OR/18/052 Emerging substances in UK groundwater

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Lapworth, D J, Crane, E J, Stuart, M E, Talbot, J C, Besien, T, and Civil, W. 2018. Micro-organic contaminants in groundwater in England: summary results from the Environment Agency LC-MS and GC-MS screening data. *British Geological Survey Internal Report*, OR/18/052.

Key substances with high frequency of detection

Table 4.1 shows the ten most frequently detected substances by the GC-MS method and summary details of their regulation. Six are pesticides, or their TPs, or halogenated solvents and are covered by the Drinking Water Directive (DWD 98/83/EC). Four of these are hazardous or priority hazardous substances under by the Priority Substances Directive (2008/105/EC). Two of these also appear in Annex XIV of the REACH Regulations. None are on the surface water watch list (SWWL), which is linked to the Water Framework Directive (2000/60/EC and later amended by 2008/32/EC).

Table 4.1 Regulation of GC-MS frequently detected substances.

Substance	**Type**	**Use**	**Regulation[a&b]**			
			DWD[a]	**Limit (µg/L)**	**Other**	**Status**
Atrazine	Pesticide	Herbicide	Y	0.1 (0.5 total)	PPP[b] PSD[a]	Withdrawn Hazardous substance
TCE	Halogenated solvent	Degreaser and feedstock for CFCs	Y	10 (PCE+TCE)	PSD[a] REACH [b]Annex XIV	Equivalent to Priority substance SVHC
BPA	Plasticiser	Polycarbonates and epoxy coatings	N		Food contact REACH[b]	Food packaging for infants ECHA candidate
Dimethyl succinate	PPCL	Flavouring fragrance plus industrial	N			
Desethyl-atrazine	Pesticide	Herbicide TP	Y	0.1 (0.5 total)		Parent withdrawn
PCE	Halogenated solvent	Degreaser, dry cleaning	Y	10 (PCE+TCE)	PSD[a] REACH [b]Annex XIV	Equivalent to Priority substance SVHC
DEET	PPCL	Insect repellent	N		Biocide regs[b]	
Cyclo-hexanone	Industrial	Nylon precursor and many other uses	N			
Fluoranthene	PAH	Waste product	Y		PSD[a]	Priority substance
Pyrene	PAH	Waste product	Y		SVHC[b]	

DWD – Drinking Water Directive, PPP – Plant Protection Products regulation, PSD – Priority Substances Directive, SVHC – substance of very high concern (REACH Regulations).
[a]end-of-pipe regulation and [b]Source regulation.

Table 4.2 shows the ten most frequently detected substances by the LC-MS method and summary details of their regulation. Six are pesticides, or their TPs, and covered by the Drinking Water Directive; four are common to Table 4.1 Three of these are hazardous or priority hazardous substances under by the Priority Substance Directive. Two are industrial/flame retardants which

appear in Annex XVII of the REACH Regulations. One of the pesticides is on the SWWL.

Table 4.2 Regulation of LC-MS frequently detected substances.

Substance	Type	Use	Regulation[a&b]			
			DWD[a]	Limit (µg/L)	Other	Status
Deisopropyl-atrazine	Pesticide	Herbicide TP	Y	0.1 (0.5 total)		Parent withdrawn
Simazine	Pesticide	Herbicide	Y	0.1 (0.5 total)	PPP[b] PSD	Withdrawn Hazardous substance
Atrazine	Pesticide	Herbicide	Y	0.1 (0.5 total)	PPP[b] PSD[a]	Withdrawn Hazardous substance
Diuron	Pesticide	Herbicide	Y	0.1 (0.5 total)	PPP[b] PSD[a]	Withdrawn Hazardous substance
Carbamazepine	Pharmaceutical	Epilepsy/bipolar disorder	N			
Clopidol	Pharmaceutical	Veterinary	N			
PFOA	Perfluorinated organic	Industrial	N		REACH [b]Annex XVII	Restricted in consumer products
Clothianidin	Pesticide	Neonicotinoid	Y	0.1 (0.5 total)	SWWL[a]	Monitored
PFOS	Perfluorinated organic	Industrial	N		PSD[a] REACH [b]Annex XVII	Priority substance Restricted

DWD – Drinking Water Directive, PPP – Plant Protection Products regulation, PSD – Priority Substances Directive, SWWL – surface water watch list.
[a]end-of-pipe regulation and [b]Source regulation.

In some cases a substance can belong to more than one regulatory regime, these are summarised by key substances types in Table 4.3.

Table 4.3 Current EU chemical substance source regulations.

Chemical Substance Type	European Legislative Body (Regulation)
Industrial & consumer chemicals	ECHA (No. 1907/2006)
Human pharmaceuticals	EMA, EMEA/CHMP/SWP/4447/0
Veterinary medicines	EMA
Plant protection products	EFSA (EC 1107/2009)
Biocides	ECHA (EU 528/2012)

ECHA – European Chemicals Agency, EMA – European Medicines Agency, EFSA – European Food Safety Authority.

Comparison with previous studies

Most of the GC-MS data is common to this study and previous BGS studies reported in 2012 and 2016 which used Environment Agency monitoring data, but the current study differs in several respects:

- It contains more recent data up to 2018
- It has been restricted to GC-MS targeted screening data only, whereas the other studies also included some data provided by other analytical methods, e.g. SVOCs
- The GC-MS method is continuously updated with new compounds being introduced and identification algorithms being improved to reduce false positives.

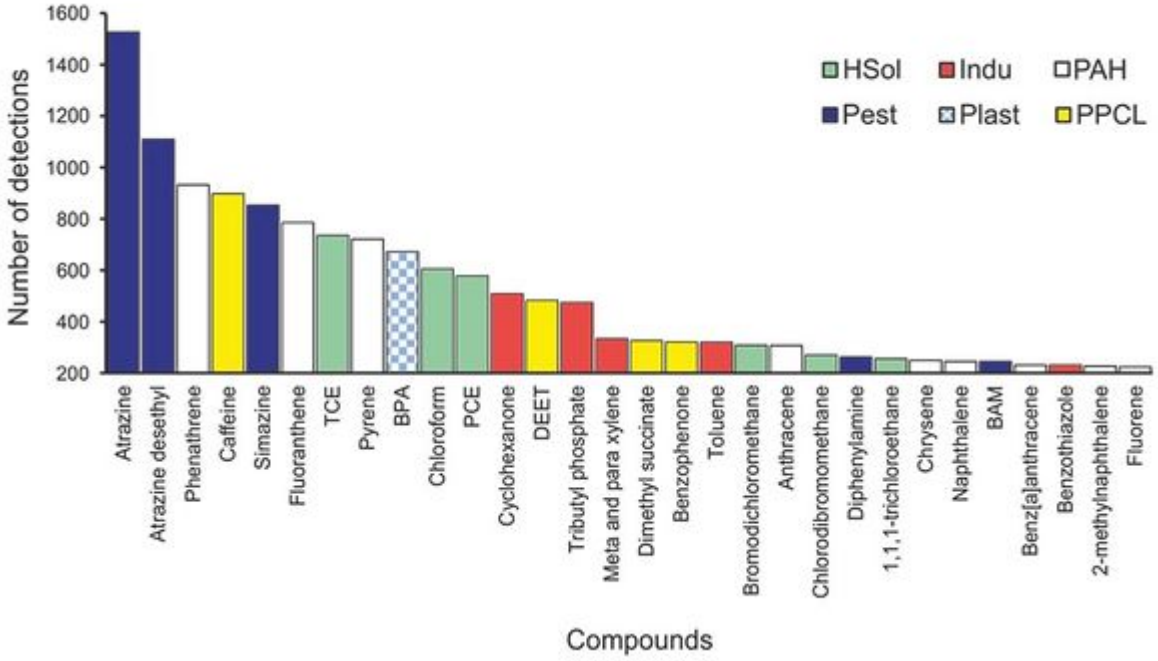

Figure 4.1 Top 30 most frequently detected compounds from 2016 assessment.

Figure 4.1 shows frequency data from the 2016 study (Manamsa et al., 2016[1]). There are fewer detections overall in the current study as results from methods other than GC-MS have been excluded. Similar compounds remain prominent in the current study in most frequent positions:

- The pesticide atrazine remains the most frequently detected compound but its desethyl TP is less prominent in this dataset
- The halogenated solvents TCE and PCE are found at higher relative frequencies as are the plasticisers BPA and DEET, and the industrial compounds cyclohexanone, dimethyl succinate and dimethyl adipate
- Caffeine has become less prominent as have some PAHs.

Figure 4.2 shows maximum concentration data from the 2016 study. Compounds in Figure 4.2 do not compare very well with the current study (*see* Figure 3.3). This reflects the exclusion of data from non-GC-MS screening methods in this review and also that these maximum concentrations may be random outliers and do not reflect typical concentrations.

The halogenated solvents are less prominent in the current study than in Figure 4.2 and particularly reflect the exclusion of solvent data from non-GC-MS methods. Plasticisers remain prominent and BBSA is the most frequently detected compound in the current study. Of the PPCL compounds, dimethyl succinate did not appear in the top 30 in 2016.

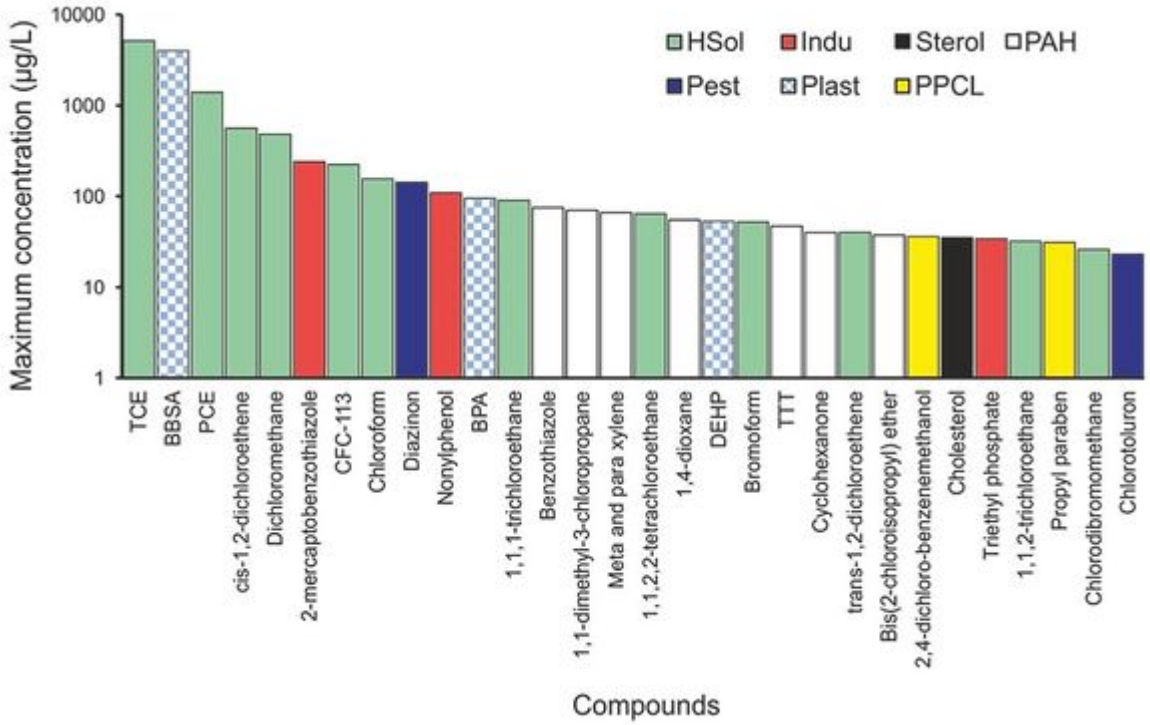

Figure 4.2 Top 30 maximum concentrations from 2016 assessment.

Implications for using quantitative analytical suites

Compounds detected

Many of the most frequently detected compounds in the GC-MS results would not be detected by the dedicated suites currently used by the Environment Agency. These dedicated suites are shown in Table 4.4.

Table 4.4 Environment Agency quantitative suites.

Suite code	Suite name	Typical member	LOD (µg/L)
GWQM01	ONP pesticides	Atrazine & TPs, diazinon	0.001–0.02
GWQM02	ONC pesticides	Trichlorobenzene, diclobenil, PCBs, aldrin	0.001–0.02
GWQM03	Acid herbicides	Bentazone, clopyralid, mecaprop	0.005–0.04
GWQM04	Urons/urocarbs	Azoxystrobin, carbendazim, isoproturon	0.005–0.1
GWQM05	Phenols	Chlorophenols	0.002
GWQM06	VOCs	Halogenated solvents, BTEX	0.01–0.5
GWQM07	PAH	Anthracene, chrysene, fluoranthene	0.01
GWQM08	Pyrethroids	Cypermethrin	0.00001–0.0001
GWQM09	Discretionary	Chlormequat, fluazaflop-butyl	0.01–0.2
	Special-site-by-site	Glyphosate, AMPA, metaldehyde	0.01–0.1
	PFOS/PFOA		0.005–0.1

Table 4.5 indicates that 60% (30/50) of the top 50 compounds found by the GC-MS method do not appear in the standard suites. These are predominantly industrial, plasticisers and PPCL compounds with a small number of pesticides and pesticide TPs.

Table 4.5 Compounds detected by GC-MS screen not present in standard suites.

Ranking	CAS Number	Analyte	Short name	Use code *
G03	80057	Bisphenol A	BPA	Plast
G04	106650	Butanedioic acid, dimethyl ester	Dimethyl succinate	PPCL
G07	134623	N,N-Diethyl-m-toluamide	DEET	PPCL
G08	108941	Cyclohexanone	Cyclohexanone	Indu
G12	123911	1,4-Dioxane	1,4-dioxane	Indu
G13	58082	Caffeine	Caffeine	PPCL
G14	117817	Bis(2-ethylhexyl)phthalate (DEHP)	DEHP	Plast
G15	627930	Dimethyl adipate	Dimethyl adipate	Indu
G18	115866	Triphenyl phosphate	TPPA	Indu
G20	2008584	2,6-Dichlorobenzamide	BAM	Pest
G21	3622842	Benzenesulfonamide, N-butyl-	BBSA	Plast
G22	119619	Benzophenone	Benzophenone	PPCL
G24	126863	2,4,7,9-Tetramethyl-5-decyne- 4,7-diol	TMDD	Indu
G25	87412	1(3H)-Isobenzofuranone	1(3H)-isobenzofuranone	Indu
G26	77732093	Oxadixyl	Oxadixyl	Pest
G27	131113	Dimethyl phthalate	DMP	Plast
G29	101371	2,4,6-Triallyloxy-1,3,5-triazine	TTT	Indu
G30	115968	Tri-(2-chloroethyl) phosphate	Tri-(2-chloroethyl) phosphate	Indu
G32	122394	Diphenylamine	Diphenylamine	Pest
G35	1241947	2-Ethylhexyl diphenyl phosphate	2-ethylhexyl diphenyl phosphate	Indu
G38	298464	Carbamazepine	Carbamazepine	PPCL
G40	128370	Butylated hydroxytoluene	BHT	PPCL
G42	131577	Benzophenone-3	Benzophenone-3	PPCL
G43	94133	Propylparaben	Propylparaben	PPCL
G44	314409	Bromacil	Bromacil	Pest
G46	96764	2,4-Di-tert-butylphenol	2,4-DTBP	Indu
G47	132649	Dibenzofuran	Dibenzofuran	Indu
G48	77907	Tributyl acetylcitrate	ATBC	Plast
G49	2440224	Drometrizole	Drometrizole	PPCL
G50	93049	2-Methyoxynaphthalene	Nerolin	Indu

Table 4.6 Compounds detected by LC-MS screen not present in standard suites.

Ranking	CAS Number	Analyte	Short name	Use code *
L06	298464	Carbamazepine	Carbamazepine	PPCL
L07	2971906	Clopidol	Clopidol	PPCL
L09	210880925	Clothianidin	Clothianidin	Pest
L11	723466	Sulfamethoxazole	Sulfamethoxazole	PPCL
L12	84057841	Lamotrigine	Lamotrigine	PPCL
L18	17254807	Chloridazon-desphenyl-methyl	CDM	Pest
L19	56038132	Sucralose	Sucralose	PPCL
L21	133855988	Epoxiconazole	Epoxiconazole	Pest

L22	188425856	Boscalid (Nicobifen)	Boscalid	Pest
L23	138261413	Imidacloprid	Imidacloprid	Pest
L25	120068373	Fipronil	Fipronil	Pest
L27	63741	Sulfanilamide	Sulfanilamide	PPCL
L28	115286	1,4,5,6,7,7-Hexachloro-5-norbornene-2,3-dicarboxylic acid	Chlorendic acid	Indu
L33	27203925	Tramadol	Tramadol	PPCL
L36	142459583	Flufenacet (Fluthiamide) (BAY FOE 5043)	Flufenacet	Pest
L38	5915413	Terbuthylazine	Terbuthylazine	Pest
L39	239110157	Fluopicolide	Fluopicolide	Pest
L41	107534963	Tebuconazole (Terbuconazole)	Tebuconazole	Pest
L42	153719234	Thiamethoxam	Thiamethoxam	Pest
L43	137586	Lidocaine (Diocaine)	Lidocaine	PPCL
L44	120983644	Desthio-prothioconazole	Desthio-prothioconazole	Pest
L45	2163691	Cycluron	Cycluron	Pest
L46	87674688	Dimethenamid (SAN 582H)	Dimethenamid	Pest
L47	422556089	Pyroxsulam	Pyroxsulam	Pest
L48	64902723	Chlorsulfuron	Chlorsulfuron	Pest
L49	21087649	Metribuzin	Metribuzin	Pest

Table 4.6 shows that the situation is similar for the LC-MS screen with 27 of 50 compounds detected not present in the standard suites. These are mainly pesticides, including TPs, and PPCL compounds.

Comparison of LODs

LODs for the top 50 compounds for the GC-MS screen are shown in Table 3.1. These are predominantly 0.01 µg/L with higher limits for four compounds, the industrial compound TMDD, the food additive BHT, and the plasticisers BBSA and DEHP.

LODs for the top 50 compounds for the LC-MS screen are shown in Table 3.2. These are predominantly an order of magnitude lower at 0.001 µg/L increasing for perfluorinated compounds, and also for the PPCLs sucralose, sulphanilamide and sulfamethoxazole, and the pesticides boscalid, trietazine and mecaprop.

The ranges of LODs for Environment Agency quantitative analytical suites are shown in Table 4.3. These are of a similar order of magnitude to the LC-MS method with higher limits for PAHs and difficult compounds, such as the pesticides chlormequat, glyphosate and metaldehyde.

Confidence

A third element must be the increased confidence in identification and quantification provided by the quantitative suites.

Case study on pesticides

Jenkins and Davy (2016)[2] report on the comparison between quantitative suites and the target based LC-MS method for pesticides in six Catchment Sensitive Farming (CSF) examples. Key determinands in this study were propyzamide, metazachlor, atrazine, diazinion, ethofumasate, MCPP, simazine, mecoprop, carbetamide and 2,4-D.

They found that overall the methods produced comparable results. There was a higher degree of scatter in the relationship at lower concentrations indicating that one or both of the methods was less accurate for concentrations close to the LOD. The target based LC-MS method was less precise and it was assessed that there was an increased risk of false positives. However the target based method had a lower LOD for many of the compounds used in this example.

References

1. ↑ MANAMSA, K, CRANE, E, STUART, M, TALBOT, J, LAPWORTH, D, and HART, A. 2016. A national-scale assessment of micro-organic contaminants in groundwater of England and Wales. Science of the Total Environment, 568, 712–726
2. ↑ JENKINS, J, and DAVEY, A. 2016. A comparison of the direct analysis and LC-MS methods for monitoring pesticides in CSF catchments. WRc Report UC111343.03 for the Environment Agency.

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