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Emerging organic compounds in European groundwater[☆]

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ABSTRACT

In Europe, emerging organic compounds (EOCs) in groundwater is a growing research area. Prioritisation for monitoring EOCs in Europe was formalised in 2019 through the development of the first voluntary groundwater watch list (GWWL). Despite this, groundwater occurrence data in the peer reviewed literature for Europe has not been reviewed to date. Questions surrounding the effect, toxicity, movement in the subsurface and unsaturated zone make the process of regulating EOC use difficult. The aim in Europe is to develop a unified strategy for the classification, and prioritisation of EOCs to be monitored in groundwater. This paper compiles evidence from the recent published studies from across Europe, since 2012, when the last major literature global review of EOCs in groundwater took place. A total of 39 studies were identified for review based on specific selection criteria (geography, publication date, sample size>10, inclusion of EOCs data). Data on specific compounds, and associated meta-data, are compiled and reviewed. The two most frequently detected EOCs, carbamazepine and caffeine, occurred in groundwater at concentrations of up to 2.3 and 14.8 μg/L, respectively.

The most frequently reported category of compounds were ‘Pharmaceuticals’; a highly studied group with 135 compounds identified within 31 of the 39 studies. In Europe, the majority of reviewed studies (23) were at a regional scale, looking specifically at EOCs in a specific city or aquifer. The use of analytical methods is not uniform across Europe, and this inevitably influences the current assessment of EOCs in groundwater. A correlation between the number of compounds analysed for, and the number detected in groundwater highlights the need for further studies, especially larger-scale studies throughout Europe. For the development of EU and national regulation, further work is required to understand the occurrence and impacts of EOCs in groundwater throughout Europe and elsewhere.

1. Introduction

The term Emerging Organic Contaminants (EOCs) (Stuart et al., 2012) is used to describe organic contaminants that are not yet regulated, but may be of current or future concern. Although defined as emerging, they may not be new contaminants, but only recently detected using improved sampling and analytical methods (Daughton, 2004), or of rising concern regarding new toxicological data. The term ‘emerging’ is therefore used in this review in the context of compounds of emerging concern. The number of EOCs is expected to increase as analytical methods develop, and new compounds continue to be released into the environment. The threat to human health has been extensively researched over the past few years (Pal et al., 2014; Pereira et al., 2015) but often requires a greater understanding of the presence, attenuation, transport and uptake of EOCs into drinking water for human exposure.

The European Commission’s Groundwater Directive (European Commission, 2006) sets out to ‘prevent and control groundwater pollution’ by a number of contaminants. However, there are no

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formal regulations to control, monitor, or report contaminants of emerging concern in groundwater. In 2014, an amendment to Annex II of the Groundwater Directive stated that a lack of information meant that new groundwater quality standards could not be set for any pollutants (European Commission, 2014). The amendment (European Commission, 2014) highlighted the need to ‘obtain new information on other substances posing a potential risk’ and this should be implemented by means of a ‘Groundwater Watch List’ (GWWL) (Voluntary Groundwater Watch List) which was first implemented in 2019 through the European working group groundwater (CIS) (Voluntary Groundwater Watch List; Lapworth et al., 2018). A major component of the GWWL is prioritisation of compounds, a dynamic process where their use, properties and hazards are considered within a prioritisation framework (Gaston et al., 2019). This is also one of the main conclusions of the OECD workshop on Managing Contaminants of Emerging Concern held on the 5 February 2018 (OECD, 2018). To improve our knowledge of EOCs and facilitate regulation, it is important to understand EOC occurrence, movement, fate, toxicity and impacts in the environment (Ghattas et al., 2017; Lapworth et al., 2018).

EOCs are often categorised by their use, rather than occurrence, transport properties or impact on the environment (Jurado et al., 2012; Lapworth et al., 2015; Sorensen et al., 2015; Manamsa et al., 2016a; Mali et al., 2017). Research studies often target one of the major usage groups, screening for selected compounds within the identified category (e.g. Bono-Blay et al., 2012; Hass et al., 2012a, b; Hillebrand et al., 2012; Paíga and Delerue-Matos, 2016; Kivits et al., 2018), limiting costs and time. However, there is sometimes significant difficulty in categorising compounds into one of these groups, especially when they may belong to more than one grouping (e.g. a number of solvents/industrial compounds). In this review, the detected compounds are categorised based upon an assessment of categories presented in the selected studies, and where this was divergent in the literature an element of expert opinion by the authors. This is not necessarily a final categorisation, but offers a basis from which to analyse the frequency of detection of different compounds.

Compared to surface water, studies of EOCs in groundwater are relatively novel, with few large-scale studies focusing on the subsurface environment e.g. (Bono-Blay et al., 2012; Lapworth et al., 2012; Lopez et al., 2015; Brueller et al., 2018). Although there are an increasing number of national-scale reviews on the occurence of EOCs in groundwater (Van Der AA et al., 2013; Petrie et al., 2015; Banzhaf et al., 2017; Cunha et al., 2017; Juliano and Magrini, 2017; Tiedeken et al., 2017); there remains no European scale review to understand the state of the science on a larger scale.

Building on previous global reviews (Lapworth et al., 2012), this paper compiles evidence from the most recent studies (since 2012) on EOCs in groundwater in Europe. The aims are to (1) understand the current state of knowledge on EOCs in Europe and the developments in recent years, (2) understand the different methods for sampling and analysing EOCs in Europe, (3) highlight ongoing research and further areas for research necessary to develop a picture of EOCs in Europe.

2. Methods

The studies included in this review were selected based on a number of criteria, explained in detail in the methods section of the Supplementary Information. These criteria were developed to identify a range of studies that would provide a overview of the current state of knowledge in the field of EOCs in European groundwater.

Using these criteria, a total of 39 studies from 16 European countries were selected for this review (Table 1).

Limitations to this review include the difference in reporting styles between European countries where the same information and level of detail is rarely reported. This is developed further in the methods section of the Supplementary Information.

3. Review

3.1. Current state of knowledge

Since the first major global review in 2012 (Lapworth et al., 2012) there have been developments in the field of EOCs in groundwater. For example, Balderacchi et al. (2014) report on the GENESIS project, which suggested amendments to the Groundwater Directive. They highlight an increasing concern about emerging contaminants and the need for monitoring for the formulation of conceptual models and the eventual improvement of legislation. Furthermore, after the implementation of threshold values across EU member states, they suggest a consistent monitoring protocol.

Studies have attempted to identify the risk to human health due to exposure to EOCs in drinking water from both surface and groundwater sources. Schriks et al. (2010) highlight a large buffer between the maximum concentration detected and provisional guideline values for a range of 50 EOCs, but many others remain unstudied. Furthermore, toxicology studies must move towards studies where multiple EOCs are present, rather than just one, as this is likely to impact the overall assessment on human health due to the presence of ‘Chemical Mixtures’ (Pereira et al., 2015). Pal et al. (2014) highlight the need for EOCs to be included in water quality models to further understand the impacts to ecosystems and the environment, but a deeper understanding of the kinetics and transformation processes undergone by EOCs is not readily available.

Previous efforts have been made to prioritise emerging compounds in surface waters including von der Ohe et al. (2011), and a list of hazardous or non-hazardous pollutants in groundwater published by JAGDAG (Joint Agencies Groundwater Directive Advisory Group) (2017) outlining the determination of these substances, using toxicity, persistence and potential to bioaccumulate. However, the 2014 amendment to Annex II of the Groundwater Directive encouraged an increase in research into organic contaminants, with the purpose of implementing management levels/concentrations for currently unregulated compounds in groundwater. One major step towards a unified understanding of the potential threat of EOCs was through the Groundwater Watch List (GWWL) (Voluntary Groundwater Watch List), developed in response to the 2014 European Commission call for increased monitoring (Lapworth et al., 2018). The voluntary GWWL broadly mirrors the mandatory surface water watch list (SWWL) (Carvalho et al., 2015a, b) in its aims and structure, where the GWWL acts to identify and monitor currently unregulated contaminants in European groundwater. The GWWL collates European monitoring data on EOCs that pose a threat to health or the environment, producing a list of substances ordered by their occurrence, potential to move toward groundwater (persistence and mobility) and toxicity (Lapworth et al., 2018). The process was documented so the list can be updated as studies further the knowledge about these attributes for different EOCs. The first GWWL contained 2 perfluoroalkyl and polyfluoroalkyl substances (PFAS) (PFDoA and PFUnA), and 9 pharmaceutical compounds (clopidol, crotamiton, amidozoic acid, sulfadiazin, primidone, sotalol, ibuprofen, erythromycin and clarithromycin). A further 4 PFAS compounds were considered further candidates for the list (4:2 monoPAP, PFDPA, PFOPA, 6:2 monoPap).

A diversity of studies is necessary in order to increase the

Table 1
Reviewed studies, including the number of groundwater sites, samples and the categories of compounds detected.

Ref	Year	Country	Scale of study	Number of groundwater sites	Number of (groundwater) samples	Our use categories of compounds detected
Brueller et al.	2018	Austria	National	22	22	Plasticisers, Industrial
van Driezum et al.	2019	Austria	Targeted	7	22	Pharmaceuticals, Industrial
Hrkal et al.	2018	Czech Republic	Targeted	6	6	Pharmaceuticals, Lifestyle, Other EOCs
Lapworth et al.[a]	2015	England/France	Regional	345	345	PCPs, Pharmaceuticals, Solvents and THMs, Plasticisers, Industrial, Lifestyle
Ahkola et al.	2017	Finland	Regional	6	Unknown	Pharmaceuticals
Lopez et al.	2015	France	National	494	988	PCPs, Pharmaceuticals, Solvents and THMs, Plasticisers, Industrial, Lifestyle, Other EOCs
Pinasseau et al.	2019	France	Regional	5	10	Pharmaceuticals, PCP's, Lifestyle
Hass et al.	2012	Germany	Targeted	9	36	Pharmaceuticals
Hillebrand et al.	2012	Germany	Targeted	1	157 (Spring)	Pharmaceuticals, Lifestyle
Müller et al.	2012	Germany	Regional	21	46	Pharmaceuticals
Hass et al.	2012	Germany	Regional	123	369	Pharmaceuticals
Reh et al.	2013	Germany	Regional	44	163	Pharmaceuticals, Industrial, Lifestyle
Spielmeyer et al.	2017	Germany	Targeted	4	88	Pharmaceuticals
Estevez et al.	2016	Gran Canaria	Targeted	7	37	Industrial, Solvents and THMs, Pharmaceuticals, Other EOCs
Nagy-Kovács et al.	2018	Hungary	Targeted	2	30	Industrial, Pharmaceuticals, Lifestyle
Pignotti et al.	2017	Italy	Regional	Unknown	17	None detected
Castiglioni et al.	2018	Italy	Regional	53	53	Pharmaceuticals, PCP's Lifestyle, Industrial
Banzhaf et al.	2012	Luxembourg	Targeted	5	47	Pharmaceuticals, Lifestyle
Kapelewska et al.	2016	Poland	Targeted	2	16	PCP's, Lifestyle, Other EOCs
Kapelewska et al.	2018	Poland	Targeted	8	23	Pharmaceuticals, PCP's, Lifestyle, Other EOCs
Carvalho et al.	2015	Portugal	Regional	13	13	Pharmaceuticals, Industrial, Other EOCs
Paíga, & Delerue-Matos	2016	Portugal	Targeted	5	10	Pharmaceuticals
Koroša et al.	2016	Slovenia	Regional	14	56	Pharmaceuticals, Industrial, Lifestyle
Mali et al.	2017	Slovenia	Regional	15	28	Pharmaceuticals, Solvents and THMs, Lifestyle Plasticisers, Industrial, Other EOCs
Bono-Blay et al.	2012	Spain	National	131 (or 91)	131 - 40 springs and 91 boreholes	Industrial, Plasticisers
Jurado et al.	2012	Spain	Regional	36	36	Lifestyle, Pharmaceuticals
Estévez et al.	2012	Spain	Regional	4	14	Pharmaceuticals, Lifestyle, Industrial, Solvents and THMs, Other EOCs
López-Serna et al.	2013	Spain	Regional	31	31	Pharmaceuticals
Jurado et al.	2014	Spain	Regional	31	31	PCP's
Jurado et al.	2014	Spain	Regional	26	26	Pharmaceuticals
Luque-Espinar et al.	2015	Spain	Regional	12	85	Pharmaceuticals, Lifestyle
Corada-Fernández et al.	2017	Spain	Regional	29	57	PCP's, Pharmaceuticals, Lifestyle, Other EOCs
Filipovic et al.	2015	Sweden	Targeted	16	16	Industrial
Eschauzier et al.	2013	The Netherlands	Regional	7	15	Industrial
Kivits et al.	2018	The Netherlands	Regional	10	46	Pharmaceuticals
Stuart et al.	2014(b)	UK	Regional	19	54	PCPs, Pharmaceuticals, Solvents and THMs, Plasticisers, Industrial, Lifestyle
White et al.	2016	UK	Regional	3	37	Solvents and THMs, PCP's, Plasticisers, Industrial, Other EOCs
Manamsa et al.	2016	UK	Regional	6	78	Plasticisers, PCPs, Pharmaceuticals, Solvents and THM's, Industrial, Lifestyle
Manamsa et al.	2016	UK	National	2650	2650	PCPs, Pharmaceuticals, Solvents and THMs, Plasticisers, Industrial, Lifestyle, Other EOCs

[a] Only groundwater from Chalk aquifers in England and France were included.

available data in a particular field of science. Large-scale studies usually report on the presence of compounds across national or continental scale. Regional and local scale monitoring is also important to understand the spatial and temporal variations in the occurrence of EOCs. Loos et al. (2013) reported on a pan-European study of 164 wate water treatment plant (WWTP) effluent samples from 23 countries completed in 2010, with particular attention to persistent organic pollutants. This study did not meet the criteria for this review due to the study of manmade effluents rather than natural groundwaters (see SI for further details on methods used to undertake this review). Since then, a number of countries have developed national scale data sets monitoring EOCs in groundwater (e.g. Bono-Blay et al., 2012; Lopez et al., 2015; Manamsa et al., 2016a).

3.2. Compound categorisation

Apart from pesticides, there is no current standard for the categorisation of contaminants in groundwater, making it potentially more difficult to identify which areas or groups of compounds need further study or a particular focus. As previously mentioned, categorisation is commonly by usage, but compounds can be categorised differently depending on the scale of the study and the area of research the study comes from. Primarily, sub-categories exist if a study is only focused on one dominant use category. These can help to build a picture of the anthropogenic uses of the contaminants, and often their sources; offering more detail than the larger scale groupings. It is important to understand what categories have been most commonly used, so these can be adapted and used to develop a more uniform classification for EOCs.

Not only does the categorisation of compounds need to be ascertained, but the terminology and size of classification group. For example, drugs of abuse are reported by Jurado et al. (2012) but may also be termed illicit drugs, as reported by Castiglioni et al. (2018). Eschauzier et al. (2013) report perfluorinated alkylated acids (PFAAs) as a category and Castiglioni et al. (2018) report perfluorinated compounds. There are discrepancies in the classification of compounds throughout Europe. Table S1 highlights a number of compounds that have irregular classifications, and how they have been classified for this review.

From a total of 39 studies considered, 36 categorise the compounds that are detected and 3 do not. Where compounds are not categorised in the literature, the study tends to look for individual target compounds. Targeting compounds in this way may reflect the nature of the study, the analytical methods that are available to the researchers, or follow an existing scoping study that highlighted compounds of concern at the site of interest.

Apart from usage, other categorisations include the potential hazards of the compounds or their source. Three studies look at endocrine disrupting compounds (EDCs) (Carvalho et al., 2015a, b; Corada-Fernández et al., 2017; Pignotti et al., 2017), or Endocrine Disrupting Chemicals in (Brueller et al., 2018) a hazard classification which includes sub-groups such as PFAA's, synthetic hormones (e.g. estrone, estradiol, 17α-ethinylestradiol) and phenols (e.g. bisphenol A, octylphenol, mestranol and nonylphenol).

An example of a use category reported was anthropogenic markers and anthropogenic contaminants (Castiglioni et al., 2018). These are primarily compounds such as caffeine and nicotine, otherwise known as lifestyle compounds that are found in high concentrations in and around densely populated or urban areas.

3.2.1. Categories used

In total 7 categories were used and proposed (Table S2), where the categories are primarily based upon the frequency of usage within the reviewed studies. Table S2 also shows the number of compounds placed into each category, and the total number of studies in which these compounds were detected. Where the group contained less than 10 compounds, these were added to the category 'Other EOCs' to prevent the overrepresentation of small categories.

3.3. Summary statistics of review studies

Summary statistics from the 39 studies were compiled to understand how EOCs have been studied across Europe. This review identifies all compounds recorded in the reviewed studies where EOCs are detected in groundwater. Any regulated compounds, such as those listed in Annex 2 of the WFD (2000/60/EC) were not considered EOCs for the purpose of this review study. For the purpose of this study, where possible, we have included compounds below the Limit of Quantification (LOQ), but above the Limit of Detection (LOD), as well as tentative detections. CAS numbers were assigned by cross-referencing the compounds with established lists e.g. NORMAN list of emerging contaminants (Dulio and Slobodnik, 2009). The categorisation adopted by the studies and known applications were used to establish a categorisation for each of the compounds detected. This is not a definitive list, but enables a greater understanding of what groups of compounds have been detected in the European studies.

It was not possible to identify all compounds detected within the reviewed studies, often due to a lack of detail in reporting, meaning not all compounds in the 39 studies are included in further analysis. Furthermore, Ahkola et al. (2017) highlight the problem of Limit of Quantification (LOQ) vs Limit of Detection (LOD). We have used their notation < LOQ differently to n.d. (no detects), and assume in this case that compounds < LOQ are detected and those with n.d. are below the LOD. These studies highlight the problem of differences in reporting between European countries, making an analysis of data across Europe challenging.

3.3.1. Distribution of studies

The distribution of studies (39) published since 2012 throughout Europe helps to understand the scale of the study area, and how this is developing spatially (Table 1; Fig. 1).

Fig. 1 (a) highlights the distribution of the studies included in this review on a European scale. The largest number of studies were located in Spain (8), followed by Germany (6). Fig. 1 (b) shows the total number of groundwater sites considered, using a summation of the number of sites used in each study within a given country. It must be noted that this does not represent the actual number of individual sites investigated, and a lack of site information means it may not be possible to determine the actual number of discrete sites used. Groundwater sites is used here to reflect only the number of individual boreholes or wells sampled, even though some sites record at different well depths. In total 4222 groundwater sites were reported, with a total of 5395 groundwater samples taken from those sites. There are still a large number of countries that have not produced publications that fits the necessary criteria to be included in this review. It may be that studies have not been carried out in these countries, they are only small scale studies, or may not be published in international journals.

3.3.2. Sampling methods

Samples are primarily taken as grab samples from existing monitoring boreholes in the studies. However, other approaches such as passive sampling (PS) can be used to determine the presence of certain EOCs (Cerar and Mali, 2016; Ahkola et al., 2017; Mali et al., 2017; Pinasseau et al., 2019). These time-integrated methods are helpful for gathering reconnaissance data on the occurrence of EOCs in groundwater, particularly where these may be more temporally dynamic in terms of contaminant occurrence. Most of the studies used POCIS (polar organic compounds integrative samplers) tools or solid disk based passive sampling (Ahkola et al., 2017; Pinasseau et al., 2019), since they are dedicated to polar to mid-polar compounds. Other passive sampling for a larger range of compounds have been developed (Mali et al., 2017), however, there are difficulties in comparing data from passive sampling and grab sampling approaches, for example, there are in-built assumptions required for translating passive sampling data to equivalent concentration data and there may be site-specific considerations/calibration of passive sampling required. Furthermore, low groundwater levels may limit contact time and can affect accumulation capabilities of the passive sampling. In light of these factors, the main use of passive sampling in groundwater is as a screening tool, rather than for quantitative assessments.

Regulatory monitoring typically follows a grab sampling protocol and it would be likely that this would be the case for EOCs in groundwater, at least for some time, particularly as in general residence times for groundwater are long, in the order of years to decades in most settings (Moreau et al., 2019) and aquifers can be

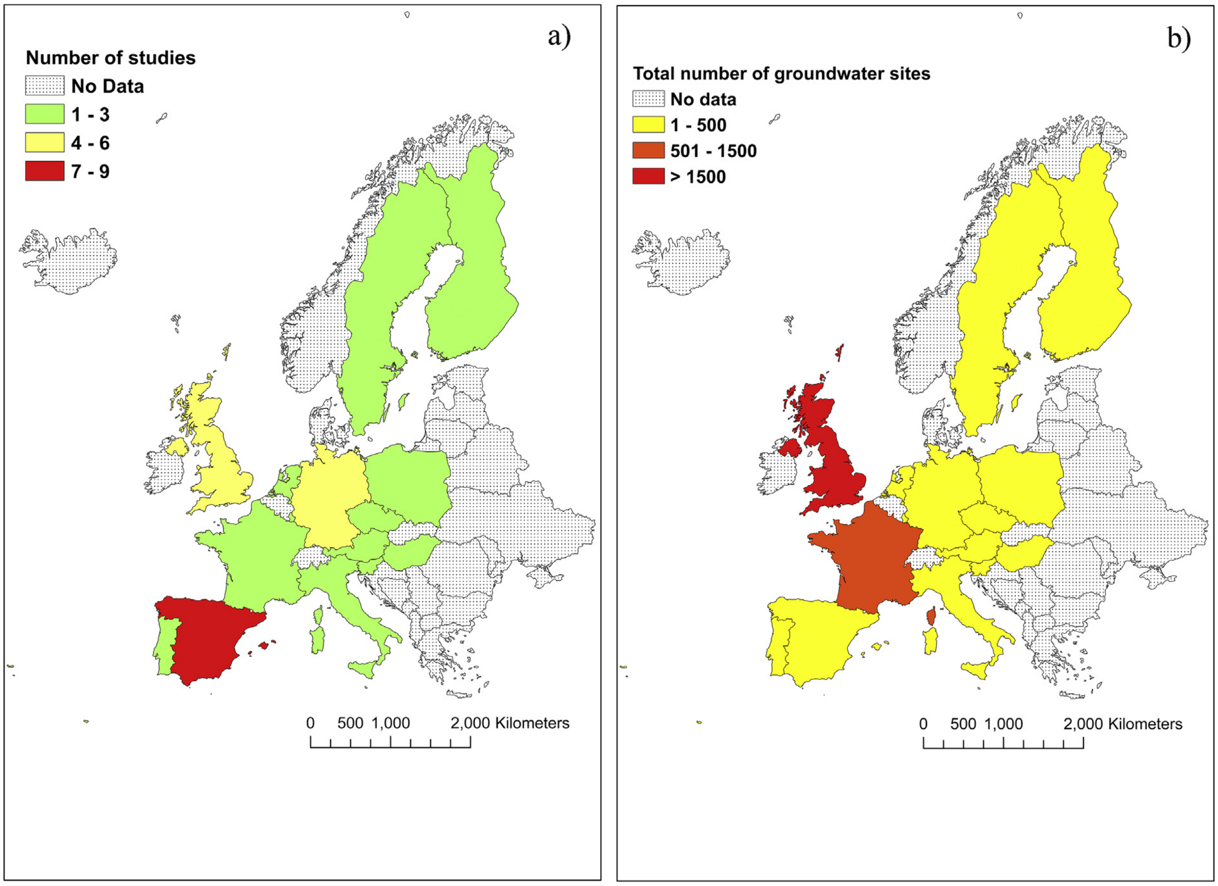

Fig. 1. EOC results for groundwater studies in Europe: (a): The number of studies used in this review from each country. (b) The total number of groundwater sites from the selected review studies. [Base map: Esri. Scale Not Given. "World Countries". January 2015. https://www.arcgis.com/home/item.html?id=ac80670eb213440ea5899bbf92a04998 (May 1, 2019)].

considered as cumulative receptors of EOCs.

Peer reviewed literature often reveals little information about the sampling regime undertaken. A number of studies complete sampling rounds at regular intervals throughout the year, some with high frequency (Hillebrand et al., 2012) and others just a single sample at multiple sites (Bono-Blay et al., 2012). Often a campaign during the summer and winter seasons are taken to reflect different groundwater table level states, for example, Jurado et al. (2014a), Lopez et al. (2015), during which different groundwater levels may affect the type and concentration of compounds detected.

3.3.3. *Analytical methods*

3.3.3.1. Preparation/extraction. In the reviewed studies, the primary analytical method implemented was solid-phase extraction (SPE), but in some cases, other methods were employed. SPE offers the benefit of extracting compounds with a wide range of properties (Martín-Pozo et al., 2019). Other methods of extraction include pressurised liquid extraction (PLE) and liquid-liquid extraction (LLE) (Estévez et al., 2012; Lopez et al., 2015; Manamsa et al., 2016b) but also more novel approaches such as ultrasound-assisted emulsification micro extraction (USAEME) (Kapelewska et al., 2016, 2018). Where passive sampling techniques are used, the extraction method is based on SPE.

3.3.3.2. Review of analytical methods. The principal analytical methods used in the studies for EOC analysis is liquid chromatography (LC) and gas chromatography (GC) coupled to mass spectrometry (MS) (Koroša et al., 2016; Mali et al., 2017; Martín-Pozo et al., 2019).

Some substances require more work to analyse than others, for example, certain PFAS compounds owing to their range of chain lengths and characteristics. Recent developments in analytical methods make screening for a large number of compounds more cost effective (Richardson and Ternes, 2017).

Petrie et al. (2015) highlight the problem with targeted screening and low resolution mass spectrometry, meaning that some metabolites are often missed, whose impacts may equal or surpeass the parent compound. Due to the large numbers of compounds detected, multiple methods are often employed within the same study e.g. Jurado et al. (2012), Stuart et al. (2014), and Lapworth et al. (2015).

High resolution mass spectrometry analysis allows conventional quantitative analysis (Brueller et al., 2018), but the development of large-scale qualitative screening methods, (Pinasseau et al., 2019), with no target compounds. allows new compounds of interest, such as EOCs transformation products, to be identified in groundwater.

3.3.3.3. Analytical methods used. Twenty-one different methods are cited in the studies, and listed in Table 2. The most popular methods are LC-MS and GC-MS methods, which both suit a wide range of compounds. The analytical method used depends on the type of EOC that has been screened for. Samples may be screened for a few specific EOCs of interest e.g. Hass et al. (2012b) and Müller et al. (2012) or a full suite of over 1000 different compounds and metabolites e.g. Manamsa et al. (2016b); White et al. (2016).

Table 2
Analytical methods used by the reviewed studies where these were reported in the associated paper.

Methods	Reference
Gas chromatography with mass spectrometry or tandem mass spectrometry (GC-MS) or (GC-MS/MS)	(Bono-Blay et al., 2012, Cabeza et al., 2012, Estévez et al., 2012, Jurado et al., 2014a, Stuart et al., 2014b, Estévez et al., 2016,Lapworth et al., 2015, Lopez et al., 2015; Kapelewska et al., 2016, 2018, Cerar and Mali, 2016, Koroša et al., 2016; Manamsa et al., 2016a, 2016b, Pitarch et al., 2016, White et al., 2016, Corada-Fernández et al., 2017, Brueller et al., 2018, Hrkal et al., 2018)
Liquid chromatography with mass spectrometry or tandem mass spectrometry (LC-MS) or (LC-MS/MS)	(Banzhaf et al., 2012, Cabeza et al., 2012, Estévez et al., 2012; Hass et al., 2012a, 2012b, Hillebrand et al., 2012; Jurado et al., 2012, 2014a, 2014b, Eschauzier et al., 2013, López-Serna et al., 2013, Reh et al., 2013, Carvalho et al., 2015a, b, Lapworth et al., 2015, Lopez et al., 2015, Antonio Luque-Espinar et al., 2015, Filipovic et al., 2015, Pitarch et al., 2016, Ahkola et al., 2017, Pignotti et al., 2017, Spielmeyer et al., 2017, Corada-Fernández et al., 2017, Brueller et al., 2018, Castiglioni et al., 2018, Hrkal et al., 2018, Kivits et al., 2018, Pinasseau et al., 2019, Van Driezum et al., 2019)
Liquid chromatography High resolution mass spectrometry (LC-TOFMS)	(Estévez et al., 2012; Pinasseau et al., 2019)
Gas chromatography—high resolution mass spectrometry (GC/HRMS)	Lopez et al. (2015)
Liquid chromatography—high resolution mass spectrometry (LC/HRMS)	Müller et al. (2012)
Continuous Flow Analysis	Lopez et al. (2015)
Semi-prep LC system with a diode-array detector (LC/DAD)	Lopez et al. (2015)
Chemical Ionization Mass Spectrometry (CI-MS/MS)	Lopez et al. (2015)
Ion chromatography	Lopez et al. (2015)

3.3.4. Screening for EOCs

In the reviewed studies, the average number of compounds screened for was 170, the largest being >1000 (Stuart et al., 2014b; Manamsa et al., 2016b; White et al., 2016) and the smallest being 4 (Hillebrand et al., 2012; Filipovic et al., 2015). Fig. 2 shows the cumulative distribution of the number of compounds screened for in the 39 reviewed studies. The largest category is the 10–100 range, representing intermediate studies where a category of compounds may be investigated or known existing EOCs are targeted (Fig. 2, Fig. S1). The number of compounds screened for does not necessarily represent the scale of the study, but may be the associated budget and aims of the study. For example, whether it is targeted study towards a few compounds, or a scoping study with a much larger number of compounds.

There appears to be no strong relationship between year and the number of compounds screened for (Fig. S2). Large-scale national studies that fit the review specifications were primarily completed in the years 2014–2017. More recently, the studies show smaller numbers of compounds are screened for, which may suggest a more targeted approach following earlier scoping studies, or the desire to characterise a few targeted compounds in more detail. These results suggest that there is an array of research taking place, both large scoping studies, and smaller, more targeted ones.

In Fig. 3a there is no strong relationship between the number of compounds detected and the number of groundwater sites in the study. Spearman's Rank correlation shows a weak negative correlation between the two variables, where $\rho = -0.26$, likely reflecting the range in results obtained from a number of large studies with around 1000 sites. Fig. 3b shows there is a strong tendency for the number of detected compounds to increase with the number of compounds screened for ($\rho = 0.89$). This is likely due to the targeted nature of the smaller scale studies, where a previous scoping study or identified target means that there is a higher hit rate of EOCs in groundwater. These results highlight the need for a prioritisation approach; showing that simply increasing the number of sites and compounds screened for will not always increase the number of detects. The number of groundwater sites and number of compounds screened have a moderate negative Spearman's Rank correlation ($\rho = -0.45$), highlighting the more detailed analysis that is carried out on smaller scale studies where fewer sites are sampled. However, we report only one study with 500+ groundwater sites (Manamsa et al., 2016a).

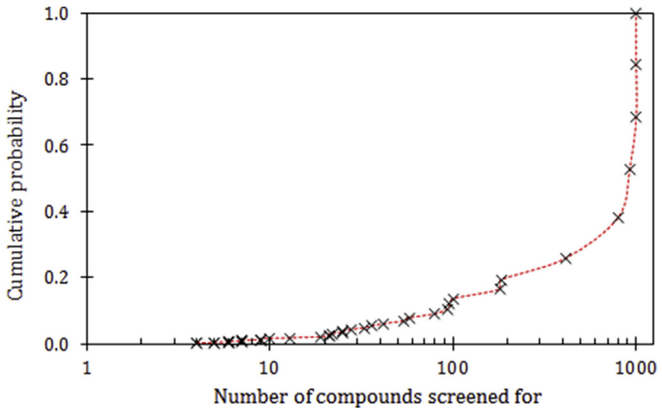

Fig. 2. Cumulative probability plot of number of compounds screened for.

Similarly, only a very weak correlation is observed between the number of groundwater sites in the 39 studies considered and the number of groundwater samples ($\rho = -0.14$) (Fig. S4), likely due to the range in scale of the studies. We might expect more targeted studies to have a smaller number of sites and therefore smaller number of samples. However, targeted studies are often sampled at a greater resolution as part of monitoring programmes (e.g. Hillebrand et al., 2012), whereas national scale groundwater EOC studies often only take samples from each site once or twice (e.g. Lopez et al., 2015).

Most of the reviewed studies do not report on their LOD and LOQ values, however large discrepancies are likely to exist in different countries and laboratories.

3.3.5. EOCs detected

Table 3 shows the top 10 compounds where one or more detections of the compound was reported in groundwater. Six of the top 10 are classified as pharmaceutical, 1 as lifestyle, 1 as a plasticiser, 1 as a personal care product and 1 as solvents and THMs (Table 3).

The GWWL incorporates hazard and toxicity, as well as prevalence, and is likely to prioritise these hazards over occurrence. Both carbamazepine and sulfamethoxazole were ranked in the top 25 pharmaceuticals and PFAS when both hazard and leaching were

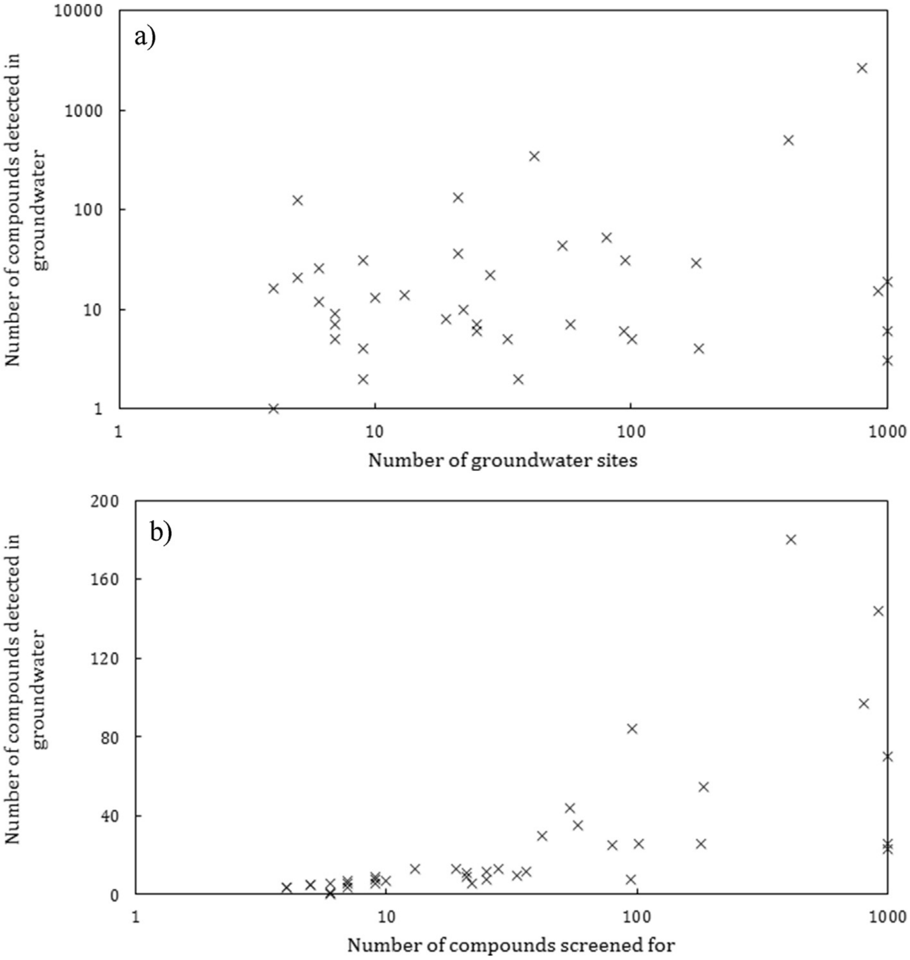

Fig. 3. (a) The number of groundwater sites sampled vs the total number of compounds detected in groundwater, and (b) The number of compounds screened for vs the number of compounds detected in groundwater.

Table 3
The top 10 compounds detected, their occurrence in number of studies in which they are detected, their use and proposed categorisation. Italics represent compounds also present in the GWWL (Voluntary Groundwater Watch List).

CAS	Compound	Number of studies reporting one or more detection	Use	Category
298464	*Carbamazepine*[a]	22	Anti-epileptic drug and other pharmaceutical applications	Pharmaceuticals
58082	Caffeine	15	Lifestyle	Lifestyle
723466	*Sulfamethoxazole*[a]	13	Antibiotics	Pharmaceuticals
80057	Bisphenol A	13	Plastics and resins for food packaging	Plasticisers
15687271	*Ibuprofen*	12	Anti-inflammatory agent with analgesic properties	Pharmaceuticals
103902	Acetaminophen (paracetamol)	9	Non-Prescription Drugs	Pharmaceuticals
134623	N,N-diethyl-m-toluamide	8	Insect repellent	PCPs
15307865	Diclofenac	8	Anti-inflammatory agent	Pharmaceuticals
108907	Chlorobenzene	8	Chlorinated solvent	Solvents and THMs
41859670	Bezafibrate	7	Lipid regulator	Pharmaceuticals

[a] Initially on the GWWL but there was adequate monitoring data for formal assessment under Annex.

considered, however, were reported in enough studies that they were removed from the initial GWWL to a list facilitating Annex I and II of the GWD, with enough evidence of potential groundwater contamination for a standard to be designed. Caffeine is widely reported, but due to its low toxicity, is not ranked highly on the watch list. Diclofenac is highly ranked in the GWWL methodology, ranking 21st in the list of pharmaceuticals considered for the watch list. Although the compound ranked highly in terms of leaching potential, the low hazard score and number of detections meant that it was not placed further up the list. Ibuprofen was also highly ranked, and the only compound in the top 10 detected compounds to be added to the GWWL (Voluntary Groundwater Watch List). The other 11 substances on the first GWWL watch list include the pharmaceuticals; clopidol, crotamiton and amidozoic acid, none of which are detected in any of the 39 reviewed studies. Since the publication of the GWWL, we would expect an increase in studies screening for these compounds, and an increase in the number of reported detections. Individual compounds in groundwater are generally found in sub µg/L concentrations (Lapworth et al., 2012) and are considered too low, by several orders of magnitude, to cause acute effects (e.g. Kim et al., 2009; Nunes et al., 2005). However, chronic exposure effects may be predicted at concentrations found in groundwater (e.g. Berninger and Brooks, 2010). The effect of compound mixing and low concentration detections, in groundwaters present remains largely unknown and needs further investigation.

Table 3 shows the number of individual compounds detected which have been assigned each category, and the number of studies that report a detection of one or more of the compounds in this category. A number of these compounds, shown to be detected in a high number of studies throughout Europe, were also considered for addition to the GWWL (Voluntary Groundwater Watch List). Carbamazepine, and sulfamethoxazole, were initially on the GWWL but it was found that there was adequate data for formal assessment under Annex I/II and were therefore removed from the first voluntary GWWL. This review corroborates some of the findings of the GWWL assessment, highlighting these as some of the most studied EOCs. Diclofenac and acetaminophen were also ranked highly on the GWWL assessment, but were not included in the final GWWL. Caffeine was ranked 4th on the GWWL ranking procedure that included PFAS and pharmaceuticals, but was removed because it poses a low potential risk to environment and health. Nonetheless, it has been widely used as a tracer of EOCs and waste water pollution in groundwater.

Fig. 4 shows the maximum reported concentrations of the two most widely detected compounds within our review studies. The maps show the maximum reported concentration, although this does not represent the background concentration in each country.

Carbamazepine is a widely prescribed anticonvulsant used to treat epilepsy, bipolar disorder, and trigeminal neuralgia (Banzhaf et al., 2012), but has been shown to threaten aquatic organisms (Oetken et al., 2005). Carbamazepine was detected in 22 of the 39 studies. The maximum reported concentration was 2325 ng/l (Müller et al., 2012), recorded in the vicinity of a waste water treatment plant (WWTP) where the groundwater is thought to be influenced by recent sewage water (Fig. 4a). In this study of pharmaceuticals as indictors of sewage-influenced groundwater, carbamazepine was reported in 20 of the 46 groundwater samples (43.5%). Hillebrand et al. (2012) reported that carbamazepine was detected in 57.3% of the 157 spring water samples taken, but was not quantified in any sample. The average sample recovery by the extraction method in the 21 groundwater studies that reported detections was 60.1%.

Caffeine was detected in 15 studies, where the maximum concentration was reported in a groundwater sample from southern Spain (Antonio Luque-Espinar et al., 2015) where a concentration of 14770 ng/L was detected in the vicinity of a wastewater treatment plant (Fig. 4b). Caffeine can fall into a number of EOC categories, but in this study has been classified as a lifestyle compound. The reported percentage of positive detections ranged between 3.1% (Manamsa et al., 2016a) and 100% (Pinasseau et al., 2019) of groundwater samples.

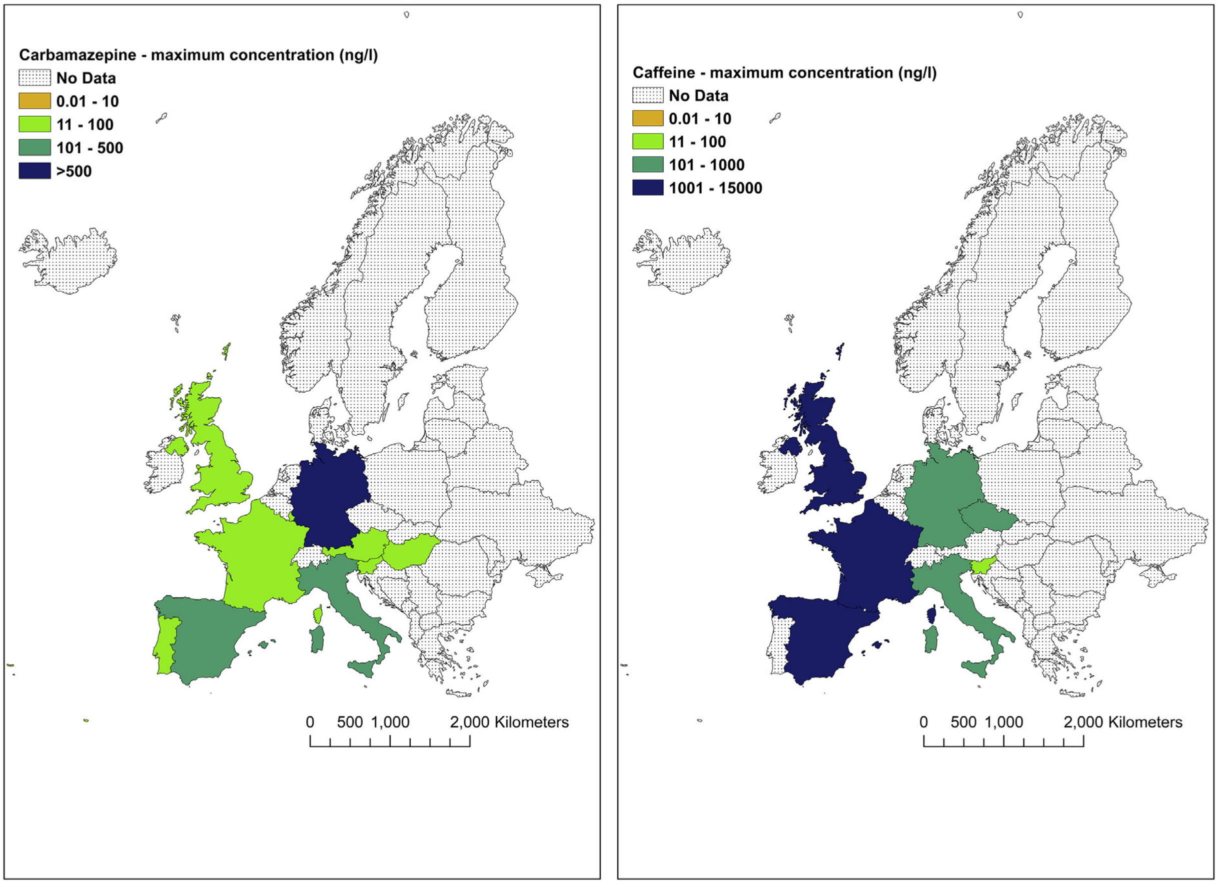

Fig. 4. Maximum concentrations of (a) Carbamazepine and (b) Caffeine in ng/L for each European country reporting detections. [Base map: Esri. Scale Not Given. “World Countries”. January 2015.https://www.arcgis.com/home/item.html?id=ac80670eb213440ea5899bbf92a04998 (May 1, 2019)].

3.3.5.1. Pharmaceuticals. Pharmaceuticals is the most widely observed category in this study, with 123 individual compounds being detected in one or more study (Fig. 5). Thirty-one studies reported the detection of one or more compound classified as a pharmaceutical (Fig. 5). The frequency of detection of pharmaceuticals is likely to be much greater, as each study is recorded here as one detection and does not reflect the number of individual positive sample detects encountered within each study. The top 5 most commonly detected pharmaceuticals are the anti-epilepsy drug carbemazepine, the antibiotic sulfamethoxazole, the anti-inflammatories diclofenac and ibuprofen and the lipid regulator bezafibrate. These EOCs are of particular concern due to their potential effects on wildlife and humans.

Pharmaceuticals are commonly used as groundwater tracers. Examples include Müller et al. (2012) who used five pharmaceuticals to indicate the presence of sewage in groundwater at 21 sites in Germany and Banzhaf et al. (2012) who used 7 EOCs to trace the interaction between surface and groundwater in riverbank deposits. The detection of pharmaceuticals after water treatment is not regularly reported, but a number of reviews showed that the process may be insufficient for the adequate removal of a number of EOCs (Yang et al., 2017). Pharmaceuticals have been widely screened for and detected in studies throughout Europe, with the data being used to assess methods of removal from drinking and aquatic water (Wang and Chu, 2016; Rodriguez-Narvaez et al., 2017; Yang et al., 2017).

3.3.5.2. Personal care products (PCPs). A total of 22 PCP compounds were detected at least once in 13 of the 39 reviewed studies (Fig. 3), where there is likely to be more than one compound from this group within the same study. The top 5 most commonly detected PCPs were the compounds benzophenone, N,N-diethyl-m-toluamide (DEET), triclosan, benzophenone-3 and propylparaben.

3.3.5.3. Endocrine disrupting compounds (EDCs). Carvalho et al. (2015a, b) analyse for 10 different EDCs in 13 groundwater samples from within a water supply system. Seven compounds were detected in 13 groundwater sites sampled. All compounds were detected at concentrations of less than 0.1 μg/L, the proposed values for some unregulated compounds such as pesticides and polycyclic aromatic hydrocarbons (PAH) (Directive, E.U., 2013). Pignotti et al. (2017) screened for six EDC's, but found that no compounds were detected in concentrations above the Method Quantification Limit (MQL) in groundwater (ranging from 0.21 to 2.02 ng/l). They conclude that dilution by rainfall makes the compounds undetectable, natural attenuation processes and distance from vulnerable recharge zones are also discussed. Brueller et al. (2018) screened for 28 compounds known or suspected of having endocrine disrupting properties. Phthalates were detected in 11 groundwater samples. Eight samples contained perfluoroalkyl substances, 4-nonylphenol monoethoxylate was found in 2 groundwater samples and bisphenol A in 1 further sample. However, 576 (93.5%) out of 616 measurements in groundwater detected no compounds above the Limit of Quantification (LOQ). Corada-Fernández et al. (2017) screened for 8 EDC's but only detected one compound (triclosan) at a concentration of 83 ± 20 ng/l.

The category EDCs is solely reported in papers where this is the only category used, as it cannot be compared to the use categories. For this reason, although a popular classification, it may not be suitable for a large-scale review, and therefore not used as a category within this study. Personal care products often contain endocrine disrupting compounds that are shown to have negative impacts on human health and the environment in which they are detected (Kabir et al., 2015).

3.3.6. Purpose and scales of studies

Current understanding of EOCs in groundwater varies considerably between European countries, highlighted by the range in the number of reported studies (Fig. 1; Table 3). The scope and scale of a study depends on funding, interest, capability, perceived threat and existence of studies on regulated compounds that remain a priority. The purpose of each study is usually well-defined and specific to the investigation work to be undertaken. A large majority of reviewed studies principally aim to investigate the occurrence; transport and fate of a group or key EOCs that have been identified in a defined catchment, area or geological unit (e.g. regional aquifer system). Others focus on the threat to a particular resource e.g. drinking water (Hass et al., 2012b; Ahkola et al., 2017) or used as tracers to develop a greater understanding of the hydrogeology of the region being studied (Stuart et al., 2014b; White et al., 2016;

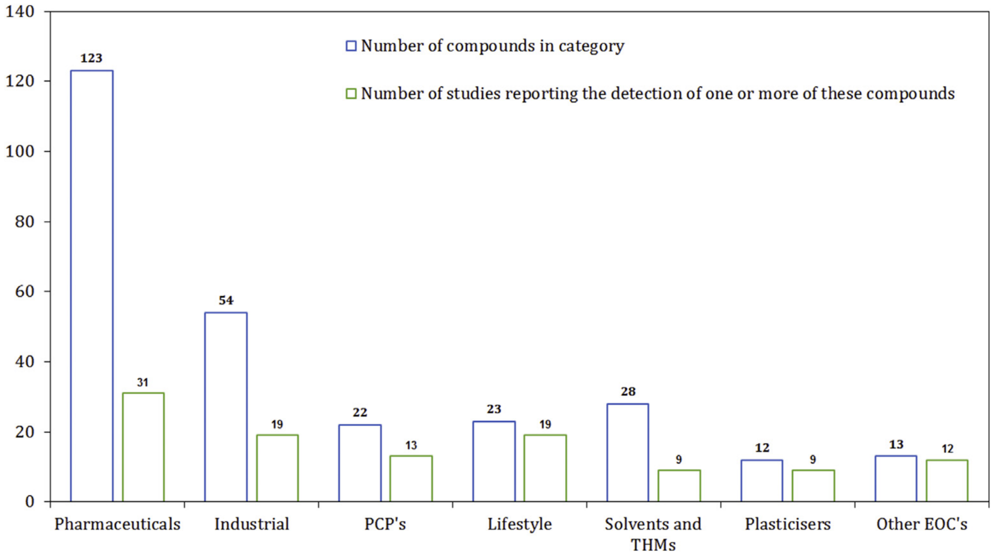

Fig. 5. The number of compounds detected in each of the 8 selected use categories and the number of studies that report a detection of one or more of the compounds in this category.

Pinasseau et al., 2019). Banzhaf et al. (2012) specifically use EOCs as tracers of surface-groundwater interactions.

Large-scale studies offer an insight into spatial occurrence and trends in EOCs, and allow researchers to understand how widespread or diffuse a particular EOC is in the groundwater system, this aspect will be an important consideration for regulating EOCs in the future. Smaller scale studies are primarily used to understand temporal variability and specific hot-spots where EOC contamination may be more likely to occur. Although the majority of studies are still focused on point sources, in areas where EOCs have previously been detected or known to have been released. There are an increasing number of regional and national studies (Lopez et al., 2015; Manamsa et al., 2016a; Brueller et al., 2018).

In this review, each study was classified to a scale to gain a greater understanding of the studies previously undertaken. Although a procedure was used, some studies may be classified differently. Where a large scale campaign was undertaken across the country as a whole, the study was classified as ‘National’. Where a range of sites around a given city/aquifer/region were studied, the study was classified as ‘Regional’. If the study focused on a specific stretch of river, WWTP or study site the study was classified as ‘Targeted’.

National scale studies principally develop the scientific understanding of EOCs in a country and act as a baseline for further studies. National scoping studies highlight areas for concern and further study, whether that is geographically or linked to the geology, land use or environmental setting. In this study, we have defined regional scale as studies that investigate the groundwater across a large geographic area. Examples include large cities, a specific geological area or aquifer system (Jurado et al., 2012, 2014b; Reh et al., 2013; Antonio Luque-Espinar et al., 2015; Koroša et al., 2016; Corada-Fernández et al., 2017; Pignotti et al., 2017; Castiglioni et al., 2018). Targeted studies focus on a particular area, often where there is a known problem or presence of EOCs. Targeted studies may then screen for a larger range of compounds to determine the scale of the contamination of groundwater in this area. Examples include wastewater treatment plants (WWTPs)(Hass et al., 2012b; Pitarch et al., 2016), current and disused landfill sites (Kapelewska et al., 2016), industrial areas (Castiglioni et al., 2018), and specific urban areas (Banzhaf et al., 2012; Hass et al., 2012a; Jurado et al., 2012; Müller et al., 2012; López-Serna et al., 2013; Rozman et al., 2015; Paíga and Delerue-Matos, 2016; Ahkola et al., 2017; Cunha et al., 2017). Out of 39 studies used in this analysis, 4 were national scale, 23 were regional and 12 were targeted studies, highlighting a consistent focus on regional and targeted studies.

There are no obvious trends in the scale of studies published in each year (Fig. 6a), however the number of studies within each category may not be large enough for any trends to be apparent.

The total number of groundwater sites, where published, totalled 4222. The total number of recorded groundwater samples was 5395. This reflects a range of scales, where large scoping studies may take one sample from a large number of sites, and local studies where 5 sites may be intensively studies at different depths. Medium scale studies were most popular, with 19 studies recording in the order of 10–100 groundwater samples (Fig. 6b).

4. Conclusions and future outlook

4.1. Ongoing research

Analytical and extraction methods continue to improve. Zhong et al. (2019) describe the development of an automated system for the extraction and analysis of 87 emerging contaminants, including those previously considered difficult to extract, in particular weakly and non-polar molecules such as PFAS. The process uses an online solid phase extraction liquid chromatography tandem mass spectrometry method, requiring just 30 min and reporting 82% of analytes with a recovery of between 70% and 130%.

Alongside EOCs, their transformation products can often be found in equal or greater concentrations (Stuart and Lapworth, 2014) and can have detrimental impacts. Stuart and Lapworth (2014) highlight the relatively few studies conducted in the area of emerging contaminant transformation products. Specific groups such as pesticides, disinfection by-products, alkyl phenols and other endocrine disruptors, and caffeine and nicotine are highlighted as some groups with transformation products of concern. Particular attention could be paid to non-relevant metabolites of pesticides that are not regulated, conversely to relevant ones, and these can be considered as emerging compounds. New methods including chemical computation methods (e.g. quantum chemical computation) (Wacławek et al., 2020) which are designed to predict the transformation of EOCs once in the environment, may be valuable to understand and predict pathways and impacts to the surrounding environment.

The recent publication of the GWWL (Voluntary Groundwater Watch List), establishes a ranking of compounds of current

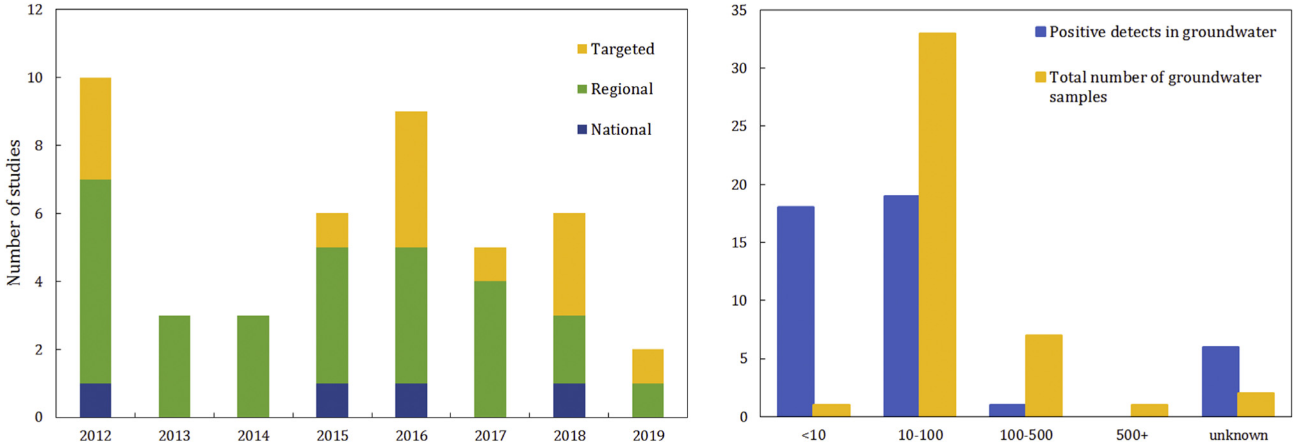

Fig. 6. (a) The scale of studies reported in each year considered in this review b) Number of groundwater samples in each research study reviewed where reported and total number of positive detects.

concern. Eleven compounds classified as either pharmaceuticals or PFAS were listed on the first published GWWL, and a further 4 PFAS selected as candidates for the list (Voluntary Groundwater Watch List). This will likely help focus efforts on priority compounds of concern in groundwater until sufficient detail is collected for a regulatory levels to be set. It is anticipated that this will be a dynamic process as compounds are studied, become regulated, and are replaced by the next highest ranking compound or a different group of compounds.

The detection of compounds continues to be a large part of the research process; assessing the presence of emerging compounds. However, the accurate quantification of compounds across a large number of geologic environments, and using a range of techniques is equally imperative. The quantification of EOC concentrations is a key component of developing standards and threshold concentrations, which may later be implemented into groundwater regulations. The transport of EOCs in aquifers in general is not well known owing to their complex behaviour and depends on the molecular structure of the compounds and the prevailing environmental conditions (Lapworth et al., 2012). Determining the transport properties of EOC in saturated and unsaturated zones remains a challenge and involves batch and column experiments in the laboratory under determined experimental conditions (Banzhaf and Hebig, 2016; Kiecak et al., 2019) as well as experiments performed in or under actual environmental field conditions (Koroša et al., 2020).

The lack of knowledge in the field of EOCs means that the majority of the studies are still at an investigative stage of data collection and collation. Aims of the studies, stated in the associated papers, are commonly to understand the occurrence, transport and fate of EOCs within a given environmental setting. A lack of knowledge on every aspect of the EOC alongside limited monitoring data mean that threshold values have not been set (Lapworth et al., 2012), and therefore remain unregulated.

4.2. *Areas for future study*

There is limited work published on the current state of EOCs in groundwater at a large-scale. In some countries, national reviews may have been undertaken; but as they are not published in English in peer-reviewed journals, they are not included here. Although interest in the topic has increased in the past years, studies still tend to focus on small pilot study areas where all aspects of the occurrence, transport, and impacts of certain EOCs are analysed. The number of large-scale studies, and those with a large number of analytes (>500) are still relatively low, owing to the high cost of screening and the logistical complexity of screening for large numbers of compounds. Currently there are a number of small-scale studies where a target compound has been identified. This allows specific compounds, like those identified on the GWWL, to receive a greater level of study than others that may not pose such a site-scale threat, or may be less mobile in the environment. The quantification of these compounds allows threshold values and water quality standards to be developed for a range of geological environments throughout Europe. There may be many more compounds present that have not yet been screened for, skewing our understanding of groundwater quality to reflect the targeted compounds. It is therefore important that the GWWL is regularly updated to encourage both targeted studies are conducted to quantify compounds of highlighted concern, whilst national and regional scale studies report the presence of other compounds of emerging concern.

The majority of studies included in this review include pharmaceutical compounds, an area that has been heavily studied in previous years. The data presented therefore shows these compounds as frequently screened for and detected, which may distract from other compounds which are screened less regularly.

An increase in the number of compounds analysed for appears to increase the number of detected compounds. This reflects the limit(s) of our current analytical scope and the number of compounds known to have the potential to reach groundwater.

The effects of complex mixtures of contaminants on biota in groundwater dependant ecosystems is an area that needs further investigation, as well as their role as drivers for anti-microbial resistance in the environment.

4.3. *Conclusions*

- There exists a high frequency of detections of a number of EOCs throughout Europe, a number of which are also detected at high concentrations. Although this helps to understand the distribution of EOCs, it does not include toxicity/hazard information and is heavily biased towards a small number of compound groups that have been more frequently investigated. Increased quantification of EOCs in groundwater is needed to aid the development of threshold values.
- For the development of European regulation on EOCs, there needs to be a greater emphasis on understanding the occurrence of EOCs in groundwater throughout Europe. It is important to continue large scale scoping studies which are invaluable for assessing the occurrence of EOCs in groundwater bodies across a range of environmental settings. Negative results must also be published to gain a greater understanding of which compounds are screened for as well as those detected.
- Meanwhile, studies on the possible impacts of the compounds must also start to develop a better understanding of the effect of the compound(s) on the aquatic environment and groundwater dependant ecosystems. While bacteria can play an important positive role in controlling groundwater pollution, the impact of EOCs on soil and subsurface biodiversity has not been intensively studied. Biodegradation of organic pollutants can favour natural attenuation of pollution, for example denitrification. The additional impact of synergistic effects, whereby an impact is compounded by the presence of more than one type of compound, must also be considered. Currently each compound is primarily assessed independently, but future studies must also assess the impact of mixtures of compounds, considering a potential cocktail effect.
- The GWWL has now been implemented throughout Europe, to help prioritise which compounds to look for. This is a relatively small list for pragmatic reasons, however, this should not detract from the need to continue to screen for a wider number of compounds that are not on the GWWL. It is important to continue advancing extraction and analytical methods which allow new EOCs to be detected.
- Increasingly, EOCs are used as tracers for surface water/groundwater interactions or interaction with infrastructure e.g. sewer networks, treatment plants (Hillebrand et al., 2012). However, we also need to improve the knowledge of relationships that link anthropogenic land uses and activities with the potential impact on groundwater quality taking into account pathways and fate of molecules that interact with physio-chemical contexts of soils and underground. This knowledge is crucial for measures to be taken on the right targets (industries, WWTP, etc.), and applied at the right scales.
- Future studies should aim to report the details of their detections, as in a number of published studies it is uncertain as to the source of a positive detection. It would also be useful to follow a standardised approach to reporting, such as the

reporting of LOQ or LOD, and the maximum concentrations and recovery rate for compounds of greater concern.

Declaration of competing interest

The authors declare that there is no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.115945.

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