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
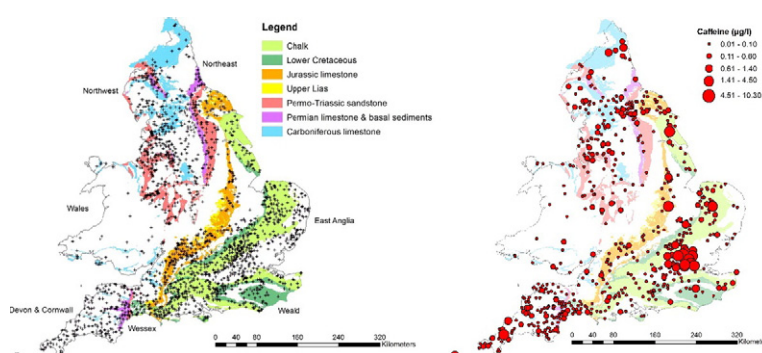
ABSTRACT

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

significant quantities of water for people", while secondary aquifers, "can provide modest amounts of water, but the nature of the rock or the aquifer's structure limits their use" (Environment Agency, 2013). Sampling has been on a broadly annual cycle since 2003 with a small number of samples collected from 1992 onwards.

The majority of the samples were collected in England. Most sampled sites (86%) had an associated aquifer, from which samples were derived, recorded in the database. Only 4% of sites in the Devon and Cornwall area had this attribution, meaning that most of the data from this area were omitted from this analysis. Other areas had >95% attribution, apart from 70% in Wessex.

129 aquifer names were used in the database, mainly at formation level (e.g. Helsby Sandstone Formation). These were aggregated into 19 groups, for example the Collyhurst, Helsby, Kinnerton, Kirklinton, Otter, Penrith, St Bees, Chester Pebble Bed and Wilmslow Sandstone formations together with areas of undifferentiated Sherwood Sandstone Group comprised the Permo-Triassic Sandstones. Groups were denoted "major aquifer", "minor aquifer" or "other" based on their productivity (Allen et al., 1997; Jones et al., 2000). Analysis of the micro-organic data associated with the sites with an aquifer designation was focussed on the four major aquifer groups with the most data (Table 1). Sites included in these four aquifer groups amount to just over half of the sites in the database, and 62% of all records (71% of records with aquifer attribute).

Land-use classification was carried out using a 500 m radius search around each site using the most recent CORINE land-use data set for Europe (EEA, 2006). A simple scheme for land-use classification was used by grouping land-use into four main categories within each search radius: (i) NGF - Natural land-use which included natural grassland and forest; (ii) UI - Urban and industrial land-use; (iii) A - Arable agricultural
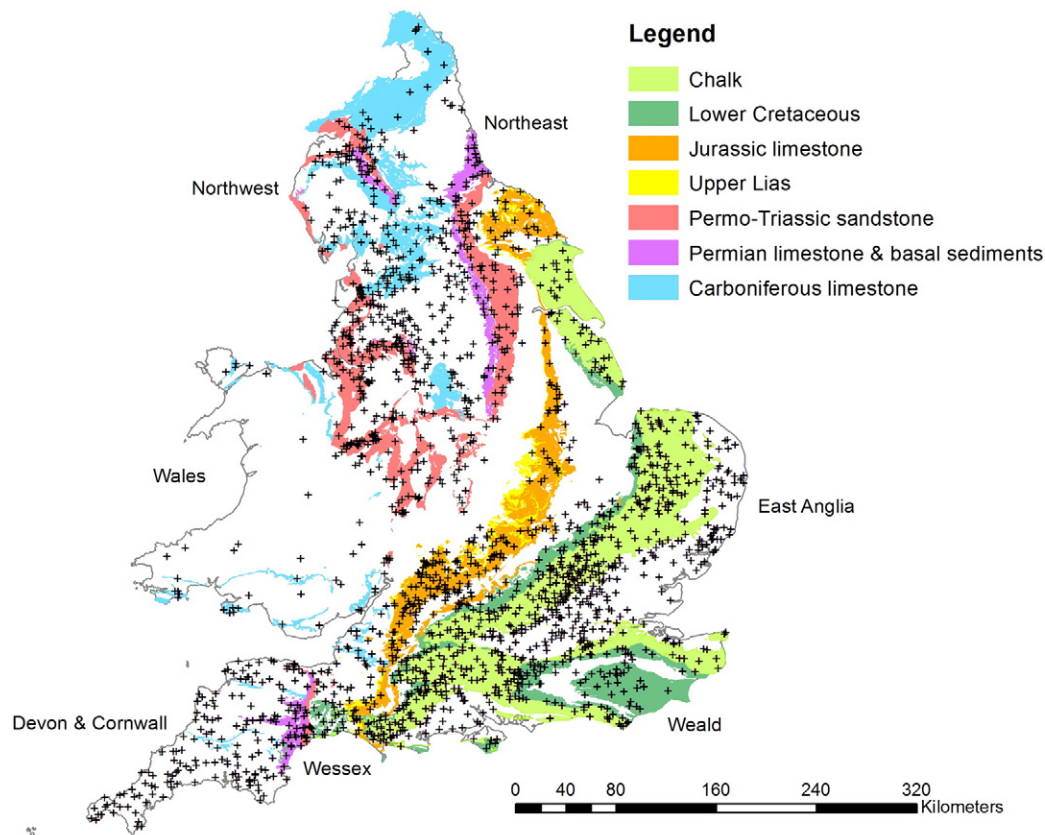
land-use and (iv) P - Pasture/grazing. Each site was then classified as a single land-use type where >60% of the area in the search radius corresponded to one of the four categories outlined above. Out of 2605 sites recorded within database, 25.11% had mixed land-use type under our classification method. Due to uncertainty associated with mixed land-use type, including mixed sources for the same compounds, these sites were excluded from subsequent analysis based on land-use.

2.4. Maximum concentrations for the 30 most frequently detected compounds

The maximum observed concentration of each detected compound was identified for each setting (e.g. by land-use classification). The 30 highest values (hereafter referred to as 'Top 30') were then plotted and assessed. This approach was employed as a useful means to compare the observed values with existing and proposed regulatory limits, for example drinking water standards or surface water thresholds. It also allowed a comparison to be made between the types of compounds observed at high concentrations and those which were detected more frequently (Section 2.5).

Table 1
MO detections in the main aquifer groupings.

Aquifer group	Number of sampled sites	Number of detections
Chalk	647	11,546
Permo-Triassic sandstones	372	2547
Jurassic limestones	248	2511
Lower Greensand	78	1288

Legend
- Chalk
- Lower Cretaceous
- Jurassic limestone
- Upper Lias
- Permo-Triassic sandstone
- Permian limestone & basal sediments
- Carboniferous limestone

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Fig. 1. Map of sample sites and aquifers in England and Wales.

2.5. Number of detections and normalisation

The number of detections were normalised to the number of samples taken, to remove the bias introduced by the uneven distribution of sampling sites/visits between different settings (e.g. aquifer group). Thus we are reporting the proportion of samples in which a compound was detected. Data for the Top 30 compounds in each land-use or aquifer setting were plotted and interpreted.

As non-detections were not recorded, for each site, the normalised frequency (%) of detections was defined as being equal to the number of actual detections per compound divided by the number of times an analytical method which could detect that compound was employed.

2.6. Categorisation of compounds

Compounds were grouped in order to more readily compare results from the different aquifer and land-use settings. Categories were based on the type of compound and/or its typical use, as summarised in Table 2 and provided in full in the Supplementary Information. Degradation products of compounds are included within the category of the parent compound (e.g. desethyl atrazine, a metabolite of atrazine, is included within the "Pesticide" category). For ease of reference, the short name "Domestic and personal" is used in the text for the category which includes lifestyle, personal care product (PCP), household, pharmaceutical and food additive compounds. Some compounds could be placed in more than one category and the most likely was chosen.

3. Results and discussion

3.1. Frequency and maximum detections in the dataset

A number of different types of organic micropollutants were detected in the groundwater in England and Wales, with multiple compounds at many sites. These include categories of compounds as described in Section 2.6.

The Top 30 most frequently detected compounds are shown in Fig 2. Frequency of detection will depend on use and persistence in the environment, as illustrated by the continuing widespread detections of atrazine (banned in the EU for all uses since 2004). Overall three out of the top five compounds are pesticides and their metabolites. Other compounds include PAHs, chlorinated solvents and THMs. Not surprisingly caffeine, which has been widely detected in other studies, is ranked fourth by frequency of detection, A number of compounds (8) within the Top 30 belong to the PAH group together with six chlorinated

solvents/THMs, four domestic and personal, four other industrial compounds, two non-chlorinated solvents and one plasticiser (BPA).

For the Chalk of England and France, Lapworth et al. (2015) found that the most frequently detected compounds were atrazine-desethyl (20% of samples), atrazine (12.5%), desisopropyl atrazine (9.6%), caffeine (8.7%), chlorodibromomethane, 2,6-dichlorobenzamide (BAM), DEHP, oxadixyl, carbamazepine and BPA (3.5%). The data from England used by Lapworth et al. (2015) were a small subset of the dataset used for the present study.

In a pan-European study, Loos et al. (2010) found very high detection frequencies with DEET (83.5%), caffeine (82.9%) and perfluorooctanoic acid (65.9%) being the most widely detected polar organics with atrazine the fourth most frequently detected, atrazine desethyl the fifth, simazine the tenth and carbamazepine the eleventh most widely detected compound. Our results broadly confirm these findings, despite results from a range of different analytical methods being summarised by these authors.

An earlier study of groundwater by the US Geological Survey (Barnes et al., 2008), using three targeted analytical methods including LC-MS, also found DEET to be the most frequently detected compound (34.7%) followed by BPA, the flame retardants tri(2-chloroethyl) phosphate and ethanol 2-butoxy-phosphate, the pharmaceutical sulfamethoxazole, plus the de-icer 5-methyl-1H-benzotriazole and 4-octylphenolmonoethoxylate, para-cresol, naphthalene, 1,4-dichlorobenzene, acetophenone, and coprostanol. In a study of untreated drinking water sources in the US, Focazio et al. (2008) frequently detected compounds not prominent in other studies, e.g. the sterols cholesterol (42%), β-sitosterol (24%) and coprostanol (18%), the nicotine metabolite cotinine (35%), 1,7-dimethylxanthine (23%) and the musk HHCB, as well as metolachlor and carbamazepine. This was probably because this study included both ground and surface water sources as well as targeting polar compounds, such as sterols.

Expressing the results from the present study as the more conventional percentage, atrazine was only detected in 5.3% of samples and caffeine in 3.1%. These percentages are substantially lower than those from the other studies discussed here. The reasons for this are not clear, but will include both differences in the target suites and the use of a non-targeted monitoring network (Lapworth et al., 2012).

The Top 30 by maximum concentration are shown in Fig 3. A different picture emerges with the top compounds being dominated by chlorinated solvents, THMs and CFCs; 6 out of the top 8 and 11 out of the Top 30 belong to this group. The highest concentration overall was for trichloroethene (TCE) (5132 µg/L). Interestingly, the PAHs are not present within the Top 30 compounds by concentration, instead 8 other industrial compounds, 3 plasticisers, 2 non-chlorinated solvents, 2 domestic and personal products and 1 sterol are present. Both the well-established endocrine disruptors BPA and nonylphenol are in the upper part of the distribution.

For the Chalk of England and France, Lapworth et al. (2015) found the highest concentrations were of BPA (100 µg/L), followed by chlorodibromomethane (29 µg/L), diethyl phthalate (DEP) (22 µg/L), diethylhexylphthalate (DEHP) (13 µg/L), the pesticide metabolite 2,6-dichlorobenzamide (BAM) (10 µg/L), boscalid (2.3 µg/L), caffeine (1.7 µg/L), oxadixyl (1.4 µg/L) and metronidazole (1.4 µg/L). Of these, the top nine compounds were detected in England. This was attributed to the much greater number of samples from England in the study. It is difficult to make direct comparisons with other national studies since the suite of compounds detected will depend on the analytical method. This study used a GCMS method which will not detect a range of polar compounds, e.g. β-blockers and surfactant metabolites. Lapworth et al. (2015) used the same method for their British data.

For polar compounds across Europe, Loos et al. (2010) found the highest maximum concentrations were for N,N-dimethyl sulfamide (52 µg/L), pesticides and their metabolites (chloridazon-desphenyl (13 µg/L), chloridazon-methyldesphenyl, bentazone dichloroprop), the pharmaceutical ketoprofen (2.99 µg/L), BPA (2.3 µg/L), the surfactants nonylphenoxy acetic acid (NP1EC) (11.3 µg/L) and nonylphenol

Table 2
Categories of compounds (see Supplementary information for full compound listing).

| Category	Members	Examples of compounds
Chlorinated solvents, THMs and CFCs	Chlorinated solvents	Trichloroethene (TCE)
	Trihalomethanes	Chloroform
	Chlorofluorocarbons	CFC-11
Non-chlorinated solvents	BTEX	Toluene, benzene, xylene
	Dioxanes	1,4-Dioxane
Poly-aromatic hydrocarbons (PAHs)		Pyrene, phenanthrene
Pesticides	Parent	Atrazine
	Metabolites	Atrazine, desethyl-atrazine
Domestic and personal	Lifestyle	Caffeine, nicotine
	Personal care products (PCP)	N,N-diethyl meta toluamide (DEET)
	Household	1H-benzotriazole, triclosan
	Pharmaceutical	Carbamazepine
	Food additives	Butylated hydroxytoluene
Plasticisers		Bisphenol A (BPA), dimethyl phthalate
Other industrial		Dimethyl succinate, tributyl phosphate
Sterol		Cholesterol
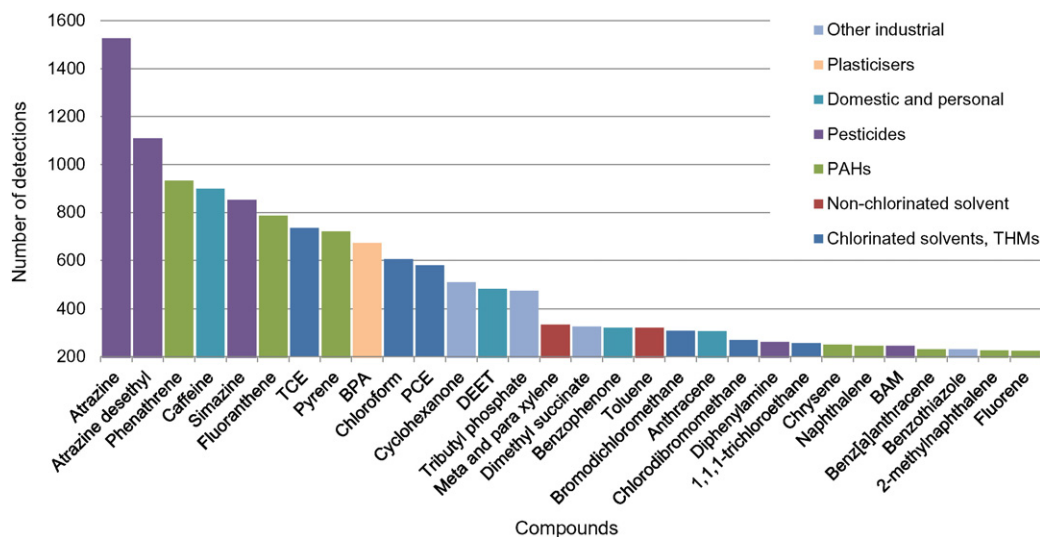
Fig. 2. The 30 most frequently detected MOs in groundwater in England and Wales.

(3.9 μg/L). These data were collated from a number of other studies and it is likely that some of these were targeted at sites with known contamination.

There are relatively few other national studies for groundwater. For the USA Barnes et al. (2008) found DEET to be detected at the highest concentrations, followed by 4-nonyl phenol diethoxylate (NP2EO), ibuprofen, acetophenone, BPA and the sterols, stigmasterol, cholesterol and coprostanol. For Spain the maximum concentrations detected were for a group containing some different compounds (Jurado et al., 2012b). These were surfactant related compounds (nonylphenoxyethoxyacetic acid (NP2EC) (11.2 μg/L), nonylphenol and linear alkyl benzene sulfonate (LAS), pesticides (alachlor, metolachlor, malathion, atrazine), DEHP and the pharmaceuticals sulfacetamide and hydrochlorothiazide. Pesticides detected will be related to the climate and agricultural practices of the study area and would not be anticipated to be similar in both Northern and Southern Europe. In Italy maximum concentrations above 0.1 μg/L for industrial compounds in groundwater were found for benzene, PCE, vinyl chloride, TCE, chloroform, a range of other chlorinated solvents and triphenyl phosphate (Meffe and de Bustamante, 2014). Evidence for other compound groups was limited but included the pharmaceuticals diazepam, the bezafibrate metabolite clofibric acid and tylosin.

3.2. Spatial distribution of selected compounds

The spatial distributions of two examples of compounds which are widely distributed in groundwater – atrazine and its metabolites and caffeine are shown in Fig. 4. All data for these compounds are plotted for all sampling dates.

For atrazine and its metabolites (Fig. 4a) the clusters in the Lee valley, East Anglia and Wessex correspond to the areas where these compounds are likely to have been used in agriculture. These data also highlight the persistence of these compounds in the subsurface. In contrast the distribution of caffeine concentrations highlights areas that are subject to urban anthropogenic impact (Fig. 4b). These are predominantly major cities underlain by groundwater. The cluster around London corresponds to the area occupied by the M25 orbital motorway.

3.3. Relationship with land-use

3.3.1. Maximum concentration

Analysis of the data for the summary land-use types is summarised in Fig. 5. Compound categories are described in Section 2.6. There is a
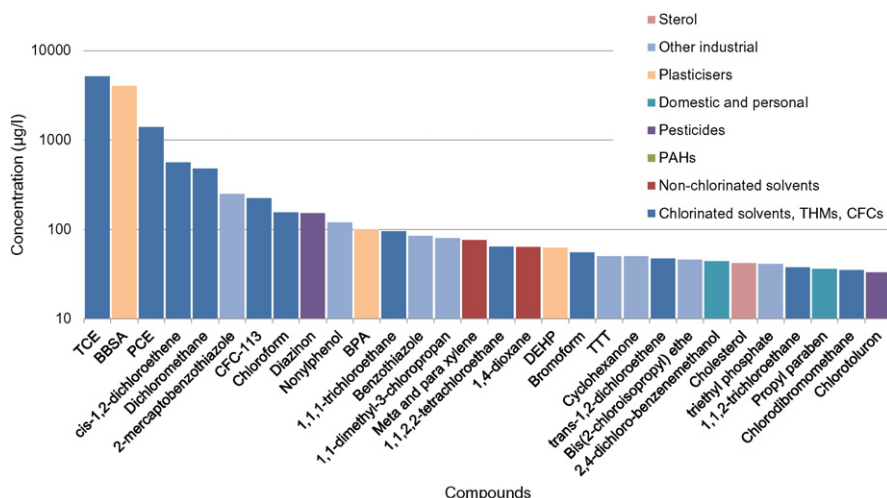

Fig. 3. Top 30 MOs by maximum concentration in groundwater in England and Wales.
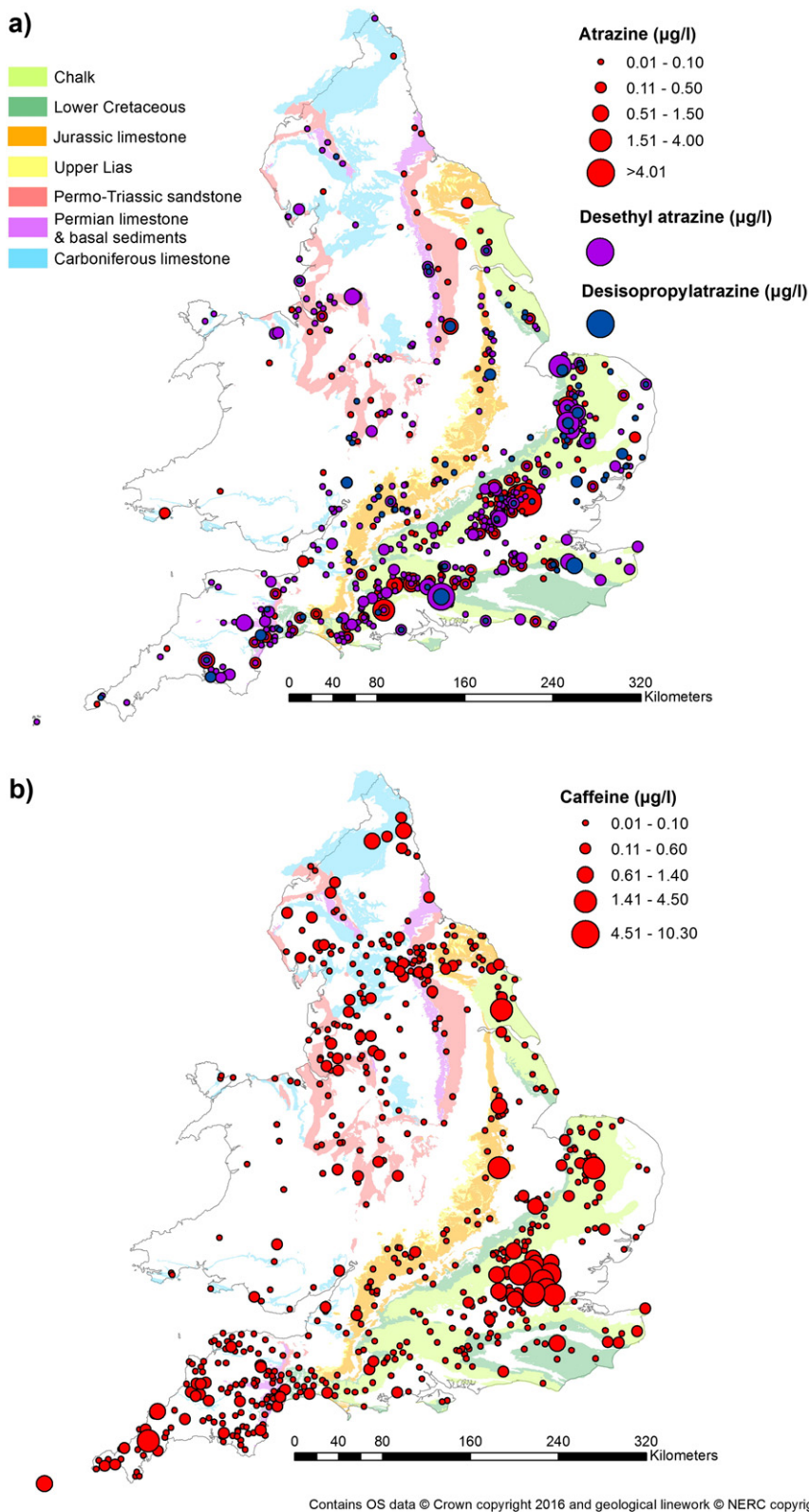
Fig. 4. England and Wales distribution of concentrations of: a) atrazine and its metabolites; b) caffeine.

clear difference in the concentration and the number of compounds found for these different land-use types.

Natural (NGF) has the lowest maximum concentrations of compounds amongst the types of land-use as well as fewer compounds – only 18 compounds with a maximum concentration of 5.5 μg/L for chlorodibromomethane. Most compounds were detected at concentrations lower than 1 μg/L. Maximum concentration for the NGF are at least an order of magnitude lower than other land-uses. Urban Industrial (UI) land-use has 13 compounds not found in other land-use types including nicotine. The highest concentrations found overall were in the UI and Arable (A) type, with most of the concentrations over 100 μg/L also found within these land-use types.
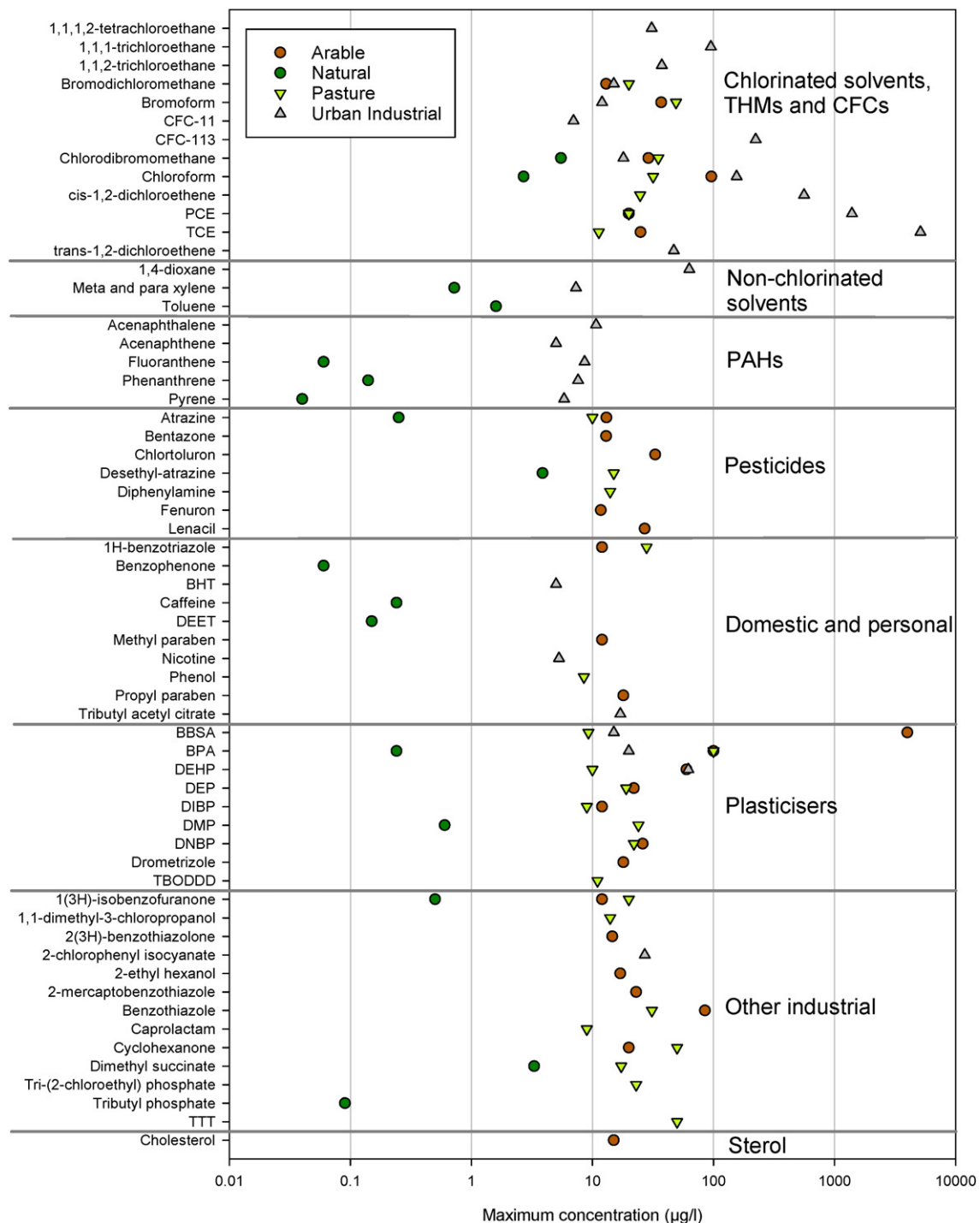
Fig. 5. Top 30 maximum concentrations of MOs by land-use.

The maximum concentrations associated with land-use A are for the plasticiser *N*-butyl benzene sulfonamide (BBSA) (4000 μg/L), followed by BPA and chloroform. Pasture (P) has the highest maximum concentration of BPA at 100 μg/l while UI has the overall highest of 5000 μg/L for TCE.

Chloroform, chlorodibromomethane and BPA are the only 3 compounds in the Top 30 found to be present within all 4 environments. Chloroform concentrations illustrate the pattern with the highest concentrations found in UI (155 μg/L) followed by A (96 μg/L), P (31.7 μg/L) and NGF (2.7 μg/L). CFC-11 and CFC-13 were exclusively detected in UI land-use, with maximum concentrations several orders of magnitude higher than modern atmospheric concentrations (270 and

70 ppt respectively (NOAA, 2015). This is strongly indicative of gross point source contamination as the detection limits for the GCMS method are above modern atmospheric concentrations and would not be able to detect any contamination introduced during sampling (Darling et al., 2012). BPA follows a similar pattern with NGF having the lowest concentration of 0.24 μg/L, 2 magnitudes lower than UI at 20 μg/L and 5 times lower than A and P both at 100 μg/L. Plasticisers and chlorinated solvents are found in all four categories of land-use while pesticides are only found within A, P and NGF.

For the Chalk of England and France Lapworth et al. (2015) did not observe a clear relationship between concentration of compounds detected and land-use. They ascribed this lack of relationship for the

Chalk to the elongated shape of typical chalk borehole catchments as opposed to the radial approach used both in their work and in this study. This study contains intergranular aquifers as well as limestones and the Chalk and the radial approach may potentially work better for these aquifers.

In their pan-French study, Lopez et al. (2015) also found the greatest occurrence of ECs where urban pressure on groundwater is associated with agricultural or industrial uses, with lower frequency of detection in predominantly agricultural areas and lower still in natural settings.

3.3.2. Frequency of detection

Fig. 6 shows the frequency of detection (data normalised as described in Section 2.5) in the four land-use types. THMs and solvents (chlorinated and non-chlorinated) dominate, followed by PAHs and plasticisers. Chlorinated solvents are found most frequently in UI, but also in P and A. Chloroform stands out as the compound detected in at least 15% of samples in all of the environments and interestingly with the highest percentage detection of 40% within NGF land-use. This could imply that its origin is within the water treatment process and
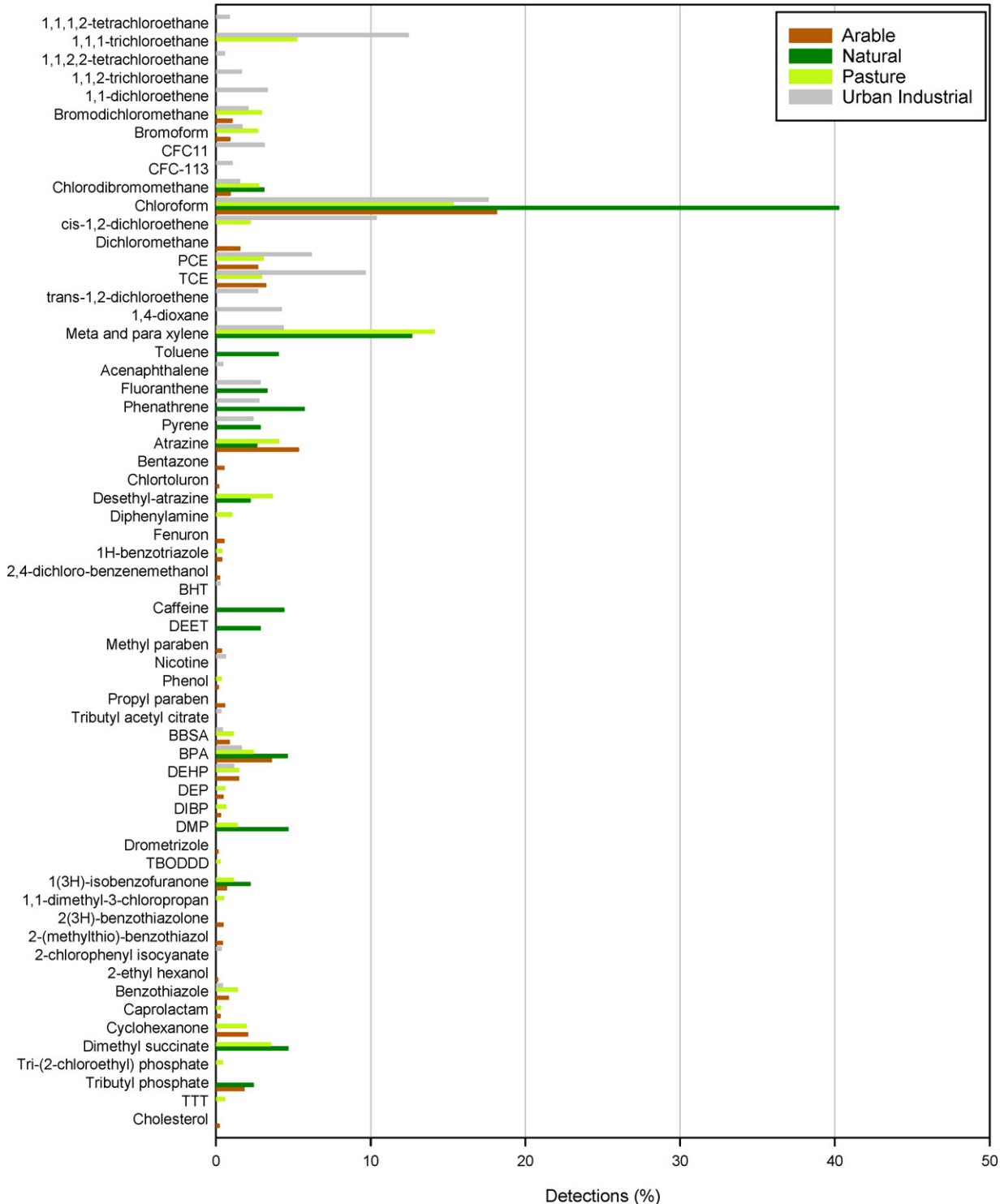

Fig. 6. Frequency of detection of MOs in land-use classes.

supports the hypothesis that chloroform is introduced via leakage into aquifers; together with plasticisers these compounds are widely detected in the environment. However, both aerial deposition (Baehr et al., 1999a) and natural production of chloroform by plants (Baehr et al., 1999b) have been proposed as contributing sources and have been detected in groundwater at comparable concentrations to those found in NGF use in this study (Hunkeler et al., 2012).

Other compounds detected at a frequency of over 10% include 1,1,1-trichloroethane and cis1,2-dichloroethene in UI. Xylene is also detected in >10% of samples in P and NGF. A has lower % detection of phthalates compared to P overall. However this trend is reversed for TCE.

The NGF setting has the fewest compound detections. Also when comparing the normalised data for the different settings NGF shows lower frequency of detection of atrazine and its metabolite compared to P and A. For other compounds, such as chloroform and BPA, this trend is reversed and NGF has a higher frequency of detection compared to other environments. However, BPA, the THMs chloroform and chlorodibromomethane, and the PAHs phenanthrene and pyrene, are detected more frequently than in other land-use types. Perhaps surprisingly, the domestic and personal compounds caffeine and DEET, are only found in the Top 30 in NGF. These compounds may be entering groundwater from leaking sewer or septic tank sources, which are present in rural areas of the UK. The result may be an artefact of the land-use methodology (Section 2.3) in which sampling sites were allocated a land-use designation on the basis of a 500 m radius around the location, which may not accurately reflect the catchment of some of the sampled boreholes (Section 3.3.1).

Arable (A) has the most frequent detections of atrazine. It also shows a significant proportion of detections of PCE and TCE as well as chloroform, BPA, DEHP and several industrial compounds. Dichloromethane, 2,4-chlorobenzene methanol, fenuron, bentazone, methyl and propyl parabens, and a number of industrial compounds are only found in A. A possible route for these compounds to enter groundwater in arable areas would be through soil application of sewage sludge. The following compounds were also only detected within the Top 30 of this setting: the industrial compounds 2-ethylhexanol and 2-mercaptobenzothiazole, the pesticides lenacil, chlorotoluron, and bentazone, the UV stabiliser drometrizole, and cholesterol.

Chloroform and xylene were detected in more than 10% of samples from P land-use (Fig. 6). Other significant detections were for solvents (1,1,1-trichloroethane, cis1,2-dichloroethene) and THMs, pesticides (atrazine, desethyl-atrazine and diphenylamine), plasticisers and industrial compounds. Compounds only detected in the P Top 30 are diphenylamine, phenol, 7,9-di-*t*-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione (TBODDD), and several industrial compounds.

Key compound detections in the UI were chlorinated solvents, THMs, CFCs and PAHs. In fact all compounds found at >10% detection were chlorinated solvents (1,1,1-trichloroethane, chloroform and 1,2-dichloroethene). A number of these solvents were only found in UI. There were few detections of other compounds in the Top 30 but 13 that are only found in this setting.

Chloroform (15.3%), xylene (14%) and 1,1,1-trichloroethane (5%) dominate P in terms of percentage detection, followed by atrazine and other compounds under 5%, while chloroform and xylene are shown to account for just under and just over 15% of samples respectively.

The absolute number of detections of the Top 30 compounds for each of the four land-use classes is shown in Fig. 7. Overall the dataset is dominated by detections in the A class and to a lesser extent the P. NGF detections are insignificant when compared to the other classes. The detection of a different range of compounds within the UI setting is clearly illustrated. Caffeine is the compound detected most times in the P land-use type, followed by atrazine.

As might be anticipated the pattern of MOs in different settings is complex. The NGF setting had both the fewest compounds detected and the lowest concentrations, as might be anticipated. There are however some compounds only detected in the Top 30 in this setting, such

as caffeine and DEET. P and A appear quite similar in both maximum concentration terms and in the range of compounds detected. These include chlorinated solvents, chloroform, plasticisers and atrazine. The UI areas are different. These show predominantly high concentrations and frequencies of chlorinated solvents and THMs, but also include nicotine and PAHs.

Clearly there are a wide range of mechanisms providing pathways to groundwater for MOs. It is simple to speculate that arable land has been subject to sewage sludge application and that some MOs will be present in animal manure in P areas, and possibly vice versa. UI areas will have had at least historical disposal and spills of industrial chemicals; chlorinated compounds are particularly persistent in groundwater. Road run off will also be a source in all land-use types.

However, chloroform, which is likely to be predominantly a by-product of mains water disinfection, is ubiquitous and surprising compounds, such as caffeine and DEET, are found in NGF areas. Chloroform can be explained in terms of natural sources, as an end product of formation of chloroperoxides by fungi or reaction of atmospheric chloroethenes with natural organic matter (Hunkeler et al., 2012), and this is supported by the lower concentrations found in NGF compared to other land-use types (Fig. 5). There is also a lack of anticipated domestic and personal compounds in UI areas which would indicate leaking sewers. López-Serna et al. (2013) found 95 pharmaceuticals in urban groundwater beneath Barcelona but in this case bank filtration from a river receiving treated effluent was thought to be the main source. Many authors have highlighted the importance of wastewater treatment works as sources of MOs in the aqueous environment (e.g. Michael et al., 2013; Musolff et al., 2010; Reinstorf et al., 2009). This suggests that treated effluent may be an important source of MOs in the environment and that groundwater/surface water interaction is an important pathway.

In developing cities a higher concentration of MOs may be likely due to more limited waste management and treatment. For example, in Hanoi and Ho Chi Mihn City, Duong et al. (2015) found in one sampling round that phthalates were detected in over 80% of wells with other plasticisers, sterols, cosmetic fragrances, fire retardants and solvents also frequently detected. In Kabwe, Zambia in the wet season, the domestic and personal compounds DEET, triclosan, caffeine, the pesticides bromacil, atrazine, and 1,3-dichlorobenzene and the surfactant 2,4,7,9-tetramethyl-5-decyne-4,7-diol were found in residential areas with DEET and chlorinated solvents TCE and PCE in industrial areas (Sorensen et al., 2014). This type of situation may represent historical activity in post-industrial developed cities in Europe, albeit with a different suite of compounds.

3.4. Relationship with geology

3.4.1. Aquifer

3.4.1.1. Maximum concentrations. The Top 30 maximum concentrations reported for the four aquifer groups (Section 2.3) are presented in Fig. 8. Maximum concentrations are lowest in the Lower Greensand (nearly all ≤10 μg/L) and highest in the Chalk, where maxima mainly fall in the 10.1–100 μg/L range. The highest concentrations, in excess of 100 μg/l, were observed in the Chalk and Permo-Triassic Sandstones; the compounds in this upper range are four chlorinated solvents, one plasticiser (BBSA), chloroform (a THM) and the industrial compound 2-mercaptobenzothiazole (a rubber accelerator).

Various plasticisers and other industrial compounds appear in the Top 30 maximum concentrations of each aquifer group. Three of the plasticisers (BBSA, BPA and DEHP) are in the Top 30 of all four aquifer groups plotted. The data are corrected for lab blanks but it is possible that these compounds have been introduced to the groundwater from the borehole casing, and may not be representative of groundwater quality more widely (Section 2.2).
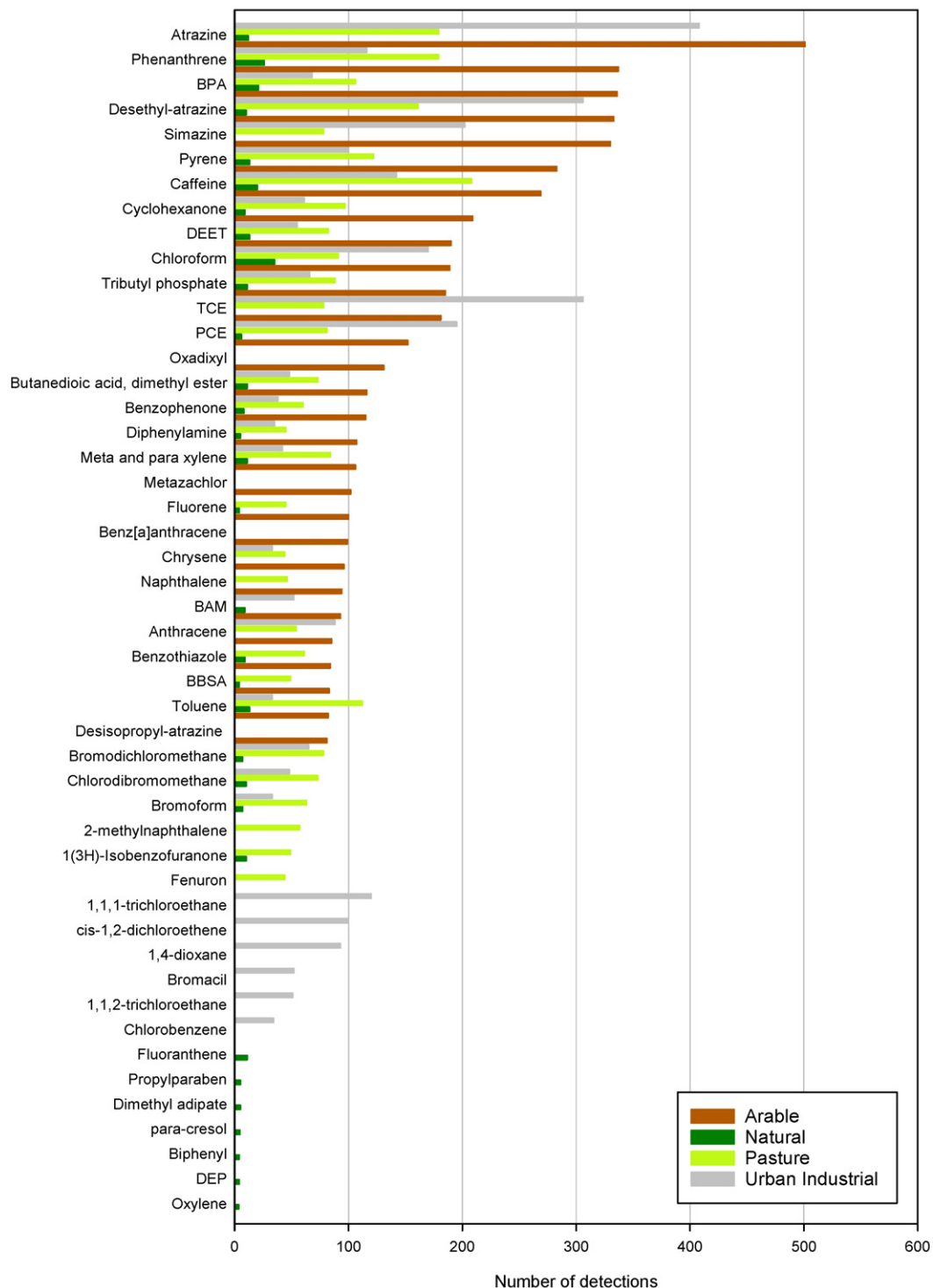
Fig. 7. Number of detections for the Top 30 compounds within different land-use settings.

As discussed in Section 2.4, some sampling bias is likely to be affecting the outcome of this analysis. For example, there is an order of magnitude more data from the Chalk aquifer than the Lower Greensand, making it more likely that higher concentrations will have been detected in the Chalk.

There are some differences between the aquifer groups in terms of the categories of compound that are in the Top 30 maximum concentrations.

• THMs (bromodichloromethane, bromoform, chlorodibromomethane and chloroform) appear in the analysis of all four aquifer groups

within the range 3.7–155 μg/L. These four compounds have a combined drinking water standard of 100 μg/l.

• PCE and TCE are both in the Top 30 of the Lower Greensand and Jurassic Limestone, while these and 8 other chlorinated solvents appear in the Chalk and Permo-Triassic Sandstones Top 30.

• PAHs arose in the Top 30 maximum concentration of the Jurassic Limestones (5 compounds), Lower Greensand (2 compounds) and the Permo-Triassic Sandstone (1 compound). All of these concentrations were considerably in excess of the 0.1 μg/L drinking water standard.
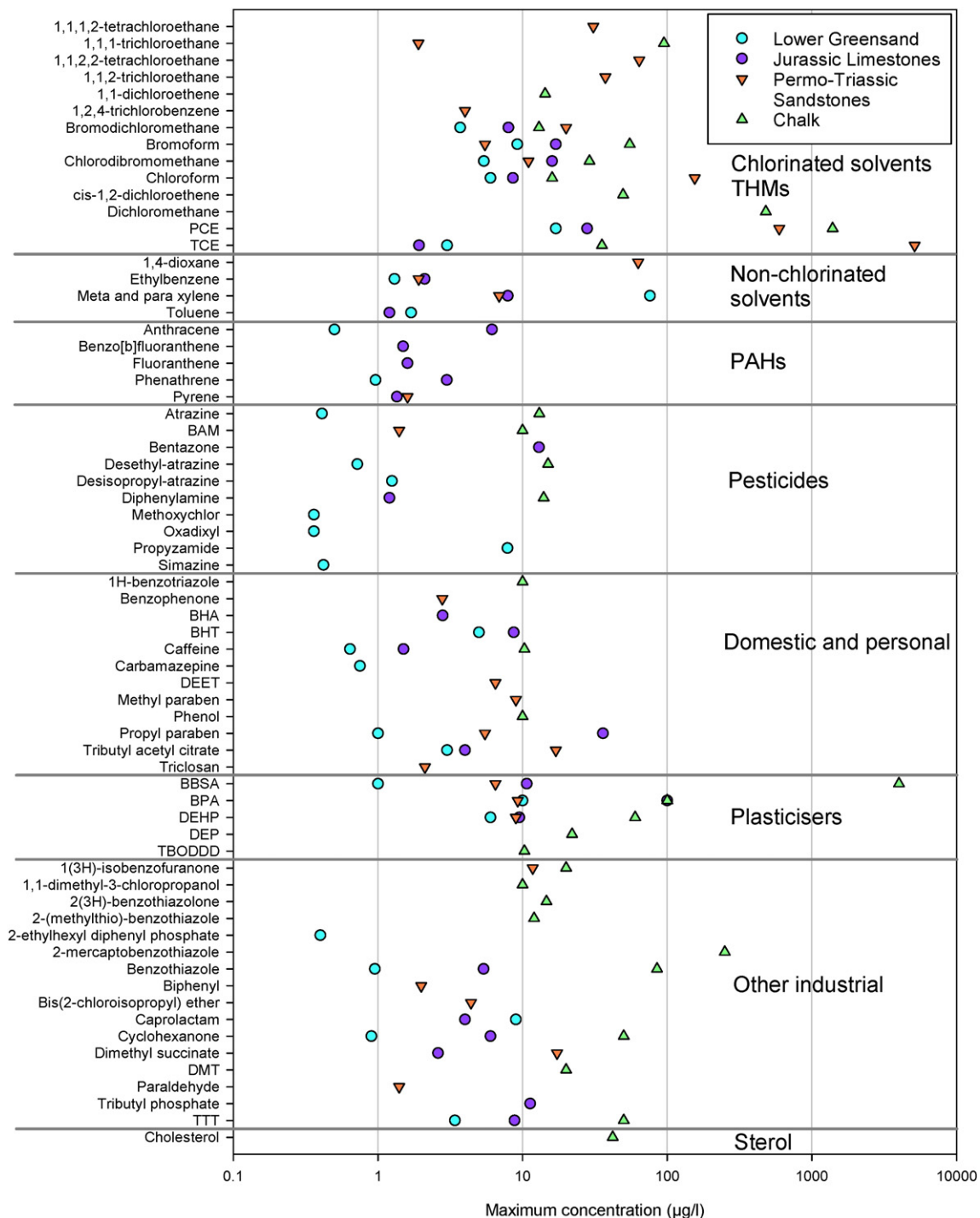
Fig. 8. Top 30 maximum concentrations by aquifer group.

• Neither PAHs nor non-chlorinated solvents appeared in the Chalk Top 30.

12 substances classified as 'domestic and personal' appear in the Top 30 lists, including DEET and triclosan in the Permo-Triassic Sandstone and carbamazepine in the Lower Greensand. Caffeine is in the Top 30 by maximum concentration of the Chalk, Lower Greensand and Jurassic Limestones.

Only one pesticide, BAM, is in the Top 30 of the Permo-Triassic Sandstones, and four (including atrazine and its daughter products) in the Chalk. Seven pesticide compounds feature in the Lower Greensand

Top 30. These compounds are all found in all aquifers, but do not all rank in the Top 30s.

The Lower Greensand is the most clearly characterised as having the lowest maximum concentrations in most of the compound groups. This is particularly marked for pesticides and personal care compounds. As stated above the Chalk has many of the maximum concentrations for both chlorinated solvents and industrial compounds. The Jurassic limestones and Permo-Triassic sandstones generally have similar values.

While controls on MOs by aquifer group are less marked than for land-use, we can observe some differences for the four aquifer groups used in this study. This may be predominantly due to the differences in outcrop area. That of the Lower Greensand is much smaller than for

the other three groups, outcropping only in the southeast, particularly around the North Downs and the Chilterns. Over substantial areas of this outcrop there is considerable topography and this may have restricted the types of surface activity.

Lopez et al. (2015) classified the sites in their national study according to aquifer type with 55% in sedimentary formations, 25% in alluvial aquifers, 15% in basement formations, 3% in low productivity aquifers and 2% in volcanic and mountain aquifers. This was stated to be representative but these authors do not discuss their results in this context.

3.4.1.2. Frequency of detection. A wide variety of micro-organic compounds have been detected in the Top 30 of all four aquifer groups. The proportion of samples in which a compound was detected in a particular aquifer group is displayed in Fig. 9, for the 30 compounds in each group which had the highest proportion of detections. Combining the four sets (one per aquifer group) of Top 30 compounds produced the list of 51 compounds shown (Fig. 9).

For the subset of samples from the four aquifers, solvents (both chlorinated and non-chlorinated) were again the most frequently detected. Chloroform was still the most frequently detected compound, being detected in about a third of samples from the Lower Greensand, and 12–16% of samples from the other aquifer groups (Fig. 9). Other THMs (bromodichloromethane, bromoform and chlorodibromomethane) were detected less frequently, in 0–3% of samples. Of the chlorinated solvents, the TCE degradation product *cis*-1,2-dichloroethene was most frequently detected, in 5–9% of samples. A higher proportion of
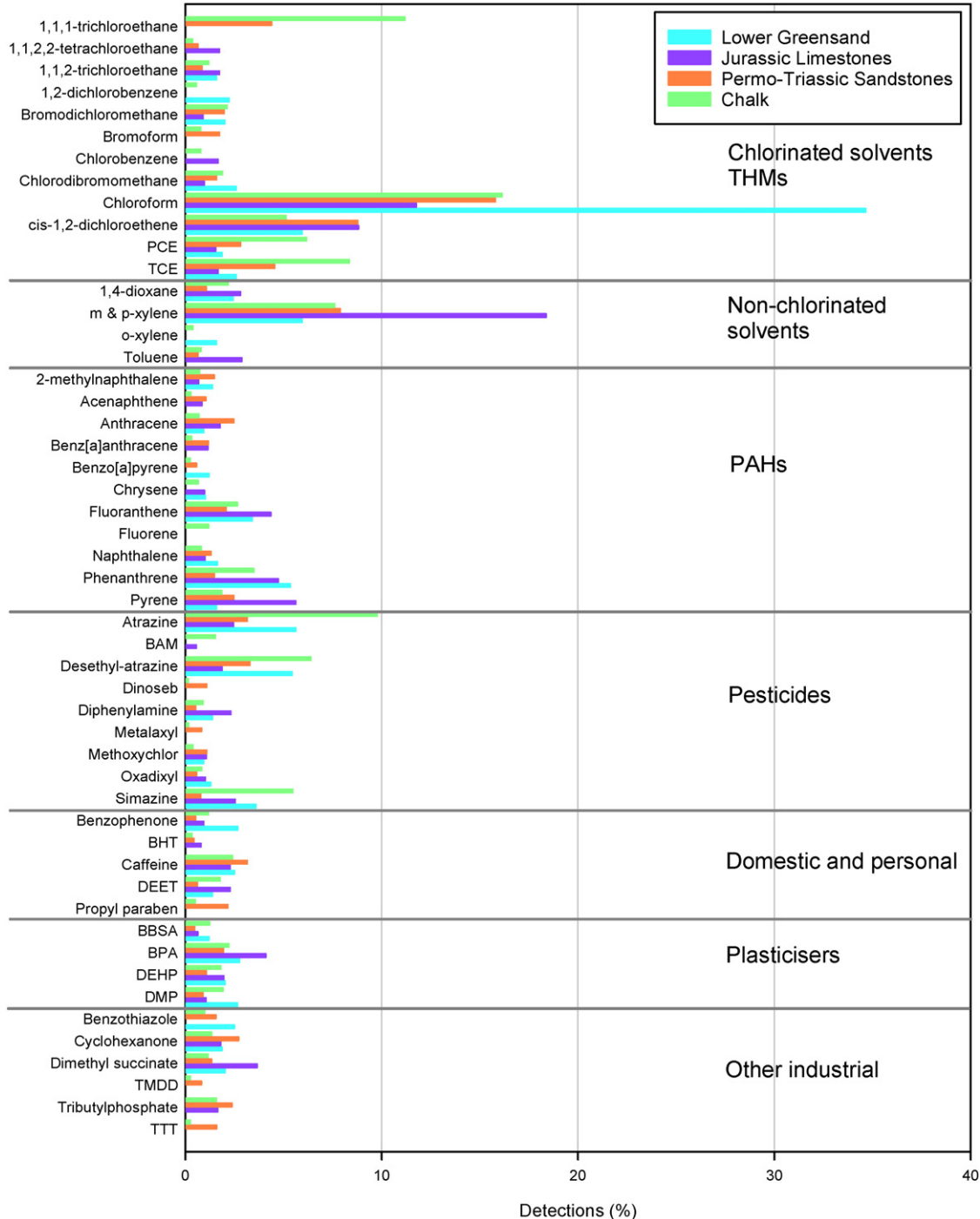

Fig. 9. Frequency of detection of MOs by aquifer group.

samples from the Chalk contained detectable concentrations of chlorinated solvents than the other aquifer groups.

For other groups of compounds detection frequencies were more uniform in aquifer types than for land-use groups. Atrazine was the only pesticide compound detected in 10% of samples from one aquifer. Eleven PAHs appear in the combined Top 30 list, indicating that they are detected relatively frequently. These compounds were detected in up to 6% of samples from the four aquifer groups, with higher frequencies in the Jurassic limestones and Lower Greensand.

Pesticides were most frequently detected in the Chalk and Lower Greensand, perhaps due to the matrix storage of water compared to the dominance of fracture storage in the limestones, which is more rapidly flushed. Atrazine was detected in 10% of samples taken from the Chalk, and the degradation product atrazine desethyl in 6%. Simazine was present at detectable concentrations in 1–5% of samples taken from the four aquifer groups.

Compounds with their origin in 'domestic and personal' products account for five of the Top 30 list (Fig. 9). DEET is found in all 4 aquifer groups in 1–2% of samples, caffeine in 2–3% and benzophenone in 1–3%.

The six compounds classified as 'other industrial' were detected in up to 4% of samples. All six compounds were detected in the Permo-Triassic Sandstones, which may reflect the location of past heavy industrial centres, and the intergranular storage which can allow contaminants to remain in the aquifer for relatively long periods. Although the frequency of detection may seem low in many cases (e.g. 1%), these represent a significant number of detections, especially in the Chalk where more samples have been taken. For example, 955 detections of atrazine and 625 of atrazine desethyl were made from Chalk samples.

3.4.2. Confinement

The database contains classification for the type of groundwater of 3 classes: confined (or captive), semi-confined and unconfined (phreatic). The unconfined groundwater class is split into depth ranges: shallow 0–5 m including springs, medium 5–15 m, deeper 15–30 m, and deep >30 m. For the above classes the data were analysed and the Top 30 compounds detected more than 10 times were analysed to see if there are any differences in frequency and maximum concentration of compounds found within settings that reflect the degree of protection or vulnerability of groundwater. In the overall database of 2545 sites 443 were classed as confined, 67 as shallow, 719 as medium, 193 as deeper and 1076 classed as deep and only 47 not classed.

The group with the largest amount of data (deep >30 m) was used to compare Chalk and Permo Triassic Sandstone (PTS). For this group 647 sites are assigned to Chalk and 372 to PTS. To put this in context there are 11,546 detections of MOs within the Chalk sites and 2547 detections within PTS sites. However it is possible to make some general observations by looking at the percentage of detections for a compound within the same setting for different aquifers. For the unconfined deep class, atrazine (pesticide) accounts for 1.96% of overall detections within the PTS while within the Chalk it is nearly 3 times that at 5.79%. Caffeine detections in the PTS accounted for 1.25% of detections similar to the Chalk at 1.02%. BPA (plasticiser) accounted for 1.37% of PTS detections and nearly half those in the Chalk at 0.71%. Cyclohexanone (other industrial) accounted for 2.04% of detections within PTS which was considerably greater than that in the Chalk of 0.65%. These findings reflect both the long residence times in the deeper Chalk, with the legacy of atrazine applications and the greater urbanised areas of the PTS.

3.5. Trends

Although a large monitoring dataset, it did not provide sufficient data for any compound for one site to determine a trend. Very few compounds have been sampled for at the same site more than 5 times. This is well below the number of values suggested as a minimum by Stuart et al. (2007) to establish a trend. Instead a qualitative assessment of temporal trends within the dataset was undertaken for the following

compounds: TCE, tributyl phosphate, atrazine, caffeine, DEET, BPA and chloroform. These compounds were selected on the basis of high frequencies of occurrence (see Top 30 section). It is difficult to establish whether there are clear trends due to:

- Irregular sampling frequency and data gaps
- Step changes which are attributed to changes or improvements in the analytical method.

Table 3 summarises trends in these datasets. It is likely that apparent trends in these data are artefacts due to changes in the density of monitoring sites or frequency of visits related to budgetary controls and to analytical method improvements. The characteristics of long-term observations and record keeping have serious implications for the interpretation of long-term observation datasets. There is a need to:

- Clearly document any and all changes to the methods of analysis or sampling during the length of the dataset
- Plan to sample the same sites consistently at consistent intervals
- Identify key determinands/sites where sampling should be continued at the expense of other sites.

4. Wider implications

4.1. Identification of key compounds

Comparison with other national surveys starts to allow us to identify key emerging contaminants either by ubiquity or by presence at high concentrations. In this study the majority of MOs detected are established pollutants, and already classed as priority substances: atrazine and its daughter products, chloroform and other THMs, PCE and TCE, PAHs, DEHP, BPA and nonylphenol. Of the emerging pollutants, caffeine is the most commonly detected (8–80%) together with DEET, BBSA and tributyl phosphate.

Concentrations of TCE, PCE and BBSA found in this study are considerably higher than in other studies apart from vinyl chloride by Meffe and de Bustamante (2014). However, overall the frequency of detection is much lower. The range of compounds found at high concentrations varies between studies and presumably contains a number of random spikes.

The widespread detection of chloroform in many studies has perhaps given the impression that mains leakage is the only source of a range of volatiles in groundwater. However as previously stated both aerial deposition (Baehr et al., 1999b) and natural production of chloroform by plants and soil bacteria (Baehr et al., 1999a) have been proposed as contributing sources. Both of these mechanisms could account for the puzzling detections of chloroform in natural and forested areas.

4.2. Monitoring strategy

Any changes over the period of the record, including both any of the sampling programme changes in terms of number of sites and frequency of visits along with the changes within laboratory analysis, need to be carefully documented and included within the database. This will add to the existing challenges of nationwide, long-term data observation recording but will add to the versatility and confidence of long-term trend analysis. This is especially important where compliance with WFD and Habitats EU Directives require evidence of the long-term improvements or prevention of deterioration of the water body status. For the establishment of trends in the study dataset, should the scope of the existing programme be reduced due to budgetary restraints at some time in the future, it would be desirable to maintain current monitoring frequency at a focussed selection of monitoring points.

Table 3
Summary of timeseries data for selected compounds.

Compound	Date range	Trend	Comments
Chloroform	2002–2010	Increase in the frequency of detection and concentration with highest recorded in 2009 and subsequent fall between 2009 and 2010	Step change and data gap in 2010
BPA	2004–2012	2009–2011 increasing trend	Many fewer detections in the period between 2004 and 2009 than the following 4 years
Caffeine	2004–2012	2004–2007 increasing trend 2008–2010 overall decreasing trend	Gap in early 2010 with data appearing again in latter part of the year
TBP	2004–2012	Slight decreasing trend over the whole dataset	Greater number of detections were found in the time period 05–08 with fewer for 09–12
DEET	2004–2012	2008–2010 decreasing trend 2011–2012 increasing trend	
Atrazine	2004–2012	Declining overall trend in both frequency and concentrations of detections from 2004 to 09 period when comparing to the subsequent 2 years	
TCE	2002–2012	No trend	

This study has shown that although land-use has a direct control on the types of contaminants found in groundwater, some compounds are very persistent in the subsurface environment (as demonstrated by atrazine and its by-products still being detected years after withdrawal from use). Land-use changes and other measures undertaken to improve the status of groundwater bodies under the WFD may take a significant time to show the desired improvements.

Although we may now be gaining a good understanding of legacy contamination in groundwater, current surface activities may be causing problems for the future. With ever improving methodologies, we will become able to detect further compounds within the aquatic environment and be better able to establish toxicological risks to receptors within the environment. To minimise the risk of new problem compounds, the need for broad screening monitoring is clear and, together with new toxicology data, could inform decision makers to prescribe realistic limits.

4.3. Policy implications

In order to prioritise monitoring and potential regulation of emerging contaminants in the aqueous environment, information on frequency and concentration of detections and on risk to receptors from these compounds is needed. Data from the reported survey contributes to our understanding of the distribution of such compounds. However, despite the wealth of monitoring data from the present study, we still know relatively little about variations in concentration over time for individual compounds and further data will be needed to establish these. Modelling of the behaviour of such compounds in the subsurface is developing quickly and this may provide another approach in the future.

Lopez et al. (2015) have put forward a practical approach based on a strategy matrix using frequency of detection plotted against the 95th percentile of concentration divided by either the threshold of regulation or the threshold of toxicological concern, to identify high concern chemicals in French groundwater. Groundwater regulatory thresholds were determined by a combination of drinking water limits, World Health Organisation (WHO) recommended limits and extrapolated surface water Environmental Quality Standards (EQSs). At this stage the threshold of toxicological concern was set at 100 ng/L. Amongst currently unregulated compounds this approach identified acetaminophen, BPA, caffeine, metformin and tolyltriazole. Also appearing in this category were the regulated compounds atrazine, desethyl atrazine, desisopropyl atrazine, desethyl desisopropyl atrazine, bentazone and DEHP. On the margins were PFHS, PFHxA, PFOS, simazine, cotinine and oxadixyl. This approach will need some real toxicological data rather than using the arbitrary 0.1 μg/L limit originally developed for pesticides and representing the lowest concentration that could be quantified at the time the regulations were developed. Stuart et al. (2012) touch on the type of data which would be required to assess for thresholds for groundwater. These include toxicology, dispersion tendency, persistence and bioaccumulation potential.

Broad screening methods such as that employed in this study will form an important part of future water quality monitoring which supplement ongoing regulatory monitoring programmes undertaken by EU member states. These supplementary monitoring programmes will continue to assist in the development of a 'Watch List' for emerging pollutants in groundwater which do not currently have water quality limits. Further work is needed to ascertain if the current watch list devised for surface waters is suitable for groundwater receptors, or if a separate watch list (for groundwater) is required given the potential differences in contaminant pathways and sources.

5. Conclusions

- This study provides a unique assessment of the long-term observations derived from a water quality dataset of national significance. Compounds found at the highest frequency included atrazine and its degradation products, simazine, PAHs, caffeine, chlorinated solvents, chloroform and BPA. In contrast those found at the highest concentrations were chlorinated solvents, THMs, plasticisers, 2-mercaptobenzothiazole, diazinon and nonylphenol.

- Spatial pesticide detections broadly correspond to the areas where these compounds are likely to have been used in agriculture and also highlight the persistence of these compounds in the subsurface. In contrast the distribution of caffeine concentrations highlights areas that are subject to urban impact.

- There are clear differences in both types of compounds and concentrations found within different land-use types on a national scale. Natural land-use had the smallest number of compounds detected and at lower concentrations compared to other land-use classes. The Urban Industrial type had some of the highest concentrations recorded overall with chlorinated solvents dominating.

- Differences between aquifers are less clear. In the four important aquifers selected for this study the Chalk had the highest concentrations and the Lower Greensand the lowest, with the Permo-Triassic sandstone and the Jurassic limestones being similar. These differences are likely to be related to aquifer flow mechanisms and land-use controls by topography

- Identification of long-term trends in the future is possible with consistent monitoring at the minimum of a focussed subset of sites at regular intervals building on the existing dataset and ensuring inclusion of information on analytical method changes.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.03.017.

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