A national-scale assessment of micro-organic contaminants in groundwater of England and Wales

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HIGHLIGHTS

- The first national-scale assessment of micro-organics in England & Wales aquifers
- Most frequently-detected MOs are established pollutants: atrazine and chloroform.
- Caffeine, DEET and bisphenol A are the most frequently detected emerging contaminants.
- There are clear differences in MOs between land-use types, but not aquifer type.
- Establishing long-term trends is not yet possible.

GRAPHICAL ABSTRACT
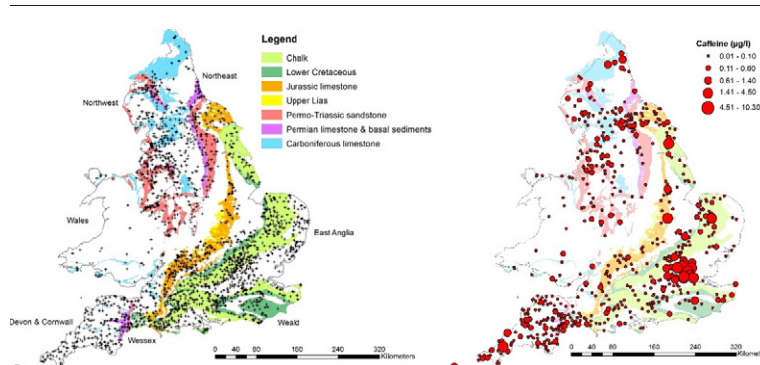
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ABSTRACT

A large variety of micro-organic (MO) compounds is used in huge quantities for a range of purposes (e.g. manufacturing, food production, healthcare) and is now being frequently detected in the aquatic environment. Interest in the occurrence of MO contaminants in the terrestrial and aquatic environments continues to grow, as well as in their environmental fate and potential toxicity. However, the contamination of groundwater resources by MOs has a limited evidence base compared to other freshwater resources. Of particular concern are newly 'emerging contaminants' such as pharmaceuticals and lifestyle compounds, particularly those with potential endocrine disrupting properties. While groundwater often has a high degree of protection from pollution due to physical, chemical and biological attenuation processes in the subsurface compared to surface aquatic environments, trace concentrations of a large range of compounds are still detected in groundwater and in some cases may persist for decades due to the long residence times of groundwater systems. This study provides the first national-scale assessment of micro-organic compounds in groundwater in England and Wales. A large set of monitoring data was analysed to determine the relative occurrence and detected concentrations of different groups of compounds and to determine relationships with land-use, aquifer type and groundwater vulnerability. MOs detected including emerging compounds such as caffeine, DEET, bisphenol A, anti-microbial agents and pharmaceuticals as well as a range of legacy contaminants including chlorinated solvents and THMs, petroleum hydrocarbons, pesticides and other industrial compounds. There are clear differences in MOs between land-use types, particularly for urban-industrial and natural land-use. Temporal trends of MO occurrence are assessed but establishing long-term trends is not yet possible.

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1. Introduction

There has been a growing interest in the occurrence of micro-organic (MO) contaminants in the last few decades within both terrestrial and aquatic environments, and in their environmental fate and potential toxicity (Halling-Sørensen et al., 1998; Kolpin et al., 2002; Kümmerer, 2009). A wide variety of MO compounds is used in huge quantities for diverse purposes including arable agriculture, human and animal healthcare, and industrial manufacturing processes. Potential sources of MOs to the environment are therefore numerous. There is relatively limited understanding of the impact of contamination of groundwater resources by MOs compared to other freshwaters. Of particular concern are newly 'emerging contaminants' (ECs), for example pharmaceuticals, household and lifestyle compounds, particularly those with potential endocrine disrupting properties (e.g. Lapworth et al., 2012; Swartz et al., 2006). The term 'emerging contaminants' is used to cover newly developed compounds, compounds newly detected in the environment due to analytical developments and compounds that have only recently been identified as having potentially harmful effects on human health or the wider environment (Lindsey et al., 2001; Petrović et al., 2006; Richardson, 2009).

Groundwaters usually have a relatively high degree of protection from pollution due to physical, chemical and biological attenuation processes in the subsurface compared to surface aquatic environments (e.g. Barnes et al., 2008). However it is clear from recent studies that trace concentrations of a large range of compounds are still detected in groundwaters (Focazio et al., 2008; Lapworth et al., 2012; Loos et al., 2010; Stuart et al., 2012). There are a number of international studies confirming that this is a global problem (Brausch and Rand, 2011; Jurado et al., 2012b; Lopez et al., 2015; Luo et al., 2014).

Research in urban environments has identified pharmaceuticals and personal care products as posing risks to groundwater (Brausch and Rand, 2011; Félix-Cañedo et al., 2013; Jurado et al., 2014; Jurado et al., 2012a; López-Serna et al., 2013; Ortiz de García et al., 2013; Sousa et al., 2014). These are now becoming a concern in the developing city context (Rehman et al., 2015). Sources include urban wastewater treatment plants (Michael et al., 2013) and lifestyle compounds, such as caffeine, are also widely detected (Lapworth et al., 2012).

In rural areas, triazine herbicides (such as atrazine) and their degradation products, as well as other pesticides, continue to be detected and remain a key concern (Baran et al., 2007; Stuart et al., 2012). Veterinary medicines have also been identified as groundwater contaminants (Boxall et al., 2004; Kemper, 2008).

Well-established industrial compounds such as chlorinated solvents, polyaromatic hydrocarbons (PAH), plasticisers and bisphenol A (BPA) are widely distributed in groundwater (Lacorte et al., 2002; Moran et al., 2006; Rivett et al., 1990) despite more recent reductions in their use and improvement in management and disposal practices. With continued development of new industries and processes there will be further impacts on groundwater, for example increase of nanoparticle uses, three dimensional printing or fracking for shale gas (Kassotis et al., 2013; Langenhoff, 2011).

Lopez et al. (2015) recently reported that a number of unregulated compounds, including the pharmaceuticals acetaminophen (paracetamol) and carbamazepine, were detected in more than 10% of samples from a national survey in France. Using reconnaissance results from studies undertaken in the Chalk aquifers of UK and France in 2011 Lapworth et al. (2015) found that MOs had some relationship to land-use but the multiplicity of sources in agricultural and urban settings meant that they were generally widespread.

The purpose of this study is to provide the first national-scale assessment of MOs in England and Wales by analysing a large dataset to determine the relative occurrence and detected concentrations of different groups of compounds and whether a relationship to land-use or aquifer type could be determined using national-scale datasets, such as European land-use and UK aquifer properties manual. The data set was also analysed for the first time to assess temporal changes in concentrations.

2. Methods

2.1. Sample collection and analysis

Groundwater samples from England and Wales were collected by the Environment Agency and analysed by their National Laboratory Service (NLS) using a target-based, multi-residue GCMS method which is semi-quantitative and screens for >800 organic compounds. An internal standard was added to each 1 L sample to correct for any loss of compound during the sample preparation or inlet stage. Due to the wide range of compounds contained within the target database and their variety of chemical characteristics, a double liquid-liquid extraction method was used, (neutral-acid) with dichloromethane. The combined extracts were then concentrated to 1 mL using a Zymark Turbo-Vap®, dried and transferred to an auto-sampler vial for analysis.

Analytes are identified using a combination of target MS libraries and quantified using response factors obtained from running a reference standard for target compounds at a known concentration, typically 1 μg/L. NLS participate in the UKAS accredited proficiency scheme Aquacheck (Group 22 'Qualitative Organics by GCMS'). The limit of detection (LOD) is dependent on compound and sample matrix and is 0.1 μg/L for the vast majority of analytes. The use of field blanks has established minimal contamination is possible during sampling, with the only significant contaminant being from plasticisers, presumably from in-situ borehole sources. Field blanks for another project collected by BGS, run blind by NLS, have been used to assess potential contamination due to sampling. Only positive detections were reported by this method, i.e. non-detections were not recorded.

The dataset also contained some analyses obtained from earlier methods, namely suites for volatiles scan, semi-volatile screen, semi-quantitative GCMS screen and cypermethrin identification. These data had differing LODs and some reported non-detections. Regulated compounds are monitored by another fully quantitative method to ensure compliance. Together these datasets are used by the Environment Agency as part of their Water Framework Directive (WFD) assessment process. Data used for this assessment were collected between February 2002 and August 2012.

2.2. Data cleaning

Duplicate records and those with a less than (i.e. below detection limit) attribute were excluded from the analysis. It is possible that some of the high concentrations reported in the database are erroneous, for example, they may result from transcription errors during manual data entry or contamination during the sampling or analysis process.

In order to reduce the likelihood of including erroneous or spurious detections, only compounds which were detected at least ten times were included in the analysis.

Compounds which could be affected by borehole installations or sample collection techniques were not excluded from the analysis. These could include plasticisers from borehole casing or pump tubing, compounds in pharmaceuticals or cosmetics associated with sampling staff. These are commented on in the discussion.

2.3. Site selection and characterisation

Samples were collected from 2650 sites as part of the then England and Wales Environment Agency's National Monitoring Programme. These are predominantly located on aquifers designated as principal and secondary by the Environment Agency (2013), with some on low permeability strata designated as unproductive, which nevertheless may provide small amounts of groundwater for private supply (Fig. 1). The definition of principal aquifers includes that they, "provide