OR/18/052 Results from GC-MS and LC-MS datasets

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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.

Top 50 GC-MS substances by frequency of detection

Data description

The top 50 substances from the GC-MS dataset selected by frequency of detection are shown in Figure 3.1. A statistical summary of the data is shown in Table 3.1. Figure 3.2 shows the distribution of the results for the 50 most frequently detected substances by GC-MS using box plots. Due to the low frequency of detections, the box plots highlight the outlier values for each substance rather than the interquartile range, which for all of these substances is below the detection limit and was not computed.

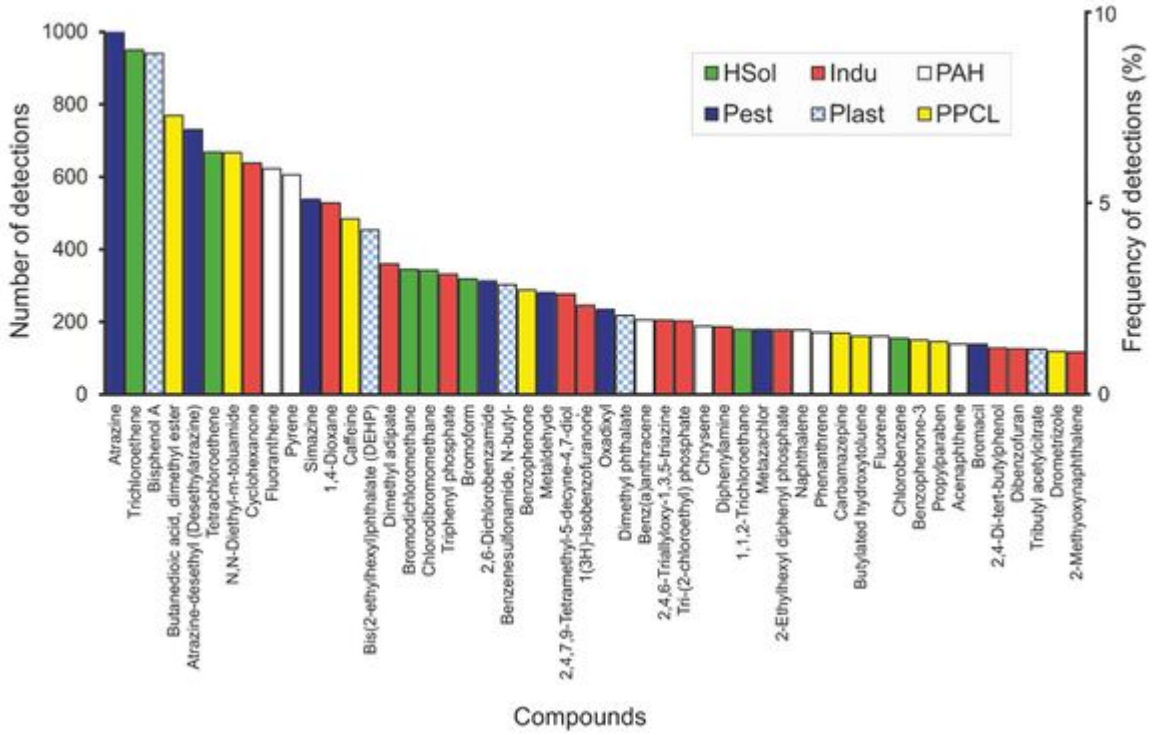

Figure 3.1 Bar chart of 50 most frequently detected substances by GC-MS screen (description of compound classes is given in Table 2.2).

Table 3.1 Summary statistics for 50 most frequently quantified substances in GC-MS screen. For all analytes the minimum concentration detected was below the LOD. The proportion of positive detections was too low to calculate a 5th percentile, median, mean or standard deviation. All concentrations are in units of µg/L.

Ranking	CAS Number	Analyte	Short name	Use code *	LOD	95th percentile concentration	Maximum concentration	Number of analyses	Number of positive detections	% analyses with positive detections
G01	1912249	Atrazine	Atrazine	Pest	0.01	0.01	0.75	11368	1069	9.40
G02	79016	Trichloroethene	TCE	HSol	0.01	0.13	184	11368	948	8.34
G03	80057	Bisphenol A	BPA	Plast	0.01	0.09	100	11368	939	8.26
G04	106650	Butanedioic acid, dimethyl ester	Dimethyl succinate	PPCL	0.01	0.02	74	11368	769	6.76
G05	6190654	Atrazine-desethyl (Desethylatrazine)	Desethyl-atrazine	Pest	0.01	0.01	1	11368	728	6.40
G06	127184	Tetrachloroethene	PCE	HSol	0.01	0.14	180	11368	668	5.88
G07	134623	N, N-Diethyl-m-toluamide	DEET	PPCL	0.01	0.01	17	11368	666	5.86
G08	108941	Cyclohexanone	Cyclohexanone	Indu	0.01	0.04	300	11368	638	5.61
G09	206440	Fluoranthene	Fluoranthene	PAH	0.01	0.01	3.4	11368	622	5.47
G10	129000	Pyrene	Pyrene	PAH	0.01	0.01	2	11368	606	5.33
G11	122349	Simazine	Simazine	Pest	0.01	0.01	0.42	11368	538	4.73
G12	123911	1,4-Dioxane	1,4-dioxane	Indu	0.01	0.01	63	11368	527	4.64
G13	58082	Caffeine	Caffeine	PPCL	0.01	0.01	1.8	11368	484	4.26
G14	117817	Bis(2-ethylhexyl) phthalate (DEHP)	DEHP	Plast	1	1	62	11368	452	3.98
G15	627930	Dimethyl adipate	Dimethyl adipate	Indu	0.01	0.01	150	11368	360	3.17
G16	75274	Bromodichloro -methane	Bromodichloro -methane	HSol	0.01	0.01	150	11368	344	3.03
G17	124481	Chlorodibromomethane	Chlorodibromomethane	HSol	0.01	0.01	180	11368	342	3.01
G18	115866	Triphenyl phosphate	TPPA	Indu	0.01	0.01	2	11368	331	2.91
G19	75252	Bromoform	Bromoform	HSol	0.01	0.01	96	11368	318	2.80
G20	2008584	2, 6-Dichlorobenzamide	BAM	Pest	0.01	0.01	70	11368	313	2.75
G21	3622842	Benzenesulfonamide, N-butyl-	BBSA	Plast	0.2	0.2	4000	11368	302	2.66
G22	119619	Benzophenone	Benzophenone	PPCL	0.01	0.01	0.8	11368	288	2.53
G23	108623	Metaldehyde	Metaldehyde	Pest	0.01	0.01	6.4	11368	280	2.46
G24	126863	2,4,7,9-Tetramethyl-5-decyne-4,7-diol	TMDD	Indu	0.03	0.03	6	11368	277	2.44
G25	87412	1(3H)-Isobenzofuranone	1(3H)-isobenzofuranone	Indu	0.01	0.01	1.2	11368	246	2.16
G26	77732093	Oxadixyl	Oxadixyl	Pest	0.01	0.01	3	11368	234	2.06
G27	131113	Dimethyl phthalate	DMP	Plast	0.01	0.01	24	11368	217	1.91
G28	56553	Benz(a)anthracene	Benz(a)anthracene	PAH	0.01	0.01	0.59	11368	206	1.81
G29	101371	2,4,6-Triallyloxy-1,3,5-triazine	TTT	Indu	0.01	0.01	62	11368	205	1.80
G30	115968	Tri-(2-chloroethyl) phosphate	Tri-(2-chloroethyl) phosphate	Indu	0.01	0.01	65	11368	202	1.78
G31	218019	Chrysene	Chrysene	PAH	0.01	0.01	0.52	11368	188	1.65
G32	122394	Diphenylamine	Diphenylamine	Pest	0.01	0.01	3	11368	187	1.64
G33	79005	1,1,2-Trichloroethane	1,1,2-trichloroethane	HSol	0.01	0.01	14	11368	179	1.57
G34	67129082	Metazachlor	Metazachlor	Pest	0.01	0.01	44	11368	179	1.57
G35	1241947	2-Ethylhexyl diphenyl phosphate	2-ethylhexyl diphenyl phosphate	Indu	0.01	0.01	1	11368	178	1.57
G36	91203	Naphthalene	Naphthalene	PAH	0.01	0.01	1.5	11368	177	1.56
G37	85018	Phenanthrene	Phenanthrene	PAH	0.01	0.01	1.2	11368	172	1.51
G38	298464	Carbamazepine	Carbamazepine	PPCL	0.01	0.01	0.26	11368	170	1.50
G39	86737	Fluorene	Fluorene	PAH	0.01	0.01	2	11368	161	1.42
G40	128370	Butylated hydroxytoluene	BHT	PPCL	0.03	0.03	8.7	11368	161	1.42
G41	108907	Chlorobenzene	Chlorobenzene	HSol	0.01	0.01	1.4	11368	155	1.36
G42	131577	Benzophenone-3	Benzophenone-3	PPCL	0.01	0.01	45	11368	150	1.32
G43	94133	Propylparaben	Propylparaben	PPCL	0.01	0.01	36	11368	146	1.28
G44	314409	Bromacil	Bromacil	Pest	0.01	0.01	3.7	11368	139	1.22
G45	83329	Acenaphthene	Acenaphthene	PAH	0.01	0.01	5	11368	139	1.22
G46	96764	2,4-Di-tert-butylphenol	2,4-DTBP	Indu	0.01	0.01	4.6	11368	128	1.13
G47	132649	Dibenzofuran	Dibenzofuran	Indu	0.01	0.01	0.61	11368	126	1.11
G48	77907	Tributyl acetylcitrate	ATBC	Plast	0.01	0.01	45	11368	125	1.10
G49	2440224	Drometrizole	Drometrizole	PPCL	0.01	0.01	18	11368	119	1.05
G50	93049	2-Methyoxynaphthalene	Nerolin	Indu	0.01	0.01	6	11368	117	1.03

** Key to use codes given in Table 2.2.*

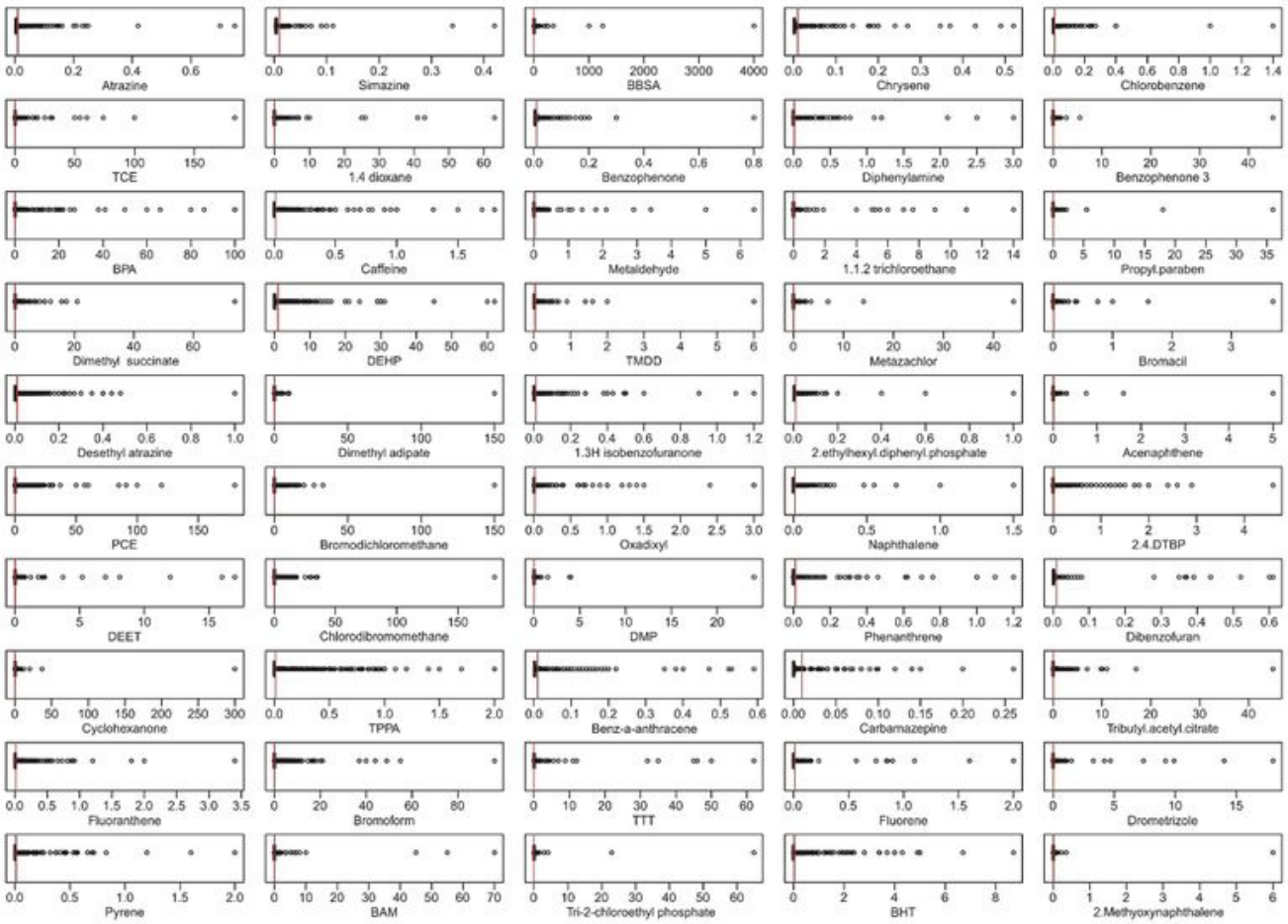

Figure 3.2 Box plots of the 50 most frequently detected substances by GC-MS screen. x-axis shown as concentration (mg/L) for all compounds. Due to the high proportion of censored data (censored level shown as red line) summary statistics below this line are not computed.

Discussion of results Pesticides (Pest)

Eight out of the top 50 most frequently detected compounds using the GC-MS method are pesticides. The triazine herbicides remain prominent. Atrazine is the most frequently detected compound with 1069 detections corresponding to 9.4% of samples, although the concentrations are relatively low, with the 95th percentile (p95) at the LOD and a maximum concentration of 0.75 µg/L. Its TP desethyl-atrazine is also prominent, the 5th most frequently detected compound, with a slightly higher maximum concentration. Simazine is also in the top 50, the 11th most frequently detected compound, but with lower maximum concentrations. Following their withdrawal from use in the UK, in 1993 for amenity use and in 2005 for agricultural uses, concentrations of atrazine and simazine have declined considerably, but concentrations not meeting the drinking water standard still persist in a few places.

The next most frequently detected compound, 2,6-dichlorobenzamide (commonly referred to as BAM) is a TP of the herbicide dichlobenil. The p95 at the LOD, but a number of high concentrations have been measured with a maximum concentration of 70 µg/L.

Metaldehyde is a molluscicide and has been a good example of an emerging contaminant with unanticipated widespread elevated environmental concentrations found over the past decade following development of a suitable analytical method. It has been detected in 2.5% of samples with a maximum concentration of 6.4 µg/L. A ban on the outdoor use of metaldehyde is to be introduced across Great Britain from Spring 2020.

Other pesticides are oxadixyl, a fungicide used in fruit growing, diphenylamine, widely used as an industrial antioxidant and reagent and also employed in agriculture as a fungicide and antihelminthic, and the herbicides metazachlor and bromacil. These are detected in fewer than 2% of samples and have maximum concentrations in the range 3–6 µg/L except metazachlor which has a maximum concentration of 44 µg/L.

These are all compounds with a well-established track record of persistence in groundwater.

Halogenated solvents (Hsol)
Seven out of the top 50 most frequently detected compounds using the GC-MS method are halogenated solvents. Trichloroethene is the most frequently detected compound in this category, and the second overall, with 948 detections corresponding to 8.34% of samples, although the concentrations are relatively low, with a p95 of 0.13 µg/L and a maximum concentration of 184 µg/L. Tetrachloroethene and the THM bromodichloromethane are found with similar maximum concentrations but in fewer samples. Other brominated THMs detected were chlorodibromomethane and bromoform in about 2% of samples. 1,1,2-trichloroethane and chlorobenzene were also found but at lower concentrations. All compounds except trichloroethane and tetrachloroethane had censored distributions with p95 concentrations at the LOD.

Plasticisers (Plast)
Five compounds classified as plasticisers were ranked in the top 50. Of these bisphenol A was the most frequently detected, and was the third most frequent in the dataset, with 939 detections corresponding to 8.26% of samples, with a p95 of 0.09 µg/L and a maximum concentration of 100 µg/L. DEHP was detected in 4% of samples with a maximum concentration of 62 µg/L. N-butylbenzene sulphonamide was much less frequently detected (2.66%) but had a very high maximum concentration (4000 µg/L). Dimethyl phthalate and ATBC were the least frequently detected, but ATBC had a maximum detected concentration of 45 µg/L.

Industrial (Indu)
This is a diverse group of 13 compounds comprising non-chlorinated solvents, industrial intermediates and flame retardants, many of which are also used as plasticisers. All compounds in this group had censored distributions with the p95 concentration at the LOD except cyclohexanone.

Non-halogenated solvents

Two compounds classed as non-halogenated solvents were detected in the top 50; 1,4-dioxane was detected in 4.6% of samples with a maximum concentration of 63 µg/L and dimethyl adipate in 3.17% of samples but at with a higher maximum concentration of 150 µg/L. As well as a solvent 1,4-dioxane is used as a stabilizer for the transport of halogenated hydrocarbons in aluminum containers. Dimethyl adipate is a nylon precursor and it is also used as a plasticiser as well as a solvent.

Intermediates

Cyclohexanone is the most frequently detected compound in the Industrial group, found in 5.61% of samples with a maximum concentration of 300 µg/L. This has a wide range of applications and has been used in the manufacture of nylon. Other compounds were found in fewer than 2.5% of samples, TMDD, 1(3H)-isobenzofuranone ((phthalide) can also be used as a food additive), TTT, 2,4-DTBP, dibenzofuran and nerolin. They had maximum concentrations of 6 µg/L or less except TTT, which was found at 62 µg/L.

Flame retardants

The aryl phosphate esters are mainly used as flame-retardant plasticisers in PVC and other polymers. Triphenyl phosphate is the most widely detected of these, found in 2.91% of samples with a maximum concentration of 2 µg/L. Tri-(2-chloroethyl) phosphate and 2-ethylhexyl diphenyl phosphate were found in 1.78% and 1.57% of samples with maximum concentrations of 65 µg/L and 1 µg/L respectively.

Polyaromatic hydrocarbons (PAHs)
There are 8 compounds in this category. PAHs are generally not very water soluble and are found at low concentrations. Fluoranthene and pyrene are the most soluble of these compounds and are detected in 5.47% and 5.33% of samples respectively with concentrations of 3.4 µg/L and 2 µg/L. Others are detected in fewer than 2% of samples with maximum concentrations of 2 µg/L or less except for acenaphthene which had a maximum concentration of 5 µg/L.

Pharmaceutical, personal care products, lifestyle (PPCL)
Nine of the top 50 compounds were in this category. The p95 of concentration for all of these compounds was below the LOD.

Personal care

Compounds in this group tend to be applied to the skin. The insect repellent DEET is the most frequently detected compound in the PPCL category and the 7th overall. It was detected in 5.85% of samples with a maximum concentration of 17 µg/L. Benzophenone, benzophenone-3 and drometrizole are UV absorbers and can be used as cosmetics, such as sunscreen, and were found in 2.53% of samples at a maximum concentration of 0.8 µg/L, 1.32% of samples at a maximum concentration of 45 µg/L and 1.05% of samples at a maximum concentration of 18 µg/L respectively. The anti-microbial propyl paraben was detected in 1.28% of samples with a maximum concentration of 36 µg/L.

Pharmaceuticals

Relatively few pharmaceuticals are detected by the GC-MS method. Carbamazepine was detected in 1.5% of samples with a maximum concentration of 0.26 µg/L.

Food additives

Butanedioic acid, dimethyl ester was the most frequently detected in this group, and the 4th most frequently overall, being detected in 6.76% of compounds with a maximum concentration of 74 µg/L. It is used as a flavouring agent but also has a wide range of industrial applications. The food antioxidant BHT was detected in 1.43% of samples with a maximum concentration of 8.7 µg/L.

Lifestyle

Caffeine was detected in 4.26% of samples with a maximum concentration of 1.8 µg/L.

Top 50 GC-MS substances by maximum concentration

Data description

The top 50 GC-MS substances ordered by maximum concentration are shown in Figure 3.3. It is worth noting that some of these maximum concentrations (i.e. outliers) are considerably higher than

the next highest concentration detected (*see* Figure 3.2), and they may represent a point source of contamination.

The top 10 highest maximum concentrations in these frequently detected compounds were for benzenesulfonamide, benzotriazole, ethylhexanoic acid, cyclohexanone, cholesterol, mercaplobenzothiazole, benzothiozole, TCE, chlorodibromomethane, and tetrachloroethene.

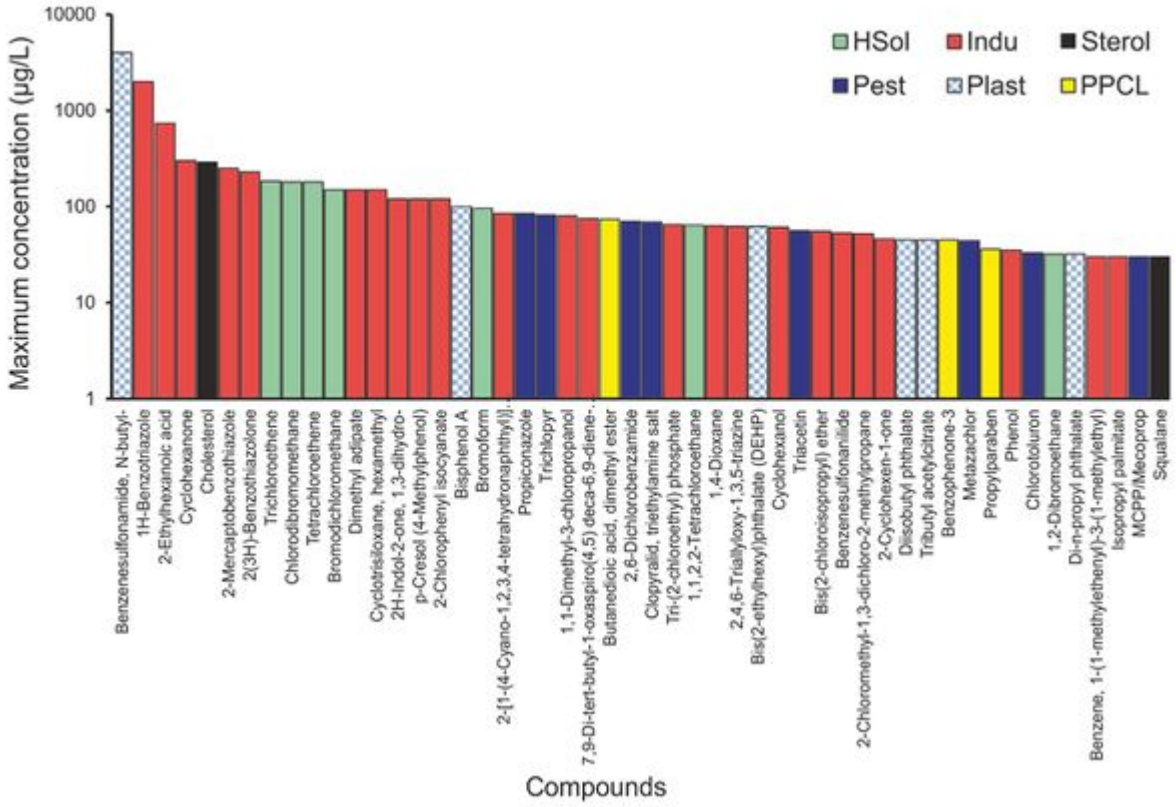

Figure 3.3 Bar chart of top 50 substances by maximum concentration by GC-MS screen.

Top 50 LC-MS substances by frequency of detection

Data description

The top 50 substances from the LC-MS dataset selected by frequency are shown in Figure 3.4. A statistical summary of the data is shown in Table 3.2. Box plots indicating data distribution are shown in Figure 3.5.

The top 18 compounds have sufficient detection data for the statistical distribution to be calculated. Many of these compounds have a median concentration considerably below the LOD. For the majority of these distributions, the p95 is at or close to the LOD. The LOD for the LC-MS method used here are much lower than the GC-MS method and this may well be the main reason why the percentage of detections is much higher.

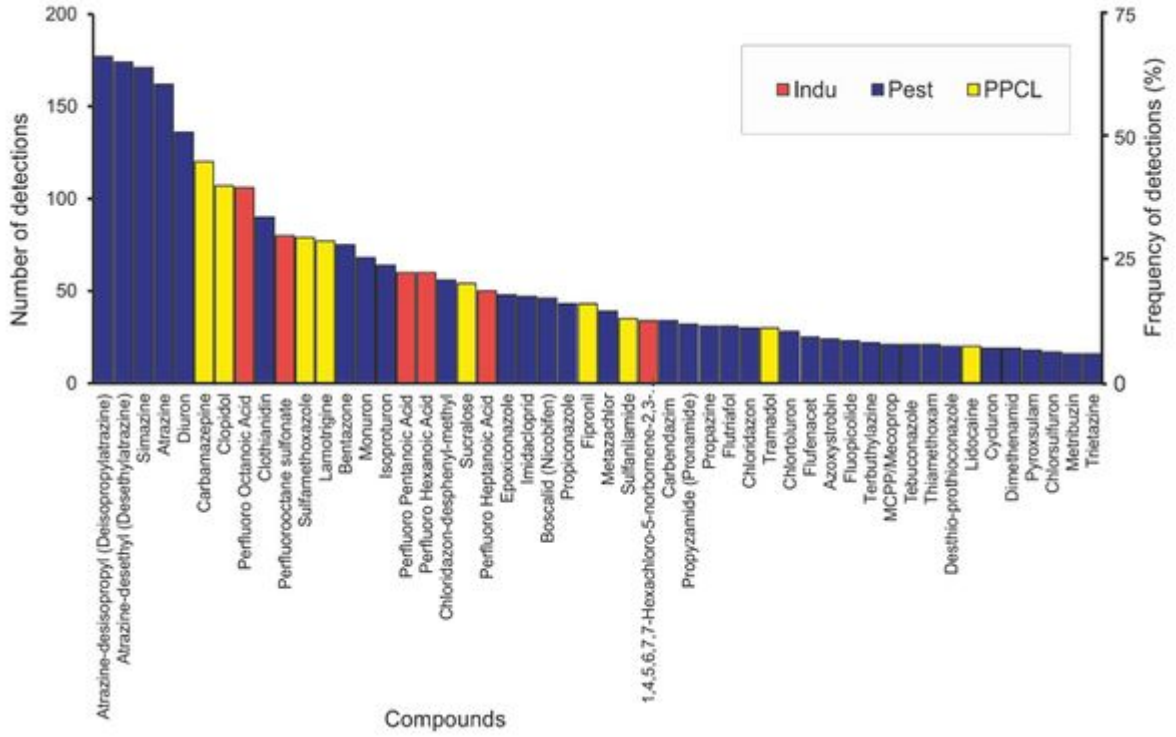

Figure 3.4 Bar chart of 50 most frequently quantified substances by LC-MS screen.

Figure 3.5 shows the distribution of the results for the 50 most frequently detected substances by LC-MS using a Tukey box plot. The box plots show the interquartile range (IQR), box whiskers (values +/- 1.5 IQR) and outliers (values >1.5 IQR). In many cases the proportion of detections is too low to calculate the IQR and in these instances, the box-plots simply illustrate the outlier concentrations.

Cumulative frequency plots for the 50 most frequently detected substances by LC-MS screens are presented in Figure 3.6.

Table 3.2 Summary statistics for 50 most frequently quantified substances by LC-MS screen. For all analytes the minimum concentration detected was below the LOD. The proportion of positive detections was too low to calculate a 5th percentile value. NA = not statistically valid. Median concentration has been rounded to 6 decimal places. All concentrations are in units of µg/L.

Ranking	CAS Number	Analyte	Short name	Use code *	LOD	Median concentration	Mean concentration	Standard deviation	95th percentile concentration	Maximum concentration	Number of analyses	Number of positive detections	% analyses with positive detections
L1	1007289	Atrazine-desisopropyl (Deisopropylatrazine)	Desisopropyl-atrazine	Pest	0.001	0.0022	0.0064	0.007	0.02	0.05	267	176	65.92
L2	6190654	Atrazine-desethyl (Desethylatrazine)	Desethyl-atrazine	Pest	0.001	0.0021	0.018	0.03	0.07	0.3	267	172	64.42
L3	122349	Simazine	Simazine	Pest	0.001	0.001	0.004	0.005	0.02	0.03	267	170	63.67
L4	1912249	Atrazine	Atrazine	Pest	0.001	0.001	0.010	0.02	0.04	0.3	267	162	60.67
L5	330541	Diuron	Diuron	Pest	0.001	0.0005	0.0021	0.008	0.01	0.08	267	133	49.81
L6	298464	Carbamazepine	Carbamazepine	PPCL	0.001	0.0006	0.0034	0.02	0.02	0.06	267	117	43.82
L7	2971906	Clopidol	Clopidol	PPCL	0.001	0.0003	0.0045	0.067	0.02	3.5	267	106	39.70
L8	335671	Perfluorooctanoic Acid	PFOA	Indu	0.005	0.0006	0.0016	0.003	0.006	0.05	267	106	39.70
L9	210880925	Clothianidin	Clothianidin	Pest	0.001	0.0003	0.003	0.025	0.01	0.09	267	89	33.33
L10	1763231	Perfluorooctane sulfonate	PFOS	Indu	0.01	0.0002	0.003	0.03	0.01	0.4	267	80	29.96
L11	723466	Sulfamethoxazole	Sulfamethoxazole	PPCL	0.005	0.0004	0.0016	0.006	0.008	0.03	267	79	29.59
L12	84057841	Lamotrigine	Lamotrigine	PPCL	0.001	0.0003	0.001	0.003	0.006	0.04	267	76	28.46
L13	25057890	Bentazone	Bentazone	Pest	0.001	0.0001	0.024	3.8	0.03	0.9	267	75	28.09
L14	150685	Monuron	Monuron	Pest	0.001	0.0002	0.001	0.005	0.005	0.05	267	67	25.09
L15	34123596	Isoproturon	Isoproturon	Pest	0.001	0.0002	0.001	0.003	0.005	0.06	267	60	22.47
L16	2706903	Perfluoropentanoic Acid	PFPeA	Indu	0.005	0.002	0.003	0.003	0.007	0.08	267	60	22.47
L17	307244	Perfluorohexanoic Acid	PFHxA	Indu	0.005	0.001	0.002	0.003	0.005	0.13	267	60	22.47
L18	17254807	Chloridazon-desphenyl-methyl	CDM	Pest	0.001	4E-05	0.04	39.3	0.04	1.1	267	56	20.97
L19	56038132	Sucralose	Sucralose	PPCL	0.01	NA	NA	NA	0.26	2.3	267	52	19.48
L20	375859	Perfluoroheptanoic Acid	PFHpA	Indu	0.005	NA	NA	NA	0.005	0.03	267	50	18.73
L21	133855988	Epoxiconazole	Epoxiconazole	Pest	0.004	NA	NA	NA	0.004	0.03	267	47	17.60
L22	188425856	Boscalid (Nicobifen)	Boscalid	Pest	0.005	NA	NA	NA	0.008	0.24	267	45	16.85
L23	138261413	Imidacloprid	Imidacloprid	Pest	0.001	NA	NA	NA	0.002	0.02	267	43	16.10

L24	60207901	Propiconazole	Propiconazole	Pest	0.001	NA	NA	NA	0.006	0.12	267	43	16.10
L25	120068373	Fipronil	Fipronil	Pest	0.001	NA	NA	NA	0.001	0.004	267	43	16.10
L26	67129082	Metazachlor	Metazachlor	Pest	0.001	NA	NA	NA	0.01	0.8	267	39	14.61
L27	63741	Sulfanilamide	Sulfanilamide	PPCL	0.01	NA	NA	NA	0.01	0.037	267	35	13.11
L28	115286	1,4,5,6,7,7-Hexachloro-5-norbornene-2,3-dicarboxylic acid	Chlorendic acid	Indu	0.005	NA	NA	NA	0.09	2.1	267	34	12.73
L29	10605217	Carbendazim	Carbendazim	Pest	0.01	NA	NA	NA	0.005	0.25	267	33	12.36
L30	23950585	Propyzamide (Pronamide)	Propyzamide	Pest	0.001	NA	NA	NA	0.001	0.044	267	32	11.99
L31	76674210	Flutriafol	Flutriafol	Pest	0.001	NA	NA	NA	0.01	0.1	267	31	11.61
L32	139402	Propazine	Propazine	Pest	0.001	NA	NA	NA	0.001	0.005	267	30	11.24
L33	27203925	Tramadol	Tramadol	PPCL	0.001	NA	NA	NA	0.001	0.048	267	29	10.86
L34	1698608	Chloridazon (PAC)	Chloridazon	Pest	0.001	NA	NA	NA	0.001	0.03	267	29	10.86
L35	15545489	Chlortoluron (Chlorotoluron)	Chlortoluron	Pest	0.002	NA	NA	NA	0.002	0.13	267	27	10.11
L36	142459583	Flufenacet (Fluthiamide) (BAY FOE 5043)	Flufenacet	Pest	0.001	NA	NA	NA	0.001	0.057	267	25	9.36
L37	131860338	Azoxystrobin	Azoxystrobin	Pest	0.001	NA	NA	NA	0.003	0.02	267	24	8.99
L38	5915413	Terbuthylazine	Terbuthylazine	Pest	NA	NA	NA	0.001	0.005	267	22	8.24	
L39	239110157	Fluopicolide	Fluopicolide	Pest	0.001	NA	NA	NA	0.001	0.008	267	21	7.87
L40	7085190	MCPP/Mecoprop	MCPP	Pest	0.005	NA	NA	NA	0.01	0.55	267	21	7.87
L41	107534963	Tebuconazole (Terbuconazole)	Tebuconazole	Pest	0.001	NA	NA	NA	0.003	0.08	267	21	7.87
L42	153719234	Thiamethoxam	Thiamethoxam	Pest	0.001	NA	NA	NA	0.001	0.003	267	20	7.49
L43	137586	Lidocaine (Diocaine)	Lidocaine	PPCL	0.001	NA	NA	NA	0.001	0.008	267	20	7.49
L44	120983644	Desthio-prothioconazole	Desthio-prothioconazole	Pest	0.001	NA	NA	NA	0.001	0.02	267	20	7.49
L45	2163691	Cycluron	Cycluron	Pest	0.001	NA	NA	NA	0.001	0.08	267	19	7.12
L46	87674688	Dimethenamid (SAN 582H)	Dimethenamid	Pest	0.001	NA	NA	NA	0.001	0.01	267	18	6.74
L47	422556089	Pyroxsulam	Pyroxsulam	Pest	0.005	NA	NA	NA	0.005	0.003	267	18	6.74
L48	64902723	Chlorsulfuron	Chlorsulfuron	Pest	0.001	NA	NA	NA	0.001	0.004	267	17	6.37
L49	21087649	Metribuzin	Metribuzin	Pest	0.002	NA	NA	NA	0.002	0.03	267	16	5.99
L50	1912261	Trietazine	Trietazine	Pest	0.005	NA	NA	NA	0.005	0.18	267	16	5.99

* *Key to use codes given in Table 2.2.*

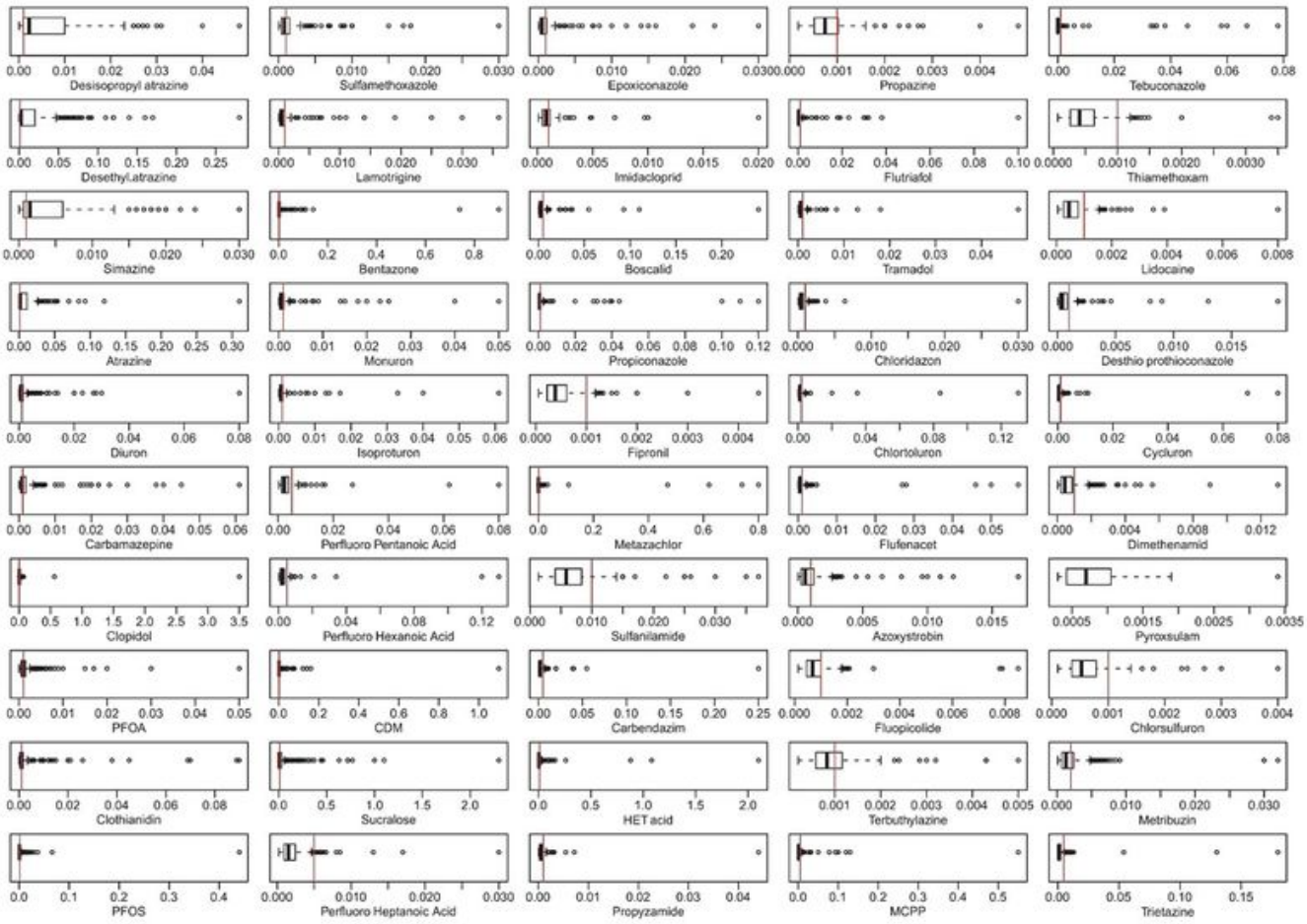

Figure 3.5 Box plots for the 50 most frequently detected substances by LC-MS. x-axis shown as concentration (µg/L) for all compounds. Percentiles below the red line, which shows the censored level, were estimated using regression on order statistics (ROS).

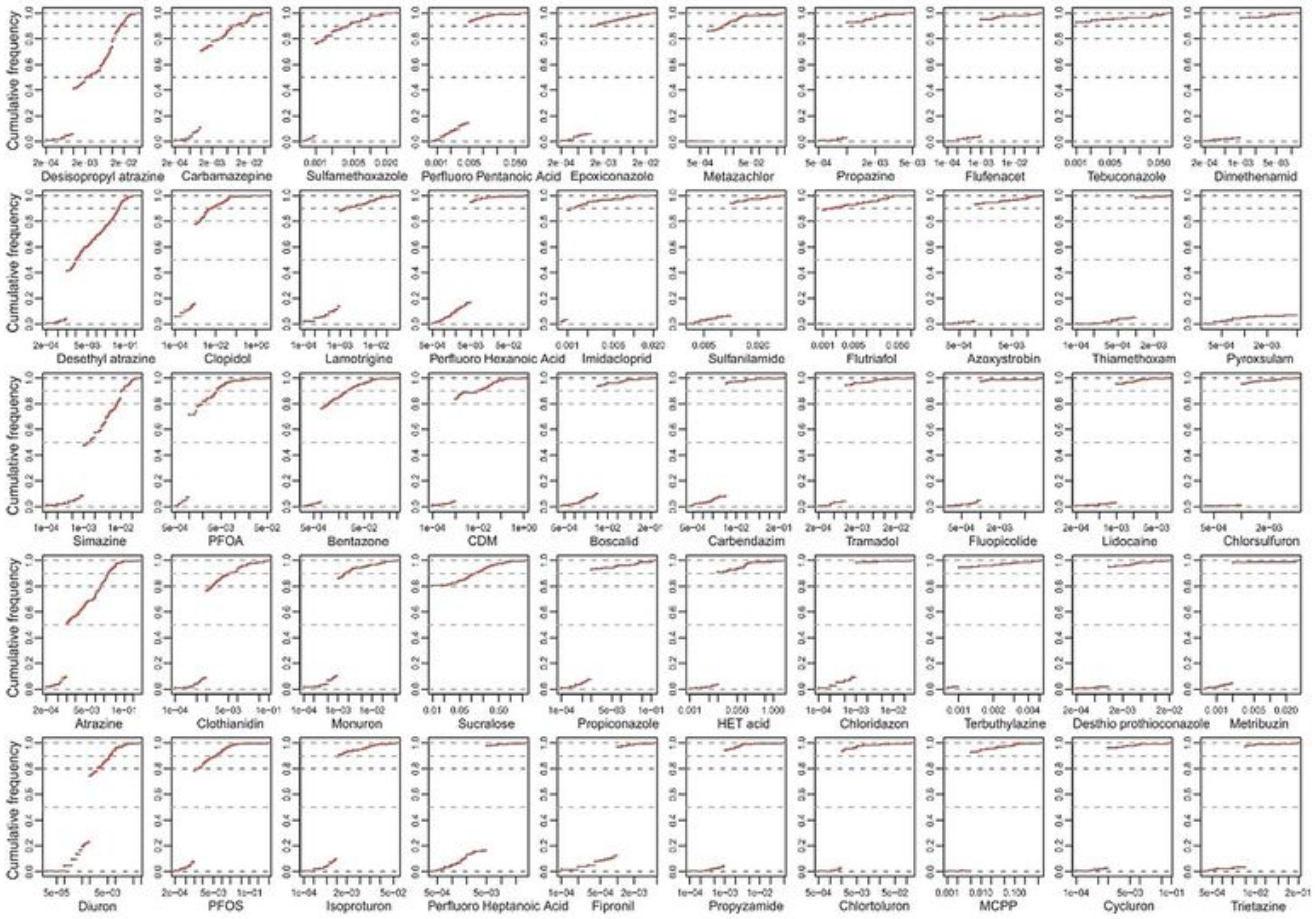

Figure 3.6 Cumulative frequency plots for 50 most frequently detected substances by LC-MS, x-axis shown as concentration units of µg/L for all compounds.

Discussion of results

Pesticides (Pest)

Thirty six of the top 50 compounds most frequently detected are pesticides. The top 4 are all triazine herbicidal compounds: atrazine, the 2 main atrazine TPs and simazine. All 4 are detected in over 50% of samples. Median concentrations ranged from 0.001 to 0.002 µg/L with maximum concentrations in the ranging from 0.03 µg/L for simazine to 0.31 µg/L for atrazine.

Three 'uron' herbicides are in the top 15 most frequently detected pesticides: diuron in 49.8% of samples, monuron in 25.1% and isoproturon in 22.5%. Other 'urons' detected were chlorotoluron, cycluron and chlorsulfuron.

Other top 50 compounds were the neonicotinoid insecticide clothianidin, the herbicide bentazone and the herbicide TP chloridazon-desphenyl-methyl, all detected in more than 20% of samples. Many of the most frequently detected pesticides are no longer approved for use. The most frequently detected pesticide that is currently approved is bentazone and that was detected in 28% of samples.

Of the other pesticide compounds detected, 2 were insecticides (fipronil and imidacloprid), 9 were fungicides (epoxiconazole, propiconazole, boscalid, carbendazim, azoxystrobin, tebuconazole, fluopicolide, thiamethoxam and the TP prothioconazole-desthio) and the remaining 12 compounds were herbicides (including the parent chloridazon). All were detected in 6% of samples or more. It is interesting that the parent prothioconazole does not appear in the top 50 compounds, although it is detectable by this method. This may relate to the rapid breakdown of the parent molecule in the environment. It was introduced in 2002 as a foliar treatment for fungal diseases in cereals and is still

used in the UK.

Compounds with maximum concentrations above the 0.1 µg/L drinking water limit, in descending order of concentration were chloridazon-desphenyl-methyl (1.1 µg/L), bentazone, metazachlor, 2-methyl-4-chlorophenoxyacteic acid (MCPA), atrazine, atrazine-desethyl, carbendazim, boscalid, trietazine, chlorotoluron, propiconazole and flutriafol.

Industrial compounds (Indu)
There are 6 compounds in this group, 5 of which are perfluorinated acids and esters. As might be anticipated, PFOA is the most frequently detected, in 39.7% of samples with a median concentration of 0.0006 µg/L and a maximum concentration of 0.05 µg/L, and PFOS is next, in 30% of samples with a median concentration of 0.0003 µg/L and a maximum concentration of 0.44 µg/L. The other three are the shorter chain acids, PFPeA, PFHxA and PFHpA, present in between 18.7 and 22.4% of samples with maximum concentrations of 0.08, 0.13 and 0.03 µg/L respectively.

Chlorendic acid is an industrial intermediate used in the synthesis of flame retardants and polymers. It is also a common breakdown product of several organochlorine insecticides. It was detected in 12.7% with a maximum concentration of 2.1 µg/L.

Pharmaceutical, personal care products, lifestyle (PPCL)

Pharmaceuticals

There are eight compounds in this group. The most widely detected compound, and 6th overall is carbamazepine, one of a number of compounds used to treat epilepsy/convulsions/bipolar disorder. This was detected in 43.8% of samples at a median concentration of 0.0006 µg/L and a maximum of 0.61 µg/L. Lamotrigine was also detected in 28.5% with a median concentration of 0.003 µg/L and a maximum of 0.036 µg/L.

Antibiotic and antibacterial compounds were detected: sulfamethoxazole in 29.6% of samples with a median concentration of 0.0004 µg/L and a maximum of 0.03 µg/L, and sulphanilamide in 13.1% with a maximum concentration of 0.037 µg/L.

The analgesics/anaesthetics tramadol and lidocaine were detected in 10.9% and 7.4% of samples respectively at maximum concentrations of 0.048 and 0.008 µg/L respectively.

The veterinary antiprotozoal substance clopidol was detected in 39.7% of samples with a median concentration of 0.0003 µg/L and a maximum concentration of 3.5 µg/L.

Lifestyle

The artificial sweetener sucralose was detected in 19.5% of samples with a maximum concentration of 2.3 µg/L. Sucralose has been suggested as an indicator of wastewater ingress to groundwater.

Top 50 LC-MS substances by maximum concentration

Data description

The top 50 LC-MS substances ordered by maximum concentration are shown in Figure 3.3. It is worth noting that some of these maximum concentrations are considerably higher than the next highest concentration detected (see Figure 3.5), and although they may represent a highly contaminated sample.

The top 10 highest maximum concentrations were for clopidol, followed by sucralose, chlorendic acid, triallate, pentobarbital, chloridazon-desphenyl-methyl, bentazone, tridimefon, metazachlor and mecoprop, with 3 of the top 5 being PPCL compounds.

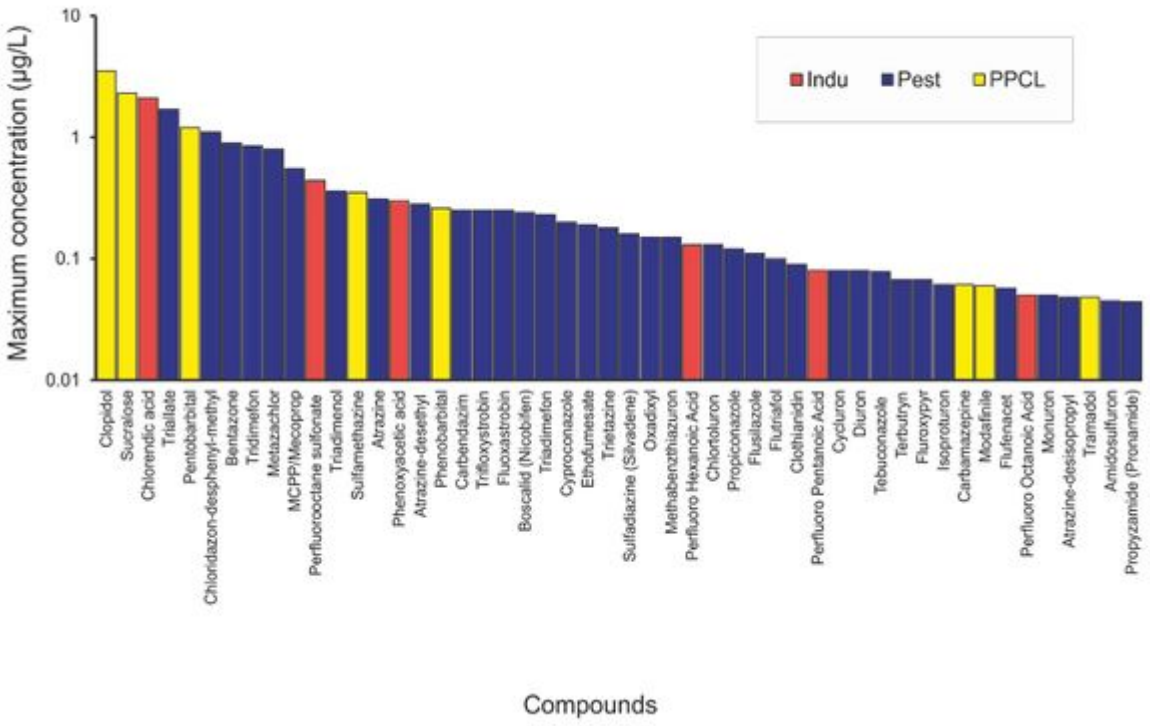

Figure 3.7 Bar chart of top 50 substances by maximum concentration by LC-MS screen.

Overlap of substances in GC-MS-LC-MS screens

Comparing the compounds listed in the Top 50 by frequency of detection and Top 50 by concentration for the GC-MS and LC-MS screens identifies 5 compounds which are detected by both methods. These compounds are listed in Table 3.3.

Table 3.3 Compounds quantified by both GC-MS and LC-MS screens, and which were ranked in the Top 50 by frequency of detection and/or concentration.

CAS Number	Analyte
122349	Simazine
298464	Carbamazepine
1912249	Atrazine
6190654	Atrazine-desethyl (Desethylatrazine)
67129082	Metazachlor

Analysis of the complete dataset indicates that the GC-MS method detected 663 substances in samples and the LC-MS detected 178 substances. Of these, 81 substances were detected by both methods: these are listed in Table 3.4.

Table 3.4 Compounds quantified by both GC-MS and LC-MS screens, in the entire BGS database.

CAS Number	Analyte
50362	Cocaine

60515	dimethoate
63252	Carbaryl
72446	Methaqualone
76744	Pentobarbital
94757	2,4-D
101428	Fenuron (N,N-Dimethyl-N-phenylurea)
121755	Malathion
122349	Simazine
125406	Butabarbital (Secubarbital)
137586	Lidocaine (Diocaine)
139402	Propazine
150685	Monuron
298464	Carbamazepine
330541	Diuron
330552	Linuron
333415	Diazinon (Dimpylate)
439145	Diazepam
470906	Chlorfenvinphos
486566	Cotinine
551928	Dimetridazole
886500	Terbutryn
1007289	Atrazine-desisopropyl (Deisopropylatrazine)
1014693	Desmetryn
1689845	Bromoxynil
1698608	Chloridazon (PAC)
1912249	Atrazine
1912261	Trietazine
2303175	Triallate
2631405	Isoprocarb
2921882	Chlorpyrifos
5915413	Terbuthylazine
6190654	Atrazine-desethyl (Desethylatrazine)
7287196	Prometryn
15299997	Napropamide
15545489	Chlorotoluron
15687271	Ibuprofen
16118493	Carbetamide
18691979	Methabenzthiazuron
19666309	Oxadiazon
21087649	Metribuzin
21725462	Cyanazine (Fortrol)
23103982	Pirimicarb
23950585	Propyzamide (Pronamide)

25057890	Bentazone
26225796	Ethofumesate
28721075	Oxcarazepine
29232937	Pirimiphos-methyl (Pirimifos-methyl)
34123596	Isoproturon
40487421	Pendimethalin (Penoxalin)
43121433	Triadimefon
51235042	Hexazinone
53112280	Pyrimethanil
55219653	Triadimenol
55335063	Trichlopyr
57837191	Metalaxyl
60142963	Gabapentin
60168889	Fenarimol
60207901	Propiconazole
66246886	Penconazole
66332965	Flutolanil
67129082	Metazachlor
67564914	Fenpropimorph (Ro 14-3169)
67747095	Prochloraz
76674210	Flutriafol
77732093	Oxadixyl
85509199	Flusilazole
87674688	Dimethenamid (SAN 582H)
107534963	Tebuconazole (Terbuconazole)
110488705	Dimethomorph
120068373	Fipronil
121552612	Cyprodinil
123312890	Pymetrozin
131860338	Azoxystrobin
133855988	Epoxiconazole
142459583	Flufenacet (Fluthiamide) (BAY FOE 5043)
153719234	Thiamethoxam
183675823	Penthiopyrad
188425856	Boscalid (Nicobifen)
239110157	Fluopicolide
361377299	Fluoxastrobin

Spatial plots of occurrence of selected substances

This section presents a series of spatial plots of key substances. These were selected on the basis of frequency of detection and/or being classed as PPCL, a large group of substances of potential emerging concern which is receiving growing attention in Europe. Concentrations (maximum per site) are shown as proportional symbols. Results are plotted on a background of a simplified 1:625 000 scale geological map as requested by the EA: the legend is provided in Figure 3.8.

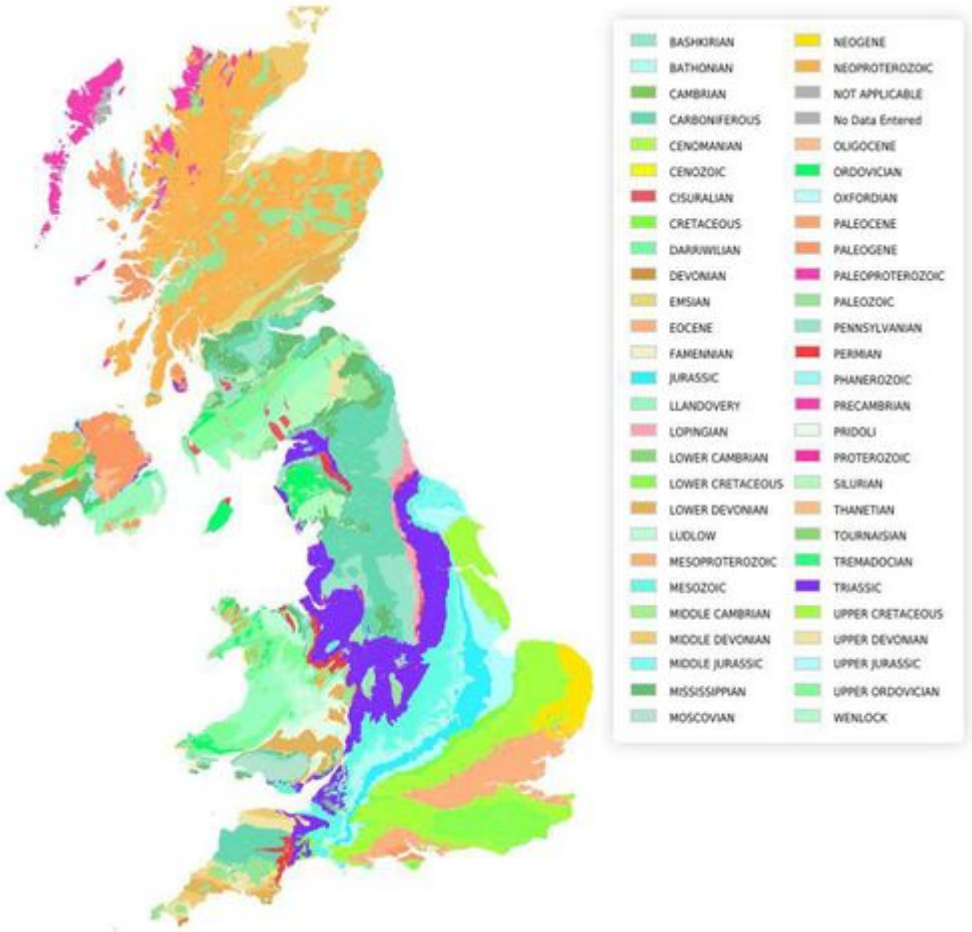

Figure 3.8 Geological map background (1:625 scale bedrock geology — UK onshore bedrock age) with legend.

GC-MS

Atrazine remains the most frequently detected compound by GC-MS. Since the database contains data collected throughout the period that this method has been used, it may give a misleading impression of current conditions. A spatial plot of these data (Figure 3.9) shows that atrazine is predominantly detected at concentrations of >0.1 µg/L in the principal aquifers of the Chalk and the Permo-Triassic sandstone. This may reflect historical usage and particularly for the Chalk the travel time from the surface through the unsaturated zone to the water table and the slow rate of flushing of these aquifers.

Historically atrazine was used for weed control, both in agriculture and for amenity use until 1992 when it was withdrawn from non-agricultural uses in the UK. There was concern that amenity use potentially allowed pesticide to enter the subsurface via soakaways, bypassing the soil. Limited agricultural uses were permitted until an EU-wide ban for all uses followed in 2003. The elevated concentrations seen in this dataset demonstrate that a precautionary approach is needed to protect groundwater from pesticides as degradation rates in the subsurface are typically very slow.

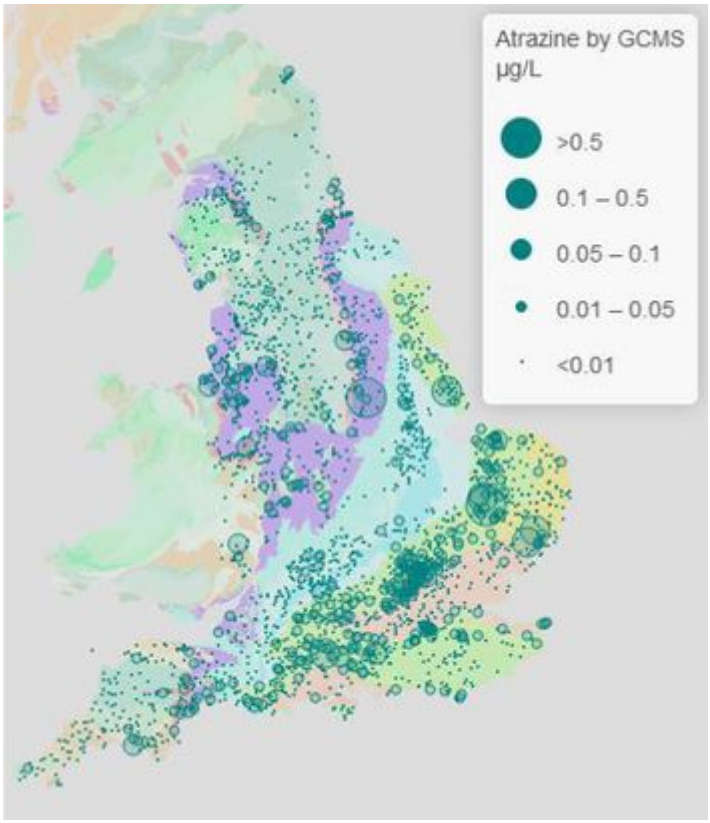

Figure 3.9 Spatial plot of atrazine concentrations by
GC-MS screen (µg/L).

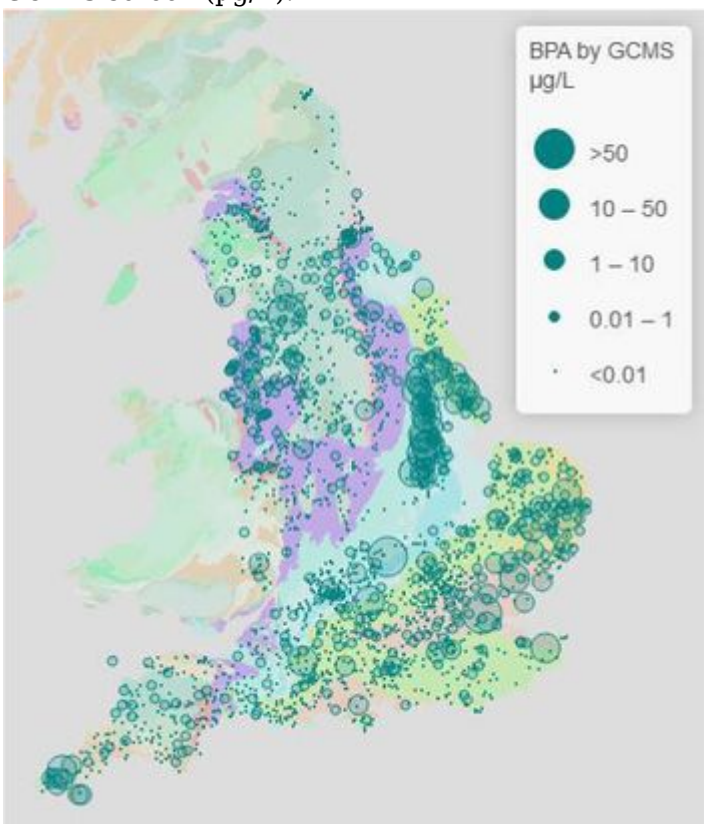

Figure 3.10 Spatial plot of BPA concentrations by GC-MS screen (µg/L).

BPA is the most frequently detected plasticiser in the dataset. The spatial plot (Figure 3.10) shows it to be widely detected across England. There are areas of concentrations >1 µg/L in the urban areas

of Greater London and the Thames Estuary, Birmingham, Liverpool and Hull areas and in the Jurassic limestones of Lincolnshire and perhaps surprisingly in the far southwest.

There are likely to be multiple sources of BPA in the environment, including wastewater, septic tanks and landfills. It is also a common component of many plastic items and care is needed to exclude these from sampling equipment. Plasticisers can be leached into groundwater from plastic well casing and pipework associated with groundwater sampling and this could explain BPA detections at some sites rather than BPA occurrence in the aquifer.

DEET is the second most frequently detected PPCL in the dataset. Figure 3.11 shows higher concentrations to be distributed with areas of central southern England, the north Yorkshire coast and the Manchester-Liverpool area with groups of values over 0.1 µg/L. The Lincolnshire Limestone and the south east of England also show scattered higher concentrations.

When used as an insect repellent, DEET is topically applied and may therefore be found in the wastewater stream (Aronson et al., 2012[1]). DEET can be readily absorbed into the body of plastic objects. The spatial coherence of DEET observations in some regions suggests that some detections may be due to contamination from samplers, but this has not been verified.

Butanedioic acid, dimethyl ester (dimethyl succinate) is detected widely across England, with surprisingly few detections in the Chalk of south-east England, the Carboniferous and Devon and Cornwall (Figure 3.12).

Caffeine is also widely detected in groundwater across England with pronounced clusters of detections in the London area, Cornwall and North Yorkshire (Figure 3.13).

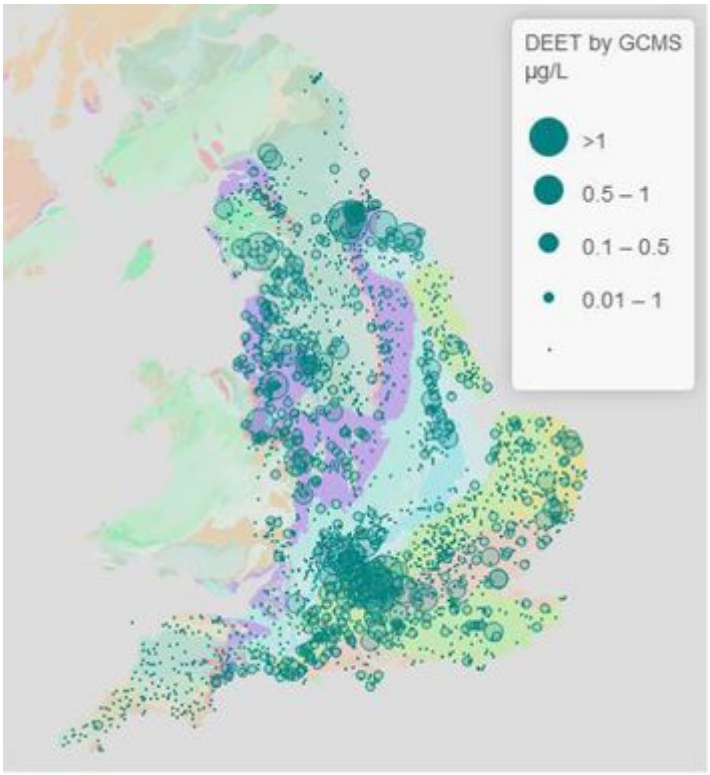

Figure 3.11 Spatial plot of DEET concentrations by GC-MS screen (µg/L).

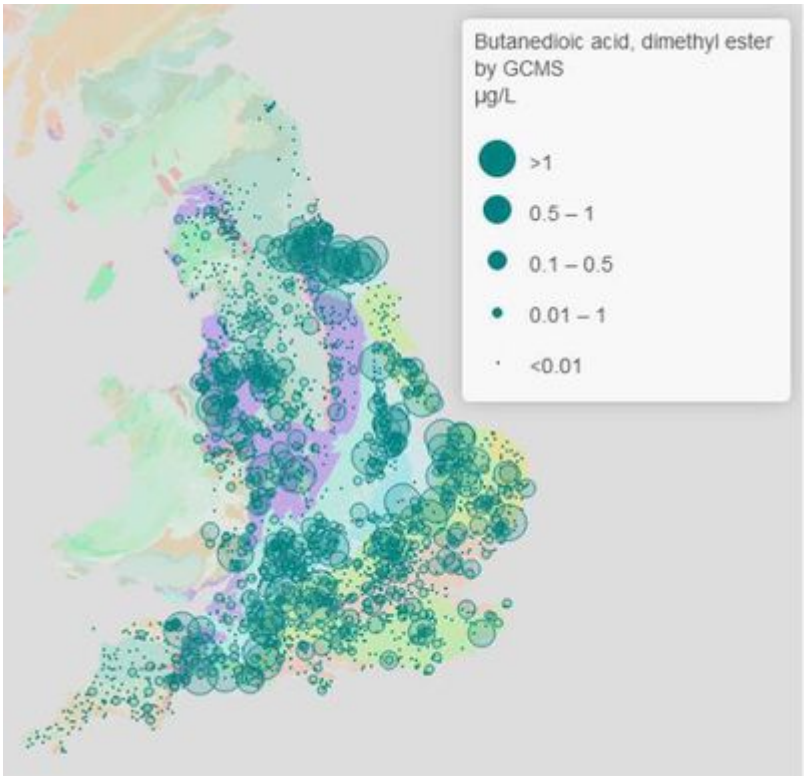

Figure 3.12 Spatial plot of butanedioic acid, dimethyl ester (dimethyl succinate) concentrations by GC-MS screen (µg/L).

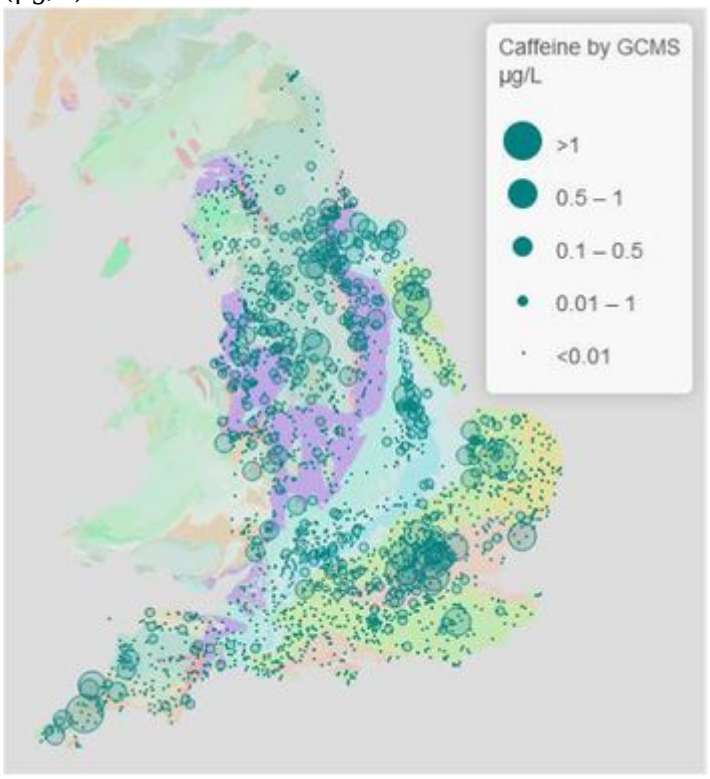

Figure 3.13 Spatial plot of caffeine concentrations by GC-MS screen (µg/L).

LC-MS

There are considerably fewer LC-MS data and these are confined to selected regions of the EA. Carbamazepine is the most frequently detected PPCL in the LC-MS database. The spatial plot (Figure 3.14) shows sampling to be mainly restricted to the central and southern areas of England,

with some sampling in the northeast. Carbamazepine is detected in the London area, in the Chalk of the southeast and in the Permo-Triassic sandstone. There is insufficient data to comment on controls on spatial distribution.

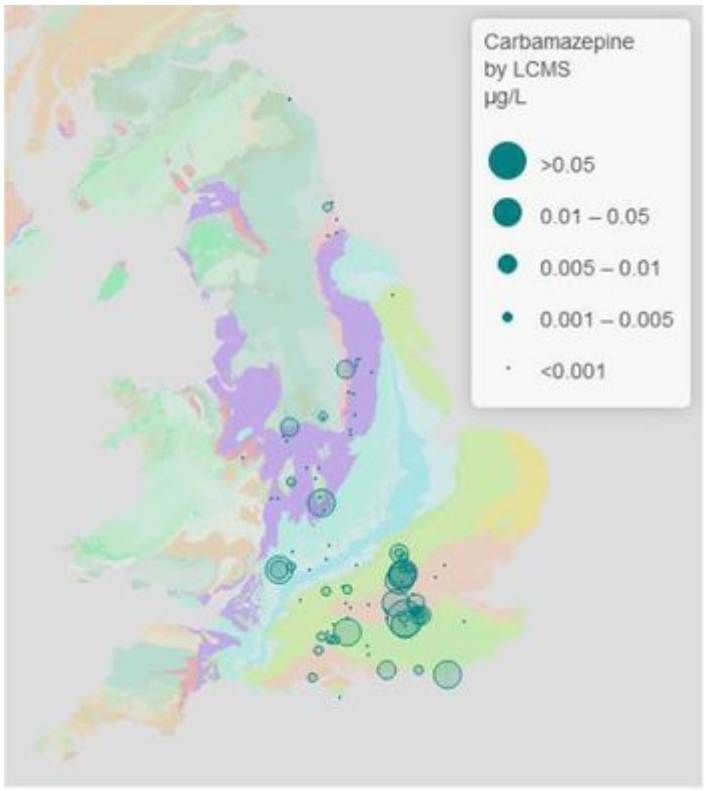

Figure 3.14 Spatial plot of carbamazepine concentrations by LC-MS screen (µg/L).

Detections of clothianidin were found in Gloucestershire and Oxfordshire, in London and in Sussex/Hampshire (Figure 3.15). Presumably, this is associated with the distribution of the target insect pests, but there are too few datapoints to allow comment on spatial distribution.

PFOS and PFOA were mainly detected in the London area, some of which are possibly associated with the Buncefield fire in 2005 and the extensive use of foams to supress the fire (Figure 3.16 and Figure 3.17). Other localised detections include in Hampshire, two sites near the coast in north east England, and a site in Birmingham. PFOS and PFOA are also degradation products of other precursor substances not reported in the LC-MS target screening method.

Clopidol was detected in µg/L concentrations at only a small number of sites, possibly associated with livestock farming and the veterinary use of this substance to treat Coccidia parasites. A high proportion of detections at low concentrations give rise to its prominence in Figure 3.18, but initial results do not indicate a wide distribution in groundwater at µg/L concentrations, however the spatial sampling is limited.

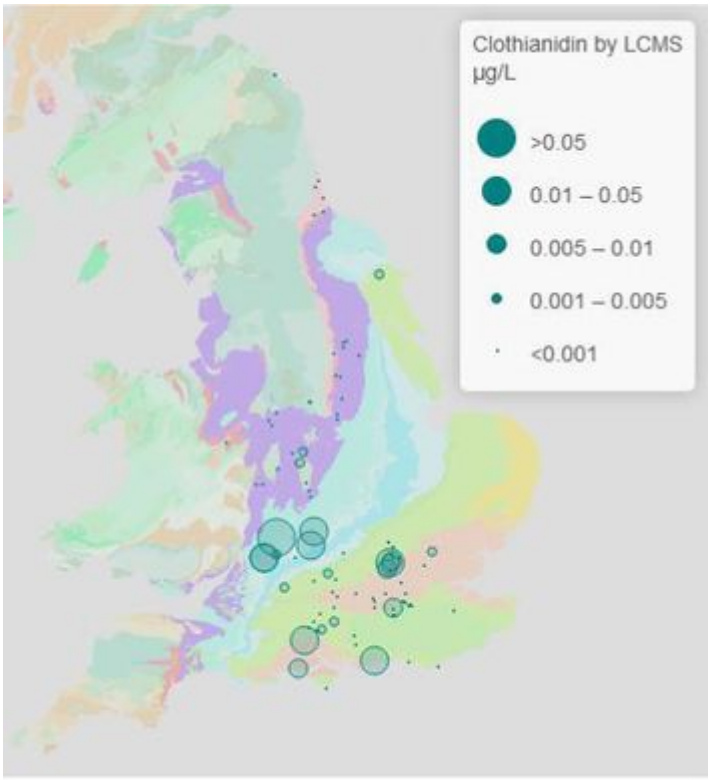

Figure 3.15 Spatial plot of clothianidin concentrations by
LC-MS screen (µg/L).

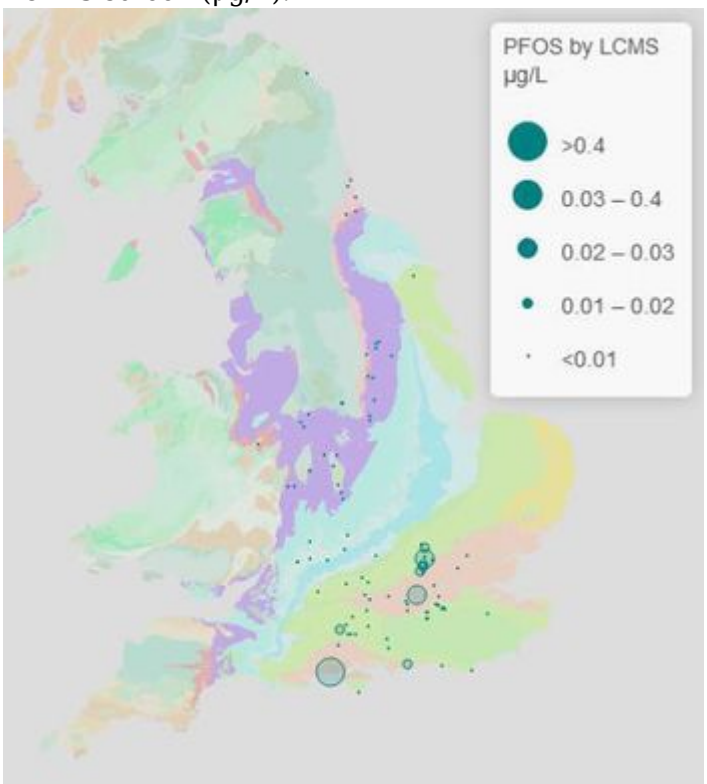

Figure 3.16 Spatial plot of PFOS concentrations by
LC-MS screen (µg/L).

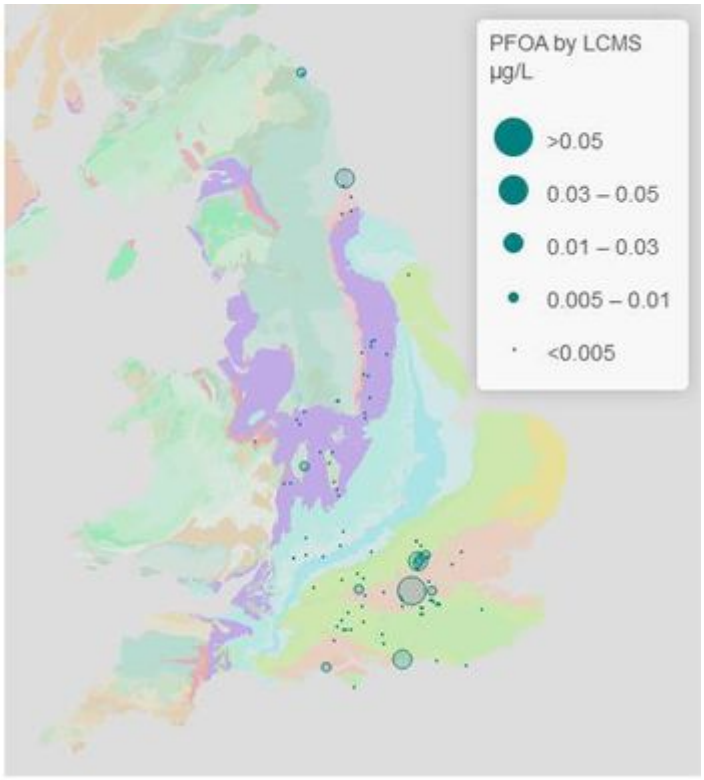

Figure 3.17 Spatial plot of PFOA concentrations by
LC-MS screen (µg/L).

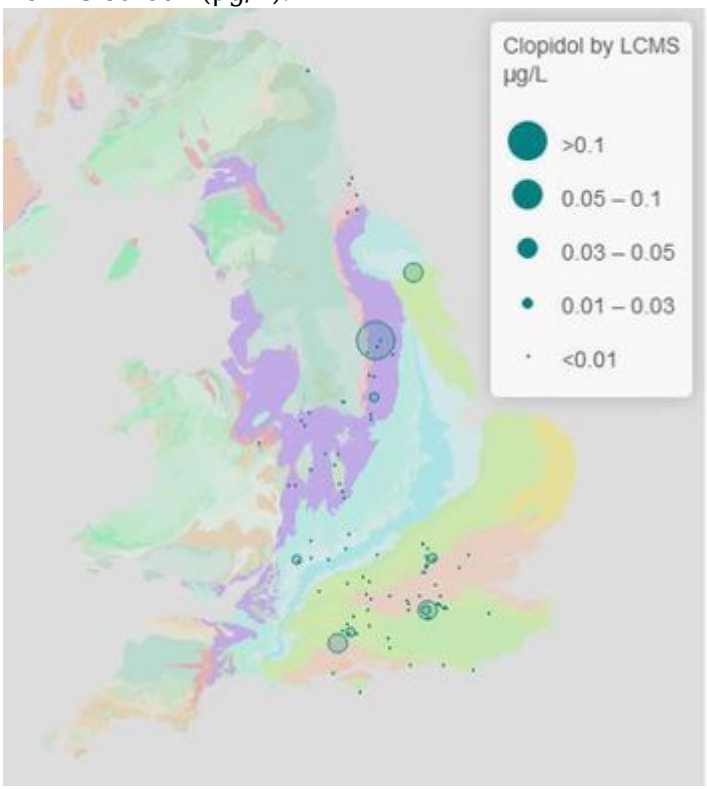

Figure 3.18 Spatial plot of clopidol concentrations by
LC-MS screen (µg/L).

References

1. ↑ ARONSON, D, WEEKS, J, MEYLAN, B, and HOWARD, P. 2012. Environmental release, environmental concentrations, and ecological risk of N,N-Diethyl-m-toluamide (DEET). Integrated Environmental Assessment and Management, 8, 1, 135–166.

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