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Screening of French groundwater for regulated and emerging contaminants

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HIGHLIGHTS

- Nationwide occurrence and distribution of emerging contaminants in groundwater
- Groundwater are impacted by the use of antibiotics in livestock
- At least one dioxin-like compound was detected in 87% of the sampling sites
- Groundwater is impacted by former anthropogenic activities
- How can groundwater quality be assessed when unregulated compounds are present?

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ABSTRACT

Nationwide screening of 411 emerging contaminants and other regulated compounds, including parent molecules and transformation products (TPs) having various uses and origins, was done at 494 groundwater sites throughout France during two sampling campaigns in the Spring and the Fall of 2011. One hundred and eighty substances (44% of the targeted compounds) were quantified in at least one sampling point. These included pharmaceuticals, industrial products, pesticides, their transformation products and other emerging compounds. Fifty-five compounds were quantified in more than 1% of the samples. Both regulated and emerging compounds were found. Among the unregulated compounds, acetaminophen, carbamazepine, perfluorinated compounds, dioxins/furans, tolyltriazole, bisphenol A, triazine transformation products, and caffeine were quantified in more than 10% of the samples analyzed. Concentrations exceeding the threshold of toxicological concern of 0.1 μg/L were found for tolyltriazole, bisphenol A and some of the triazine transformation products (DEDIA). These new results should help the water resource managers and environmental regulators develop sound policies regarding the occurrence and distribution of regulated and emerging contaminants in groundwater.

1. Introduction

The global demand for fresh water continues to grow. Nearly half of the world's population now depends on groundwater for drinking water and other uses (e.g., agriculture, industry). Groundwater resources are, however, increasingly threatened by chemical and biological contamination (Fogg and LaBolle, 2006; Schwarzenbach et al., 2006). Man-made chemicals and natural organic compounds are synthesized and used to meet the demands of industrial and agricultural activities, for medical and personal care products and cosmetics, and for many other ordinary consumer products. Due to this wide variety of uses and pressure, to (bio)geochemical transformations, and to different levels of effectiveness of wastewater and drinking water treatment, many of these substances can reach the environment (Duirk et al., 2011; Fatta-Kassinos et al., 2011; Focazio et al., 2008; Kormos et al., 2010; Loos et al., 2010; Salgado et al., 2013; Schulz et al., 2008). The presence of these Emerging Contaminants (ECs), also known as Contaminants of Emerging Concern (CECs), in surface and groundwater has been reported by numerous researchers over the last decade and is a growing concern of the scientific community and of society in general (Barnes et al., 2008; Kolpin et al., 2002; Lapworth et al., 2012; Ortiz de García et al., 2013; Stuart et al., 2012; Ternes et al., 1998). The effects of some of these substances on the aquatic environment and human health have already been demonstrated (Correa-Reyes et al., 2007; Cunningham et al., 2006; Farre et al., 2008; Lapworth et al., 2012; Triebskorn et al., 2004). However, for many of the contaminants, little is known about any potential human health effects of low doses and long-term exposure (Schwarzenbach et al., 2006).

In the European Union, water pollution assessment is based on the Water Framework Directive (WFD, Directive 2000/60/EC), which established a framework for Community action in the field of water

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policy. For groundwater, a specific text was written in 2006 (Directive 2006/118/EC) and reviewed in 2014 (Directive 2014/80/EU) concerning protection against pollution and deterioration. European regulations set Environmental Quality Standards (EQS) for priority substances (Directive 2013/39/EU) and certain other pollutants. EQS, given only for inland surface waters, other surface waters and biota, are concentrations of pollutants or groups of pollutants that must not be exceeded in order to protect human health and the environment. Many families of compounds, including ECs, are not included and are still unregulated. An effort is currently being made to identify new substances that might contaminate the aquatic environment, including groundwater, and put human health and/or the environment at risk.

This is a major concern for national, regional and local agencies that are not able to fund long-term monitoring programs for thousands of substances. For this reason, the number of field reconnaissance studies of the occurrence of a variety of organic contaminants that are likely to be released into the environment has increased in recent years. Several large-scale reconnaissance studies have been carried out in the US (Barnes et al., 2008; Focazio et al., 2008; Kolpin et al., 2002) and in the EU (Loos et al., 2009; Loos et al., 2010; Jurado et al., 2012; Stuart et al., 2012) to provide an initial overview of the occurrence and distribution of these contaminants in the environment. In France, there have been few studies of the occurrence of ECs and their transformation products in groundwater and these are primarily interested in pharmaceutical compounds at local scales (Miège et al., 2006; Quoc Tuc et al., 2011; Togola and Budzinski, 2007, 2008; Vulliet and Cren-Olive, 2011). As a result, although there is a growing need to assess the environmental risk associated with these substances, there is a lack of information concerning actual exposure to many other anthropogenic compounds in natural environments at the national scale. The French Ministry of Ecology and the French National Agency for Water and Aquatic Environments have initiated a national reconnaissance study of emerging (or poorly monitored) contaminants of various possible origins (e.g., pharmaceutical products, industrial compounds, pesticides and personal-care products). Analyses were done to detect 411 emerging contaminants in samples collected at 494 groundwater sites throughout France during two campaigns in 2011. The results of these two campaigns are reported here.

2. Materials and methods

2.1. Targeted compounds

The primary aim of the screening was to identify the presence in French groundwater of compounds that are monitored rarely or not at all. Following a review of national uses, fates, occurrences in groundwater, and toxicological/ecotoxicological properties, a specific prioritization scheme was created to target relevant compounds and the analytical capabilities of participating laboratories were taken into account. Four hundred and eleven compounds, including parent molecules and transformation products (TPs), were selected for the study (Tables S1 and S2).

These compounds were divided into 19 groups and 4 major families (pharmaceutical products, industrial compounds, pesticides and other emerging contaminants) based on the type of compound or general category of use. Because usage can vary widely for any given compound, the tabulated usage categories are given for illustrative purposes only and are not necessarily all inclusive. To simplify, TPs were placed in the same group as their parent molecule. One hundred and thirty one pharmaceutical products (37 antibiotics, 17 steroids and hormones, 6 non-prescription drugs, 5 biocides and 66 other prescription drugs), 143 industrial compounds (36 PCBs, dioxins and furans, 25 dyes, 13 perfluorinated compounds, 11 flame retardants, 10 plasticizers and 48 other industrial compounds), 103 pesticides (48 herbicides, 29 fungicides and 26 insecticides), and 34 other emerging pollutants (13 lifestyle products, 10 cosmetics, 4 disinfection by-products, 4 toxins and 3 organotins) were sought in the groundwater samples.

2.2. Sampling sites

Samples were collected at 494 groundwater sites (springs, wells, and boreholes) throughout France during two campaigns in the Spring (485 sites) and the Fall (475 sites) of 2011 (Fig. 1). Sampling was done by the teams responsible for national WFD regulatory monitoring with the same technical requirements.

The sites were selected to include a wide variety of both lithological and hydrogeological conditions, anthropogenic pressures (agricultural (both crop production and animal husbandry), urban, mixed, and natural or semi-natural environments) and uses (drinking water, irrigation, industrial water, etc.). The proportion of different types of hydrogeological environments sampled is representative of what is observed at the national level: 55% of the groundwater was collected from sedimentary formations, 25% from alluvial aquifers, 15% from basement formations, 3% from low production aquifers, and 2% from volcanic and mountain aquifers. The land surrounding the sampled sites was classified according to principal land use as agricultural, urban-agricultural, urban-industrial, or natural. The number of selected sampling sites classified according to hydrogeological and land-use characteristics is given in Table 1. More than half of the sites (282) are used for drinking water supply.

2.3. Analytical methods

The groundwater samples were analyzed by two private French laboratories currently participating in regulatory monitoring. Given the number of target compounds, a wide range of analytical methods (extraction and analysis) were used (Tables S1 and S2).

Most of the polar compounds (i.e., the pharmaceuticals, most of the pesticides (77 out of 103), and the perfluorinated compounds) were measured after solid phase extraction (SPE) by LC/MS/MS. Monochloroacetic acid, acrylamide, ethylene thiourea, fosetyl, fentin hydroxide, propylene thiourea, 1,2,4-triazole, mepiquat, chlormequat and choline chloride were measured after direct injection by LC/MS/MS, and dithiocarbamates were analyzed by GC/MS after acidic hydrolysis and measure of produced carbon disulfide.

Non-polar compounds (e.g., plasticizers, disinfection by-products, musks) were measured by GC/MS after liquid/liquid extraction (LLE) or SPE. Organotin compounds were analyzed by L/L extraction, ethylation and GC/MS. PCB and dioxin substances (36) and BDEs (6) were measured by LLE combined with GC/HRMS using the isotope dilution method. Volatile compounds were determined with headspace or purge and trap by GC/MS. A few compounds were analyzed using specific methods: free cyanides (Continuous Flow Analysis), acetaldehyde, nitrilotriacetic acid, formaldehyde and bisphenol A (LC/DAD), monochloroacetic acid (CI-MS/MS) and bromates (ion chromatography with suppressed conductivity detection).

The laboratories are accredited in compliance with the NF EN ISO 17025 standard. Given the emerging state of research for many of the substances, only 130 out of 411 are covered by the scope of accreditation. Accreditation includes quality assurance procedures, method validation, internal quality controls (blank, recovery test), participation in proficiency testing when available, and periodic third-party evaluation. When the method includes an extraction step, results are corrected for extraction yield. The limits of quantification (LOQs in Tables S1 and S2) for a large number of substances have been estimated according to AFNOR XP T90-210 or NF T90-210 standards. This entails verifying the accuracy of the method for reproducibility and repeatability at the LOQ on a natural representative matrix. Laboratory LOQ takes into account typical lab blanks as in the classical accreditation procedure. Lab blanks are regularly checked by batch analyses.