0.6 | 1.1 | 3.5 | – | 3.7 |
| Pesticides | Acetochlor ESA | Acetochlor | 2 | – | – | 4.1 | – | – | – | 2.6 | – | – | – | – |
| | Atrazine | – | 1 | 4.2 | – | – | – | 3.5 | – | 2.4 | – | 4.5 | – | – |
| | 2OH-At | Atrazine | 1 | – | – | – | 2.0 | – | 1.4 | – | – | 5.1 | – | – |
| | DEA | Atrazine | 2 | 19.5 | – | – | 5.9 | 7.4 | – | 3.0 | – | 6.2 | – | – |
| | DIA | Atrazine | 1 | 1.1 | – | – | – | 10.0 | – | 2.9 | – | 1.3 | – | – |
| | Diuron | – | 1 | – | – | – | – | – | – | – | – | – | – | 3.3 |
| | Hexazinone | – | 1 | – | – | – | – | – | 1.4 | – | – | – | – | – |
| | Metolachlor ESA | Metolachlor | 5 | – | – | 13.7 | 7.5 | – | 20 | 28.2 | – | – | – | – |
| | Metolachlor OXA | Matolachlor | 4 | – | – | – | – | – | – | 4.5 | – | – | – | – |
| | Simazine | – | 1 | – | – | – | – | 1.4 | – | – | – | 4.9 | – | – |
| | Desethyl-terbuthylazine | Terbuthylazine | 1 | – | 1.1 | – | – | – | – | – | – | – | – | – |

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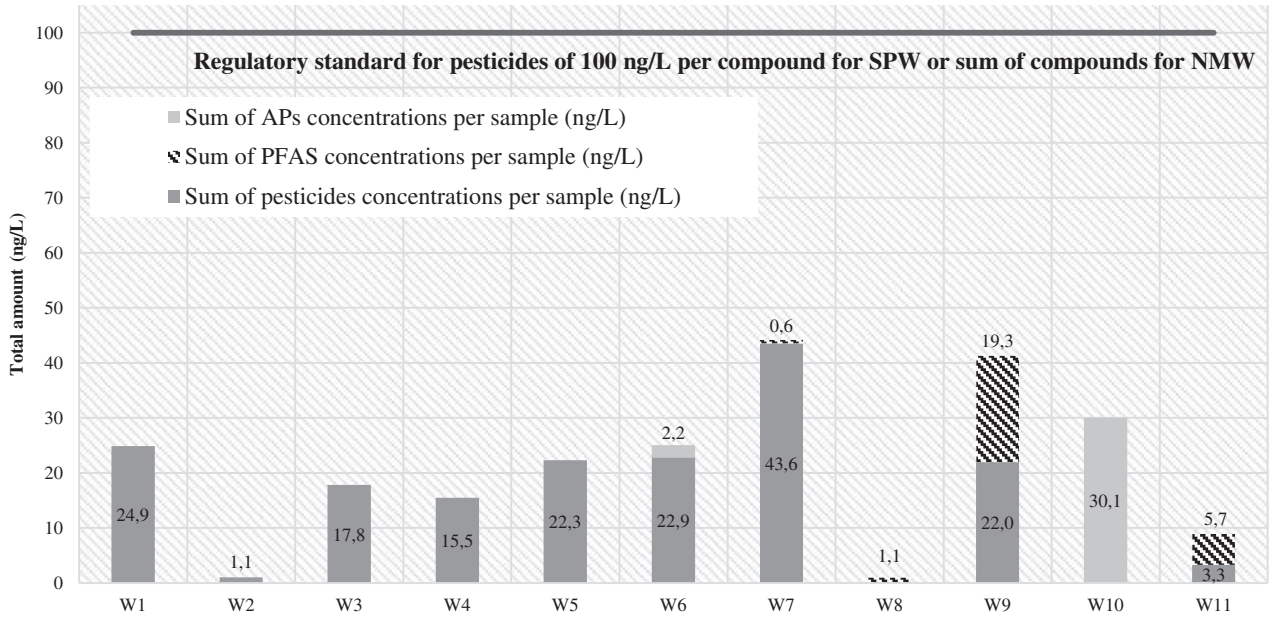


**Fig. 2.** Distribution of APs, PFAS and pesticides in the 11 positive samples. All values are given in $ng \cdot L^{-1}$.

PFAS sources are currently mostly unknown due to their ubiquity in rivers (Munoz et al., 2015), groundwaters (Boiteux et al., 2012; Lopez et al., 2015; Loos et al., 2010), sediments and drinking waters (Ericson et al., 2008; Gellrich et al., 2013), even in areas with low anthropogenic pressures such as the Artic (Ellis et al., 2004; Wania, 2007). In our case, the protection measures taken to preserve the exploited aquifers from anthropogenic contamination did not totally prevent the presence of PFAS. Their occurrence could be linked to long-range atmospheric transport of PFSAs, PFCAs and of their precursors (i.e. fluorotelomer alcohols or carboxylic acids, fluorotelomer unsaturated carboxylic acids, etc.) that have been reported in atmospheric deposition samples (Kim and Kannan, 2007; Loewen et al., 2005; Scott et al., 2006; Taniyasu et al., 2013). Finally, among the 4 samples positive to PFAS, 3 showed interclass contamination with ancient pesticides, suggesting another possible origin from pesticide adjuvants (POP review committee, 2013). Further studies should be carried out in order to better understand the origin and possible sources of such low levels of PFAS in these types of matrices with, at first, the analysis of raw water and finished products to investigate possible origin from the bottling equipments, such as some gaskets present inside the flanges between stainless steel pipes.

Low concentrations of PFAS are usually found in bottled waters. In this study, when considering $\sum$PFAS, 95% of the samples were below 2 ng/L with a maximum value of 19.3 ng/L, which is consistent with Gellrich et al. (2013) and Ericson et al. (2008) with 95% and 100% of their samples ($n = 119$ and $n = 4$ respectively) quantified below 5 ng/L and with maximum $\sum$PFAS values of 24.2 ng/L and 1.3 ng/L respectively. Surprisingly, Schwanz et al. (2016) reported a different trend in 10 Spanish and 19 French bottled waters as clearly shown in Fig. 4, with a maximum $\sum$PFAS value at 118 ng/L and a majority of the samples leaning towards the high concentrations. Moreover, in a few samples, long-chain PFCAs were found to mainly contribute to the $\sum$PFAS, with the quantification of PFTeA, PFxDA and PFODA, while they are usually not detected or at very low levels in groundwaters or surface waters (Labadie and Chevreuil, 2011; Munoz et al., 2015). As the levels of procedural blanks are usually not clearly specified, such discrepancies could potentially be explained by a contamination during the sample storage, handling or analysis. In order to exclude any doubt regarding the analytical methodology applied, procedural blank levels must be clearly explained (see Table S8) along with the use of very stringent QAQC (see Section 2.4.4).

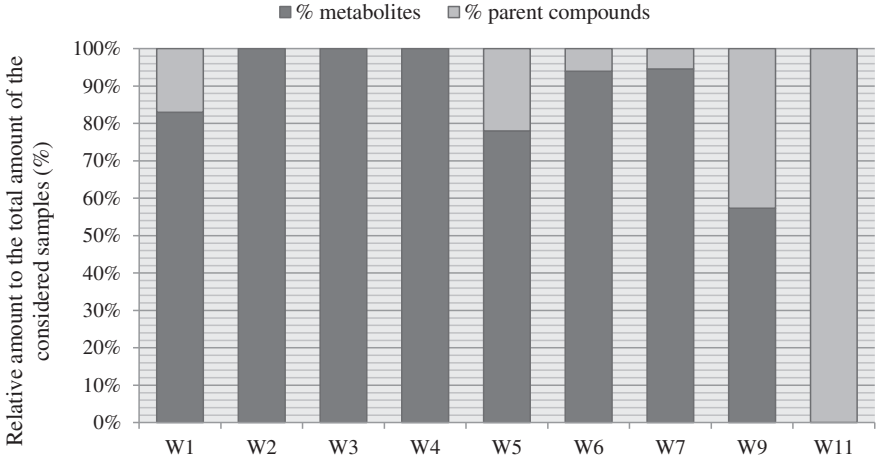


**Fig. 3.** Distribution of parent compounds and metabolites in the 9 samples positive for pesticides.

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**Table 3**
Regulatory status and environmental fate of the quantified pesticides (University of Hertfordshire).

| Compounds *: metabolite H: herbicide | Parent compound | GUS[a] | Relevant 91/414[b] | Introduction date of parent compounds | Banishment of parent compounds in France | Countries where the parent compound is still in use[c] |
|---|---|---|---|---|---|---|
| Acetochlor ESA* | Acetochlor | 3,88 | ✓ | 1985 | 2011 | – |
| Atrazine (H) | – | 3,8 | | 1957 | 2003 | – |
| 2OH-At* | Atrazine | – | | 1957 | 2003 | – |
| DEA* | Atrazine | 3,2 | ✓ | 1958 | 2004 | – |
| DIA* | Atrazine | – | ✓ | 1959 | 2005 | – |
| Diuron (H) | – | 1,83 | | 1951 | 2003/2008 | ES, BG |
| Hexazinone (H) | – | 4,58 | | 1975 | 2004 | – |
| Metolachlor ESA* | Metolachlor | 6,46 | ✓ | 1976 | 2003 (Metolachlor) S-metolachlor still in use | S-metolachlor: AT, BE, BG, CY, CZ, DE, EL, ES, FR, HR, HU, IE, IT, LU, NL, PL, PT, RO, SI, SK, UK |
| Metolachlor OXA* | Metolachlor | 6,61 | ✓ | 1977 | 2003 (Metolachlor) S-metolachlor still in use | S-metolachlor: AT, BE, BG, CY, CZ, DE, EL, ES, FR, HR, HU, IE, IT, LU, NL, PL, PT, RO, SI, SK, UK |
| Simazine (H) | – | 2 | | 1960 | 2003 | – |
| Terbutylazine desethyl* | Terbuthylazine | 3,9 | ✓ | 1967 | 2003 | AT, BE, BG, CY, CZ, DE, EL, ES, HU, IE, IT, LU, NL, PL, PT, RO, SI, SK, UK |

[a] Groundwater Ubiquity Score (GUS) is a calculated indicator correlating the persistence of compounds in soils ($t^{1/2}_{soil}$) and their mobility (Koc) in order to better anticipate their potential leaching into groundwater.
[b] Directive 91/414 states on the ability of a compound to be introduced in the market: a metabolite is considered to be 'relevant' if there is reason to believe that it has comparable intrinsic properties to those of the parent chemical in terms of biological target activity, or if it has toxicological properties that are considered severe, and poses comparable or even higher risks to organisms than the parent substance.
[c] AT = Austria; BE = Belgium; BG = Bulgaria; CY = Cyprus; CZ = Czech Republic; DE = Germany; EL = Greece, ES = Spain; HR = Croatia; HU = Hungary; IE = Ireland; IT = Italy; LU = Luxembourg; NL = Netherlands; PL = Poland; PT = Portugal; RO = Romania; SI = Slovenia; SK = Slovakia; UK = United Kingdom.

### 3.4. Alkylphenols (APs)

Out of the 8 investigated alkylphenols (APs) in the 40 bottled waters, only the 2 parent compounds were quantified, each in two different samples: 4-nonylphenol (4-NP) at 30 ng/L and 4-octylphenol (4-t-OP) at 2 ng/L (LOQ level). None of the alkylphenoxy acetic acids (AP1EC) and alkylphenol polyethoxylates (APnEO) (n = 1, 2) were quantified (Table 2).

In the present study, the single quantification of 4-NP at 30 ng/L, i.e. three times higher than the LOQ, is the only meaningful quantification in the 40 bottled waters analyzed. In order to investigate its possible origin, i.e. contamination of the exploited groundwater or contamination occurring within the bottling plant or via the packaging, further analyses were carried out. A second sampling of raw water collected at the factory inlet and of the finished product was performed concomitantly, and showed absence of 4-NP in both matrices. This punctual contamination was not originating from the exploited groundwater, which is coherent with the literature data. Moreover, as discussed below, PET packaging could not be a spot of AP contamination and neither could the bottling line, APs being usually voluntarily banned by the bottled water industry from cleaning agents used in the factories due to their inclusion into the REACH regulation on chemical substances (REACH regulation 1907/2006/EC). Nevertheless, HDPE caps cannot be excluded as a potential contamination source.

The results of this study are consistent with those of the study of Bono-Blay et al. (2012) where 4-NP and 4-t-OP were occasionally detected with mean concentration values of 2 ng/L (n = 1) and 58 ng/L (n = 4) respectively in groundwater intended for bottling. As for studies on bottled finished products, variability in the results exists regarding 4-NP and 4-t-OP (Colin et al., 2014; Dévier et al., 2013; Guart et al., 2014b;

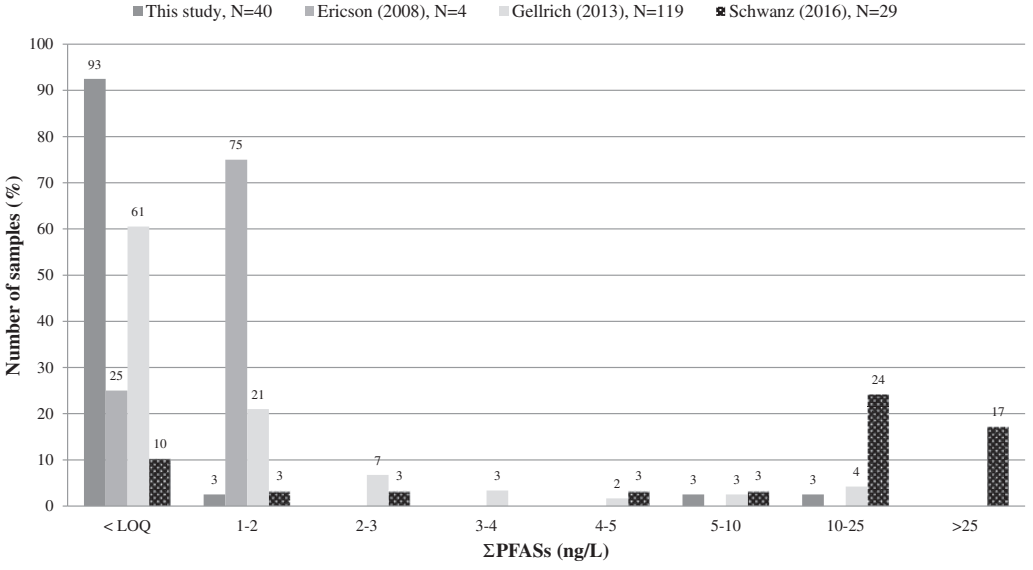


**Fig. 4.** Sample distribution in reconnaissance studies considering ∑PFAS abundance of eight common compounds (PFBS, PFDA, PFHpA, PFHxA, PFHxS, PFNA, PFOA and PFOS), N = number of bottled waters investigated.

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Amiridou and Voutsa, 2011). These contradictory results could be explained either by the diversity of implemented methodologies and achieved LOQs or by the lack of information about packaging and storage conditions (Bach et al., 2012). In fact, some authors underlined the presence of background contamination regarding 4-NP and decided to increase the LOQ, in order to avoid false positive even though some comprehensiveness could be lost (Colin et al., 2014). Moreover, contamination by plastic materials during the analytical procedure has also been demonstrated by Capdeville and Budzinski (2011) which makes the APs analysis significantly impacted by the type of laboratory equipment used. By applying an adapted analytical procedure, a reliable background contamination level (below 3 ng/L), could be achieved for 4-NP, 4-t-OP and nonylphenol diethoxylate ($NP_2EO$) (Dévier et al., 2013; Salgueiro-González et al., 2012). When considering migration tests on PET bottled waters closed with HDPE caps, none of the investigated APs were quantified by Dévier et al. (2013) in fresh bottled waters or in aged samples, whereas 4-NP and 4-t-OP were quantified by Guart et al. (2014a) in 2% and 4% of fresh samples and in 7% and 8% of the same samples after one year of storage respectively. Nevertheless, PET resin used to produce PET bottles intended for water does not contain APs or other substances that may lead to their generation (Bach et al., 2012). When considering AP ethoxylates (APnEC($n = 1,2$) and APnEO ($n = 1, 2$)), very few studies have been carried out on their occurrence or persistence in groundwater or drinking waters, as compared to 4-t-OP and 4-NP (Barnes et al., 2008; Colin et al., 2014; Dévier et al., 2013; Focazio et al., 2008; Loos et al., 2007; Tubau et al., 2010). For bottled water, none of them were quantified in a previous study (Dévier et al., 2013) (i.e. NP1EC, NP1EO and NP2EO) and in (Colin et al., 2014) (i.e. nonylphenol ethoxyacetic acid (NP1EC), nonylphenol monoethoxylate (NP1EO), NP2EO, octylphenol monoethoxylate (OP1EO) and octylphenol diethoxylate (OP2EO)), which is coherent with our results.

### 3.5. Hormones and pharmaceutical substances

To our knowledge, this is the first study to focus on such a wide range of pharmaceuticals and hormones in bottled waters. None of the 172 pharmaceuticals and 11 hormones investigated were detected in the 40 investigated bottled waters. Even those considered as robust wastewater tracers, such as carbamazepine, and despite the very low and robust LOQs reached, ranging from 1 to 315 ng/L for pharmaceuticals and from 1 to 3 ng/L for hormones.

From a hydrogeological standpoint, even if these data were obtained from 40 different aquifers, the overall result is rather consistent as (i) the watersheds of the sampled aquifers don't have significant urban landcover, (ii) there are no interactions with river waters, in which wastewaters may be released upstream. Moreover, it underlines that the wastewaters from the villages belonging to the watershed either did not reach the bottled aquifers, as a result of efficient wastewater collection, treatment and release outside the watershed, or did not yet reach the aquifer as a result of long water transit time, or, for instance for wastewater issuing from septic tanks, were eliminated in the soil or diluted enough. In most of the watersheds where protection policies were implemented by the bottling companies, wastewater collection and treatment, and rehabilitation of individual wastewater treatment facilities (such as septic tanks and infiltration trenches) are parts of the first policies implemented (see for instance references provided in Section 1).

When comparing these results with the literature, there are consistent with the very few studies involving hormones in bottled waters, generally coming to an absence of quantification (Dévier et al., 2013; Gottschall et al., 2013). Regarding the pharmaceutical substances, they belong to the most studied class of emerging contaminants in aquatic compartments, especially groundwater, with the highest detection frequencies (Lapworth et al., 2012; Meffe and de Bustamante, 2014) (see occurrence data and discussion in Table S10). While comparing concentrations of pharmaceuticals in European bottled waters reported in the literature, it can be noted that they are more or less consistent with each other (Table 4).

Only one study (Carmona et al., 2014) quantified a huge amount of pharmaceuticals with 10 among the 12 investigated compounds including bezafibrate and salicylic acid in 18% and 100% of the samples respectively. Interpreting this systematic detection of salicylic acid at the ng/L is tricky, since the levels of blanks are not clearly specified and only one transition for identification and confirmation is being used. In fact, salicylic acid and some other pharmaceuticals are already known to be sensitive to false positive results due to chronic blank issues (see Table S8; Focazio et al. (2008); Dévier et al. (2013)). Consequently, when targeting low LOQs in aquatic matrices, extreme precautions must be taken in order to avoid possible sources of contamination and high rate of false positives (Capdeville and Budzinski, 2011). Similarly, González Alonso et al. (2012) detected nicotine in 50% of the samples but not cotinine, its human metabolite which excludes pollution by wastewater. Indeed, up to 80% of nicotine is metabolized into cotinine by the human body (Yildiz, 2004) and can be used as an anthropogenic marker of urban wastewater in groundwater (Van Stempvoort et al., 2013). Other compounds such as ketoprofen and caffeine were detected in procedural blanks by Dévier et al. (2013) confirming the need to clearly specify the types of QAQC applied and levels of blanks for such compounds, in order to produce reliable results. Finally, sulfamethoxazole and other sulfonamides were quantified by Perret et al. (2006) and could be attributed to breeding activity on the infiltration spot, these compounds being mostly used as veterinary drugs and not only linked to wastewater contamination (Dévier et al., 2013; Postigo and Barceló, 2015).

### 3.6. Phthalates

In our study, none of the 11 phthalates investigated were quantified in the 40 bottled waters. Very few studies exist on the occurrence of phthalates in aquifers intended for bottled waters. In fact, to our knowledge, only Bono-Blay et al. (2012) have investigated 6 phthalates in 131 Spanish source waters intended for bottling, and only diethyl phthalate (DEP) was quantified at 1115 ng/L (LOQ = 837 ng/L) in a single sample coming from a borehole near an industrial area, and diéthylhexyladipate (DEHA) at 192 ng/L (LOQ = 180 ng/L) in one SPW, showing that phthalates are not relevant contaminants of protected groundwaters intended for bottling which is coherent with our study. More studies exist on the fate of phthalates in bottled finished products associated with the type of packaging, but they show contradictory results. (Amiridou and Voutsa, 2011; Guart et al., 2014a; Casajuana and Lacorte (2003); Dévier et al., 2013; Jeddi et al. (2015); Keresztes et al., 2013). Nevertheless, it is well-known that no plasticizer is used in the manufacturing process of PET bottles (EFBW, 2013) and that contamination could neither originate from the bottling process in the plant nor migration from the PET bottles or caps as highlighted by Dévier et al. (2013) and Jeddi et al. (2015). It was also demonstrated that traces of phthalates quantified in NMW, as well as in aquatic matrices, were a consequence of the unavoidable laboratory background contamination which led to the high levels of blanks (INERIS, 2009; Dévier et al., 2013; Marega et al., 2013). Contradictory results could then be explained by the wide variety of extraction procedures used in these studies (i.e. SPE, Magnetic Solid Phase Extraction (MSPE), Liquid-Liquid extraction, SPME), or by external contaminations. This background contamination could be minimized using on-line technologies enabling reliable background contamination levels (see Table S8). Pollution could also originate from the matrix used as blank: NMW, Milli-Q water or fiber desorption. In the present study, phthalates were quantified using an external calibration (Section 2.4.4).This innovative calibration of phthalates enabled us to be emancipated from the contamination induced by ISs-spiked samples (Dévier et al., 2013). In addition, the use of NMW as reference water was chosen in order to take into account the matrix effect induced by the dissolved minerals contained in the

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**Table 4**
Comparison of reconnaissance studies involving pharmaceuticals in bottled waters.

| References (Area) | Type of sample (number) | LOQ range (ng/L) | Investigated pharmaceuticals (quantified) | pharmaceuticals in common with this study (quantified) | Quantified pharmaceuticals (number of positive samples ; LOQ ; mean or range* concentration ; nc: not investigated in this study) |
|---|---|---|---|---|---|
| Present study (France) | NMW & SPW (40) | 1 – 90 | 172 (0) | | – |
| Dévier et al 2013 (France) | NMW (2) | 1–150 | 97 (0) | 97 (0) | – |
| Perret et al 2006 (Italy) | NMW (8) | 5 – 21 | 11 (3) | 6 (3) | Sulfamethizole (n=1 ; 7ng/L ; 9ng/L)<br>Sulfamethoxazole (n=2 ; 9ng/L ; 13–80ng/L*)<br>Sulfadimethoxine (n=1 ; 8ng/L ; 11ng/L) |
| Gonzàlez Alonso et al 2012 (Spain) | NMW (10) | 1–125 | 58 (1) | 39 (0) | Nicotine (n=5 ; 4ng/L ; 7–15ng/L* ; nc) |
| Carmona et al 2014 (Spain) | NMW (11) | 0.1–3.4 | 12 (10) | 8 (7) | Salycilic acid (n=11 ; 0.1ng/L ; 33ng/L)<br>Clofibric acid (n=11 ; 0.6ng/L ; 21ng/L)<br>Indomethacin (n=10 ; 1.3ng/L ; 7ng/L ; nc)<br>Naproxen (n=9 ; 0.5ng/L ; 25ng/L)<br>Gemfibrozil (n=9 ; 0.3ng/L ; 8ng/L)<br>Ibuprofen (n=8 ; 5ng/L ; 12ng/L)<br>Thiamphenicol (n=7 ; 3.4ng/L ; 7ng/L ; nc)<br>Diclofenac (n=6 ; 1ng/L ; 25ng/L)<br>Flufenamic acid (n=2 ; 0.1ng/L ; 4ng/L ; nc)<br>Bezafibrate (n=2 ; 0.2ng/L ;1ng/L) |

matrices of bottled waters and to replace Milli-Q water which is a well-known vector of contamination for phthalate analysis (Cao, 2008; Dévier et al., 2013). As for the risk of blank contamination, most of the studies do not clearly specify the levels of blanks reached or even the strategy used to determine the LOQs. LOQs obtained by SPE-GC/MS were then 10 to 20 times higher than those obtained using on-line SPME as it was the case in our study. Di(2-ethylhexyl)phthalate (DEHP), DEP and di-n-butyl phthalate (DBP) were analyzed by Lopez et al. (2015) using liquid-liquid extraction followed by GC/MS achieving LOQs of 400 ng/L for each compounds. Finally, thanks to the introduction of a wide range of QAQCs (Section 2.4.4), blank levels of such ubiquitous compounds could be limited and therefore the LOQs reached in the present study stand among the lowest reported for phthalates ranging from 5 ng/L for dimethyl phthalate (DMP), DEP, DBP and dibenzyl phthalate (DBzP) to 50 ng/L for DHP and DEP.

## 4. Conclusion

Among the 330 compounds investigated in the 40 bottled waters, no phthalate, hormone or pharmaceutical substances was quantified. Nineteen compounds were quantified at the low-ng/L level in 11 samples: 11 herbicides or their metabolites, 6 PFAS and 2 APs. The analytical challenge of achieving low LOQs for such a wide range of compounds in clean bottled water matrices was taken up by lowering background laboratory contamination and setting robust and efficient QAQC. Nevertheless, even using an on-line extraction procedure as well as dedicated glassware and room enabling reliable and lower levels of blank to be achieved, it has become a real matter of concern for analytical laboratory practices as blank levels now define the reachable LOQs.

Levels and quantification frequencies obtained in this study were generally lower than those obtained in groundwaters subject to anthropogenic pressures (Lapworth et al., 2015). However, it was not always possible to compare the results due to the wide range of LOQs used. Also, some disparities between studies on the analysis of PFAS, phthalates or APs underline the need to clearly specify the QAQC put in place in order to obtain robust and comparable results. This study confirmed, in a larger amount of samples, the previous results obtained by Dévier et al. (2013) and suggests that the springs used for bottling in France are well-protected from contamination, such as river waters or wastewaters, with the absence of quantification of hormones and pharmaceuticals, contrary to lots of aquifers having significant relationships with surface water (such as alluvial aquifers for instance). However, the natural geological protection of the exploited aquifers could not prevent the presence, at low levels (far below the applicable French regulation for pesticides) and in only a few samples, of some PFAS, herbicides and their metabolites, originating mostly from former application. Thus, it is important to underline the need to pursue the protection policies already in place on their watersheds by more strictly regulating the overall use of very stable organic substances. In addition, most of the aquifers tapped for bottling are directly recharged by rainfall which is known to be a possible vector of contamination regarding PFAS and pesticides and could explain the low level of contamination quantified here (Scheyer et al., 2007; Scott et al., 2006).

Finally, ultra-trace analysis is an interesting monitoring tool for the bottled water industry and could even help improve their practices by using reliable methodologies that are able to avoid issues like false positive or false negative results when reaching the ultra-trace level (low ng/L). It may be interesting to repeat this type of study in the coming

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years in order to monitor the evolution of detected compounds and their attenuation rate.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.11.174.

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