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# A field based method for pre-concentration of micro organics using solid phase extraction

Groundwater Programme

Open Report OR/17/011





BRITISH GEOLOGICAL SURVEY

GROUNDWATER PROGRAMME

OPEN REPORT OR/17/011

# A field based method for pre-concentration of micro organics using solid phase extraction

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# Foreword

This report is the product of a study by the British Geological Survey (BGS) to test the suitability of a field based method to pre-concentrate micro-organics from surface and groundwaters using solid phase extraction. The reason for this is two-fold; i) to reduce the weight of transporting samples, particularly for overseas applications, ii) to reduce the potential impact of sample degradation during storage prior to solid phase extraction.

# Acknowledgements

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# Summary

British Geological Survey (BGS) have been researching micro-organic pollutants for many years in the UK (Goody et al 2004, Stuart et al 2012, White et al 2016) and overseas (Sorensen et al 2015). A hindrance to the research, especially overseas, has been the need to transport large volumes of water back to the laboratory and the worry of degradation during transportation prior to LCMS or GCMS analysis. The first step in the LCMS analytical procedure is the solid phase extraction of the micro-organic contaminants onto a small cartridge. This report details the field trial where by BGS, working in conjunction with NLS, carried out the pre-concentration step of sample processing in the field. NLS provided pre-conditioned sorbent Oasis® HLB cartridges supplied in sealed Corning centristar centrifuge tubes. Water samples were run through the cartridges by the field team using a small peristaltic pump prior to sending to NLS for semi-quantitative broad screen LCMS analysis. To check the repeatability and the stability of this method the sorbed samples were analysed in duplicate and replicate analysis was carried out over set periods after storage for up to a month. The results from the duplicate replicates are compared to results from the original water sample analysed immediately after sampling. Laboratory and field equipment blanks were included in the trial to check for any contamination introduced by the sampling method and extraction process.

Preliminary results demonstrate that for a large range of compounds, and different types of matrices, this method was able to preserve samples for up to a month. Once the procedure had been validated, it was used to investigate the occurrence of micro-pollutants in a rural groundwater, estuarine waters and a range of surface waters receiving treated sewerage outflows.

The work was funded under the BGS Development Capabilities programme, and was also supported by the BGS Groundwater Science programme under the Groundwater Protection team. Analytical aspects of this work was undertaken in collaboration with Wayne Civil based at Star Cross National Science Laboratory (NLS).

# 1 Introduction

Micro-organic (MO) pollution from anthropogenic sources in groundwater (Lapworth et al 2012) and surface waters (Pal et al 2010) is of growing concern. Recent studies show that groundwaters are polluted with a wide range of regulated legacy contaminants and emerging micro-organic pollutants (Stuart et al 2012). These compounds include pharmaceuticals, personal care products, industrial compounds veterinary medicines and pesticides. A diverse range of micro-organic compounds are found in the outflow from sewerage treatment works which are only partially removed by conventional treatment processes and impact the quality of receiving surface water bodies (Pal et al 2010). Micro-organic pollutants are also seen in the run off from agricultural land and urban areas. New broad screening methods are an important way of quantify the diversity of MO pollution in a cost effective way. However, this type of analysis requires highly specialised techniques which are only possible in a limited number of laboratories.

The National Laboratory Service (UK) have developed techniques such as the LC-MS based screening technique to semi-quantify a broad range of polar organic compounds. Additional compounds continue to be added to the list. The LC-MS technique requires a litre of water to be collected in a glass bottle and sent to the lab. For this type of water quality assessment to be made overseas, or in remote areas, water sampling campaigns are often hampered by the need to carry and ship large volumes of liquid. This can be both expensive and cumbersome. Equally, sample storage and preservation is a concern and there is potential for degradation in transit.

## 2 Method

### 2.1 SAMPLE COLLECTION

#### 2.1.1 Sample site collection

The objective of the initial trial was to test how stable a selection of compounds were on the cartridges and if the compounds detected in a conventional bottled water sample reflected those sorbed onto the cartridge. Sample sites OSP, East Hanney and East Shefford, were all surface waters receiving input from sewage treatment works of differing sizes, two of these were in rural areas and the other in an urban area. The groundwater sample from Boxford was from a previously well characterised borehole in a rural area. These sites were selected to find a wide range of contaminants.

#### 2.1.2 Sample handling precautions

All through the process, from sample collection to pre-concentration onto the cartridges all precautions were taken to reduce the possibility of contaminating the samples with personal care products including insect repellents, sun screens, medicated ointments, as well as vehicle fuel, grease or any other possible contaminant.

Samples were collected in clean glass bottles supplied by the National Laboratory Services (NLS) which were inspected for cleanliness prior to use. No bottles were re-used. Bottles were stored away from sources of contamination with the lids tightly closed. Bottles were labelled using only the labels provided by NLS and no permanent marker was used.

Sample handling in the laboratory was carried out using nitrile gloves.



### 2.1.3 Sample collection methods

For the field trial, samples from surface waters were either collected directly from the stream or by using a pump where it was either too hazardous or difficult to do so. A Solinst 410 peristaltic pump was used together with pump tubing and rigid HDPE tubing that had previously been washed in a solution of Virkon and rinsed with deionised water. During the initial field trial each site had dedicated tubing to prevent carry over.



**Plate 1 Surface water sampling. Direct sampling from the bank at Maidenhead and the use of the peristaltic pump at Hanington Wick during flood conditions.**

For the groundwater sample a Waterra 3-stage pump was used to purge the borehole then samples were taken with the Solinst peristaltic pump with dedicated, Virkon washed and deionised water rinsed tubing. Each surface water site sampled during the initial study had dedicated, washed pump and HDPE tubing stored in separate plastic bags before and after use.

All samples were refrigerated at 4 °C on return to the laboratory and left to stand at least over night for any particulate matter to settle.

## 2.2 SAMPLE METHOD BLANKS

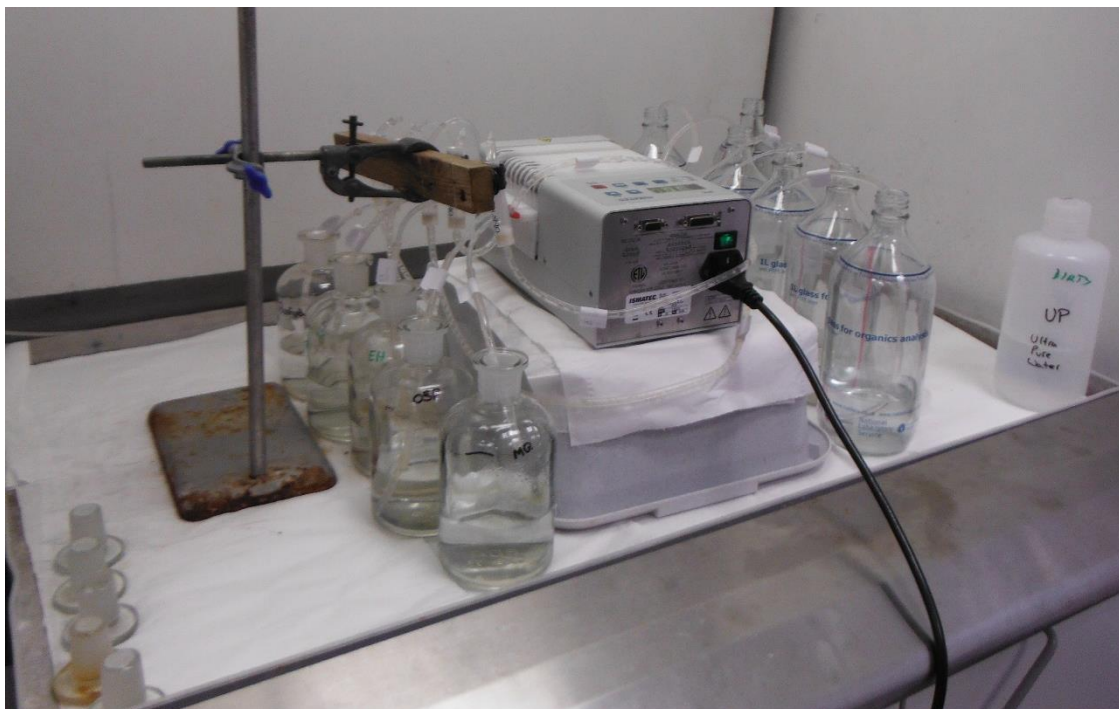
To test the likely inputs of contaminants from different stages of the sampling process a blank was taken.

*Sample bottle blank.* Ultra-pure water direct from the dispenser was run into an NLS glass bottle to test NLS bottles for contamination. This was run through the system and onto the cartridge, replicating the procedure for other samples.

## 2.3 SAMPLE PROCESSING SET UP

Pre-conditioned, numbered and dated sorbent Oasis® HLB cartridges were supplied by NLS in sealed Corning centristar centrifuge tubes to protect the cartridges and stop them drying out. Nitrile gloves were worn during the handling of the cartridges, tubing and samples to avoid contamination. As the system was run in a laboratory, the whole system was put in a fume cupboard to stop possible contamination from volatiles within the laboratory environment.

A 12-channel Ismatec high precision multichannel dispenser was used to drip the sample onto the pre-treated cartridge using new red-red (1.14 mm internal diameter) or yellow-yellow (1.42 mm internal diameter) double-bridge Tygon® auto analyser pump tubes. Additional new Tygon® tubing was attached from the influent end of the pump tube into the sample bottle, carefully making sure the input was above the bottom of the bottle to avoid disturbance of settled particulate matter.



**Plate 2** Details of system using the 12-channel high precision multichannel dispenser

**Table 1** Details of Tygon© tubing used.

Product code	Description	Use
ACF00007-CP	Tygon© Lab Tubing, Non-DEHP, 1/8"ID x 1/4"OD	Extension tube
WZ-96449-48	Ismatec SC0430 2-Stop, E-LFL Tubing, 2.79mm (Purple-white)	Effluent
WZ-96449-30	Ismatec SC0421 2-Stop, E-LFL Tubing, 1.14mm (red-red)	Influent
WZ-96449-34	Ismatec 2-Stop, E-LFL Tubing, 1.42mm (yellow-yellow)	Influent

The effluent from the cartridge was pumped into an effluent container using purple-white (2.79 mm internal diameter) double bridge Tygon© auto analyser pump tubes. The effluent tubes were larger than the influent tubes to allow for the resistance of the sample passing through the resin.

Tygon© tubing was used for any extensions needed between the pump tubes and sample bottle, cartridge or effluent containers. Where needed, 0.5cm length of purple-white Tygon© were pushed over the end of the smaller diameter pump tubes to act as seals and size changers before connecting the larger diameter Tygon© tubing. All influent tubing was changed between each sample and the effluent tubing was changed as needed.

Five samples could be run at once with the 12 channel Ismatic pump but not all samples ran at the same speed. Due to particulate matter collecting onto the resins the influent pump speed was reduced during pumping or specific sample lines were interrupted to stop loss of sample.

Effluent from the cartridge was collected in a bottle and when approximately 500 ml had successfully gone through the cartridge, pumping was stopped and the effluent tubing run dry. The resulting effluent was poured into a measuring cylinder, the volume was noted and the cartridge was put back in the centrifuge container. The centrifuge container was labelled in pencil with the sample name, the volume of effluent and the date of processing. An additional NLS sample ID

label was attached to the centrifuge tube and the corresponding label, together with the sample information was recorded on the NLS sample log sheet.

During the initial set-up both the influent and effluent pump tubes were controlled by the same dispensing pump. This caused a problem when needing to reduce the speed of the influent when the cartridges became blocked as the effluent was reduced at the same time. When a second peristaltic pump was available the system was modified so that the influent and effluent were controlled by separate pumps. This made the system easier to control especially with the high particulate concentrations found in some of the surface water samples.



**Plate 3** Details of the system using separate pumps for the influent and effluent.

## 2.4 EVIDENCE FROM THE INITIAL TRIAL

To check the repeatability of the process across different concentrations and for different compounds samples were taken from sites likely to have different contaminant loads. A groundwater sample was taken from a previously characterised borehole know to have a fewer contaminants at low concentrations. Several surface water samples were taken from downstream of sewage treatment works of differing sizes from the small local works to the main area works. A laboratory blank was also taken.

To check the repeatability and stability of the samples, 5 water samples were collected into NLS bottles at each site and on returning to the laboratory 4 of the samples were split between 2 pre-conditioned sorbent Oasis® HLB cartridges. This yielded 1 water sample and 8 cartridges for each sample site. The water samples and sorbed samples were sent to NLS for semi-quantitative, analysis using a multi residue LCMS scan with the following timetable for each sample site:

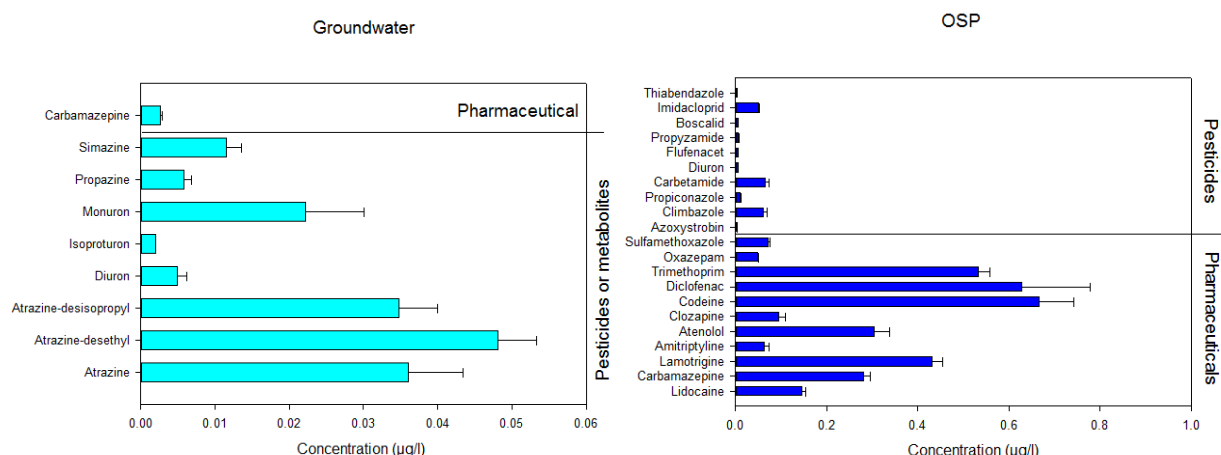
**Table 2** Sample analysis timetable

Week	Analysis
1	Water sample, cartridge 1 and 2
2	Cartridge 3 and 4
3	Cartridge 5 and 6
4	Cartridge 7 and 8

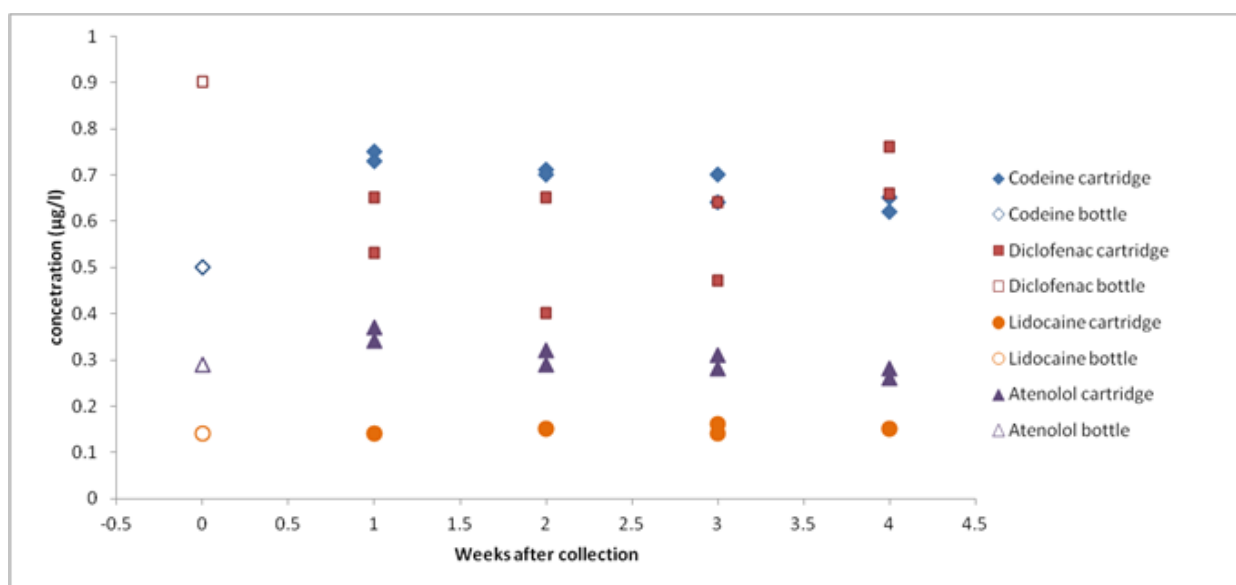
No compounds were detected in any of the blank samples; from this we could conclude that the Tygon tubing, NLS bottles and lab method used was not contributing contamination to the samples. Appendix 1 gives details of the results for the bottled water and sorbed cartridge replicate duplicate samples from the trial.

Bar charts (Figure 1) show the average concentration of all the cartridges and bottled water sample for the pumped groundwater and the surface water sample OSP which had the greatest contaminant load, the error bar is one standard deviation. Full data is given in Appendix 1.

Figure 3 shows the variability in reported selected contaminants and concentrations with time between the duplicate, replicate samples as well as the un-processed water sample from the highly impacted OSP site. Compounds were selected due to their relatively high concentrations in the sample. As can be seen, some compounds look very stable at the reported concentrations, while there is slight variation in others. Detection limits for Atenolol, Codeine and Lidocaine is 0.001 µg/l, there is no reported LOD for Diclofenac.



**Figure 1** Bar charts to show the average concentration of each compound with error bars at one standard deviation for two sample sites. Oxford Science Park (OSP) is from a stream after the input of a major sewage treatment works.



**Figure 2** Plot to show the change over time of selected substances sorbed to the replicate duplicate cartridges for the Oxford Science Park samples. The concentrations of the selected substances in the initial water sample are also shown.

The results from each cartridge was compared to results from the original water sample analysed soon after sampling. This is shown for some of the compounds from one of the sites



## 2.5 THAMES SURFACE WATER FIELD TRIAL, UK

After the initial success of the technique, the trial was expanded and samples were taken along the length of the River Thames. The River Thames rises as groundwater fed streams in the Cotswolds, and flows through rural areas, towns and cities before flowing through London and out to sea. There are a series of locks on the river which restrict the tidal range to below Teddington lock and through most of London. Surface waters in the Thames are impacted by rural (agriculture, small sewage treatments works), urban (industry, larger sewage treatments works) and saline conditions, this was seen to be a good test of the field procedure. The Thames was in flood during parts of the study with the river containing higher particulate load.

A total of 34 samples were taken along the length of the Thames from the source to the sea in January and February 2016. Most samples in this project were taken direct from the bank without the use of a pump, however, the Solinst peristaltic pump was used where it was too hazardous to sample in this manner. The tidal part of the Thames (consisting of 15 samples) was sampled from a boat using the Solinst pump with the inlet 1 m below the water surface. When the pump was used all tubing was rinsed thoroughly with sample water prior to sampling. Duplicate samples were processed and additional blanks were run during this study to test the field procedures.

- *Sample bottle blank.* Ultra-pure water direct from the dispenser was run into an NLS glass bottle to test NLS bottles for contamination. This was run through the system and onto the cartridge, replicating the procedure for other samples.
- *Peristaltic pump method blank.* A solution of Virkon was run through the Solinst peristaltic pump tubing and HDPE tubing (plus PE connector), the tubing was run dry followed by ultra-pure water to rinse. A glass beaker was used. A sample of ultra-pure was then pumped into an NLS bottle through the clean tubing to test the tubing for contamination.
- *Post-sampling peristaltic pump blank.* After sampling the tidal Thames (15 samples) one litre of Ultra-pure water was used to rinse the Solinst peristaltic pump tubing, PE connectors and HDPE rigid tubing. After this the procedure in the field was followed, the sampling beaker was rinsed three times and then filled with 600ml of water before filling a clean NLS bottle. This was to test for carry over between samples as we were unable to wash the tubing between samples.

**Table 3 Thames study blank results.**

Blank sample description	Compound detected (LOD µg/l)	Concentration (µg/l)
Peristaltic pump method blank.	no compounds detected	
Post-sampling peristaltic pump blank (post-tidal Thames survey)	Mepronil (0.001)	0.0024
	Carboxin (0.001)	0.014
Post-sampling peristaltic pump blank (post source to Oxford sampling)	Tramadol (0.001)	0.0001
Laboratory blanks	no compounds detected	

A total of 84 compounds were detected above the LDO in the samples from the Thames; 38 pesticides, 37 pharmaceuticals, 6 surfactants, a fire retardant, sucralose and cocaine.

### 2.5.1 Thames study conclusions

The post-sampling blanks highlight the importance of cleaning the peristaltic sampling tubing correctly between sample sites and has led to the data being blank corrected for possible carry over.

No problems were encountered when processing sea-water influenced samples during the field solid phase extraction however, processing samples with higher particulate matter was more difficult. Where higher particulate matter was seen, samples needed to be left to settle at least over night, the input had to be above the bottom of the sample bottle and the influent line pump speed had to be reduced or stopped more often as the cartridges became blocked. This meant that the process took longer.

Processing of the cartridges at NLS was more difficult for some parts of the Thames due to the amount of contaminants found in the samples. After correcting for detection limit and blank contaminants, between 10 and 62 compounds were reported in the Thames samples.

## 2.6 FIELD-TRIAL IN VARANASI, INDIA

The city of Varanasi, India, is situated on the banks of the Ganges River and has a population of over 1 million. The city obtains a significant proportion of its drinking water from the sedimentary aquifer system beneath the city. Municipal drinking water supply is from groundwater sources distributed across the city as well as surface water from the River Ganges. Private groundwater supply is common across the city. A campaign of fieldwork to characterise the groundwater quality of drinking water sources within the aquifer system included sampling and broad screening for micro-organic contaminants.

A total of 29 groundwater sites were sampled from paired shallow (<50 mbgl) and deep sites (>100 mbgl) to profile depth changes in environmental tracers as well as spatial variation. Broad screening for micro-organics was carried out by the UK National Laboratory Service following solid phase extraction of groundwater samples in the field. A blank sample was taken out in a sample bottle from the UK and processed in the field to quantify procedural contamination.



**Plate 4** Solid Phase extraction of micro-organics from water samples in Varanasi, India.

### 2.6.1 Varanasi Preliminary results

The field blank was found to be contaminated with 7 substances, two analgesics and 4 insecticides and a pesticide. With the exception of dichlorvos and trinexepac these the concentrations found in the blank sample were <0.015 µg/L.

**Table 4 Varanasi blank sample results**

CAS#, Substance (Common name)	Group	Concentration (LOD), µg/L
Cas# 103-90-2 Acetaminophen (Paracetamol)	Analgesic	0.012 (0.005)
Cas# 63-25-2 Carbaryl	Insecticide	0.0079 (0.001)
Cas# 62-73-7 Dichlorvos	Insecticide	0.82 (0.005)
Cas# 138261-41-3 Imidacloprid	Insecticide	0.0057 (0.001)
Cas# 52-68-6 Trichlorfon (Metrifonate)	Insecticide	0.0029 (0.001)
Cas# 143294-89-7 Trinexepac	Pesticide	0.18 (0.1)
Cas# 15687-27-1 Ibuprofen	Analgesic	0.014 (0.001)

For the 30 samples analysed the most frequently detected groups included pesticides, pharmaceuticals and perfluorinated alkylated substances (PFAS). One the bank data had been screened out a total of forty separate compounds were considered true detections in the study, 22 pesticides, 14 pharmaceuticals, 3 PFAS and sucralose. Although mostly detected in low ng/L concentrations in groundwater there are a broad range of compounds that are consistently detected in shallow groundwater and surface waters including frequent detection of sulphonamides.

## 3 Conclusions

The results from the trial concluded that the method was valid and the technique was portable and easy enough to run in a field laboratory or hotel room. Considerable resources could be saved by transporting the processed samples sorbed onto the cartridges instead of as 1 litre water samples. Samples were also seen to be stable over time although some change over time was seen with some compounds.

After the initial trial the technique was used to sample the River Thames from the source to the sea most samples in this project were taken direct from the bank without the use of a pump, however, the Solinst™ peristaltic pump was used where it was too hazardous to sample in this manner. The tidal part of the Thames was sampled from a boat using the Solinst™ pump. At the sites the pump was needed all tubing was rinsed thoroughly with sample water prior to sampling. Additional blanks were run during this study to test the field procedures and a small number of compounds were found in the field blanks run through the Solinst™ pump post sampling

This field-based technique was successfully trailed in India, where samples were extracted in the field, and shipped back to the UK for broad-screen LC-MS analysis. Using the field based SPE method reduced uncertainty regarding sample degradation and reduced shipping costs and allowed the project to analyse more samples than would have been possible without the field based SPE method.

## Appendix 1 Trial Results

**Table A1 Full results for the groundwater sample**

<b>Groundwater - Boxford</b>		Water Sample	WEEK 1 03.12.2014		WEEK 2 10.12.2014		WEEK 3 17.12.2014		WEEK 4 23.12.2014	
Substances Identified	LOD µg/l approx.	3029102	Cartridge 1 3029108	Cartridge 2 3029113	Cartridge 3 3029118	Cartridge 4 3029123	Cartridge 5 3029128	Cartridge 6 3029133	Cartridge 7 3029138	Cartridge 8 3029143
Atrazine	0.001	0.05	0.03	0.033	0.03	0.03	0.035	0.032	0.045	0.04
Atrazine-desethyl	0.001	0.06	0.05	0.048	0.05	0.046	0.045	0.042	0.048	0.044
Atrazine-desisopropyl	0.001	0.04	0.045	0.037	0.036	0.034	0.031	0.03	0.03	0.03
Carbamazepine	0.001	0.003	0.0025	0.0025	0.0025	0.0025	0.003	0.0025	0.0025	0.0025
Carboxin	0.001	0.0009	0.0003	0.0004	0.0009	0.001	0.0009	0.0008	0.0007	0.0007
Diuron	0.001	0.007	0.004	0.005	0.0035	0.0035	0.005	0.0045	0.006	0.006
Isoproturon	0.001	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Monuron	0.001	0.038	0.014	0.02	0.015	0.015	0.023	0.02	0.03	0.025
Propazine	0.001	0.008	0.005	0.005	0.005	0.005	0.006	0.0055	0.0065	0.0065
Simazine	0.001	0.015	0.01	0.01	0.01	0.01	0.012	0.01	0.014	0.013



Table A2 Full results for the OSP surface water sample

OSP			WEEK 1 03.12.2014		WEEK 2 10.12.2014		WEEK 3 17.12.2014		WEEK 4 23.12.2014	
Substances Identified	LOD	Water Sample 3029099	Cartridge	Cartridge	Cartridge	Cartridge	Cartridge	Cartridge	Cartridge	Cartridge
	µg/l approx.		1 3029105	2 3029110	3 3029115	4 3029120	5 3029125	6 3029130	7 3029135	8 3029140
Amitriptyline	0.005	0.07	0.055	0.05	0.055	0.07	0.064	0.063	0.07	0.08
Atenolol	0.001	0.29	0.37	0.34	0.29	0.32	0.31	0.28	0.26	0.28
Azoxystrobin	0.001	0.005	0.004	0.0035	0.003	0.004	0.004	0.004	0.004	0.005
Boscalid	0.005	0.008	0.004	0.004	0.004	0.005	0.005	0.005	0.006	0.006
Carbamazepine	0.001	0.27	0.27	0.27	0.27	0.29	0.3	0.27	0.3	0.3
Carbetamide	0.001	0.07	0.05	0.06	0.065	0.07	0.07	0.06	0.08	0.07
Climbazole	0.001	0.07	0.05	0.05	0.06	0.065	0.06	0.06	0.07	0.07
Clozapine	0.001	0.06	0.1	0.1	0.085	0.1	0.1	0.1	0.1	0.11
Codeine	0.001	0.5	0.75	0.73	0.71	0.7	0.7	0.64	0.62	0.65
Diclofenac		0.9	0.65	0.53	0.4	0.65	0.47	0.64	0.66	0.76
Diuron	0.001	0.006	0.0045	0.005	0.005	0.005	0.006	0.006	0.006	0.006
Flufenacet	0.001	0.007	0.005	0.005	0.005	0.006	0.006	0.006	0.006	0.006
Imidacloprid	0.001	0.05	0.055	0.055	0.045	0.05	0.05	0.05	0.05	0.046
Lamotrigine	0.001	0.45	0.45	0.44	0.38	0.44	0.45	0.43	0.41	0.44
Lidocaine	0.001	0.14	0.14	0.14	0.15	0.15	0.16	0.14	0.15	0.15
Oxazepam	0.001	0.05	0.05	0.045	0.05	0.05	0.05	0.045	0.05	0.05
Propiconazole	0.001	0.014	0.008	0.008	0.008	0.01	0.009	0.01	0.01	0.011
Propyzamide	0.001	0.009	0.0045	0.005	0.006	0.006	0.006	0.006	0.008	0.008
Sulfamethoxazole	0.005	0.07	0.075	0.07	0.065	0.07	0.08	0.07	0.07	0.075
Thiabendazole	0.001	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004
Trimethoprim	0.001	0.47	0.55	0.54	0.53	0.53	0.56	0.52	0.54	0.55

Table A3 Full results for the East Hanney surface water sample

<b>East Hanney</b>		Water Sample 3029100	WEEK 1 03.12.2014		WEEK 2 10.12.2014		WEEK 3 17.12.2014		WEEK 4 23.12.2014	
Substances Identified	LOD µg/l approx.		Cartridge 1 3029106	Cartridge 2 3029111	Cartridge 3 3029116	Cartridge 4 3029121	Cartridge 5 3029126	Cartridge 6 3029131	Cartridge 7 3029136	Cartridge 8 3029141
Amitriptyline	0.005	0.025	0.018	0.02	0.02	0.023	0.02	0.025	0.028	0.024
Atenolol	0.001	0.45	0.55	0.58	0.44	0.44	0.39	0.23	0.35	0.37
Azoxystrobin	0.001	0.003	0.0025	0.003	0.0025	0.0025	0.0025	0.003	0.003	0.003
Carbamazepine	0.001	0.085	0.077	0.094	0.084	0.081	0.085	0.08	0.089	0.087
Climbazole	0.001	0.015	0.009	0.011	0.01	0.011	0.01	0.011	0.013	0.013
Codeine	0.001	0.6	0.74	0.78	0.63	0.6	0.59	0.58	0.54	0.55
Diclofenac		0.27	0.18	0.19	0.18	0.19	0.18	0.21	0.25	0.23
Diuron	0.001	0.004	0.0025	0.0035	0.003	0.003	0.0035	0.0035	0.0035	0.0035
Flufenacet	0.001	0.006	0.0035	0.004	0.004	0.0045	0.0045	0.004	0.005	0.0045
Gabapentin	0.1	4.3	3.7	4	3.1	2.9	3.1	3.1	2.7	2.6
Hydrocodone	0.001	0.14	0.1	0.1	0.1	0.1	0.1	0.09	0.11	0.11
Imidacloprid	0.001	0.055	0.055	0.065	0.05	0.05	0.05	0.045	0.045	0.045
Lamotrigine	0.001	0.25	0.22	0.25	0.24	0.24	0.23	0.24	0.22	0.22
Lidocaine	0.001	0.07	0.075	0.085	0.07	0.07	0.065	0.06	0.065	0.065
Morphine	0.001	0.17	0.15	0.27	0.21	0.15	0.17	0.06	0.17	0.17
Propiconazole	0.001	0.006	0.0035	0.004	0.0035	0.004	0.0035	0.004	0.004	0.004
Propyzamide	0.005	0.0025	0.0015	0.002	0.002	0.0015	0.0015	0.0015	0.0025	0.002
Sulfamethoxazole	0.005	0.05	0.06	0.06	0.055	0.05	0.05	0.055	0.05	0.05
Trimethoprim	0.001	0.15	0.17	0.2	0.17	0.15	0.16	0.15	0.15	0.15

Table A4 Full results for the East Shefford surface water sample

<b>East Shefford</b>			WEEK 1 03.12.2014		WEEK 2 10.12.2014		WEEK 3 17.12.2014		WEEK 4 23.12.2014	
Substances Identified	LOD µg/l approx.	Water Sample 3029101	Cartridge 1 3029107	Cartridge 2 3029112	Cartridge 3 3029117	Cartridge 4 3029122	Cartridge 5 3029127	Cartridge 6 3029132	Cartridge 7 3029137	Cartridge 8 3029142
Atenolol	0.001	0.05	0.08	0.06	0.048	0.045	0.033	0.042	0.033	0.043
Carbamazepine	0.001	0.025	0.022	0.023	0.02	0.02	0.02	0.021	0.021	0.022
Climbazole	0.001	0.0035	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.003	0.003
Diclofenac		0.13	0.07	0.055	0.07	0.07	0.07	0.065	0.085	0.075
Flufenacet	0.001	0.001	0.0008	0.0009	0.0009	0.0009	0.0009	0.001	0.0011	0.001
Gabapentin	0.1	0.9	0.99	0.75	0.62	0.58	0.58	0.54	0.5	0.53
Hydrocodone	0.001	0.02	0.019	0.02	0.019	0.017	0.018	0.017	0.016	0.019
Imazalil	0.001	0.0007	0.0006	0.0006	0.0005	0.0005	0.0006	0.0005	0.0007	0.0006
Imidacloprid	0.001	0.015	0.022	0.018	0.015	0.015	0.014	0.014	0.013	0.014
Lamotrigine	0.001	0.078	0.083	0.078	0.074	0.072	0.072	0.072	0.066	0.07
Lidocaine	0.001	0.01	0.014	0.011	0.01	0.01	0.008	0.009	0.008	0.0085
Metazachlor	0.001	0.002	0.002	0.002	0.0015	0.0015	0.0015	0.0015	0.0015	0.002
Morphine	0.001	0.018	0.03	0.025	0.007	0.014	0.006	0.008	0.006	0.013
Oxazepam	0.001	0.024	0.025	0.023	0.022	0.02	0.02	0.019	0.022	0.022
Propiconazole	0.001	0.001	0.0007	0.0006	0.0007	0.0007	0.0007	0.0007	0.0007	0.0008
Simazine	0.001	0.002	0.0016	0.0019	0.0015	0.0016	0.0014	0.0014	0.0018	0.0019
Sulfadiazine	0.005	0.025	0.045	0.033	0.031	0.027	0.027	0.025	0.023	0.023
Sulfamethoxazole	0.005	0.021	0.033	0.027	0.023	0.023	0.023	0.023	0.023	0.023
Thiabendazole	0.001	0.0004	0.0006	0.0005	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004
Trimethoprim	0.001	0.017	0.026	0.022	0.017	0.017	0.017	0.017	0.015	0.017

Table A4 Full results for the equipment blank samples

<b>Blank</b>			WEEK 1 03.12.2014		WEEK 2 10.12.2014		WEEK 3 17.12.2014		WEEK 4 23.12.2014	
Substances Identified	LOD µg/l approx.	Water Sample 3029103	Cartridge 1 3029104	Cartridge 2 3029109	Cartridge 3 3029114	Cartridge 4 3029119	Cartridge 5 3029124	Cartridge 6 3029129	Cartridge 7 3029134	Cartridge 8 3029139
None										

## References

British Geological Survey holds most of the references listed below, and copies may be obtained via the library service subject to copyright legislation (contact libuser@bgs.ac.uk for details). The library catalogue is available at: <https://envirolib.apps.nerc.ac.uk/olibcgi>.

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