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Source / Izvornik: **Journal of Hydrology, 2021, 604**

Journal article, Published version
Rad u časopisu, Objavljena verzija rada (izdavačev PDF)

https://doi.org/10.1016/j.jhydrol.2021.127242

Journal of Hydrology 604 (2022) 127242

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Emerging organic contaminants in karst groundwater: A global level assessment

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ARTICLE INFO

This manuscript was handled by Huaming Guo, Editor-in-Chief

Keywords:
Emerging organic contaminants
Karst
Groundwater
Vulnerability
Aquifer characterisation
Tracers

ABSTRACT

A quarter of the world's population uses groundwater from karst aquifers. A range of emerging organic contaminants (EOCs) are considered a potential threat to water resources and dependant ecosystems, and karst aquifers are the most vulnerable groundwater systems to anthropogenic pollution. This paper provides the first global compilation (based on 50 studies) of EOCs in karst aquifers and explores EOC occurrence and the use of EOCs to understand karst systems. Of the 144 compounds detected in the reviewed studies, the vast majority in karst groundwater are pharmaceuticals and pesticides. Maximum concentrations of compounds varied over five orders of magnitude, and nearly half of the detected compounds exceed 100 ng/L. Karst groundwater is shown to have lower frequency of detection and lower concentrations compared to surface waters and local shallow intergranular aquifers, but overall higher concentrations compared to other major aquifer types. A growing number of studies have demonstrated the utility of EOCs and some legacy compounds for groundwater quality assessment and as tracers for characterising karst systems. They can improve understanding of vulnerability, storage, attenuation mechanisms, and in some cases have been used to assist with catchment delineation. This is a growing research area for karst hydrogeology, and more research is needed to understand EOC contamination of karst aquifers, and to develop EOCs as tracers within karst to improve our understanding of this critical water resource.

1. Introduction

Emerging organic contaminants (EOCs) are anthropogenic chemicals (e.g. pharmaceuticals, personal care products and lifestyle compounds (PCP-LS), pesticide compounds, and per and polyfluoroalkyls) that have been detected in the environment due to advances in analytical techniques (Muter and Bartkevics, 2020; Richardson and Kimura, 2020; Schmidt, 2018) and for which there are growing concerns regarding their potential harmful impact on the environment. However, most EOCs are not regulated in the environment or routinely monitored in groundwater (Lapworth et al., 2019). Their properties, environmental behaviour and toxicological effects are still poorly understood (Brack, 2012; Halden, 2015; Kurwadkar, 2014; Lapworth et al., 2019; NORMAN, 2019; Pal et al., 2014; Petrie et al., 2015; Poynton and Vulpe, 2009; Sauvé and Mélanie, 2014; Schriks et al., 2010; Stuart et al., 2012; Thomaidi et al., 2015). There are 30,000 to 70,000 registered chemicals in daily-used products (Schwarzenbach et al., 2006), and about 4000 new chemicals are registered every day (Dulio et al., 2018). There are many newly emerging substances present in the environment, which may have adverse impacts on human health and ecosystems, for which limited occurrence data are available (Bolong et al., 2009; Brack et al., 2015; Brion et al., 2019; Freeling et al., 2019; Gavrilescu et al., 2015; Geissen et al., 2015; Legradi et al., 2018; Lindsey et al., 2001; Stefanakis and Becker, 2016). Micro-plastics are also a potentially important emerging organic contaminant group in groundwater, this topic was recently reviewed by Re (2019); and broader reviews by Wong et al. (2020) and Stock et al., (2020).

Groundwater is a vital global water resource and is under increasing pressure from contamination due to anthropogenic activities (Collet et al., 2015; Gleeson et al., 2012; Lapworth et al., 2017; Lukač Reberski et al., 2019; Simonffy, 2012; Taylor et al., 2012). Groundwater is generally less vulnerable to contamination by EOCs than surface water (White et al., 2019), but trace concentrations of many pollutants, including EOCs, are still commonly detected in groundwater (Cabeza et al., 2012; Lapworth et al., 2012, 2019; Lopez et al., 2015; Moreau et al., 2019). Moreover, some substances present in groundwater are persistent and difficult to treat.

Many studies of EOCs in aquatic environments have been undertaken

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https://doi.org/10.1016/j.jhydrol.2021.127242
Received 11 November 2020; Received in revised form 17 November 2021; Accepted 20 November 2021
Available online 27 November 2021

for wastewater (ww) effluents (Bueno et al., 2012; Petrović et al., 2003) and surface waters (Houtman, 2010; Loos et al., 2009; Matamoros et al., 2012). Fewer studies have been undertaken for groundwater (Bexfield et al., 2019; Lapworth et al., 2012; Loos et al., 2010; Sanchez-Vila et al., 2015; Stuart et al., 2012; Sui et al., 2015). Karst aquifers are a particularly important source of groundwater, with approximately 14 % of the earth's land surface covered by karst (BGR et al., 2017) and 25% of the global population completely or partially dependent on drinking water from karst aquifers (Chen et al., 2017; Hartmann et al., 2014).

Compared to other rock types, karst aquifers are especially vulnerable to pollution due to direct infiltration via stream sinks, shafts, and caves (Ford and Williams, 2007; Goldscheider and Drew, 2007). Groundwater flow can be rapid over long distances as shown by the median velocity of 1940 m/d from 3015 karst tracer tests between stream sinks and springs (from 34 countries); with 595 over distances of > 10 km (Worthington and Ford, 2009). It might therefore be expected that karst aquifers are more impacted by EOCs than some other aquifer types.

There have been some previous studies that have reviewed EOCs in karst aquifers. Notably, Mahler and Musgrove (2019) provide a very useful introduction to different types of emerging contaminants (Pharmaceuticals, Personal care products and hormones; flame retardants; Perfluorinated and Polyfluorinated Alkyl Compounds; Nanoparticles; and Microplastics), together with an overview of studies that have detected these different types of emerging contaminants in karst groundwater. They highlight the vulnerability of the Edwards Aquifer in Texas to pollution from Emerging Contaminants and recommend future work to investigate this. Padilla and Vesper (2018) provide a comprehensive review of contaminant transport processes and modelling approaches within karst aquifers, with a focus on the transport of both legacy and emerging contaminants (phthalates).

The initial objective of this paper is to provide the first compilation of EOC data from previous studies of EOCs in karst aquifers and review how the types and concentrations of EOCs present compare to their occurrence in surface water and other types of groundwater system. In the second part of the paper we review how EOCs can assist with karst hydrogeological characterisation, for example through contributing to understanding of aquifer vulnerability and rapid groundwater flow, identifying connecting with wastewater, identifying pollutant sources, delineating catchments, and investigating contaminant attenuation mechanisms.

2. Methods

An extensive literature search was undertaken using Google scholar, Web of Science, ScienceDirect, ResearchGate, and Microsoft Academic (Supplementary Material, Figure S1). > 10,000 published papers relating to groundwater and EOCs were identified covering a range of topics and groups of EOCs (Fig. 1) using the following key word combinations: karst groundwater, contaminants of emerging concern, PCP-LS, industrials, emerging pollutants, pharmaceuticals, emerging organic contaminants. The review and searches were limited to dissolved organic compounds; nano-materials and micro-plastics were not considered in this paper, as there are very few studies on these new types of contaminants in karst systems (e.g. Panno et al., 2019) and their fate and behaviour in groundwater may be quite different compared to dissolved compounds (see Re, 2019). The literature search was also limited to English publications. Several hundred papers were initially evaluated based on a brief survey of titles, key words and abstracts, of which 50 publications related specifically to karst aquifers and containing EOC occurrence data were selected and form the basis of this review.

In previous research on emerging organic contaminants, different authors include different ranges of compounds and classified them differently (Lapworth et al., 2012; Mahler and Musgrove, 2019; Zhao

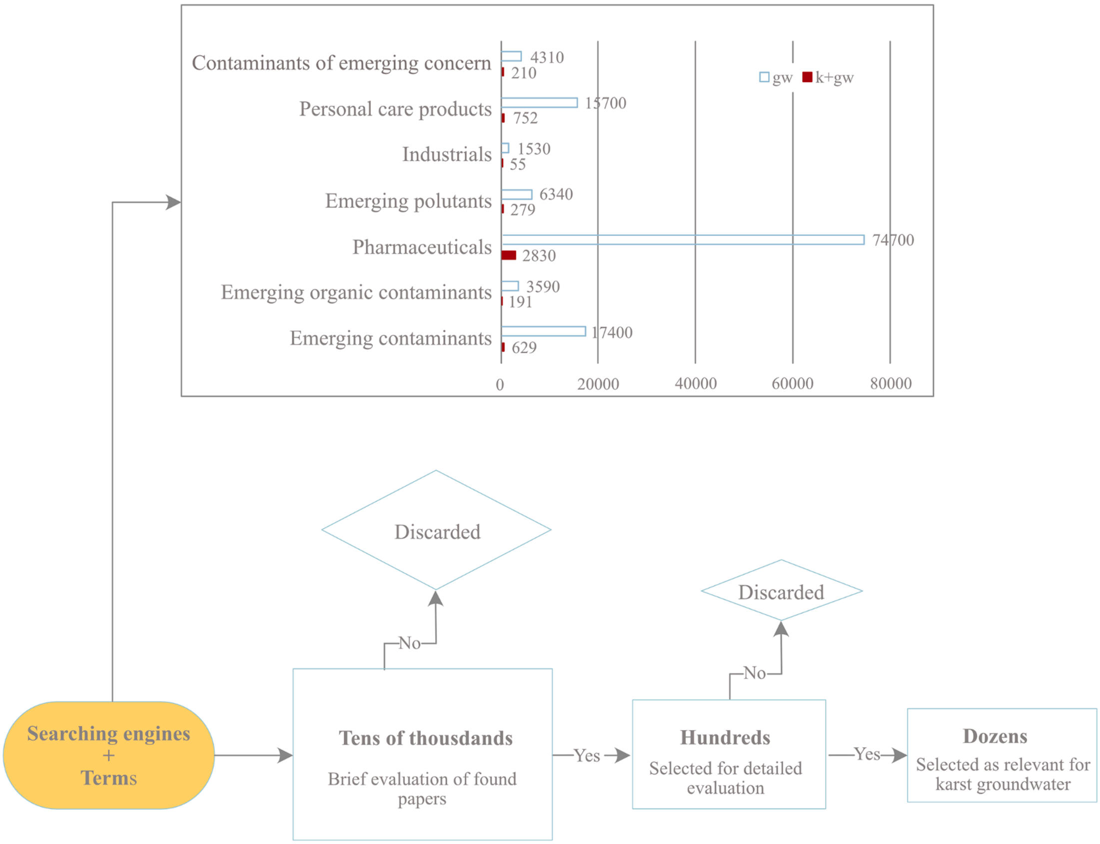

Fig. 1. Flowchart of literature selection process with the number of articles found after searching with different terms and including groundwater (gw) or karst and groundwater (k + gw).

et al., 2018; Bunting et al., 2021). This is partly because the status of a compound as ’emerging’ is regionally dependant and may change with time, thus newer studies may include compounds that were classified as ’emerging’ many years ago. However, there are also a wide range of compounds that are routinely measured as part of the analysis suite for emerging contaminants, even though some of these compounds have been around for a long time and would not be defined as ’emerging’. This may be partly because some types of emerging contaminant classes include both new and legacy compounds (e.g. some pesticides) and the analytical suites (e.g. LC-MS/MS) used to look for these compounds include both legacy and more recently added compounds such as pharmaceuticals.

New compounds are being manufactured and utilised all the time, the EOCs of today will be legacy contaminants in the future. In some countries, compounds suspected of harmful health impacts are put on the watch list and are monitored for several years after which they are either transferred to the priority list or removed from that list (European Commission Directive 2006/118/EC.; Lapworth et al., 2019; https://www.epa.gov/dwucmr, 2021). Another challenge is the differences in legislation in different countries. When regulated, microorganics are not regulated globally, but at the country/and sometimes regional level. In the EU pesticides are regulated both as an entire group and on an individual basis in some cases (WFD 2006/118/CE Annex I). However, there are many other parts of the world where this is not the case. For example, atrazine, widely considered a legacy compound in Europe, is regulated in only 28 of the 104 countries that belong to the World Health Organisation (WHO, 2018), and is not banned from use in parts of North America. Given the focus of this study is a global data compilation we have used the current WHO guidelines (WHO, 2018) as the benchmark for defining if a contaminant is emerging or not; all compounds with a WHO guideline value or deemed not to need a limit because concentrations found in groundwater are too low to be considered a health concern are excluded from the data compilation part of this paper. All degradation compounds of pesticides are considered EOCs. Some former EOCs (e.g. atrazine) are discussed in the second part of the paper in relation to the review of the applications of EOCs in karst hydrogeology.

For the data compilation, EOCs were divided into four broader groups: Pharmaceuticals comprising hormones, human and animal drugs; Personal Care Products and Lifestyle compounds (PCP-LS) comprising fragrances, cosmetics, artificial sweeteners, stimulants and their metabolites; Industrial compounds comprising flame retardants and plasticisers; and Agricultural products comprising pesticides, herbicides, fungicides, algicides and their metabolites. Some of the compounds have multiple uses in which case they are classified according to the most common use. The list of compounds is in the Supplementary Material Table S1.

Maximum concentrations of compounds are used in the data presentation as this was the only parameter that was consistently available from the studies reviewed. There are limitations to this approach due to the presence of outliers, but we were not able to use a more suitable measures such as the 90th or 95th percentile due to limited reporting in the reviewed literature and lack of access to the raw data from the majority of studies.

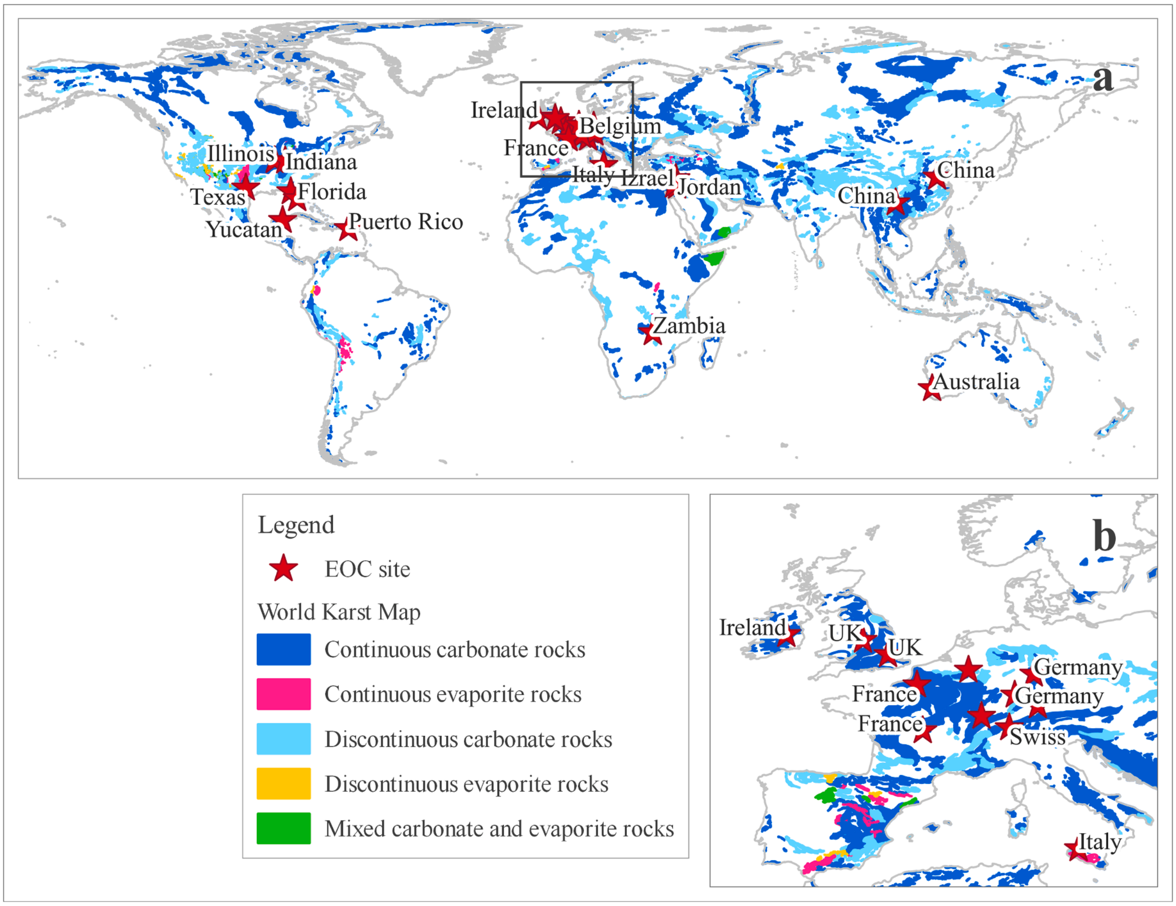

Fig. 2. Locations of EOC studies in karst, a) Global distribution of studies, b) Studies in European Karst. Karst geology shown (source of the World karst map is https://www.whymap.org/whymap/EN/Maps_Data/Wokam/wokam_node_en.html).

3. Results and discussion

3.1. Occurrence of EOCs in karst aquifers

The 50 publications of EOCs in karst were from studies in 21 countries (Fig. 2). In some countries more research has been done, sometimes in the same location (e.g. Germany); and in some countries, extensive regional monitoring has been carried out in many locations (e.g. USA, UK, France, China). Most studies have been carried out in Europe and the USA, with few or no studies in many other parts of the world. The different types of karst covered by the investigations of EOCs included in this study differ significantly in age and degree of karstification. They range chronostratigraphically from the older karst of Palaeozoic age, characterised by low matrix porosity; to younger Cenozoic karst with high matrix porosity. Comparative hydrological characteristics of some of the springs, or karst regions they belong to, can be found in the WoKaS database (Olarinoye et al., 2020).

Despite the relatively small number of studies in karst areas, they provide key insights into patterns of EOCs in karst aquifers and have been used for a wide range of applications (Table 1). Many other studies (e.g. D'Alessio and Ray, 2016; Dong et al., 2018; Gavrilescu et al., 2015; Lopez et al., 2015; Meffe and de Bustamante, 2014; Moreau et al., 2019; Murray et al., 2010; Postigo and Barceló, 2015) sampled EOCs from karst, but karst samples were not distinguishable from other lithologies and they are therefore not included in Table 1.

A total of 144 compounds from different groups of contaminants were identified in studies of karst aquifers (data are available in supplementary material). Most were pharmaceutical and pesticide compounds used in agriculture, with fewer industrial compounds and personal care products and lifestyle compounds detected (Table 1, Fig. 3). Carbamazepine (anticonvulsant) and caffeine (stimulant) were the most frequently detected compounds, whilst many compounds were detected in just a single study (See Supplementary Material Table S1). Most studies aimed to determine the occurrence (type and concentrations) of emerging contaminants. However, the number of sample locations and sample frequencies; and the number, type and group of analysed compounds for particular investigations varied greatly between studies. The way the results of the analyses were reported varied as well; some studies reported medians, some mean values, thus maximum concentrations were used for comparison as the only data available in all studies. This review highlights the need to report high percentiles (such as the 95th percentile) and for studies to make the full set of results available so that these can be calculated as these would help to avoid the issue of small numbers of outliers skewing results.

Maximum concentrations of compounds varied over 5 orders of magnitude (Fig. 4), and nearly half of the detected compounds exceed 100 ng/L, the current EU drinking water limit for individual pesticides. Many of the highest concentrations were industrial compounds (Fig. 4), although the highest concentration was of the antibiotic sulphanilamide (6.5×10^8 ng/L – not included in Fig. 4 to retain the clarity of the figure), which was detected in the Chalk aquifer beneath a chemical plant in the UK (Bennett et al., 2017). Bisphenol A (BPA), paracetamol, and 2,6-dichlorobenzamide (BAM) are among the top 20 compounds in terms of both concentration and detection frequency, and hence indicate the greatest risk to karst aquatic ecosystem.

Individual compounds in karst aquifers are typically found in concentrations that are considered too low, by several orders of magnitude, to cause acute toxicity effects (e.g. Costanzo et al., 2007; Kim et al., 2009; Nunes et al., 2005). In exceptional circumstances, detections in relation to some point sources can lead to high concentrations in groundwater that approach or exceed acute toxicity thresholds (e.g. Bennett et al., 2017). One recent study by Geiger et al. (2016) found that mixtures of pharmaceuticals were more toxic to algae (inhibiting algal growth) than single compounds. However, the concentrations used are not representative of typical environmental concentrations and further work is needed using more realistic concentrations which reflect environmental exposure by organisms. There is little information on the impact of mixtures of EOCs on chronic responses in organisms, but some studies have shown chronic exposure effects are predicted at levels found in karst groundwater in this review (e.g. Berninger and Brooks, 2010).

In Fig. 5 maximum concentrations of EOCs in karst aquifers are compared with values found in a range of aquifers globally (Lapworth et al., 2012) and surface waters in Europe (Loos et al., 2009). Maximum concentrations depend upon the presence and nature of contaminant sources within the catchment, which was not assessed in this literature review. However, maximum concentrations appear lower in karst groundwater compared to other aquifer types for carbamazepine, caffeine, ibuprofen, nonylphenol, hormones; but are higher for sucralose, metoprolol, tetracycline; and are comparable for paracetamol, oxazepam, and 1H-benzotriazole (Fig. 5). While overall maximum concentrations appear lower in karst groundwater, nearly 25% of compounds had comparable or greater maximum concentrations in karst compared to other aquifers (Fig. 5). Maximum concentrations reported in Lapworth et al. (2012) were often from shallow alluvial aquifers, and as such represent highly vulnerable groundwater systems that are often at least periodically in hydraulic continuity with surface waters, and hence may have high concentrations of microorganic contamination, much like karst systems.

McManus et al. (2017) found significant differences and a lower detection frequency in fractured/karstified limestones compared to overlying shallower intergranular aquifers but showed that many of the substances reached the deeper karst aquifers as well (e.g. pesticides and their metabolites). Extensive national monitoring of hormones and pharmaceuticals conducted in the United States (Bexfield et al., 2019) showed that at least one compound was detected to a greater extent in samples from carbonate rocks (26%) compared to non-carbonate rock rocks (19%), but concentrations and frequency of detections of most compounds were higher in non-carbonate rocks. Results from a large national study in England and Wales (Manamsa et al., 2016b) showed that Chalk and Jurassic Limestone (carbonate aquifers with some karstification) had higher maximum concentrations for most microorganic contaminants, including EOCs, compared to other important aquifer types (e.g. Permo-Triassic Sandstone and Greensand). The percentage frequency of detections for the different aquifer types varied depending on the compound, but was overall comparable for the karst and sandstone aquifers and was typically below 5% (Manamsa et al., 2016b). Comparing the results of two investigations of karst groundwater with surface water, detection frequency and concentrations of all detected PPCPs were higher in surface water compared to karst groundwater except for fenofibrate (Zemann et al., 2015) and acesulfame-K (Doummar and Aoun, 2018b).

It appears that EOCs may have a lower frequency of detection and lower concentrations in karst groundwater compared to surface waters and local shallow intergranular aquifers, but higher concentrations than other major aquifer types such as sandstones and other unconsolidated sedimentary aquifers. However, systematic sampling studies are needed to confirm more conclusively how EOC occurrence in karst groundwater compares to surface waters and other aquifers; and in all springs/abstractions, the occurrence and magnitude of EOC contamination will vary substantially depending on the type of catchment and pollution sources found within them and timing of sampling the flow characteristics of spring sources.

It is clear that karst is highly vulnerable to EOC contamination with potentially serious impacts on both drinking water supplies, and karst dependent ecosystems. However, the limited number of studies undertaken in karst globally currently restricts our understanding of the extent of pollution from EOCs in this vulnerable setting.

3.2. Applications of EOCs in karst hydrogeology

The increasing number and presence of EOCs in groundwater present

Table 1

Summary of investigations related to emerging contaminants in karst areas. Explanation: OCC – occurrence, SSI – source specific indicators, ENV – tracers present in environment, TRA – artificial tracers, CKA – characterisation of karstic aquifers, ML – mass loads, ATT – attenuation, PC – predicting contamination, MC – modeling capabilities; PPCP-LS – pharmaceuticals, personal care products and lifestyle compounds.

Reference	Country	Type of karst	Catchment area (km^2)	Analysis method	Total number of samples	Number of sampling sites and sample type (spring, well.)	Sampling frequency	EOC types/ number	Application of results
Bekele et al. 2011	Perth, Australia	karstified limestone	local test site		33	3 wells	–	Pharmaceuticals/5	ATT
Bennett et al. 2017	UK	chalk	local test site	HPLC	19	9 wells	1 sampling campaign	Sulphanilamide	ATT
Bexfield et al. 2019	USA	carbonate aquifers	regional	HPLC/MS/MS	191	wells	1 sampling campaign	Pharmaceuticals/13 Hormone/5 Industrial/1 PCP-LS/2	OCC
Chiffre et al., 2016	E France	highly karstified limestone	2320 km^2	UHPLC -MRM	12	spring	Half-year (2 campaign)	Pharmaceuticals/21 Hormone/10	OCC
Morasch, 2013	Swiss Jura	highly karstified limestone	c. 6 km^2	UPLC-MS/MS	35	2 springs ponor	Monthly plus one additional campaign	Pharmaceuticals/10 Pesticides/8 Industrial/2	OCC, SSI, ENV
Deleu, 2018	Liège, Belgium	highly karstified limestone and sandstone aquifer	15.6 km^2	LC-MS	1	spring	1 sampling campaign	PPCP-LS/49	OCC
Dodgen et al. 2017	SW Illinois, USA	karstified dolostone and limestone	600 km^2	LC-MS/MS	58	8 springs 5 cave streams	quarterly	PPCP-LS/12 Hormones/7	OCC, SSI
Dong et al. 2018	Xuzhou China	karstified limestone	regional			Karst pore water		Industrial/1	OCC
Doummar et al. 2014	Beirut, Lebanon	highly karstified limestone with dolostone, Jurassic	150 km^2	SPE-HPLC-MS/MS)	28	spring	3–6 h	PPCP-LS/2	CKA, ENV, ATT
Doummar and Aoun 2018a	Lebanon	highly karstified limestone with dolostone, Jurassic	250 km^2	HPLC/MS–MS	8	spring 2 wells	48 h (through 9 days)	PPCP-LS/9 Industrial/1	OCC, SSI
Doummar and Aoun 2018b	Lebanon	highly karstified limestone with dolostone, Jurassic	50 km^2	SPE-HPLC-MS/MS)	20	spring	4–8 h (3 events)	PPCP_LS/4	ENV, CKA
Dvory et al. 2018a	Jerusalem, Israel	karst/fractured-porous carbonates	88 km^2	GC/MS LC/MS/MS	23	well	1–56 days (through 310 days)	PPCP-LS/2	MC, CKA, PC
Dvory et al. 2018b									ENV, ATT, SSI
Einsiedl et al. 2010	Southern Germany	karstified limestone and dolostone, Carboniferous	127 km^2	HPLCMS/MS	8	4 springs	2 campaigns (February and May)	Pharmaceuticals/2	ENV, OCC
Heinz et al. 2009	SW-Germany	karstified limestone and marly limestone, Upper Jurassic	45 km^2	GC–MS	57	spring	1 per week 4–6 h after events	Industrials/8 PPCP-LS/3	ENV, SSI, ATT
Hillebrand et al. 2012a	SW-Germany	karstified limestone and marly limestone, Upper Jurassic	45 km^2	HPLC/MS-MS)	157	spring	3–24 h (1.5 month)	PPCP-LS/4	ENV, SSI, ML
Hillebrand et al. 2012b	SW-Germany	karstified limestone and marly limestone, Upper Jurassic	45 km^2	HPLC-ESI-MS/MS	93	spring	10 min – few hours (7 days)	PCP-LS/1	ATT, TRA, CKA
Hillebrand et al. 2014	SW-Germany	karstified limestone and marly limestone, Upper Jurassic	45 km^2	HPLC-ESI-MS/MS	263	spring	Few hours - weekly (1 year)	Pesticides/2	CKA, VA, SSI
Hillebrand et al. 2015	SW-Germany	karstified limestone and marly limestone, Upper Jurassic	45 km^2	HPLC-ESI-MS/MS	76	spring	0.5 – 12 h (event)	PPCP-LS/7	ATT, TRA, CKA
Huang et al. 2019, Zou et al. 2018	SW China, Kaiyang	karstified carbonates	59 km^2	UPLC-MS/MS	41	3 springs 4 rivers *	Half-year (4 sampling campaigns)	Pharmaceuticals/35	OCC, SSI, PC
Indelicato et al. 2017	Sicily, Italy	karstified limestone and marly limestone- Mesozoic	8x8 km^2 10x10 km^2	GC-LC-MS	30	13 wells	3 campaigns/3 months intervals	Industrial/1	VA

(continued on next page)

Table 1 (*continued*)

Reference	Country	Type of karst	Catchment area (km^2)	Analysis method	Total number of samples	Number of sampling sites and sample type (spring, well.)	Sampling frequency	EOC types/ number	Application of results
		and Cenozoic							
Katz et al. 2010	Florida, USA	karstified limestones, Cenozoic	1100 km^2	GC–MS		wells	3 sampling campaigns	Pharmaceuticals/ 16	SSI
Lapworth et al. 2015	SE England NW France	Chalk	regional	LC-MS/MS GC/MS	300 England 45 France	wells	1 sampling campaign	Industrial/14 Pesticides/14 Pharmaceuticals/ 11	OCC
Leal-Bautista et al. 2011	Riviera Maya, Yucatan	highly karstified carbonates, Cenozoic	10 × 10 km^2	HPLC	7	5 wells 2 cenotes	1 sampling campaign	Caffeine	SSI
Mahler and Musgrove 2019	Global and local (Texas)	vary		–	–	–	–	–	OCC, ENV, VA
Manamsa et al. 2016a	England and Wales	Jurassic limestone chalk	regional	GC–MS	248 limestone 647 chalk	wells	1 sampling campaign	Wide range	OCC
Manamsa et al. 2016b	Berkshire, UK	chalk	local test site	GC–MS	87	1 piezometer	Monthly through (13 months)	Industrials/4 PCP-LS/3 Pesticides/4 Pharmaceuticals/ 1	OCC
McManus et al. 2017	Ireland	karstified limestone	regional	UHPLC – MS-MS	730	springs Piezometers	Monthly through 2 years	Pesticides/9 Pesticide metabolites/8	OCC
Metcalfe et al. 2011	Riviera Maya, Yucatan	highly karstified carbonates, Cenozoic	local recharge area	LC-MS/MS GC-ECD GC-LRMS	5	4 caves 1 cenote	Passive samplers	Industrials PPCP-LS Pesticides Pharmaceuticals	SSI
Mooney et al. 2020	Ireland	Classical karst	regional	UHPLC – MS-MS	54	Springs wells	One sampling campaign	Pharmaceuticals/ 7	OCC, ENV
Morasch, 2013	Swiss Jura	Classical	Cca. 6 km^2	UPLC-MS/MS	35	2 springs 1 swallow hole	Monthly + one additional campaign	Pharmaceuticals/ 7 Pesticides/5 Industrial/2	OCC, SSI, ENV
Padilla and Vesper, 2018	N Puerto Rico	karstified limestones, Cenozoic	regional	–	–	–	–	–	MC, CKA
Panno et al. 2019	NW Illinois, USA	Dolomites	Cca. 1000 km^2	LC-MS/MS	11	8 springs 3 shallow wells	One sampling campaign	Pharmaceuticals/ 2 PPCP-LS/2	SSI, ENV
Reh et al. 2013, 2014	Central Germany	less karstified carbonates	65 km^2	HPLC–MS/MS	163	springs Wells (44 gw locations)	Half-year (4 campaign)	PPCP-LS/34 Pesticides/48 Industrial/2	OCC, CKA, ATT
Schiperski et al. 2015	SW-Germany	karstified limestone, Upper Jurassic	45 km^2	HPLC-ESIMS/ MS	54	spring	45 min –11 h (7 days)	Pesticides/12 PPCP-LS/1	SSI, CKA, PC
Sorensen et al. 2015	Kabwe, Zambia	karstified dolostone	cca. 120 km^2	GC–MS	21	wells	2 sampling campaign (dry and wet season)	Pesticides/34 Industral/3 PCP-LS/1	OCC
Talarovich and Krothe, 1998	Central Indiana, USA	highly karstified carbonates	1.4 km^2	na	38	1 spring	Storm event	Industrial/1	VA
Torres et al. 2017, 2018	N Puerto Rico	karstified limestones, Cenozoic	cca. 800 km^2	na	201	4 springs 17 wells	Spring, fall (3 years)	Industrial/6	OCC
					1803	historical data	1981–2013		
Zemann et al. 2015	Jordan	karstified limestone	cca. 300 km^2	HPLC–ESI-MS–MS	66	5 springs 2 wells	Yearly (4 campaigns)	Pharmaceuticals/ 25	OCC, SSI
Zhang et al. 2015	SW China	karstified and highly karstified carbonates	300 km^2	GC–MS	196	springs ponors	Through 4 years	Industrials/1	OCC, SSI
Zirlewagen et al. 2016	SW-Germany	karstified limestone and marly limestone, Upper Jurassic	45 km^2	HPLC–ESI–MS/ MS	51	spring	6 h – 1 day (winter and spring event)	Pesticides/3 PCP-LS/2	SSI, ENVNAT

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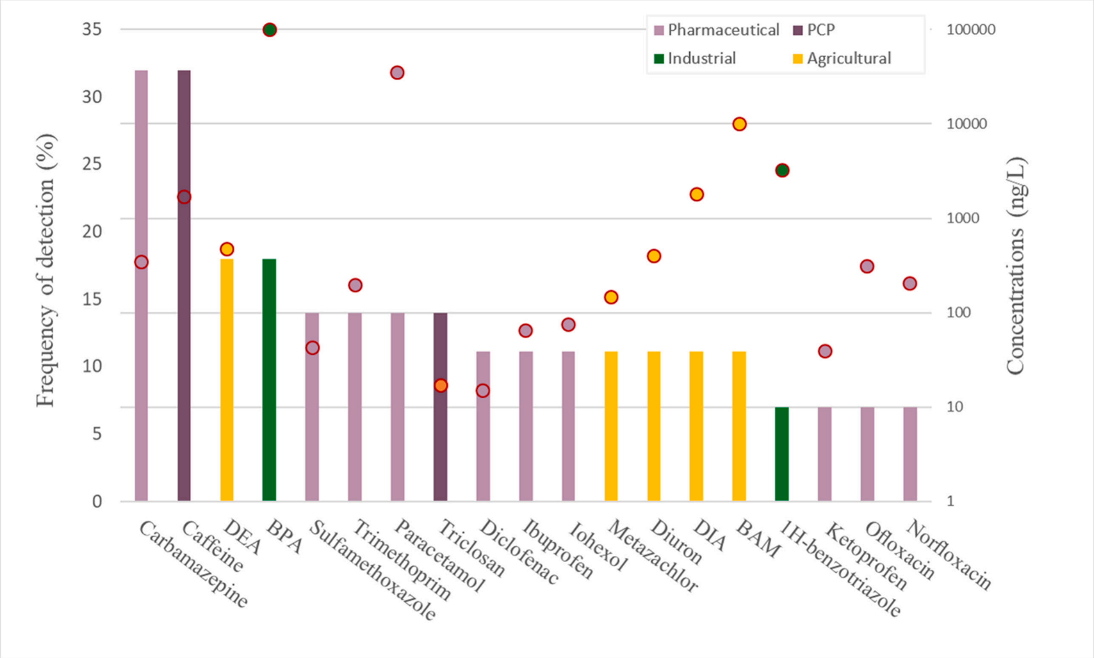

Fig. 3. The 20 most frequently detected compounds and their concentrations detected in karst groundwater. Bars show frequency (%) of studies that detected substance, circles show concentrations.

many challenges due to the detrimental impacts on the quality of water used for supply and which sustains rivers and ecosystems. However, EOCs can also provide information to assist with karst hydrogeological studies. In this section the use of these compounds in karst hydrogeological studies are considered, with a summary of the applications in Table 3.

Understanding the degradation properties of EOCs is a prerequisite for their use in aquifer characterisation and therefore in this section studies on the degradation properties of compounds are reviewed (Section 3.2.1). The use of EOCs in characterising vulnerability is then discussed (Section 3.2.2), followed by the use of EOCs for identifying longer term storage (Section 3.2.3). EOCs have also been used to investigate attenuation mechanisms within karst aquifers and these studies are discussed in Section 3.2.4. The final section (3.2.5) discusses the use of EOCs as a tool for better defining catchment areas.

3.2.1. *Degradation properties of EOCs.*

The presence of rapidly degrading compounds is a useful indicator of rapid groundwater flow and vulnerabilty. Studies of compound degradation are summarized in Table 2.

Caffeine has been observed to degrade relatively rapidly, with half lives of less than 104 h (Dvory et al., 2018b; Hillebrand et al., 2012a, Hillebrand et al. 2015; Table 2), and an estimate of 12 days for degradation in a lake (Buerge et al., 2003). However, Hillebrand et al. (2012b) suggested wastewater leakage and the subsurface redox condition may have contributed to the high biodegradation of caffeine that they observed; and longer degradation times of 30 to 69 days have been estimated for caffeine in intergranular aquifers (Gonçalves et al., 2017; Koroša et al., 2020).

Other compounds have also been found to have high degradation rates. A study of the UK Chalk aquifer beneath a pharmaceutical factory found sulfanilamide concentrations decreased from 650 to 10 mg/L over a distance of about 500 m. 56% of this reduction was attributed to biodegradation processes and 42% to processes within the aquifer such as dilution and dispersion (Bennett et al., 2017). Some papers suggested biodegradation as the main cause of decreasing concentrations of caffeine in groundwater (Dvory et al. (2018b) and Hillebrand et al. (2015). Heinz et al. (2009) suggest the same process for plasticizers, flame retardants and PPCPs. Some studies have suggested that non-chlorinated organophosphates degrade more rapidly than chlorinated ones (Andresen et al., 2004; Heinz et al., 2009; Meyer and Bester, 2004) and that substances with higher octanol–water partition coefficient (K_{ow}) values have higher degradation.

Some compounds, such as carbamazepine (Table 2) and atrazine (Hillebrand et al., 2014; Morasch, 2013; Schiperski et al., 2015), are more resistant to degradation. Atrazine has been found in karst aquifers many years after it was banned in Europe (Chen et al., 2019; Lapworth and Gooddy, 2006). Persistence in karst aquifers was also evident for a range of EOCs: acesulfame (Doummar and Aoun, 2018b; Zirlewagen et al., 2016); phthalates (Padilla and Vesper, 2018); sucralose, gemfibrozil, iohexol (Doummar and Aoun, 2018b); primidone, tamoxifen and analgesic phenazone, which had a particularly high detection frequency even though it has not recently been prescribed in significant quantities (Reh et al., 2013).

Overall it appears that EOCs have very variable degradation properties. EOC compounds like caffeine, ibuprofen, atenolol which degrade more rapidly in groundwater (Hillebrand et al. 2012b, Hillebrand et al., 2015; Reh et al. 2013,) could be used as evidence of rapid groundwater flow and high vulnerability. In contrast others (e.g. carbamazepine, acesulfame and the former EOC atrazine) are more persistent. However, the degradation properties of EOCs are still poorly understood, and the extent to which observations reflect degradation or other attenuation processes such as sorption and dilution is often unclear and there have been few laboratory studies of EOC properties. Further work on the properties of current and former EOCs would be very useful to improve understanding of their persistence in groundwater. In addition, the degradation products of EOCs can potentially be as toxic and persistent as parent compounds, and this topic has also received little attention.

3.2.2. *Investigating vulnerability using EOCs*

A useful potential application of EOCs in karst hydrogeology is for assessing the vulnerability of a spring or abstraction. In karst aquifers indicators such as rapidly fluctuating spring discharge (Butscher and Huggenberger, 2008), high turbidity (Fournier et al. 2006), or high coliforms (Mahler et al., 2000) are used as evidence that springs or abstractions have high vulnerability. EOCs provide further evidence of

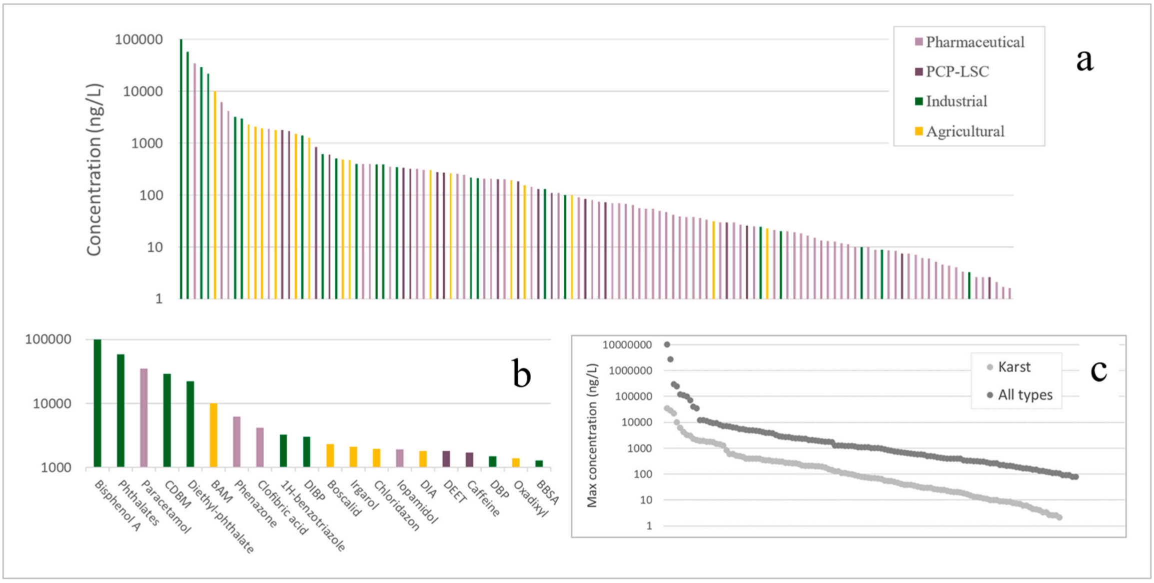

Fig. 4. Maximum concentrations of detected substances a) maximum concentrations of all detected compounds (antibiotic sulphanilamide is not presented in graph due to much higher concentration than other compounds at 6.5 × 10^8 ng/L, see Supplementary Material Table S1), b) maximum concentrations of first 24 compounds, c) maximum concentrations of all detected EOCs in karst groundwater in relation to groundwater in all rock types (according to Lapworth et al., 2012); compounds at x axes are different.

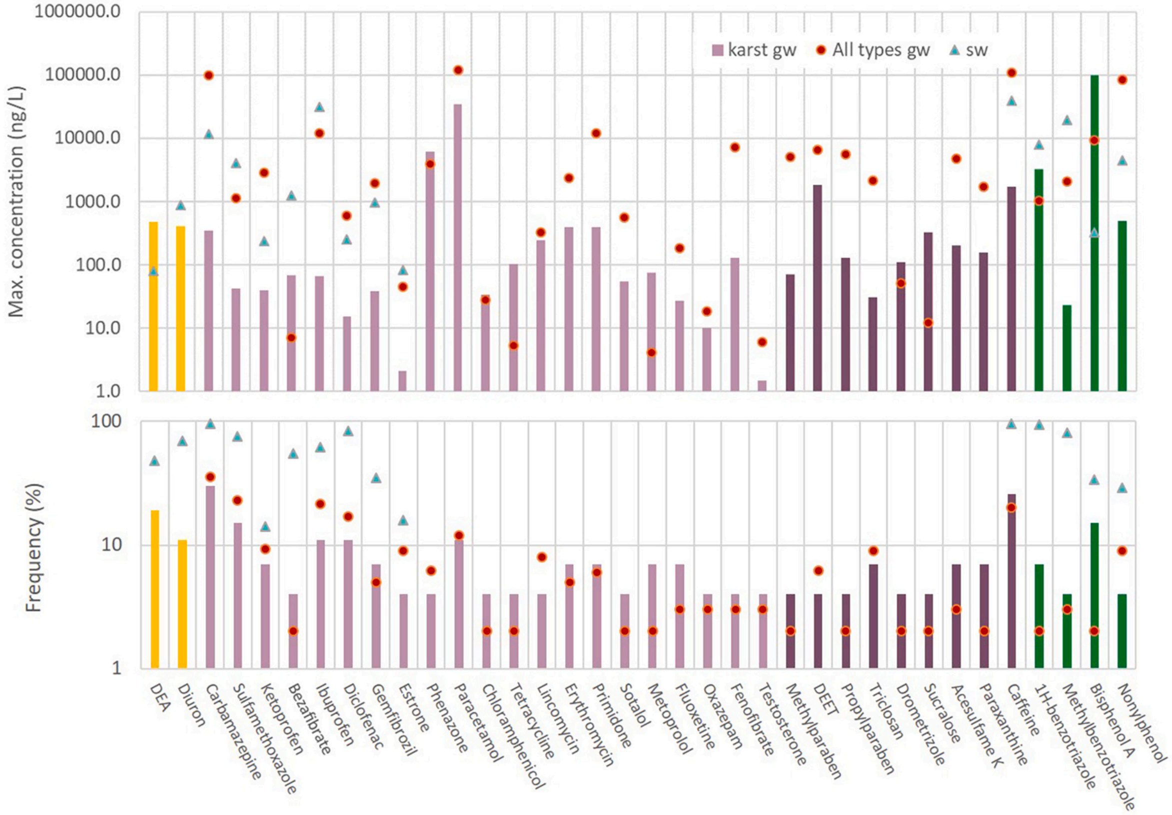

Fig. 5. Comparison of maximum concentration and frequency of microorganics detected in karst groundwater with groundwater globally from a range of aquifers types and surface waters in Europe. Bars show karst groundwater, dots and triangles show results for all aquifer types (Lapworth et al., 2012) and surface waters (Loos et al., 2009).

vulnerability if rapidly degrading compounds are present indicating rapid groundwater flow and low residence times; where particularly high concentrations of EOC compounds are present (Meffe and de Bustamante, 2014); or where there are a wide range of different types of EOC compounds.

There are examples of studies that have demonstrated high vulnerability using EOCs. High vulnerability from fast flow events in a karst aquifer with a leaking sewage pipe was identified using carbamazepine

Table 2
The use of EOCs (and other substances analysed as part of EOC analysis suites) for karst hydrogeological investigations.

Type of Karst Hydrogeological investigation	EOCs/other indicator substances	References
Identifying vulnerability and rapid groundwater flow	Caffeine Nonchlorinated organophosphates Ibuprofen, theophylline and metoprolol	Dvory et al., 2018b and Hillebrand et al., 2012a, Hillebrand et al. 2015; Heinz et al., 2009; Reh et al. (2013
Identifying long residence time components in karst groundwaters	Carbamazepine, Atrazine Acesulfame Phthalates Sucralose, gemfibrozil, iohexol Primidone, tamoxifen, phenazone,	Dvory et al. 2018b; Hillebrand et al. 2014, Morasch, 2013; Schiperski et al., 2015; Doummar and Aoun, 2018b; Zirlewagen et al., 2016; Padilla and Vesper, 2018; Doummar and Aoun, 2018b; Reh et al., 2013
Investigating subsurface contaminant attenuation mechanisms	Diclofenac, ibuprofen Carbamazepine	Einsiedl et al. (2010; Dvory et al. (2018a)
Identifying connectivity of groundwater with wastewater	Carbamazepine - for treated and untreated ww Caffeine-for recent inputs Cyclamate-for raw ww Acesulfame-K, gemfibrozil, iohexol Sucralose	Hillebrand et al., 2012a; Hillebrand et al., 2012a; Zirlewagen et al., 2016; Doummar and Aoun, 2018a; Doummar and Aoun, 2018b
Investigating whether nitrate sources are agricultural (or urban?)	Diatrizoic acid	Zemann et al., 2015
Identifying catchment areas/pollution sources from source specific pollutants (i.e. substances that are not widely used and can usually be traced to a single source)	Paraxanthine Caffeine Triazines-ternary diagrams Pharmaceuticals-fingerprinting different sources of anthropogenic pollution	Hillebrand et al., 2012a; Leal-Bautista et al., 2011; Chiffre et al. (2016); Keifer et al (2021)
Investigations of groundwater flowpaths and contaminant attenuation using introduced tracers	Caffeine	Hillebrand et al., 2012b, Hillebrand et al., 2015
Calculating ww rate in gw resource	Caffeine	Hillebrand et al. (2012b)
Statistical analyses for determing pollutant sources and/or catchment area	Group of different EOCs compounds	(Dodgen et al., 2017; Huang et al., 2019; Kiefer et al., 2021

and caffeine by Dvory et al. (2018a). Sorenson et al. (2015) found that deep groundwater in a karst aquifer was more vulnerable than previously thought. Clay-rich superficials were thought to provide significant groundwater protection to the karst aquifer, but high concentrations of DEET, with more than a five-fold increase after the wet season, showed that contaminants can transit rapidly from the surface to the bedrock aquifer.

In some cases, EOCs have been used in conjunction with other parameters for vulnerability assessment. For example, Doummar and Aoun (2018b) found that the mass flux of turbidity and chlorides were strongly correlated with those of the two artificial sweeteners sucralose and acesulfame-K. Schiperski et al. (2015) obtained good correlations between atrazine, metazachlor, cyclamate and SEC and turbidity in hysteresis plots.

Although the presence of EOCs can indicate rapid groundwater flow and high vulnerability, the absence of EOCs does not necessarily indicate low vulnerability if there are limited sources of EOC contaminants in the catchment. The large numbers of EOC compounds that can be measured, including some that indicate short residence times are clearly useful as indicators of vulnerability. These are best used in conjunction with other evidence, such as turbidity, coliforms, and discharge variability; and a good understanding of the land use in the catchment to enable assessment of the likely contaminant loads that could impact the spring or abstraction.

3.2.3. Identification of longer term storage in karst

Karst aquifers have extremely high hydraulic conductivities and generally have large components of short residence time groundwater (Ford and Williams, 2007). Nevertheless, even in highly karstified aquifers, there may be a substantial component of longer term storage (Ford and Williams, 2007; Atkinson, 1977; Smart and Friederich, 1986). Understanding longer term storage in karst aquifers is an important component of aquifer characterisation and EOCs could contribute to this understanding.

In some locations banned substances (such as atrazine) can provide evidence that karst aquifers could have significant contaminant storage and or longer residence time pathways (Einsiedl et al., 2010; Hillebrand et al., 2014; Reh et al., 2013; Schiperski et al., 2015; Zirlewagen et al., 2016). For example, even though atrazine was prohibited in Europe>20 years ago, it is still widely detected in karst aquifers (Hertzman, 2017; Iker et al., 2010; Lapworth and Gooddy, 2006; Morasch, 2013). It has been suggested that this is because atrazine is stored and persists in the matrix which slowly leaks into the fracture and conduit flow system (Hillebrand et al., 2014; Morasch, 2013; Schiperski et al., 2015). Atrazine and its metabolites have been detected at ng/L-µg/L concentrations in a range of karst studies and it appears that it may pose a continued risk to humans and microbiological communities long after it has been banned from use (Huang et al., 2019; Qin et al., 2020; Xiang et al., 2020). In other cases, the start date for the use of a particular EOC, such as artificial sugars or pharmaceuticals, can be obtained for a particular country or region and may help constrain the residence time of the groundwater system under investigation.

Zemann et al. (2015) found the most frequently detected compounds in karst groundwater samples were two standard substances used in X-ray diagnostics, diatrizoic acid (DA), whose use has been significantly reduced since 2008, and iopamidol (IP), which is the usual replacement for DA. During this five-year investigation, DA was detected only a few times in wastewater, and IP occurred more commonly in wastewater and groundwater, suggesting a more recent wastewater input to groundwater. The low, but continuous DA concentrations in groundwater suggest that there is also a longer term storage component with the residual concentrations of DA in the matrix of the unsaturated zone being slowly being released into the more permeable parts of the karst system (solutional fractures and conduits).

3.2.4. Attenuation mechanisms in karst aquifers

Within aquifers, a range of processes such as dilution, dispersion, diffusion, and sorption are important for controlling natural attenuation. Conduit rich karst is generally thought to have poor attenuation capabilities due to rapid and focussed groundwater inputs via streams sinks and rapid groundwater flow which can exceed a velocity of 30 km/d (Petrič et al., 2020), and because they are oligotrophic (Gibert et al., 1994; Hirsch, 1986). However, even in highly karstified aquifers, contaminants can be attenuated. Studies of EOCs have contributed to understanding of attenuation mechanisms (Einsiedl et al., 2010; Hillebrand et al., 2012b; Zemann et al., 2015). In particular, studies have considered attenuation via diffusion between different void types (e.g. conduits, fissures and fractures) (Dvory et al., 2018a, 2018b; Einsiedl et al., 2010). Other studies have indirectly provided information on attenuation processes (Bekele et al., 2009; Doummar and Aoun, 2018b; Heinz et al., 2009; Hillebrand et al., 2012b, 2015; Katz et al., 2010; Reh et al., 2013; Zemann et al., 2015).

Einsiedl et al. (2010) used two pharmaceuticals, diclofenac and ibuprofen, from wastewater effluents in springs, to compliment

Table 3
EOC degradation rates.

Compound	Recovery rate/recovery rate related to uranine (%)	Half life (h)/ Degradation rate (d^{-1})	Method	Key processes identified	Reference
Caffeine	27/55	104 h 0.16 d^{-1}	Simultaneous tracing with caffeine and uranine	ww leakage and the redox condition	Hillebrand et al 2012a
	41.4/67.2	89.1 h 0.19 d^{-1}	Simultaneous tracing with eight tracers	Biodegradation	Hillebrand et al. 2015
	82.1 ± 10.2	0.091 d^{-1}	Transport modelling (ww releases over the outcrops of the carbonate aquifer)	Biodegradation and sorption in to lesser extent. Caffeine was completely degraded a few months after the sewage spill	Dvory et al. 2018b
Atenolol	30.6/50	61.8 h	Simultaneous tracing with eight tracers	Biodegradation	Hillebrand et al. 2015
Ibuprofen	31.3/51.1	79.9 h			
Paracetamol	17.6/28.8	37.5 h			
Acesulfame	67.8/100				
Cyclamate*	63.8/94.1	1366 h			
Carbamazepine	61.2/100				
Carbamazepine	86.2 ± 14.2	less than0.05	Transport modelling (ww releases over the outcrops of the carbonate aquifer)	95 % of carbamazepine mass remained in the vadose zone 6 months after its peak concentrations	Dvory et al. 2018b
Atrazine	4–7.5 % of total applied mass have been discharged through 45 years	na	Assumptions based on total applied mass to total mass discharged at spring	Rock matrix storage, low to nonexistent degradation rates	Hillebrand et al. 2014

*less reliable data due to short residence time in the aquifer during the tracer test (Hillebrand et al., 2015).

modelling and tracer testing studies of attenuation. They concluded that contaminant transport is significantly influenced by diffusion between the mobile fracture flow component of the aquifer and groundwater in the matrix.

Dvory et al. (2018a) investigated attenuation processes by simulating carbamazepine transport in the saturated and unsaturated zones of a karst aquifer to investigate processes during fast flow events and baseflow. The modeling results suggested low solute exchange and less diffusion of contaminant into the matrix during fast flow events with more carbamazepine reaching the saturated zone from the unsaturated zone. In contrast, during low flow conditions, high storage in the porous matrix of the unsaturated zone was thought to provide a continuous supply of carbamazepine to the saturated zone.

3.2.5. *Identifying pollutant sources*

EOCs can help identify the origin of pollution (Stuart et al., 2014; Kiefer et al., 2021). Unlike many conventional indicators (e.g. inorganic ions, electrical conductivity), they do not have natural background concentrations. Some EOCs also have a unique source type, which makes them particularly useful source specific indicators. When used in combination with other tracers and tools they may provide useful insights into the sources of pollution in the catchment. EOCs are particularly useful for identifying connectivity with wastewater and the compounds that have been most useful for this are discussed in Section 3.2.5.1. Their use for identification of other pollutant sources are discussed in Section 3.2.5.2

3.2.5.1. Identifying connectivity with wastewater effluents. Wastewater (ww) poses a major risk to groundwater, especially in vulnerable karst areas. EOCs have been successfully used to provide information on how effective ww treatments are and detect pollution incidents, and specific indicators are reviewed below.

Carbamazepine

Several studies have shown that carbamazepine is a conservative indicator for both treated and untreated wastewater (Clara et al., 2004; Dvory et al., 2018b; Fenz et al., 2005; Gasser et al., 2010). However, carbamazepine concentrations in effluent are often relatively low and therefore may be a poor indicator where only small quantities of ww are discharged into highly diluting systems (Hillebrand et al., 2012a).

Caffeine and its metabolites

Many surface water investigations found caffeine to be a good ww indicator (Buerge et al., 2003, 2006; Edwards et al., 2015, Gonçalves et al., 2017). Caffeine has also been used as a ww indicator in karst groundwater systems. Caffeine degrades in groundwater (Section 3.2.1), and is not a good indicator in systems with long transit times, but can determine recent ww inputs (Hillebrand et al., 2012a). It is especially useful where carbamazepine concentrations are low (Dvory et al., 2018b) because ww can contain caffeine concentrations several orders of magnitude higher than carbamazepine (Miao et al., 2005). In one study, a positive correlation of caffeine with its predominantly human metabolite paraxanthine suggested a connection with domestic ww (Hillebrand et al., 2012a) while in another it has been used as an indicator of the impact of tourism on water quality in an area of the Yucatan (Leal-Bautista et al., 2011).

Hillebrand et al. (2012b) used caffeine concentrations in spring water and untreated ww, water consumption rates, and spring discharge data, to calculate that the average amount of domestic ww discharging at a karst spring was approximately 0.4% of the total amount of ww within the spring catchment. This is a relatively low fraction compared to those calculated by Rutsch et al. (2006) for other catchments which were found to be in the range of 1–13 %. Doummar and Aoun (2018a) suggested that compounds more resistant to high degradation would be more suitable for estimating exfiltration rates of ww into the environment. Using a mixing model based on chloride mass fluxes, they defined exfiltration rates in a karst catchment of 0.7–4 % in low to medium flow and 5–10 % at high flow.

Cyclamate

Cyclamate (CYC) could be used as a tracer of raw ww sources (Zirlewagen et al., 2016). It has similar concentrations in ww to caffeine and was shown to be a more sensitive indicator for untreated ww than caffeine because it is less degradable. However, its detection does not necessarily indicate a recent input of ww to karst systems, and therefore the combined use of caffeine and cyclamate may be useful (Hillebrand et al., 2015). Zirlewagen et al. (2016) suggested using the ratio of cyclamate and another, much more persistent, artificial sweetener, acesulfame (ACE) as indicator for raw wastewater as it is not affected by uncertainties associated with dilution. The high CYC/ACE ratio indicates fresh inputs of untreated ww. In the same investigation concentration curves of cyclamate were similar to those of the faecal indicator bacteria suggesting that they had the same origin and that ww is the main source of bacterial pollution in the catchment.

Other EOC tracers

Other EOCs that have been shown to be good wastewater indicators are acesulfame-K, gemfibrozil, iohexol (Doummar and Aoun, 2018a), sucralose (Doummar and Aoun, 2018b), DEET, caffeine metabolites theophylline, triclosan, and atenolol (Upton et al., 2020), and chlorinated organophosphate, tris-2-chloro-1-chloromethyl-ethyl-phosphate (Heinz et al., 2009). Acesulfame-K, gemfibrozil and iohexol may be indicators of domestic ww effluents, or pollution from specific point sources such as poultry farms and hospitals (Doummar and Aoun, 2018a). Sucralose has a high detection limit of 100 μg/L but it has still been detected and indicated the presence of wastewater in a karst groundwater system (Doummar and Aoun, 2018b). There is inconclusive evidence on whether diclofenac is a good ww tracer. Reh et al. (2013) suggested that diclofenac has high attenuation. However, Einsiedl et al. (2010) reported frequent detections of diclofenac which they attributed to high concentrations in treated WW effluent, widespread long term use, and low sorption properties. Ibuprofen was thought to be poor ww indicator in a study by Einsiedl et al. (2010) due to its low detection in karst samples, despite its high concentrations in raw ww. High biodegradation rates were suggested as the most likely explanation for this.

3.2.5.2. Identifying other sources of pollution. EOCs and other legacy microorganic pollutants also point to other non-ww sources of pollution in karst, i.e. agriculture (Chiffre et al., 2016; Dong et al., 2018; Hillebrand et al., 2014; Morasch, 2013; Reh et al., 2013) or industrial activities (Dong et al., 2018). Reh et al. (2013) separated different sources of pollutants using ternary diagrams of triazines (atrazine and its degradation products DEA and DIA). Samples from agricultural areas had high fractions of DEA, whilst those from urban areas had a higher DIA fraction. Chiffre et al. (2016) detected pharmaceuticals at sample locations in rural sparsely populated areas not just downstream of ww treatment plant as expected, but upstream as well.

A good example of the application of EOCs as source specific indicators is the study where sources of groundwater nitrate pollution were identified by correlation with diatrizoic acid (Zemann et al., 2015). It is well known that nitrate can reach groundwater from various sources such as sewage and agriculture. However, as diatrizoic acid had not been used in agriculture, but is found in urban ww, it was most likely that ww was the source of nitrate in the groundwater. Much like Stuart et al. (2014), and more recently Keifer et al (2021), they identified pharmaceutical detection rates as a suitable tool for fingerprinting different sources of anthropogenic pollution.

3.2.6. Catchment delineation

Catchment delineation in karst can be challenging due to the high heterogeneity and changes in groundwater divides under different water level conditions. Many EOCs have limited numbers of potential sources, and the occurrence of specific EOCs at a groundwater abstraction could indicate connectivity with a particular contaminant source and thereby demonstrate that it is in the catchment. For example, by intensive monitoring of micropollutants (pharmaceuticals, corrosion inhibitor, pesticides), Morash (2013) found that the main source of the pollutants at two observed springs in a Swiss karst catchment was a swallow hole draining an agricultural plain, indicating that this site is within the spring catchment area. In another example, Reh et al. (2014) used detections of triazines to help with catchment delineation by distinguishing agricultural and urban pollutant sources. While in areas with multiple potential sources, and high levels of contamination, it may be difficult to determine the exact source of a contaminant (Lapworth et al., 2015; Reh et al., 2013), the use of statistical methods (e.g. correlations, clustering) can help to determine pollutant sources and thus catchment areas (Dodgen et al., 2017; Huang et al., 2019; Stuart et al., 2014).

Although by definition EOCs are contaminants and should not be knowingly introduced to groundwater, some newly measured compounds could have suitable properties for use as artificial tracers if they are non toxic. Artificial tracers should be conservative, absent from but readily soluble in water, easy to detect quantitatively, inexpensive, and easy to handle (Goldscheider and Drew, 2007; Käss, 1998). Karst groundwater tracer tests have been conducted using caffeine and results were obtained (Hillebrand et al., 2012b, Hillebrand et al., 2015). Caffeine is cheap but is degradable and present in the environment, so is not an ideal tracer, but it could possibly be useful for tracer tests to delineate catchments in small highly karstified areas in the case of known or low background concentrations.

4. Conclusions

This paper reviewed 50 studies on EOCs in karst from 21 countries. EOCs are clearly an important threat to karst groundwater quality which could impact drinking water sources, rivers and other dependant ecosystems. A total of 144 compounds were detected in spring and groundwater samples. The most frequently detected compounds were pharmaceutical products as well as pesticides used in agriculture, with fewer industrial compounds and personal care products and lifestyle compounds (PCP-LS) detected. Carbamazepine and caffeine were the most frequently detected compounds, whilst many compounds were detected in just a single study.

Maximum concentrations of compounds varied over 5 orders of magnitude, and nearly half of the detected compounds exceed 100 ng/L, the current EU drinking water limit for individual pesticides. Many of the highest concentrations were industrial compounds, although the highest concentration was of the antibiotic sulphanilamide (6.5×10^8 ng/L).

This review suggests that overall EOCs may have a lower frequency of detection and lower concentrations in karst groundwater compared to surface waters and local shallow alluvial aquifers, but higher concentrations compared to other major aquifer types such as sandstones.

This paper also reviews the use of EOCs in karst hydrogeological studies. EOCs represent a potentially very large range of anthropogenically introduced tracers with a wide range of physical and chemical properties and different subsequent fate in karst. The presence of rapidly degrading EOCs (e.g. caffeine) can be an indicator of rapid groundwater flow and vulnerability; and aquifer vulnerability is also indicated by high concentrations of EOCs or a wide range of different EOCs at a site. In contrast, persistent, former EOCs that are banned or no longer used (e. g atrazine, diatrizoic acid) can indicate a component of longer term storage in karst aquifers. Furthermore, the transport of EOCs in karst may help improve understanding of attenuation mechanisms, for example, exchange between the matrix, fractures and larger conduits.

EOCs are useful to identify sources of pollution in karst. Several EOC compounds have been shown to be good indicators of connectivity with wastewater. More persistent compounds (e.g. carbamazepine, acesulfame) can be used as indicators for both treated and untreated wastewater, while readily degradable compounds (e.g. caffeine, cyclamate) indicate more recent wastewater inputs. Some EOCs also have a unique source, which makes them particularly useful for source identification and catchment delineation.

5. Future outlook

Studies of EOCs in karst are a fairly new area of research. The relatively small number of studies (50) found in our review highlights the need for further research on EOCs in karst aquifers, to improve understanding of their impacts on karst environments, and to develop their use for karst aquifer characterisation. More studies employing more frequent monitoring are required to assess temporal changes, particularly important for dynamic karst systems; and more sensitive analytical methods are also required to improve assessments of EOC contamination. The lack of data on microplastics in karst groundwaters is also an important area requiring future research.

The data compiled here are limited because the only parameter that was consistently reported in the studies reviewed was maximum concentration. A collaborative project with a full analysis of all the EOC data in karst aquifers would be extremely useful to provide more robust conclusions on EOCs in karst aquifers.

The relationships between EOC occurrence and other drivers of stress and the prevalence of anti microbial resistance should be further assessed in these highly vulnerable (in many ways sentinel) karst groundwaters systems. Given the role of karst as a host for a range of important stygofauna (Maurice et al., 2016), it is also recommended that further research is done to assess the fate of hazardous EOCs, as well as their interaction and potential accumulation in dependant ecosystems within karst.

Selected EOCs are now beginning to be included more widely within some national monitoring plans (Glassmeyer et al., 2017; Bunting et al., 2021), a recent example being the introduction of a Groundwater Watch list in Europe (Lapworth et al., 2019). However, as this review has shown, even in karst, which are amongst the most vulnerable groundwater systems, there are relatively few studies that have been undertaken on EOCs. There is a requirement for more research and monitoring of EOCs in karst, and a need for better prioritisation of screening for EOCs in groundwater and dependant ecosystems (e.g. Gaston et al., 2019), particularly given the importance of karst for drinking water supplies globally and its role as a unique and vulnerable ecosystem.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This paper is partly the result of collaboration, training and education conducted through GeoTwinn project that has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement no. 809943. BGS authors publish with the permission of the BGS-UKRI director.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jhydrol.2021.127242.

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