

New organic groundwater pollutants in the national groundwater monitoring network of Poland

Anna KUCZYŃSKA^{1, *}

¹ Polish Geological Institute – National Research Institute, Rakowiecka 4, 00-975 Warszawa, Poland;
ORCID: 0000-0002-9455-1166



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This article reports on emerging organic compounds (EOCs) discovered in groundwater samples collected within the national groundwater monitoring network of Poland. EOCs are very toxic substances that can significantly disrupt the functioning of living organisms. Monitoring of EOCs is not yet regulated within EU groundwater legislation, and so is rarely undertaken at national levels. In Poland EOCs are mainly monitored at local scales, usually undertaken by academic centres, except for the Polish Geological Institute – National Research Institute (PGI), which undertakes studies at broader scales, collecting samples from the national groundwater monitoring network. Data collected in 2016–2017 proved the presence of pharmaceutical substances in 53% of monitoring sites. Between 2022–2024 PGI continued sampling for pharmaceuticals, nonylphenol, 17- β -estradiol, PFAS, solvents and chelating agents. The results demonstrated the presence of EOCs in groundwater in Poland, especially in areas exposed to agriculture and industry, and in urban agglomerations. Pharmaceuticals have been found in 21%, PFAS compounds in 19%, nonylphenol in 17% and solvents and chelating substances in 45% of the boreholes sampled. Four substances were found sufficiently frequently to be placed on a list of substances to be regulated at EU level. These were carbamazepine, PFPeA, nonylphenol and 2-Ethoxy-2-methylpropane (ETBE).

Key words: emerging organic contaminants, groundwater pollution, water quality, pharmaceuticals, PFAS, nonylphenol, PMT.

INTRODUCTION

Emerging organic compounds are synthetic or natural organic compounds such as pesticides, pharmaceuticals, oestrogens, surfactants, personal hygiene products, food additives and industrial additives, which are commonly used in many sectors of the economy and industry worldwide, and which enter the environment as a result of anthropogenic activities. They commonly pose a threat to the health and life of organisms by causing changes in the hormonal, immune, and endocrine systems and leading potentially to the development of serious illnesses. Research on the presence of EOCs in groundwater and their interactions and negative effects on living organisms has been conducted for several decades (Seiler et al., 1999; Sacher et al., 2001; Kolpin et al., 2002; Cordy et al., 2004; Verstraeten et al., 2005; Barnes et al., 2008; Zuccato et al., 2008; Loos et al., 2010; Vulliet and Cren-Olive, 2011; Stuart et al., 2012; Lapworth et al., 2012; de Jesus Gaffney et al., 2015)

but it is the last decade that has provided the most information about their wide presence in groundwater (Bexfield et al., 2019; Bunting et al., 2021). This is linked to the development and improvement of analytical techniques capable of detecting small concentrations of EOCs. In Poland, monitoring of emerging contaminants in groundwater, despite overall good awareness of this problem worldwide, is still not included in the framework of the State Monitoring Programme. As such, funding is limited and the problem is addressed only in research projects. As reported by Ślósarczyk et al. (2021), only 14 scientific publications on the presence of pharmaceuticals and personal care products in Polish groundwater were available by 2021, the majority of which had limited spatial extent, being focused on local problems. Since then, four more publications appeared, and these were also focused on local problems such as landfill leachate (Ślósarczyk and Dąbrowska, 2025), drinking water quality (Sikora et al., 2025; Ślósarczyk et al., 2025) and general characterisation of urban groundwater in the Kraków area (Rusiniak et al., 2021). Most of the Polish publications on emerging contaminants report studies of pharmaceuticals and personal care products (Caban et al., 2015; Kapelewska et al., 2016; Kuczyńska, 2017, 2019; Kuczyńska and Janica, 2017; Kruć et al., 2019a, b, 2022, 2023; Szymczycha et al., 2020; Kmiecik et al., 2020; Rusiniak et al., 2021; Ślósarczyk and

* E-mail: anna.kuczynska@pgi.gov.pl

Dąbrowska, 2025; Ślósarczyk et al., 2025). Studies on other groups of emerging contaminants, such as industrial chemicals including PMT (persistent, mobile and toxic) and PFAS (per- and polyfluorinated) substances are still very few (Kapelewska et al., 2016, 2018; Sikora et al., 2025).

This article reports the results of pilot monitoring studies focused on a total of 72 emerging contaminants analysed by the Polish Geological Institute – National Research Institute (PGI) between 2022–2024, as a follow up of EOCs studies carried out by PGI in 2016–2017 (Kuczyńska, 2019). This included 11 pharmaceutical active substances, 16 PFAS compounds, nonylphenol, 17- α -estradiol, and 43 solvents and chelating agents. Samples were taken from monitoring boreholes included in the national groundwater monitoring network. As such, despite the pilot character of the research, the results provide more nationwide cover than the other studies so far reported from Poland.

PROPERTIES OF EOCs INCLUDED IN THE REVIEW

Pharmaceuticals are chemical substances that are biologically active and used in human and veterinary medicine. High production and consumption of drugs is recognised as a global problem, causing pharmaceuticals and their metabolites to pollute the environment, including groundwater (Kuczyńska, 2017). Per- and polyfluoroalkyl substances (PFAS) are a large class of thousands of synthetic chemicals that are used throughout society. Their global use started in the 1940s and led to environmental pollution that is linked to negative effects on human health. Due to carbon-fluorine bonds being one of the strongest chemical bonds in organic chemistry, PFAS are resistant to degradation processes. For that reason they are often called “forever chemicals”. Most PFAS are also easily transported over long distances in the environment. Nonylphenol (NP) is an anionic surfactant, a substance similar to detergents with a wide range of applications, leading to their common presence in the environment. NP is produced in large quantities and is used in both industrial processes and in consumer laundry detergents, personal hygiene products, products containing polyvinyl chloride (PVC), automotive applications, in latex paints, epoxy and phenolic resins, and in lawn care products and pesticides (Lacorte et al., 2002; Soares et al., 2008). NP is highly toxic to aquatic organisms. It can accumulate in tissues and leads to the feminization of aquatic organisms, reducing male fertility, and impacts the viability of young individuals. 17- α -estradiol (E2) is a natural oestrogen that is known to cause endocrine-disturbing effects, being toxic to aquatic ecosystems and dangerous for human health (SCHEER, 2022). Specifically it has been associated with increased rates of breast and prostate cancer, decreased sperm quality, premature menopause and virilization in young girls. Estradiol is widely used for oral contraception and in post-menopausal hormonal therapy. Solvents and chelating agents are synthetic organic chemicals of common use in many fields of industry. Due to their intrinsic properties, such as persistence, mobility and toxicity they are very dangerous to the environment and to human health. They can travel long distances and stay in the environment bounded to soil, which makes them a long-lasting threat to drinking water resources (Hale et al., 2020).

MATERIALS AND METHODS

Data reported in this article were gathered within three separate sampling campaigns, for which separate research objectives and funding were set, hence the number of sampling loca-

tions and the number of analysed parameters in every campaign were different. Some campaigns included more than one group of chemicals.

ANALYTES

The selection of pharmaceutical and PFAS compounds analysed in 2022 was based on recommendations given by the CIS Working Group Groundwater in 2019 (CIS, 2019a, b) and reflected parameters considered in the selection of candidates for either inclusion in the voluntary groundwater watch list or in regulations under the Groundwater Directive. This included the following substances (Table 1): pharmaceuticals – sulfadiazine, erythromycin, clatromycin, clopidol, crotamiton, primidone, sotalol, ibuprofen, diatrozoic acid, sulfametoxazole and carbamazepine; PFAS compounds – perfluorobutanoic acid (PFBA), 4:2 monoPAP, perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorobutane sulfonic acid (PFBS), 6:2 monoPAP, perfluoroheptanoic acid (PFHpA), perfluorodecylphosphonic acid (PFDPA), perfluorooctanoic acid (PFOA), perfluorohexane sulfonic acid (PFHxS), perfluorononanoic acid (PFNA), perfluorooctylphosphoric acid (PFOPA), perfluorodecanoic acid (PFDA), perfluorooctane sulfonic acid (PFOS), perfluoroundecanoic acid (PFUnA) and perfluorododecanoic acid (PFDoA). According to analysis done by the CIS Working Group Groundwater these pharmaceuticals and PFAS compounds either frequently occur in groundwater or have large potential to be present in groundwater across the EU and therefore require further monitoring (CIS, 2019a, b). NP and 17- α -estradiol were chosen for the study in 2023 because of concerns over their endocrine-disrupting properties, which was addressed in Drinking Water Regulation 2020/2184. The group of 43 solvents and chelating agents surveyed in 2024 was selected following a methodology used by experts of the CIS Working Group Groundwater, who selected them from a group of PMT (permanent, mobile, toxic) substances as defined by the German Federal Environmental Agency (Neuman and Schliebner, 2019) for the purpose of selecting candidates for either inclusion in the voluntary groundwater watch list or in regulations under the Groundwater Directive. The list of substances included: 1,1,1-Trichlorethane, 1,1,2,2-Tetrachlorethane, 1,1,2-Trichlorethane, 1,1-Dichlorethylene, 1,1-Dichloroethane, 1,2,3-Trichlorobenzene, 1,2,4-Trichlorobenzene, 1,2,4-Trimethylbenzene, 1,2-Dichlorobenzene, 1,2-Dichloroethane, 1,2-dichloropropane, 1,3,5-Trimethylbenzene, 1,4-Dioxane, 2-Ethoxy-2-methylpropane, benzene, bromdichlormethane, carbon tetrachloride, chlorobenzene, chloroethane, chloroform, chloromethane, cis-1,2-Dichloroethene, dibromochlormethane, dichloromethane, diethylene glycol dimethyl ether, diisopropylether, EDTA, ethylbenzene, isopropylbenzene, n-butylbenzene, n-propylbenzene, NTA, tert-butanol, tert-butyl methyl ether, tetrachloroethene, tetraglyme, tetrahydrofuran, toluene, trans-1,2-Dichloroethene, tribromomethane, trichloroethene, trifluoroacetic acid and vinyl chloride.

SAMPLING LOCATIONS

Locations selected for groundwater sampling were chosen from the points belonging to the national groundwater monitoring network used for WFD water quality monitoring and located throughout the entire country. To optimise resources for the research, sampling was done in parallel to the operational monitoring. For that reason the majority of sampling sites were located within GWBs identified to be at risk of not achieving environmental objectives, which is either in GWBs being of poor status or where pressures threatening the status were identified.

Table 1

Characteristics of chemicals and analytical methods described in the article

No.	Parameter	Group	CAS number	Analytical method	Limit of Quantification [µg/L]
1	Diatrozoic acid	pharmaceutical	117-96-4	LC-MS/MS SPE	0.023
2	Sotalol	pharmaceutical	3930-20-9	LC-MS/MS SPE	0.015
3	Sulfadiazine	pharmaceutical	68-35-9	LC-MS/MS SPE	0.014
4	Clopidol	pharmaceutical	2971-90-6	LC-MS/MS SPE	0.017
5	Primidone	pharmaceutical	125-33-7	LC-MS/MS SPE	0.012
6	Sulfametoxazole	pharmaceutical	723-46-6	LC-MS/MS SPE	0.013
7	Carbamazepine	pharmaceutical	298-46-4	LC-MS/MS SPE	0.011
8	Erythromycin	pharmaceutical	114-07-8	LC-MS/MS SPE	0.013
9	Clarithromycin	pharmaceutical	81103-11-9	LC-MS/MS SPE	0.014
10	Crotamiton	pharmaceutical	483-63-6	LC-MS/MS SPE	0.014
11	Ibuprofen	pharmaceutical	15687-27-1	LC-MS/MS SPE	0.024
12	PFBA	PFAS	375-22-4	LC-MS/MS SPE	0.006
13	4:2 monoPAP	PFAS	150065-76-2	LC-MS/MS SPE	0.026
14	PFPeA	PFAS	2706-90-3	LC-MS/MS SPE	0.020
15	PFHxA	PFAS	307-24-4	LC-MS/MS SPE	0.019
16	PFBS	PFAS	375-73-5	LC-MS/MS SPE	0.011
17	6:2 monoPAP	PFAS	57678-01-0	LC-MS/MS SPE	0.028
18	PFHpA	PFAS	375-85-9	LC-MS/MS SPE	0.013
19	PFDDPA	PFAS	52299-26-0	LC-MS/MS SPE	0.016
20	PFOA	PFAS	335-67-1	LC-MS/MS SPE	0.013
21	PFHxS	PFAS	355-46-4	LC-MS/MS SPE	0.016
22	PFNA	PFAS	375-95-1	LC-MS/MS SPE	0.012
23	PFOPA	PFAS	40143-78-0	LC-MS/MS SPE	0.031
24	PFDA	PFAS	335-76-2	LC-MS/MS SPE	0.011
25	PFOS	PFAS	1763-23-1	LC-MS/MS SPE	0.017
26	PFUnA	PFAS	2058-94-8	LC-MS/MS SPE	0.012
27	PFDoA	PFAS	307-55-1	LC-MS/MS SPE	0.011
28	17-β-estradiol	endocrine disruptant	50-28-2	LC-MS/MS SPE	0.3
29	4-nonylphenol	endocrine disruptant	84852-15-3	LC-MS/MS SPE	0.1
30	1,1,1-Trichlorethane	solvent and chelating agents	71-55-6	HS-GC-MS	0.25
31	1,1,2,2-Tetrachlorethane	solvent and chelating agents	79-34-5	HS-GC-MS	0.25
32	1,1,2-Trichlorethane	solvent and chelating agents	79-00-5	HS-GC-MS	0.25
33	1,1-Dichlorethylene	solvent and chelating agents	75-35-4	HS-GC-MS	0.25
34	1,1-Dichloroethane	solvent and chelating agents	75-34-3	HS-GC-MS	0.25
35	1,2,3-Trichlorobenzene	solvent and chelating agents	87-61-6	HS-GC-MS	0.25
36	1,2,4-Trichlorobenzene	solvent and chelating agents	120-82-1	HS-GC-MS	0.25
37	1,2,4-Trimethylbenzene	solvent and chelating agents	95-63-6	HS-GC-MS	0.25
38	1,2-Dichlorobenzene	solvent and chelating agents	95-50-1	HS-GC-MS	0.25
39	1,2-Dichloroethane	solvent and chelating agents	107-06-2	HS-GC-MS	0.25
40	1,2-dichloropropane	solvent and chelating agents	78-87-5	HS-GC-MS	0.25
41	1,3,5-Trimethylbenzene	solvent and chelating agents	108-70-3	HS-GC-MS	0.25
42	1,4-Dioxane	solvent and chelating agents	123-91-1	GC-MS/MS	0.5
43	2-Ethoxy-2-methylpropane	solvent and chelating agents	637-92-3	HS-GC-MS	0.02
44	Benzene	solvent and chelating agents	71-43-2	HS-GC-MS	0.25
45	Bromdichlormethane	solvent and chelating agents	75-27-4	HS-GC-MS	0.25
46	Carbon tetrachloride	solvent and chelating agents	56-23-5	HS-GC-MS	0.25
47	Chlorobenzene	solvent and chelating agents	108-90-7	HS-GC-MS	0.25
48	Chloroethane	solvent and chelating agents	75-00-3	HS-GC-MS	0.25
49	Chloroform	solvent and chelating agents	67-66-3	HS-GC-MS	0.25
50	Chloromethane	solvent and chelating agents	74-87-3	HS-GC-MS	0.25
51	cis-1,2-Dichloroethene	solvent and chelating agents	156-59-2	HS-GC-MS	0.25
52	Dibromochlormethane	solvent and chelating agents	124-48-1	HS-GC-MS	0.25

Tabl. 1 cont.

No.	Parameter	Group	CAS number	Analytical method	Limit of Quantification [µg/L]
53	Dichloromethane	solvent and chelating agents	75-09-2	HS-GC-MS	0.25
54	Diethylene glycol dimethyl ether	solvent and chelating agents	111-96-6	GC-MS/MS	1
55	Diisopropylether	solvent and chelating agents	108-20-3	HS-GC-MS	2
56	EDTA	solvent and chelating agents	60-00-4	LC-UV	1
57	Ethylbenzene	solvent and chelating agents	100-41-4	HS-GC-MS	0.25
58	Isopropylbenzene	solvent and chelating agents	98-82-8	HS-GC-MS	0.25
59	n-Butylbenzene	solvent and chelating agents	104-51-8	HS-GC-MS	0.25
60	n-Propylbenzene	solvent and chelating agents	103-65-1	HS-GC-MS	0.25
61	NTA	solvent and chelating agents	139-13-9	LC-UV	1
62	Tert-butanol	solvent and chelating agents	75-65-0	HS-GC-MS	2
63	Tert-butyl methyl ether	solvent and chelating agents	1634-04-4	HS-GC-MS	0.5
64	Tetrachloroethene	solvent and chelating agents	127-18-4	HS-GC-MS	0.25
65	Tetraglyme	solvent and chelating agents	143-24-8	LC-MS/MS	0.03
66	Tetrahydrofuran	solvent and chelating agents	109-99-9	HS-GC-MS	0.05
67	Toluene	solvent and chelating agents	108-88-3	HS-GC-MS	0.25
68	trans-1,2-Dichloroethene	solvent and chelating agents	156-60-5	HS-GC-MS	0.25
69	Tribromomethane	solvent and chelating agents	75-25-2	HS-GC-MS	0.25
70	Trichloroethene	solvent and chelating agents	79-01-6	HS-GC-MS	0.25
71	Trifluoroacetic Acid	solvent and chelating agents	76-05-1	LC-MS/MS	10
72	Vinylchlorid	solvent and chelating agents	75-01-4	HS-GC-MS	0.25
LC-MS/MS – Liquid Chromatography coupled with Tandem Mass Spectrometry LC-MS/MS SPE – Liquid Chromatography coupled with Tandem Mass Spectrometry and Solid Phase Extraction HS-GC-MS – Headspace Gas Chromatography-Mass Spectrometry GC-MS/MS – Gas Chromatography-Mass Spectrometry LC-UV – Liquid Chromatography-Ultraviolet					

Sampling points were analysed in terms of location and the construction of the borehole, following the criteria: a. shallow occurrence of the monitored aquifer with no or a limited confining layer; b. location within or in close proximity to urban agglomerations or unsewered rural areas; c. location at short distances from documented contamination sources such as cemeteries, hospitals, sewage treatment plants; or, at short distances from surface water courses. Samples were taken in a total of 268 locations situated within 96 GWBs. Pharmaceuticals and PFAS compounds were surveyed in 106 monitoring points that were located within an area of 63 groundwater bodies (GWBs). Nonylphenol and 17- β -estradiol were surveyed in 151 monitoring boreholes spread within 72 GWBs and solvents and chelating agents were studied in 56 monitoring boreholes located within 29 GWBs. Monitoring boreholes were mostly screened in porous deposits (over 90% of monitoring points) of Quaternary age (75%). Depth to the aquifer varied from 0 to 240 m b.g.l.; however in 75% monitoring boreholes did not exceed 25 m b.g.l. Characteristics and locations of water sampling locations are provided in [Figure 1](#) and [Supplementary data Table 1](#), respectively.

SAMPLING PROCEDURES AND TRANSPORTATION

To collect representative groundwater samples, the wells from which water samples were taken were previously pumped using portable pumping sets, suction pumps, or Gigant or Gigant & While type pumps. During the pumping, measurements of the stabilization of the following parameters were

made: temperature, pH level, and electrolytic conductivity (EC), which aimed to establish inflow of fresh water from the aquifer to the well. Depending on the stability of the substances monitored, the volume of water pumped from the wells ranged from 3 to 5 times the volume of stagnant water. Samples were collected according to “clean hands-dirty hands” protocol. Water samples for pharmaceuticals, nonylphenol, 17- β -estradiol and PMT substances were collected into dark brown glass bottles (40–1000 ml volume), samples for PFAS were collected into HDPE bottles of 1000 ml volume. Depending on the analyte, samples were conditioned with HCl, Na₂SO₄ or H₂SO₄. The sampling team was asked not to use any pharmaceuticals, sunscreen or other personal care products on the day of sampling. Samples were delivered to analytical laboratories packed in coolboxes within 24 hours from sampling.

ANALYTICAL PROCEDURES

Water samples for pharmaceuticals, PFAS, NF and 17- β -estradiol were analysed in the Chemical Laboratory of the Polish Geological Institute using the LC-MS/MS method with SPE extraction. Samples for solvents and chelating agents were analysed in an external, commercial laboratory and the analytical methods used included LC-MS/MS, LC-UV, HS-GC-MS and LC-MS/MS. Limits of quantification for every analyte were defined based on information gathered in reports from CIS Working Group Groundwater, which collected a large amount of data on analytical methods during the voluntary groundwater watch list process (CIS, 2019a, 2024). For

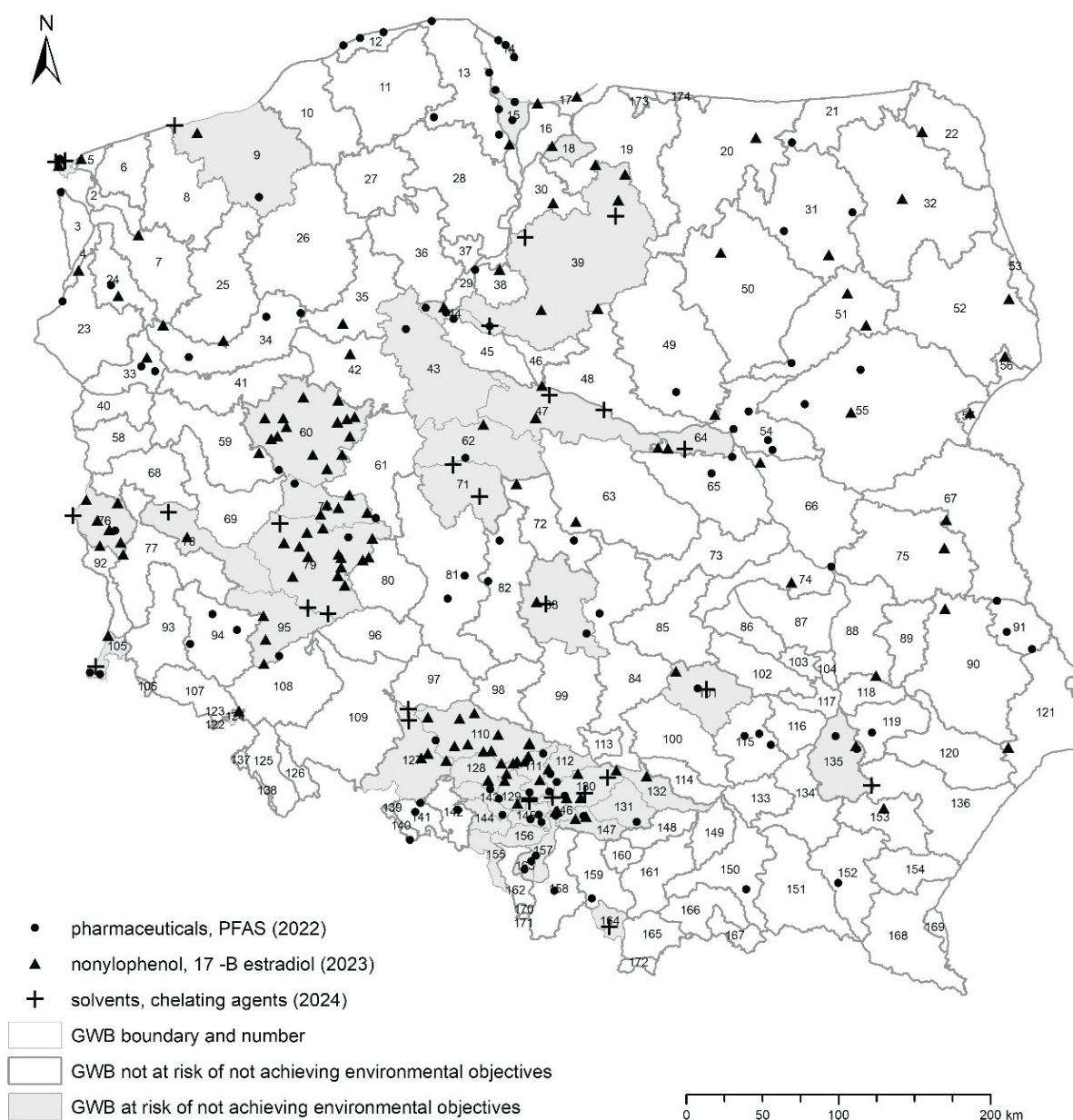


Fig. 1. Sampling locations

NF and 17- β -estradiol the limits of quantification were defined to fulfill recommendations of the Drinking Water Directive 2000/2184 (Polish version). In the Polish version of the directive, recommended guidance values for NF and 17- β -estradiol were 0.3 $\mu\text{g/l}$ and 1 $\mu\text{g/l}$ and therefore LOQ levels for these substances were defined at 0.1 $\mu\text{g/l}$ and 0.3 $\mu\text{g/l}$. It was later discovered that in the original, English text of the directive, the guidance value for 17- β -estradiol was 1 ng/l and therefore the LOQ value for the study was too high to detect it. Parameters of analytical methods used in this study are given in [Table 1](#).

RESULTS

The research on pharmaceuticals carried out between 2022–2024 showed the presence of their active substances in 22 out of 106 monitoring boreholes, which is 21% of the samples. 7 out of 11 pharmaceuticals included in the study were found: these were diatrizoic acid, sotalol, clopidol, primidone, sulfametoxazole, carbamazepine and ibuprofen. The pharmaceutical that was most often found was carbamazepine, which was recorded in 10 locations (9% of sampling locations). The second most often found was sulfametoxazole, recorded at 4

Table 2

Maximum concentrations of analytes included in the study

Analyte	LOQ [$\mu\text{g/l}$]	No of samples collected	No of samples with results > LOQ	Maximum concentration [$\mu\text{g/l}$]
Diatrozoic acid	0.05	100	1	0.05
Sotalol	0.01	106	1	0.01
Clopidol	0.01	106	2	0.04
Primidone	0.01	106	2	0.03
Sulfametoxazole	0.01	106	4	0.04
Carbamazepine	0.01	106	10	0.23
Ibuprofen	0.05	106	2	0.09
PFPeA	0.01	106	15	0.12
PFBS	0.01	106	2	0.02
6:2 monoPAP	0.01	106	3	0.02
PFDPA	0.01	106	2	0.02
PFOA	0.01	106	1	0.03
PFHxS	0.01	106	1	0.02
PFOPA	0.01	106	1	0.01
PFUnA	0.01	106	1	0.01
nonylphenol	0.1	151	25	0.93
2-Ethoxy-2-methylpropane (ETBE)	0.02	56	12	0.17
Benzene	0.25	56	3	0.4
Carbon tetrachloride	0.25	56	1	2.1
Chloroform	0.25	56	1	13
cis 1,2-Dichloroethene	0.25	56	3	1.2
Dibromochloromethane	0.25	56	1	6
Dichloromethane	0.25	56	1	1.7
EDTA	1	56	5	6
Ethylbenzene	0.25	56	5	0.43
NTA	1	56	3	3
Tetraglyme	0.03	56	1	0.13
Toluene	0.25	56	8	2.5
Tribromomethane	0.25	56	1	1.1
Trichloroethene	0.25	56	1	1.1

locations (4% of sampled sites). Other pharmaceuticals were found in 1 or 2 monitoring boreholes only. With respect to concentrations, these were generally low. The highest concentration of an active substance was carbamazepine, found at 0.23 $\mu\text{g/l}$ (Table 2).

Out of 16 per- and polyfluoralkyl substance selected for the study, 8 were identified in samples collected in 2022. These were PFPeA, PFBS, 6:2 monoPAP, PFDPA, PFOA, PFHxS, PFOPA and PFUnA. The substance most often found was PFPeA, which is used in production of grease and waterproof packaging, carpets and furniture textiles. It was found at 15 locations (14% of all samples). Other PFAS compounds were found in 1–3 locations. In total PFAS compounds were located in 20 monitoring boreholes (19% of all sampling locations). With respect to concentrations, the highest, at 0.12 $\mu\text{g/l}$, was found for PFPeA. The remaining analytes were found at levels of <0.01–0.03 $\mu\text{g/l}$ (Supplementary data Table 2).

NF and 17- β -estradiol were surveyed in 151 monitoring boreholes. NF was found at 25 sampling locations, which constitutes 17% of all sites. 17- β -estradiol was not found in any of sampling points included in the study, most likely due to the too high LOQ. Concentrations of NF in the groundwater samples varied from 0.14 to 0.93 $\mu\text{g/l}$, Supplementary data Table 3.

The last study of solvents and chelating agents revealed their presence at 25 out of 56 sampling locations, which constitutes 45% of all points included in the study, Supplementary data Table 4. Fourteen chemicals from this group were found and these included 2-Ethoxy-2-methylpropane (ETBE), benzene and carbon tetrachloride, chloroform, cis 1,2-Dichloroethene, dibromochloromethane, dichloromethane, EDTA, ethylbenzene, NTA, tetraglyme, toluene, tribromomethane and trichloroethene. 2-Ethoxy-2-methylpropane (ETBE) was the most often found chemical (11 out of 56 sampling locations, 20% of samples). ETBE is an additive to petroleum products.

Its highest concentration was at 0.17 µg/l. Toluene, which is a solvent used in many industries including paint production, cosmetics (nail polish), pharmaceutical and military products, was found in 8 locations (14% of samples) and its highest concentration was at 2.5 µg/l. TFA, a commonly used organic acid often found in groundwater, was not detected in this research, probably due to a too high LOQ level.

In total, emerging organic contaminants were found in 69 out of 268 sampling points (26%) in which the depth to the aquifer varied from 0 to 69.7 m b.g.l. 87% of these boreholes were screened in porous, Quaternary deposits. Only 9 represented fissured aquifers. At over 90% of these points, depth to an aquifer was <20 m and in 45% <5 m depth. The water table was phreatic in 71%, which shows that the most vulnerable aquifers are shallow and unconfined.

DISCUSSION

The research was directed towards delivering information on the presence of selected emerging contaminants in groundwater in Poland. The results reported here follow previous pilot studies undertaken within the national groundwater monitoring network (Kuczyńska, 2017) and corroborate the presence of emerging contaminants in groundwater in Poland.

Return of samples with positive results of emerging contaminants was relatively high, though sampling was undertaken at a limited number of places. The selection of monitoring sites was aimed at places where impact from anthropogenic pressures was anticipated and where hydrogeological conditions would facilitate their occurrence. It is expected that returns would be lower if more monitoring boreholes were included in the study and if they were spread more evenly across the country. Since sampling was done at selected sites, drawing conclusions about the correlation of relationships with the conditions of occurrence seems unjustified and could differ if the number of points covered by the studies were larger.

Nonetheless, according to the methodology of the CIS WG Groundwater strategy (CIS, 2019b) for selection of chemicals to be recommended for consideration of inclusion into the Groundwater Directive regulation, the number of sites with a positive result per country was defined at 10 per substance. Occurrence of a substance in 10 sites in at least 4 EU countries makes a substance fulfil the criteria of so-called List Facilitating (LF), which includes substances considered to be of high concern for groundwater quality at EU level and as such to be regulated at European level. Based on the pilot studies reported in this article, 4 substances meet these criteria, which are carbamazepine, PFPeA, NF and 2-Ethoxy-2-methylpropane (ETBE). Carbamazepine, PFPeA and ETBE are already included in LF based on information gathered from other EU countries (CIS, 2019b, 2024). NF has not been analysed by the CIS Groundwater WG.

The other factor limiting positive results in this study could be the limits of quantification. Chemicals covered in this research are generally expected to occur in low concentrations, hence analytical methods with low limits of quantifications are needed to detect them. Lower limits of quantification are often associated with increased uncertainty of results. For that reason the analytical methods and their limits of quantification should be chosen with respect to required guidance values. Unfortunately, the majority of substances covered in this research are not yet regulated under EU and national regulations. Lack of regulations defining acceptable levels of concentrations of these substances makes it difficult to decide what limit of quantification is required, even for a pilot study. Despite efforts taken to assure the best LOQ for the study, it is still possible that for some substances the limits of quantifications were set too high, including 17- β -estradiol and TFA.

CONCLUSION

This article presents previously unpublished results of concentrations of emerging contaminants in groundwater in Poland, confirming their presence in groundwater within the national groundwater monitoring network. The presence of a wide range of different groups of chemicals indicates the necessity of carrying further investigations and scientific research, especially with respect to chemicals that are not regulated in national and international legislations, but are already documented to be harmful to the environment and to have intrinsic properties allowing them to travel across large distances and to bioaccumulate in the subsoil environment. The presence of these substances may be harmful not only to humans and animals via drinking contaminated water, but also to microfauna living underground (stygo fauna), which influence microbiological processes taking place in the groundwater environment. These results demonstrate further that regulations of emerging contaminants in groundwater are urgently needed as well as regular monitoring of these compounds in groundwater. One shall also expect that when regulations are in place this will impact upon our perception of groundwater quality and groundwater status across Poland and EU, which will result in a need to develop new strategies towards the protection of groundwater.

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Supplementary data Table 1. Charateristics of sampling points

Groundwater body	Water table	Monitoring borehole depth [m b.g.l.]	Depth to aquifer top [m b.g.l.]	Depth to aquifer bottom [m b.g.l.]	Stratigraphy	Aquifer type	Pharmaceuticals	PFAS	Nonylofenol	17-β-estradiol	Solvents	Chelating agents
91	phreatic	90.0	28.2	90	K2	porous-fissured	yes	yes				
79	confined	114.5	70.5	109	Pg+Ng+Q	porous			yes	yes	yes	yes
71	confined	69.7	14.7	69.7		porous-fissured			yes	yes	yes	yes
91	phreatic	60.0	12	60	K2	porous-fissured	yes	yes	yes	yes		
9	phreatic	20.0	3.2	18	Q	porous			yes	yes		
51	confined	57.5	31	55	Q	porous			yes	yes		
54	phreatic	53.5	5.06	50	Q	porous	yes	yes	yes	yes		
66	phreatic	59.0	5.4	55	Q	porous			yes	yes		
64	confined		12.8	15	Q	porous	yes	yes	yes	yes	yes	yes
95	phreatic	23.0	5.7	21	Q	porous	yes	yes	yes	yes	yes	yes
110	phreatic	95.0	2.6	87	Q	porous			yes	yes		
94	phreatic	7.0	4.8	7.3	Q	porous	yes	yes				
44	confined	312.0	240		K	fissured-karstic			yes	yes		
153	phreatic	21.3	2.4	18.3	Q	porous			yes	yes		
15	confined	38.0	15	36	Q	porous	yes	yes	yes	yes		
63	confined	205.0	105	205	K2	porous-fissured			yes	yes		
110	confined	50.0	23	50	T1	fissured-karstic			yes	yes		
128	phreatic	139.0	23	139	T2	fissured-karstic			yes	yes		
110	confined	253.0	36	248	T1+2	fissured-karstic			yes	yes		
48	confined	174.0	127.5	173	K+Pg+Ng	porous			yes	yes		
13	phreatic	5.8	2.5	15.6		porous	yes	yes				
52	confined	151.0	103	151	Q	porous			yes	yes		
39	confined	98.0	49	100	Q	porous			yes	yes		
74	confined	100.0	40	100	K	porous-fissured			yes	yes		
75	confined	62.0	34	62	Q	porous			yes	yes		
64	phreatic	60.8	4.5	61	Q	porous			yes	yes		
54	phreatic	35.0	2	35	Q	porous	yes	yes				
90	confined	100.0	32	100	K2	porous-fissured			yes	yes		
121	phreatic	80.0	27.2	80	K2	fissured-karstic			yes	yes		
49	phreatic	70.0	27.6	72.5	Q	porous			yes	yes		
22	confined	76.8	35	72	Q	porous			yes	yes		
31	confined	51.0	25	47	Q	porous			yes	yes		
32	confined	38.8	17	35	Q	porous			yes	yes		
56	confined	156.0	133	152	PgOl	porous			yes	yes		
51	confined	81.5	62.5	80.6	Q	porous			yes	yes		
110	confined	167.0	54	167	T1+2	porous-fissured-karstic			yes	yes		
130	spring				J3	porous-fissured			yes	yes		
110	phreatic	70.0	2	67	Q	porous			yes	yes		
159	phreatic	8.0	1.85	6	Q	porous	yes	yes				
72	confined	37.0	13	38.8	Q	porous	yes	yes				
47	confined		21	36	Ng	porous			yes	yes		
101	phreatic		22.29	60	D2	fissured-karstic			yes	yes	yes	yes
39	confined	21.0	6	20	Q	porpus					yes	yes
43	confined	43.0	14	43	Q	porous	yes	yes				
21	phreatic	14.5	0.95	11	Q	porous	yes	yes				
119	phreatic	21.0	1.4	18	Q	porous	yes	yes				
141	phreatic	14.2	6.5	14.2	K2	fissured-karstic	yes	yes				
127	phreatic	11.0	1.5	9	Q	porous					yes	yes
34	phreatic	7.2	2.5	6.5	Q	porous	yes	yes				
76	phreatic	40.0	2.6	38	Q	porous			yes	yes		
79	phreatic	13.7	2.6	14	Q	porous			yes	yes	yes	yes
79	phreatic	22.0	5.9	20	Q	porous			yes	yes		
158	phreatic	12.0	1.5	9	Q	porous	yes	yes				
131	phreatic	21.5	9.9	21	Q	porous	yes	yes			yes	yes
15	confined	32.3	14	31	Q	porous	yes	yes				
39	confined	50.5	36	48.5	Q	porous			yes	yes		
127	phreatic	37.0	2	36	Q	porous					yes	yes
60	phreatic	18.0	1.99	16	Q	porous	yes	yes			yes	yes
111	phreatic	70.0	22.7	70	T1+2	fissured-karstic			yes	yes		
110	confined	149.0	89	149	T2	fissured-karstic			yes	yes		
64	phreatic	14.2	1.9	13.8	Q	porous					yes	yes
49	phreatic	15.0	1.1	11.2	Q	porous	yes	yes				
47	confined	18.0	12.1	18.7	Q	porous					yes	yes
47	confined	96.0	16	96.7	Q	porous					yes	yes
45	phreatic	15.0	1	14	Q	porous	yes	yes				
13	confined	150.0	127	150	K2	porous-fissured			yes	yes		
101	phreatic	25.0	0.9	19.3	T1+Q	porous	yes	yes			yes	yes
115	confined	20.5	16	20.5	NgM	porous-fissured	yes	yes				
65	phreatic	85.0	0.5	82	Q	porous	yes	yes				
65	phreatic	15.0	0.6	16	Q	porous	yes	yes				
65	phreatic	5.7	0.6	16	Q	porous	yes	yes				
39	phreatic	30.0	3.1	30	Q	porous					yes	yes
13	confined	21.5	15	21	Q	porous	yes	yes				
20	confined	87.5	69	87.5	Q	porous			yes	yes		
39	phreatic	63.0	34.91	63	Q	porous			yes	yes		
83	phreatic	87.1	13.1	87.1	K2	porous-fissured	yes	yes			yes	yes
13	confined	166.0	144	161	PgOl	porous	yes	yes				
115	phreatic	42.0	17	37	NgM	porous-fissured	yes	yes				
65	confined	30.0	9.4	27.5	Q	porous			yes	yes		
71	phreatic	80.0	0.14	80	K2+Q	porous					yes	yes
76	phreatic	28.0	0.89	28	Q	porous					yes	yes
105	phreatic	11.6	1.2	11.6	Q	porous			yes	yes	yes	yes
23	phreatic	8.8	1.1	6.8	Q	porous	yes	yes				
60	phreatic	21.5	3.3	20.5	Q	porous			yes	yes		
25	phreatic	30.0	5	30	Q	porous			yes	yes		
111	phreatic	24.0	10.56	31	T1+2	porous-fissured	yes	yes				
50	phreatic	29.4	2.4	30.2	Q	porous			yes	yes		
91	phreatic	45.0	2.7	45	K	porous-fissured	yes	yes				
84	phreatic	15.1	1.8	9.6	Q	porous	yes	yes				
3	phreatic	15.0	1.5	20	Q	porous	yes	yes	yes	yes		
15	confined	33.4	18.3	33.7	Q	porous	yes	yes				
12	phreatic	20.0	5	20	Q	porous	yes	yes				
15	phreatic	5.0	2.4	5	Q	porous	yes	yes				
15	phreatic	50.0	0.9	50	Q	porous	yes	yes				
15	confined	17.65	8.5	18.1	Q	porous	yes	yes	yes	yes	yes	yes
15	phreatic	7.0	1.52	6	Q	porous	yes	yes				

14	phreatic	20.0	3.1	20	Q	porous	yes	yes				
62	confined	9.0	3.3	9	Q	porous	yes	yes				
163	phreatic	10.0	1.2	8.1	Q	porous	yes	yes				
157	phreatic	23.0	14.3	21	Q	porous	yes	yes				
142	phreatic	17.8	1	13.8	Q	porous	yes	yes				
44	phreatic	10.5	1	10.5	Q	porous	yes	yes				
17	confined	26.5	18	38	Q	porous			yes	yes		
152	phreatic	5.0	3.7	5	Q	porous	yes	yes				
140	phreatic	7.0	1.73	4.5	Q	porous	yes	yes				
129	confined	24.6	13.1	20.7	Q	porous					yes	yes
146	confined	82.0	36	82	T1+2	fissured-karstic			yes	yes		
112	phreatic	53.2	13.6	53.2	C	porous-fissured	yes	yes				
146	phreatic	28.0	13	24	Q	porous					yes	yes
66	phreatic	10.0	5.1	10	Q	porous	yes	yes				
5	phreatic	74.0	30.5	78	Q	porous			yes	yes		
55	confined	106.5	68	101.5	Q	porous			yes	yes		
57	confined	132.0	90	130	Q	porous			yes	yes		
111	phreatic	130.0	21	130	T2	fissured-karstic			yes	yes		
129	phreatic	23.0	5.7	23	T+Q	porous-fissured			yes	yes	yes	yes
112	confined	35.0	28.4	32.4	C3	porous-fissured	yes	yes			yes	yes
130	confined	45.0	23	40	P	porous-fissured			yes	yes		
146	confined	88.0	34	88	T2	fissured-karstic			yes	yes		
147	phreatic	60.0	35.7	60	T2	fissured-karstic			yes	yes		
147	phreatic	23.0	10	19.7	Q	porous			yes	yes	yes	yes
24	confined	22.0	12	19	Q	porous			yes	yes		
18	confined	38.0	16	35	Q	porous			yes	yes		
24	phreatic	23.5	9.8	20	Q	porous	yes	yes				
29	phreatic	17.0	2.1	14	Q	porous	yes	yes				
29	confined	55.3	32	54	Q	porous			yes	yes		
60	confined	90.0	58	88	Q	porous			yes	yes		
60	confined	150.0	129	150	NgM	porous			yes	yes		
60	confined	78.5	45	78.5	Q	porous			yes	yes		
60	confined	61.0	32	61	Q	porous			yes	yes		
60	confined	88.0	46	86	Q	porous			yes	yes		
60	phreatic	30.5	17.9	24.5	Q	porous			yes	yes		
60	confined	76.0	51	76	Q	porous			yes	yes		
76	confined	40.0	21	40	Q	porous			yes	yes		
76	phreatic	30.5	1.6	29	Q	porous			yes	yes		
76	confined	15.0	7	13	Q	porous			yes	yes		
76	phreatic	32.0	1.1	35	Q	porous	yes	yes	yes	yes	yes	yes
76	confined	40.0	14	39	Q	porous			yes	yes		
76	confined	41.0	23.5	38	Pg+Ng	porous			yes	yes		
70	confined	40.0	27	38	Q	porous			yes	yes		
60	confined	108.0	82	107	NgM	porous			yes	yes		
70	phreatic	26.0	11.5	21	Q	porous			yes	yes	yes	yes
70	confined	89.0	68.6	87.5	Q	porous			yes	yes		
61	phreatic	14.5	1.5	10.5	Q	porous	yes	yes				
60	phreatic	48.0	8.23	22	Q	porous			yes	yes		
79	phreatic	62.0	6	61	Q	porous			yes	yes		
79	phreatic	42.0	15	40	Q	porous			yes	yes		
79	confined	34.0	14	32	Q	porous			yes	yes		
79	confined	69.0	57	61	Q	porous			yes	yes		
79	confined	45.0	19.1	50.2	Q	porous			yes	yes		
79	phreatic	33.0	2.6	30.5	Q	porous			yes	yes		
79	phreatic	68.0	13.3	86	Q	porous			yes	yes		
79	confined	48.0	12	46	Q	porous			yes	yes		
79	confined	39.0	24	37	Q	porous			yes	yes		
79	confined	43.5	35	42.5	Pg+Ng	porous			yes	yes		
79	phreatic	40.0	9	40	Q	porous	yes	yes	yes	yes		
79	confined	56.0	13	56	Q	porous			yes	yes		
79	confined	29.5	15.6	26	Q	porous			yes	yes		
79	confined	77.0	51	75	Q	porous			yes	yes		
110	confined	69.0	42	65	T1	fissured-karstic			yes	yes		
127	confined	83.5	27.5	75.5	T1	fissured-karstic			yes	yes		
127	confined	72.0	50	70	T1+2	porous-fissured-karstic			yes	yes		
110	confined	108.0	70.9	108	T2	fissured-karstic			yes	yes		
110	phreatic	34.0	1	34	Q	porous			yes	yes		
110	phreatic	24.5	8	23	Q	porous			yes	yes		
127	phreatic	60.0	9.3	60	T2	fissured-karstic	yes	yes	yes	yes		
141	phreatic	70.0	36	67	Q	porous	yes	yes				
129	confined	173.5	52.5	167	T2	fissured-karstic			yes	yes		
128	phreatic	126.0	61.9	126	T2	fissured-karstic			yes	yes		
110	confined	101.0	54	101	T1+2	fissured-karstic			yes	yes		
111	phreatic	35.0	14	33	T2	fissured-karstic	yes	yes				
129	confined	75.0	30	73	Q	porous					yes	yes
130	phreatic	39.0	16.7	39	Q	porous					yes	yes
130	confined	70.0	11.8	70	C	porous-fissured	yes	yes				
112	confined	48.0	32.5	46	P	porous-fissured			yes	yes		
111	confined	19.0	13	20	Q	porous	yes	yes			yes	yes
130	confined	88.0	8.5	88	T2	fissured-karstic			yes	yes		
1	confined	35.0	14	35	Q	porous	yes	yes				
1	phreatic	32.0	0.44	32.4	Q	porous					yes	yes
105	confined	36.0	18.5	20	Pg+Ng	porous					yes	yes
105	phreatic	35.0	5	29	Pg+Ng	porous	yes	yes			yes	yes
12	confined	23.0	11.5	23	Q	porous	yes	yes				
135	phreatic	24.5	3	22.5	Q	porous					yes	yes
135	phreatic	13.0	1.9	11	Q	porous	yes	yes				
67	confined	49.0	30	48	Q	porous			yes	yes		
35	confined	65.0	29.5	63.5	Q	porous			yes	yes		
135	confined	19.0	4.5	17.1	Q	porous	yes	yes			yes	yes
14	phreatic	20.0	1.15	20	Q	porous	yes	yes				
145	confined	8.0	2.9	4.90	Q	porous	yes	yes			yes	yes
145	phreatic	29.0	8.61	30	C3	porous-fissured	yes	yes				
112	phreatic	11.5	5.1	11	Q	porous	yes	yes			yes	yes
9	phreatic	19.4	10.6	19.4	Q	porous	yes	yes				
130	confined	101.5	8.5	94	T2	fissured-karstic			yes	yes		
127	confined	88.0	21	80	Ng	porous			yes	yes		
31	confined	9.25	6.7	9.25	Q	porous	yes	yes				
1	phreatic	33.6	6.08	36	Q	porous			yes	yes		
34	phreatic	9.5	1.6	13	Q	porous	yes	yes				
55	phreatic	9.7	1.3	9.1	Q	porous	yes	yes				

55	phreatic	7.0	0.9	7.2	Q	porous	yes	yes				
60	confined	75.0	63	74.5	Q	porous			yes	yes		
42	confined	44.0	15	45	Q	porous			yes	yes		
7	confined	78.0	58	79	Q	porous			yes	yes		
60	phreatic	33.0	11.5	30	Q	porous			yes	yes		
60	confined	59.0	39	56	Q	porous			yes	yes		
143	phreatic	44.5	0.8	41	Q	porous	yes	yes	yes	yes	yes	yes
110	phreatic	85.0	10	85	T2	fissured-karstic			yes	yes		
88	phreatic	80.0	45.9	80	K2	porous-fissured			yes	yes		
128	phreatic	17.0	7.2	12	Q	porous	yes	yes	yes	yes	yes	yes
130	confined	117.4	50	117.4	T1+2	fissured-karstic			yes	yes		
59	confined	80.0	41.5	79	Q	porous			yes	yes		
143	phreatic	13.0	1	11.5	Q	porous	yes	yes	yes	yes	yes	yes
145	phreatic	33.0	4.4	29.5	Q	porous	yes	yes			yes	yes
33	phreatic	9.7	1.8	10	Q	porous	yes	yes				
115	confined	8.7	1.2	5.6	Q	porous	yes	yes				
31	phreatic	7.0	1.78	15	Q	porous	yes	yes				
150	phreatic	5.0	2.5	4.6	Q	porous	yes	yes				
70	phreatic	10.4	1.2	9.3	Q	porous			yes	yes		
70	phreatic	12.0	0.8	12	Q	porous	yes	yes	yes	yes		
128	confined	210.0	41.5	208	T1+2	fissured-karstic			yes	yes		
83	phreatic	8.3	1.15	26	Q	porous					yes	yes
81	phreatic	8.0	1.34	5.7	Q	porous	yes	yes				
81	phreatic	7.4	3.43	6.6	Q	porous	yes	yes				
13	phreatic	15.4	1.2	15.4	Q	porous	yes	yes				
12	confined	7.15	2.34	8	Q	porous	yes	yes				
78	phreatic	40.0	3.03	55	Q	porous					yes	yes
82	phreatic	13.0	5.3	13	Q	porous	yes	yes				
54	phreatic	16.5	2.8	13	Q	porous	yes	yes				
34	phreatic	6.0	2.5	11	Q	porous	yes	yes				
33	phreatic	23.8	4	21.6	Q	porous	yes	yes				
34	phreatic	33.0	10.2	23.5	Q	porous			yes	yes		
1	phreatic	8.0	0.3	9	Q	porous					yes	yes
1	confined	19.0	15	31	Q	porous					yes	yes
94	phreatic	13.0	6.43	11.3	Q	porous	yes	yes				
95	confined	51.0	39	49	Ng	porous			yes	yes		
95	confined	97.5	81.5	93.5	Ng	porous			yes	yes		
33	confined	64.3	33	60	Q	porous			yes	yes		
82	phreatic	10.8	5.1	9.5	Q	porous	yes	yes				
54	phreatic	30.0	1.8	31	Q	porous	yes	yes				
94	phreatic	22.0	5.9	21	Q	porous	yes	yes				
39	confined	80.0	69.7	80	K	porous-fissured					yes	yes
39	phreatic	10.5	3.9	7.6	Q	porous	yes	yes			yes	yes
95	phreatic	18.0	7	14.2	Q	porous			yes	yes		
17	phreatic	43.0	5.2	43	Q	porous			yes	yes		
147	phreatic	8.0	1.29	8	Q	porous	yes	yes			yes	yes
51	phreatic	20.7	1.4	20.7	Q	porous	yes	yes				
62	confined	60.0	45.5	60	K	porous-fissured			yes	yes		
72	confined	104.0	14	104	K	porous-fissured			yes	yes		
79	confined	18.0	14	18	Q	porous					yes	yes
132	phreatic	80.0	7	80	K2	fissured-karstic			yes	yes		
101	confined	90.0	74	90	T2	fissured-karstic			yes	yes		
30	confined	76.0	54.5	76	Q	porous			yes	yes		
44	phreatic	15.9	5.7	15.8	Q	porous	yes	yes				
14	phreatic	11.0	1.29	11	Q	porous	yes	yes				
163	phreatic	12.0	3.5	8	Q	porous	yes	yes				
146	phreatic	17.0	6	14.7	Q	porous	yes	yes			yes	yes
105	phreatic	16.0	5.1	12	Q	porous	yes	yes			yes	yes
164	confined	24.0	3.2	22	Q	porous					yes	yes
23	confined	20.0	14	20	Q	porous			yes	yes		
76	phreatic	27.0	6.5	25	Q	porous			yes	yes	yes	yes
78	phreatic	28.5	8.92	26.5	Q	porous			yes	yes		
70	confined	33.0	8	30	Q	porous			yes	yes		
130	phreatic	31.5	8.5	33	J3	porous-fissured					yes	yes
83	confined	31.0	26	33	Q	porous			yes	yes		
135	phreatic	28.0	4.6	25.8	Q	porous			yes	yes		
124	phreatic	88.0	81	86	P	porous-fissured			yes	yes		
9	confined	20.5	14.8	18.2	Q	porous					yes	yes
39	confined	32.0	18	30	Q	porous			yes	yes		
39	phreatic	23.5	5	21.5	Q	porous			yes	yes		
60	confined	59.0	41	56	Q	porous			yes	yes		
							106	106	151	151	56	56

Supplementary data Table 3. Results of nonylfenol and 17-β-estradiol

Analyte		17-beta-estradiol	4-nonylfenol
unit		ug/l	ug/l
LOQ		0.3	0.3
No.	ID Monitoring	1	2
1	5915	<0.30	<0.30
2	8	<0.30	<0.30
3	29	<0.30	<0.30
4	57	<0.30	<0.30
5	66	<0.30	<0.30
6	69	<0.30	<0.30
7	74	<0.30	<0.30
8	75	<0.30	<0.30
9	76	<0.30	<0.30
10	91	<0.30	<0.30
11	123	<0.30	<0.30
12	151	<0.30	<0.30
13	173	<0.30	<0.30
14	203	<0.30	<0.30
15	206	<0.30	<0.30
16	231	<0.30	<0.30
17	232	<0.30	<0.30
18	233	<0.30	<0.30
19	238	<0.30	<0.30
20	263	<0.30	<0.30
21	276	<0.30	<0.30
22	279	<0.30	<0.30
23	291	<0.30	<0.30
24	297	<0.30	<0.30
25	300	<0.30	<0.30
26	305	<0.30	<0.30
27	307	<0.30	<0.30
28	309	<0.30	<0.30
29	312	<0.30	<0.30
30	314	<0.30	<0.30
31	315	<0.30	<0.30
32	321	<0.30	<0.30
33	331	<0.30	<0.30
34	333	<0.30	0.54
35	336	<0.30	<0.30
36	439	<0.30	<0.30
37	446	<0.30	<0.30
38	665	<0.30	<0.30
39	679	<0.30	0.93
40	685	<0.30	0.86
41	786	<0.30	<0.30
42	857	<0.30	<0.30
43	858	<0.30	<0.30
44	1027	<0.30	<0.30
45	1112	<0.30	<0.30

Analyte		17-beta-estradiol	4-nonylphenol
unit		ug/l	ug/l
LOQ		0.3	0.3
No.	ID Monitoring	1	2
46	1127	<0.30	<0.30
47	1297	<0.30	<0.30
48	1941	<0.30	0.61
49	1978	<0.30	<0.30
50	2018	<0.30	<0.30
51	2148	<0.30	<0.30
52	2225	<0.30	<0.30
53	2250	<0.30	<0.30
54	2427	<0.30	<0.30
55	2489	<0.30	<0.30
56	2541	<0.30	<0.30
57	2545	<0.30	<0.30
58	2546	<0.30	<0.30
59	2580	<0.30	<0.30
60	2605	<0.30	<0.30
61	2609	<0.30	<0.30
62	2611	<0.30	<0.30
63	2615	<0.30	<0.30
64	2616	<0.30	<0.30
65	2640	<0.30	<0.30
66	3306	<0.30	<0.30
67	3335	<0.30	<0.30
68	3347	<0.30	<0.30
69	3349	<0.30	<0.30
70	3355	<0.30	<0.30
71	3358	<0.30	<0.30
72	3364	<0.30	0.41
73	3366	<0.30	0.53
74	3372	<0.30	<0.30
75	3375	<0.30	<0.30
76	3377	<0.30	<0.30
77	3379	<0.30	<0.30
78	3381	<0.30	<0.30
79	3383	<0.30	<0.30
80	3384	<0.30	<0.30
81	3388	<0.30	<0.30
82	3392	<0.30	<0.30
83	3403	<0.30	<0.30
84	3411	<0.30	<0.30
85	3415	<0.30	<0.30
86	3422	<0.30	<0.30
87	3426	<0.30	0.37
88	3427	<0.30	0.44
89	3428	<0.30	<0.30
90	3430	<0.30	<0.30
91	3431	<0.30	<0.30
92	3433	<0.30	<0.30

Analyte		17-beta-estradiol	4-nonylphenol
unit		ug/l	ug/l
LOQ		0.3	0.3
No.	ID Monitoring	1	2
93	3436	<0.30	<0.30
94	3437	<0.30	<0.30
95	3439	<0.30	<0.30
96	3441	<0.30	<0.30
97	3444	<0.30	<0.30
98	3448	<0.30	<0.30
99	3450	<0.30	<0.30
100	3455	<0.30	<0.30
101	3456	<0.30	<0.30
102	3459	<0.30	<0.30
103	3460	<0.30	<0.30
104	3461	<0.30	<0.30
105	3462	<0.30	<0.30
106	3464	<0.30	<0.30
107	3473	<0.30	<0.30
108	3474	<0.30	<0.30
109	3476	<0.30	<0.30
110	3485	<0.30	<0.30
111	3492	<0.30	<0.30
112	4644	<0.30	<0.30
113	4648	<0.30	<0.30
114	5609	<0.30	<0.30
115	5610	<0.30	<0.30
116	5712	<0.30	<0.30
117	5869	<0.30	<0.30
118	5870	<0.30	<0.30
119	5873	<0.30	<0.30
120	5894	<0.30	<0.30
121	5897	<0.30	<0.30
122	5899	<0.30	<0.30
123	5909	<0.30	<0.30
124	5910	<0.30	<0.30
125	5913	<0.30	<0.30
126	5914	<0.30	<0.30
127	5916	<0.30	<0.30
128	6431	<0.30	<0.30
129	6432	<0.30	<0.30
130	6530	<0.30	<0.30
131	6918	<0.30	<0.30
132	7026	<0.30	<0.30
133	7027	<0.30	<0.30
134	7029	<0.30	<0.30
135	7329	<0.30	<0.30
136	7592	<0.30	<0.30
137	7929	<0.30	<0.30
138	7935	<0.30	<0.30
139	8269	<0.30	<0.30

Analyte		17-beta-estradiol	4-nonylphenol
unit		ug/l	ug/l
LOQ		0.3	0.3
No.	ID Monitoring	1	2
140	8272	<0.30	<0.30
141	8273	<0.30	<0.30
142	8936	<0.30	<0.30
143	8938	<0.30	<0.30
144	8939	<0.30	<0.30
145	8942	<0.30	<0.30
146	9409	<0.30	<0.30
147	9410	<0.30	<0.30
148	9412	<0.30	<0.30
149	9730	<0.30	<0.30
150	9732	<0.30	<0.30
151	9990	<0.30	<0.30

Supplementary data Table 4. Results of solvents and chelating agents

Analyte	1,1,1-Trichloroethane	1,1,2,2-Tetrachloroethane	1,1,2-Trichloroethane	1,1-Dichloroethylen	1,1-Dichloroethane	1,2,3-Trichlorobenzene	1,2,4-Trichlorobenzene	1,2,4-Trimethylbenzene	1,2-Dichlorobenzene	1,2-Dichloroethane	1,2-dichloropropane	1,3,5-Trimethylbenzene	1,4-Dioxane	2-Ethoxy-2-methylpropane (ETBE)	Benzene	Bromodichloromethane	Carbon tetrachloride	Chlorobenzene	Chloroethane	Chloroform	Chloromethane	cis 1,2-Dichloroethene	Dibromochloromethane	Dichloromethane	Diethylene glycol dimethyl ether	Diisopropyl ether	EDTA	Ethylbenzene	Isopropylbenzene	n-Butylbenzene	n-Propylbenzen	NTA	tert-butanol	Tert-butyl methyl ether	Tetrachloroethene	Tetraglyme	Tetrahydrofuran	Toluene	trans-1,2-Dichloroethene	Tribromomethane	Trichloroethene	Trifluoroacetic acid	Vinylchlorid		
unit	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l		
LOQ	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.5	0.02	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	1.00	2.00	1.00	0.25	0.25	0.25	0.25	1.00	2.00	0.5	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
No.	ID Monitoring	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	
1	8	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
2	29	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
3	76	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	0.03	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
4	91	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	2	0.41	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25		
5	446	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
6	486	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
7	569	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
8	679	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
9	704	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	0.28	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	01.lip	<0.25	<0.25	<10	<0.25			
10	814	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
11	830	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
12	865	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
13	993	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
14	1004	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	2	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
15	1047	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
16	1083	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	0.04	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
17	1161	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
18	1315	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
19	1924	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	0.05	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	2	<2.0	<0.50	<0.25	0.13	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
20	1941	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
21	2250	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
22	2483	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	3	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
23	2491	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.02	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<1.00	<2.0	<1.0	<0.25	<0.25	<0.25	<0.25	<1.0	<2.0	<0.50	<0.25	<0.03	<0.05	<0.25	<0.25	<0.25	<10	<0.25			
24	2605	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0																																