Electronic Supplementary Material (ESI) for Analytical Methods.

Electronic supplementary information

Use of Chemcatcher® passive sampler with high-resolution mass spectrometry and multi-variate analysis for targeted screening of emerging pesticides in water

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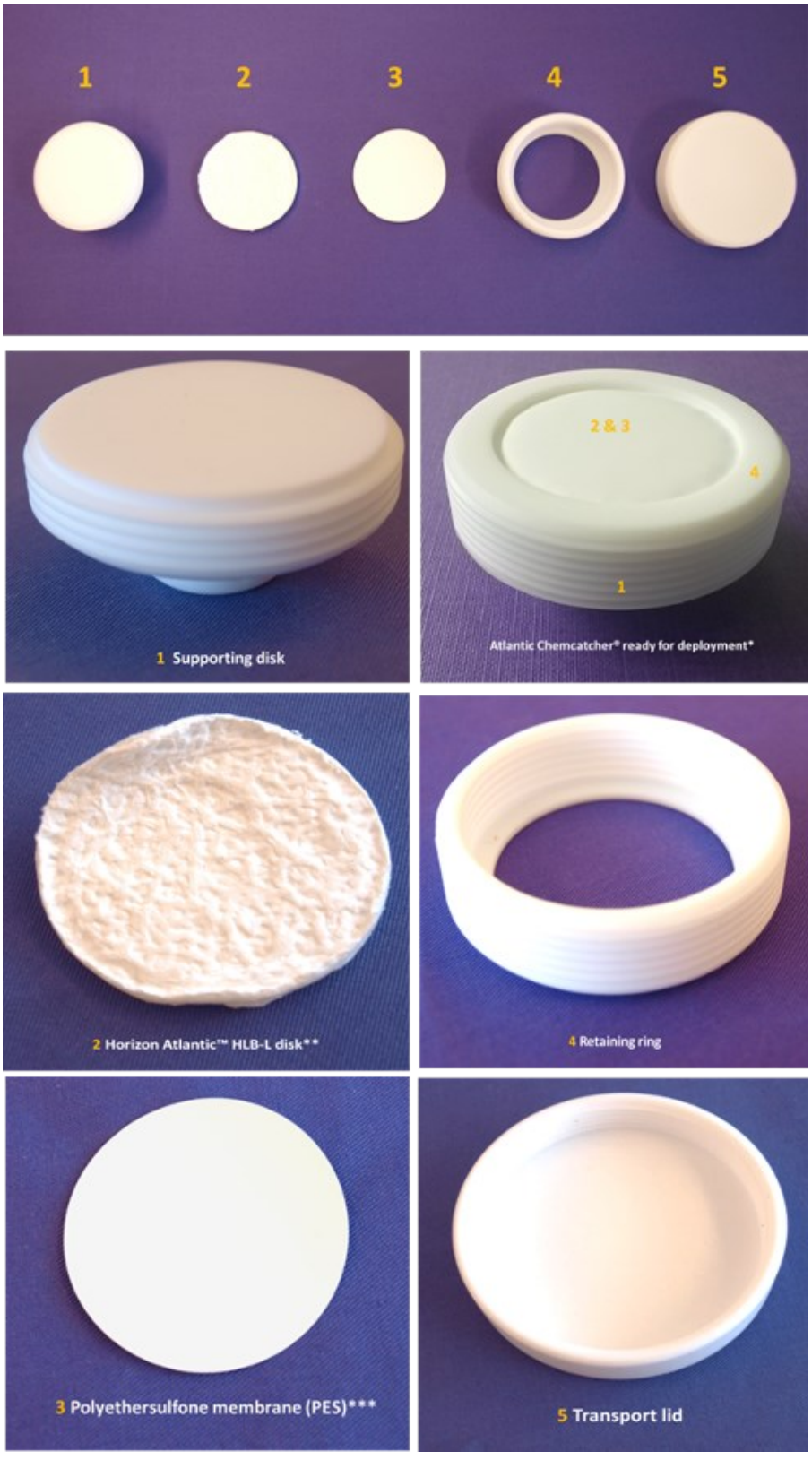


Fig. S1 Components of the Atlantic® version of the Chemcatcher® PSD. *The Chemcatcher® is made of machined PTFE, **Atlantic® HLB-L disk (47 mm diameter) and ***PES, Supor®200, pore size: 0.2 µm, 52 mm diameter disk.

Study area

The Arun and Western Rother river catchment (AWRRC) in South East England is used for the capitation of potable water and has diverse hydrology, land use, and pollution sources. The major rivers within the AWRRC are the Western Rother draining 350 km^2 and the Arun draining 380 km^2. These rivers meet at Pulborough, where there are surface water abstractions for public supply on each river, alongside a groundwater (greensand) abstraction for public supply. Land use within the catchment is primarily arable or pasture, with scattered urban conurbations (e.g. Horsham, Petersfield, Midhurst and Pulborough), industry, woodland, meadow and amenity grassland. Chalk and lower greensand aquifers underlie much of the Western Rother catchment and contribute to the headwaters of many of the tributaries. Tributaries underlain by the upper greensand on the Arun are not primarily groundwater fed and run-off following precipitation and discharges constitute the majority of flow. Consequently, where the influence of groundwater is lower the hydrological regime is flashier as run-off and discharges are precipitation dependant. For these reasons' natural low flows on the Western Rother are high, and relatively stable and natural low flows on the Arun are comparatively low at 5 ML day^{-1}. This is augmented by daily discharges (primarily wastewater treatment works (WWTW) outfalls totalling 18 ML day^{-1}, meaning tangible low flow on the Arun is 23 ML day^{-1}.[28] The river Arun is tidal below the confluence of the Arun and the Western Rother.

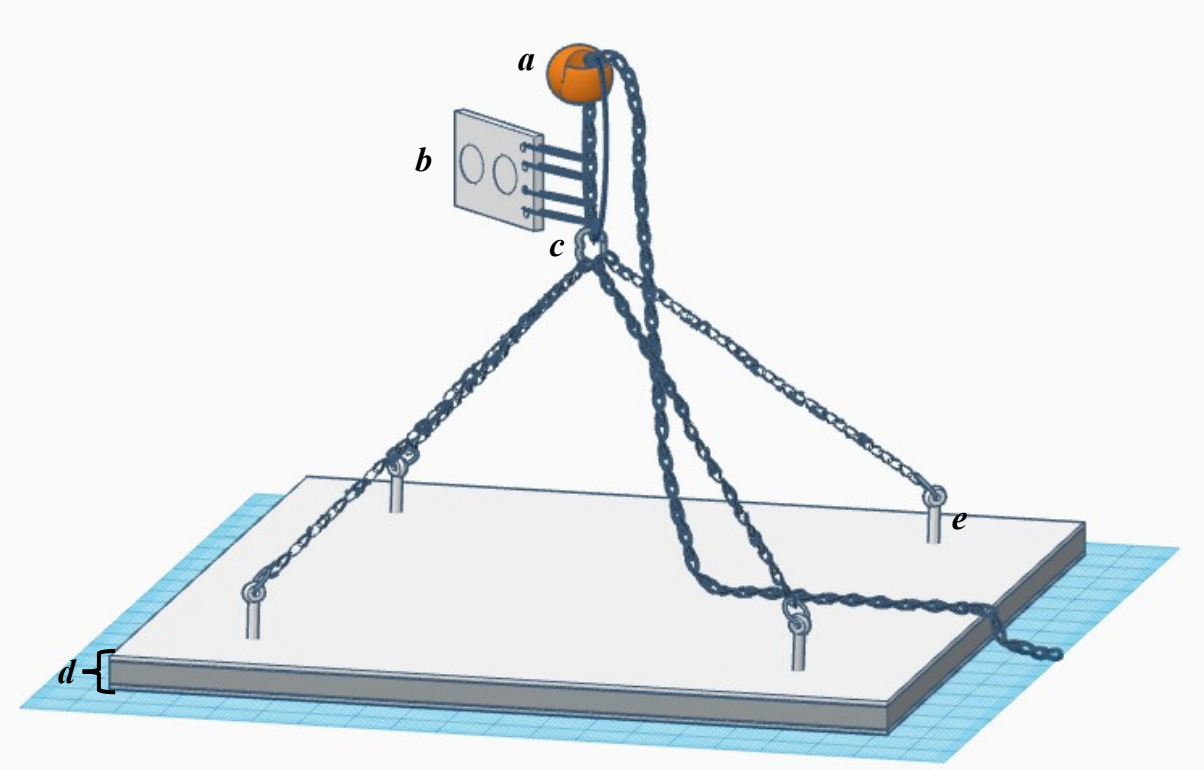


Fig. S2 Schematic of Chemcatcher® deployment apparatus for *in-situ* deployment on the riverbed. (a) Dummy buoy sits below surface and helps position rig and Chemcatcher® PSDs in the water column; (b) Chemcatcher® PSDs inset in sheet of cast acrylic and to rig with polypropylene rope; (c) Carabiner clip connecting all components of rig; (d) concrete slab sandwiched between two cast acrylic sheets (450 x 450 x 35 mm); (e) Stainless steel (marine grade) eyebolt with ring attached to japanned chain at each corner; (g) Japanned chain, running slack along riverbed to a point on bank where chain is secured with a padlock.

Fig. S3 Photographs of a rig type deployment system, showing Chemcatcher® devices during deployment (A), (B), during retrieval (C), and 4 Chemcatcher® devices secured in a plastic mount after retrieval (D).

Table S1 Details of analytes detected in solvent and blank samples (SB = solvent blank; PB = procedural blank; FB = field blank)

Sample type	Sample name	No. runs*	No. analytes

Solvent	Mobile phase A & B (Total)	47	8
Sample	SB (Total)	66	28
Sample	PB (Total)	66	28
Sample	FB (Total)	78	26
Sample	(Combined) SB,PB,FB	210	30

*Number of instrumental runs.

Table S2 Treatment of analytes present in blank and solvent samples.

Analyte	**Treatment**
1,2,3,6-Tetrahydrophthalimide (*cis*-)	False negatives: Left in data (blank subtraction)
Carbofuran	False positives: removed from data
Carvone	False positives: removed from data
Diethyltoluamide (DEET)	False negatives: Left in data (blank subtraction)
Dimethylphthalate	False positives: removed from data
Hymexazol	False positives: removed from data
Melamine	False positives: removed from data
Methoprene Peak 1 Fragm 279	False positives: removed from data
Methoprene Peak 2 Fragm 279	False positives: removed from data
Metolcarb Fragm 109	False positives: removed from data
Pyrethrin I	False positives: removed from data
Spiroxamine Peak 1	False positives: removed from data
Spiroxamine Peak 2	False positives: removed from data
Thiabendazole	False positives: removed from data
Trimethacarb (2,3,5-) Fragm 137	False positives: removed from data
Triphenylphosphate	False negatives: Left in data (blank subtraction)
Halofenozide Fragm 105	False positives: removed from data
Methoxyfenozide Fragm 149	False positives: removed from data

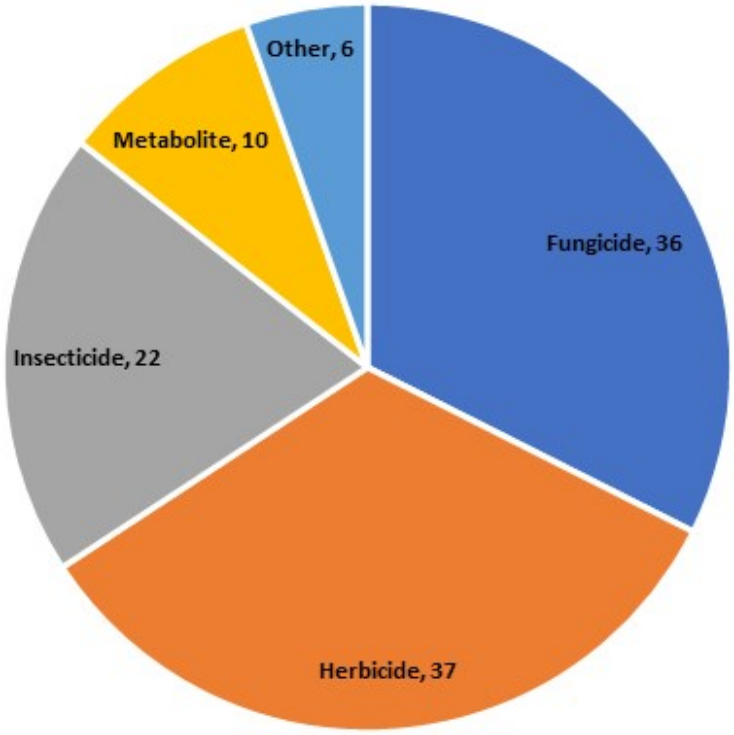


Fig. S4 Number of types of polar pesticides detected with Chemcatcher® PSDs during 25 consecutive deployments at three sites on the River Arun occurring over one year.

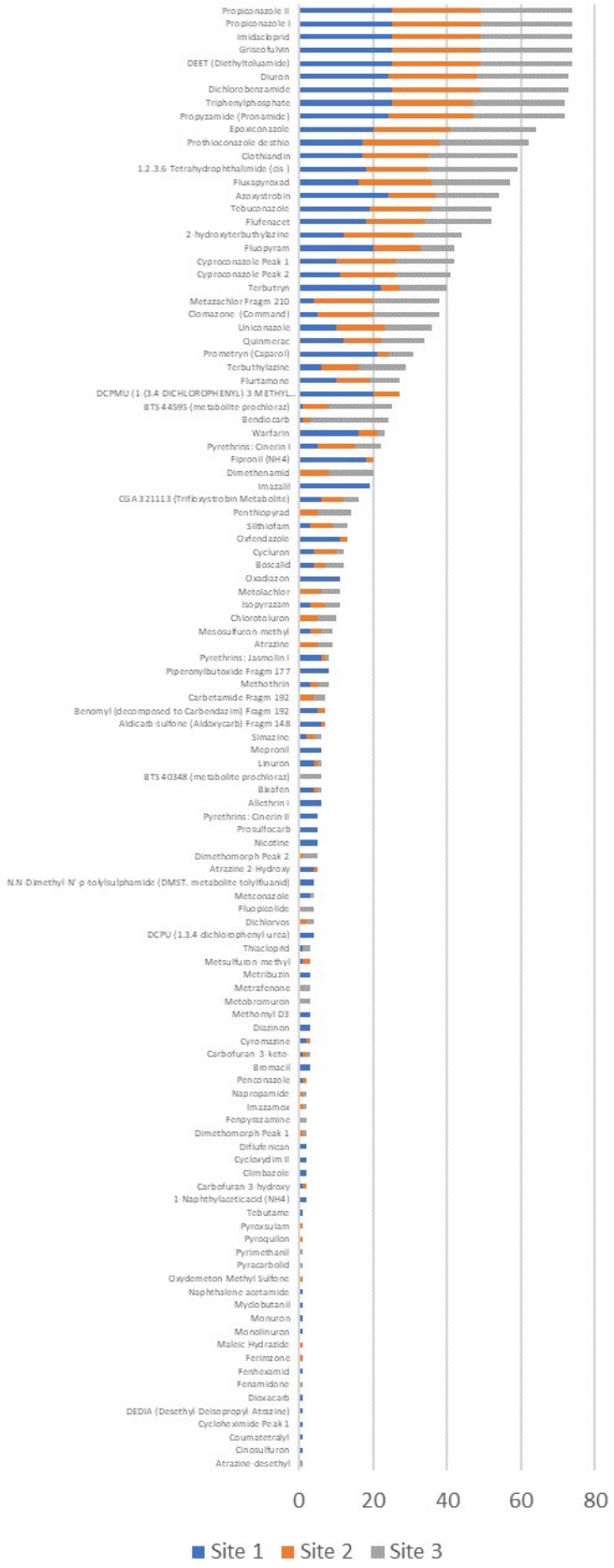


Fig. S5 Number of detections of polar pesticides with Chemcatcher® PSDs during 25 consecutive deployments at three sites on the River Arun occurring over one year.

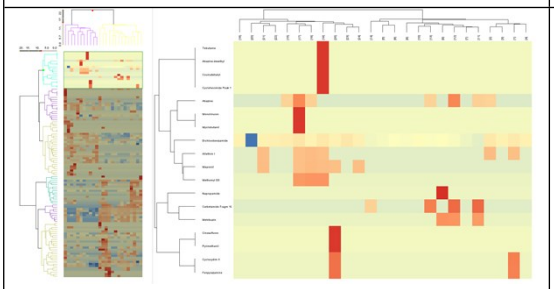
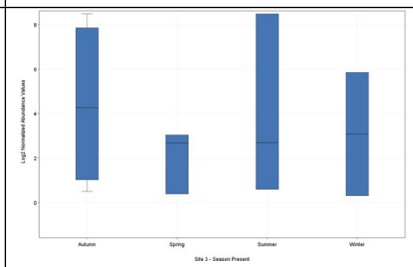
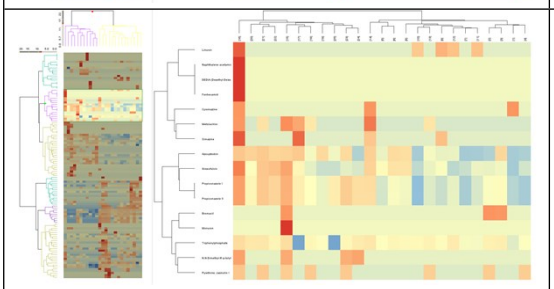
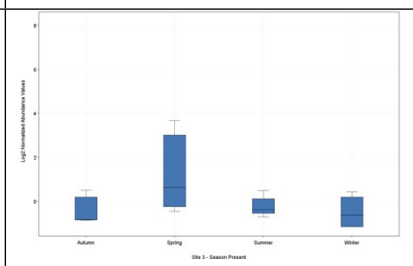
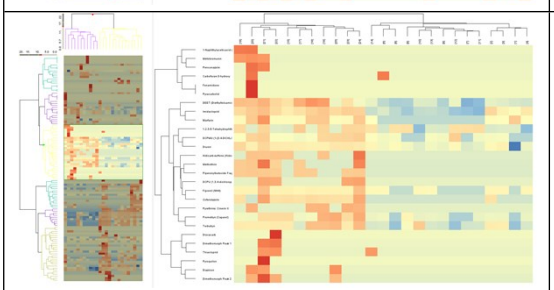
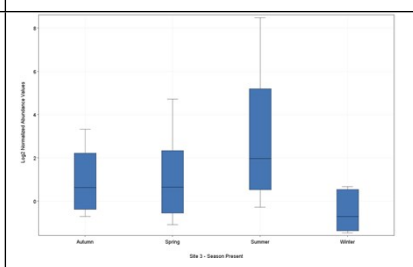
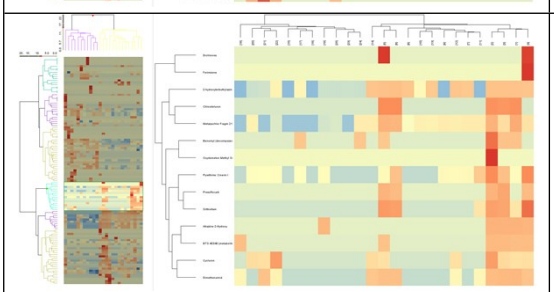
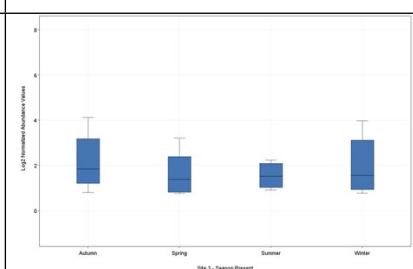
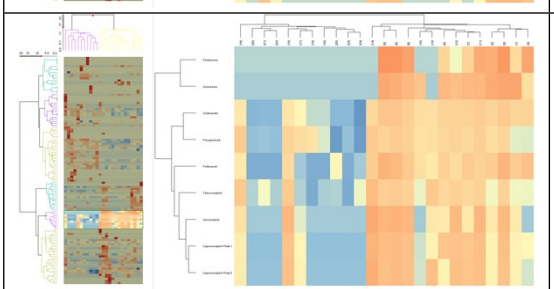
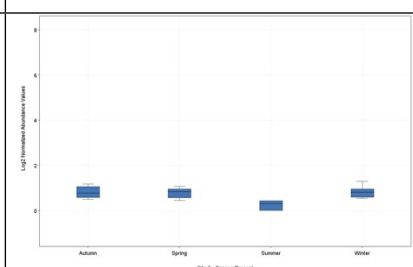
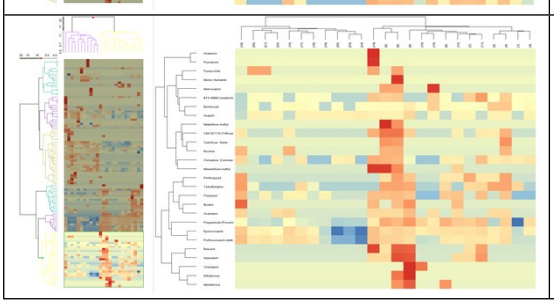
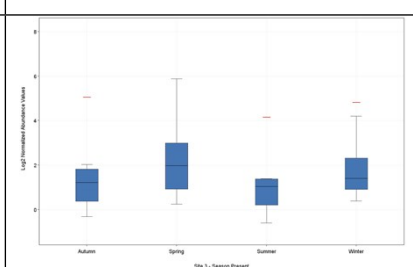
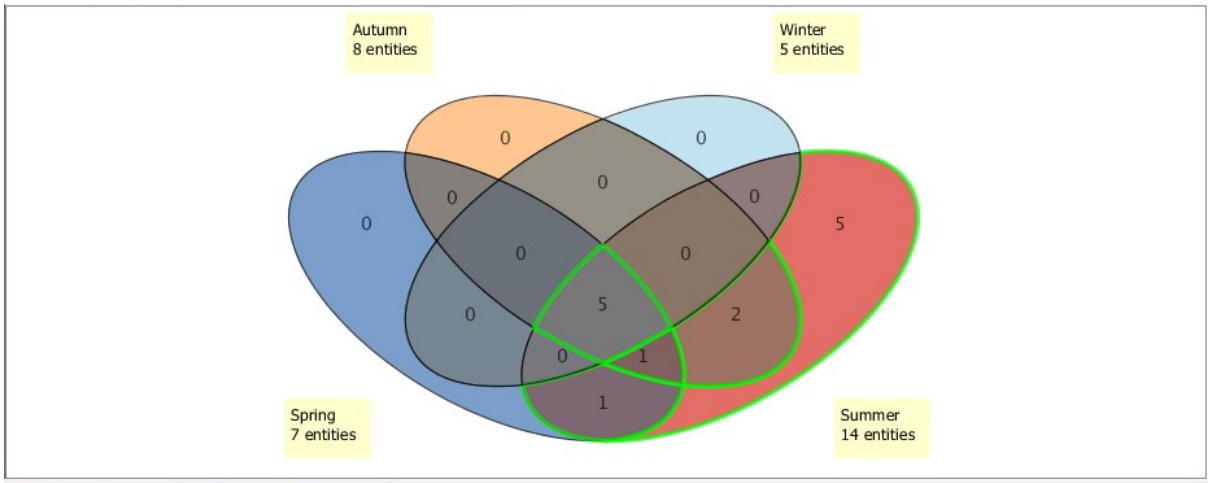
Cluster Summary	Box and Whisker	Cluster No.	No. Analytes
		1	18
		2	16
		3	27
		4	14
		5	9
		6	27

Fig. S6 HCA and box and whisker plots of analytes present in clusters 1-6.

Table S3 Properties of analytes present in cluster 3.

Sub Cluster No.	Compound	Chemical class	Pesticide type	Status	Pest	Applications
1	1-Naphthylacetic acid (NH_4)	Synthetic auxin	Plant growth regulator	Approved, 31/12/2021	Fruit drop	Apples, Pears, Plums, Cherries; Potatoes
	Metobromuron	Urea	Herbicide	Approved, 31/12/2024	Broad-leaved weeds (various)	Sunflowers; Potatoes; Tomatoes; Soybeans; Tobacco
	Penconazole	Triazole	Fungicide	Approved, 31/12/2021	Powdery mildew; Scab; Ring spot; Rusts	Vines, Apples, Pears, Peaches, Plums, Apricots, Strawberries, Ornamentals, Hops, Vegetables, Cucumbers, Tomatoes
2	Carbofuran-3-hydroxy	Carbamate	Insecticide, Nematicide, Acaricide, Metabolite	Transformation product	Spider mites; Nematodes; Aphids; Corn rootworms; Weevils	Potatoes; Corn; Rice; Soybean; Fruit including Citrus, Grapes; Vegetables; Cotton; Alfalfa
	Fenamidone	Imidazole	Fungicide	Not approved	Early and Late blight, Downy mildew, Alternaria leaf spot, Purple blotch	Bulb vegetable crops; Potatoes; Tomatoes; Lettuce; Curcubits
	Pyracarbolid	Anilide	Fungicide	Not approved	Rusts; Smuts; Damping-off; Blister blight	Coffee; Vegetables; Tea; Ornamentals
3	Diethyltoluamide (DEET)	Unclassified	Insecticide, Repellent	Not approved	Mosquitoes; Ticks; Fleas; Chiggers; Leeches; Gnats; Sand flies; Stable flies; Harvest mites	Human skin; Clothing
	Imidacloprid	Neonicotinoid	Insecticide, Veterinary substance	Approved, 31/07/2022	Plant hoppers, Aphids, Termites, Colorado beetle, Fleas, White grubs, Crane flies; Crickets, Ants	Lawns and turf; Domestic pets; Rice, Cereals; Maize; Potatoes; Sugar beet
	Warfarin	Coumarin anticoagulant	Rodenticide	Not approved	Rats; Mice; Grey squirrels; Gophers	Pharm* A rarely used anticoagulant rodenticide
4	1.2.3.6-Tetrahydrophthalimide (*cis*-)	Dicarboximide	Fungicide	Transformation product	Seed rot; Damping-off; Grey mold; Berry rot; Spur blight; Brown rot; Leaf spot; Downy mildew; Bunch rot; Scab	Apples, Apricots, Blueberries, Blackberries, Cherries, Grapes, Raspberries, Nectarines, Plums, Peaches; Almonds; Grasses; Roses
	DCPMU (Monomethyldiuron)	Phenylurea	Herbicide	Transformation product	Bermuda grass; Fathen; Pigweed; Charlock; Sow thistle; Wild radish; Wild turnip; Cape weed; Dead nettles; Poppies; Barnyard grass	Vegetables Including Asparagus, Peas, Pulses; Fruit Including Bananas, Pineapples, Grapes; Cotton; Lucerne; Lupins; Sugarcane; Cereals Including Wheat, Barley, Oats, Triticale; Tea; Ornamentals including tulips, daffodils, iris
	Diuron	Phenylurea	Herbicide	Approved, 30/09/2020	Bermuda grass; Fathen; Pigweed; Charlock; Sow thistle; Wild radish; Wild turnip; Cape weed; Dead nettles; Poppies; Barnyard grass	Vegetables including Asparagus, Peas, Pulses; Fruit Including Bananas, Pineapples, Grapes; Cotton; Lucerne; Lupins; Sugarcane; Cereals Including Wheat, Barley, Oats, Triticale; Tea; Ornamentals including tulips, daffodils, iris
5	Aldicarb-sulfone (Aldoxycarb) Fragm 148	Carbamate	Insecticide, Nematicide, Metabolite	Not approved	Honey locust; Gall midge; Nematodes	Cotton; Potatoes; Sugar beet; Ornamentals
	Methothrin	Pyrethroid	Insecticide	None	-	-
	Piperonylbutoxide Fragm 177	Synergist		None		Synergist (carbamates, pyrethrins, pyrethroids, and rotenone)
	DCPU (1.3.4-dichlorophenyl-urea)	Phenylurea	Herbicide	Transformation product	Bermuda grass; Fathen; Pigweed; Charlock; Sow thistle; Wild radish; Wild turnip; Cape weed; Dead nettles; Poppies; Barnyard grass	Vegetables including Asparagus, Peas, Pulses; Fruit Including Bananas, Pineapples, Grapes; Cotton; Lucerne; Lupins; Sugarcane; Cereals Including Wheat, Barley, Oats, Triticale; Tea; Ornamentals including tulips, daffodils, iris
	Fipronil (NH_4)	Phenylpyrazole	Insecticide, Veterinary substance	Not approved	Ants, Beetles, Cockroaches, Fleas, Termites, Thrips, Black vine weevil and other insects	Hardy ornamentals; Non-edible ornamentals; Turf
	Oxfendazole	Benzimidazole	Insecticide, Veterinary	None	Round worms, strongyles and pin	

			substance		worms for a range of livestock	
6	Pyrethrins: Cinerin II	Pyrethrum	Insecticide	Approved, 31/08/2022	Various insect pests	A non-persistent insecticide extracted from Pyrethrum, used to control a variety of pests on crops, in domestic and public health situations
	Prometryn (Caparol)	Triazine	Herbicide	Not approved	Grasses including barnyard grass, goose grass, ryegrass, prairies grass; Broad-leaved weeds including dead nettle, nightshade, chickweed, fathen, common spurry	A herbicide used to control annual grasses and broad-leaved weeds in a variety of crops
	Terbutryn	Triazine	Herbicide	Not approved	Chick weed; Poppies; Black grass; Annual meadow grass; Dead nettle; Cape weed; Hedge mustard; Shepherd's purse; Bind weed; Lupins	A pre-emergence herbicide used to control some grasses and broad-leaved weeds. Also used to control aquatic algae. Also a pesticide transformation product.
7	Dioxacarb	Carbamate	Insecticide	Not approved	Potato bugs, Phyllotreta undulata and Ceutorrhynchus; Leafhoppers; Aphids; Beetles; Cockroaches; Colorado beetle	An obsolete insecticide once used to control pests on potatoes, other crops and non-agricultural sites
	Dimethomorph Peak 1	Morpholine	Fungicide	Approved, 31/07/2020	Downy mildew; Anthracnose; Phytophthora cactorum, Septoria leaf spot; Late blight; Root rot; Crown rot	A fungicide effective against various fungal pathogens in vines and other crops
	Thiacloprid	Neonicotinoid	Insecticide	Approved, 30/04/2020	Aphids; Pollen beetles; Blossom midge; Codling moth; Wireworm; Fruit fly	A chloronicotinyl insecticide for use on apples and other crops to control sucking and chewing insects
	Pyroquilon	Unclassified	Fungicide	Not approved	Rice blast	An unclassified, systemic fungicide used on rice
	Diazinon	Organophosphate	Insecticide, Acaricide, Repellent, Veterinary substance	Not approved	Bean fly; Thrips; Caterpillars; Cabbage white butterfly; Loopers; Cutworms; Livestock pests including mites, ticks, lice and biting flies	A broad spectrum insecticide used to control sucking and chewing insects on a wide range of crops including top fruit. Also has livestock applications.
	Dimethomorph Peak 2	Morpholine	Fungicide	Approved, 31/07/2020	Downy mildew; Anthracnose; Phytophthora cactorum, Septoria leaf spot; Late blight; Root rot; Crown rot	A fungicide effective against various fungal pathogens in vines and other crops



Venn Summary | Entity Match Inspector

Unique ID [Venn]	EL1 : Compound	EL2 : Compound	EL3 : Compound	EL4 : Compound
1.2.3.6-Tetrahydrophthalimi...	1.2.3.6-Tetrahydrophthalimi...	1.2.3.6-Tetrahydrophthalimi...	1.2.3.6-Tetrahydrophthalimi...	1.2.3.6-Tetrahydrophthalimi...
DEET (Diethyltoluamide)	DEET (Diethyltoluamide)	DEET (Diethyltoluamide)	DEET (Diethyltoluamide)	DEET (Diethyltoluamide)
Dimethomorph Peak 2	Dimethomorph Peak 2		Dimethomorph Peak 2	
Diuron	Diuron	Diuron	Diuron	Diuron
Imidacloprid	Imidacloprid	Imidacloprid	Imidacloprid	Imidacloprid
Methothrin	Methothrin		Methothrin	
Prometryn (Caparol)	Prometryn (Caparol)	Prometryn (Caparol)	Prometryn (Caparol)	
Terbutryn	Terbutryn	Terbutryn	Terbutryn	Terbutryn
Metobromuron		Metobromuron	Metobromuron	
Dimethomorph Peak 1			Dimethomorph Peak 1	
Fenamidone			Fenamidone	
Pyracarbolid			Pyracarbolid	
Thiacloprid			Thiacloprid	
Warfarin			Warfarin	

Fig. S7 Seasonality of cluster 3 pesticide detections at site 3. Highlighted sections in the Venn diagram show the number of detected pesticides. Data table lists pesticides detected in each season (using the colour format from the Venn diagram).

Table S4 Prioritisation and risk assessment of analytes present at site 3.

Compound	Site 1	Site 2	Site 3		Risk Score	Venn*	Cluster no
Dichlorobenzamide			A, W, Sr, Su	73	High	ABC	1
Griseofulvin	Sr	Sr	A, W, Sr, Su	74	High	ABC	2
Propiconazole I	Sr	Sr	A, W, Sr, Su	74	High	ABC	2
Propiconazole II	Sr	Sr	A, W, Sr, Su	74	High	ABC	2
Triphenylphosphate	Sr	Sr	A, W, Sr, Su	72	High	ABC	2
Diethyltoluamide (DEET)	A, W, Sr, Su	Su	A, W, Sr, Su	74	High	ABC	3
Diuron	A, W, Sr, Su	Su	A, W, Sr, Su	73	High	ABC	3
Imidacloprid	A, W, Sr, Su	Su	A, W, Sr, Su	74	High	ABC	3
1,2,3,6-Tetrahydrophthalimide (*cis*-)	A, W, Sr, Su	Su	A, W, Sr, Su	59	High	ABC	3
Clothiandin	A, W, Sr	A, W, Sr	A, W, Sr, Su	59	High	ABC	5
Fluxapyroxad	A, W, Sr	A, W, Sr	A, W, Sr, Su	57	High	ABC	5
Propyzamide (Pronamide)	W, Sr	W, Sr	A, W, Sr, Su	72	High	ABC	6
Prothioconazole desthio	W, Sr	W, Sr	A, W, Sr, Su	62	High	ABC	6
Epoxiconazole	W, Sr	W, Sr	A, W, Sr, Su	64	High	ABC	6
Bendiocarb	W, Sr	W, Sr	A, W, Sr, Su	24	High	ABC	6
Azoxystrobin	Sr	Sr, Su	A, W, Sr, Su	54	Medium	ABC	2
Terbutryn	Su	Su	A, W, Sr, Su	40	Medium	ABC	3
Metazachlor Fragm 210	A, W, Sr, Su	A, W, Sr, Su	A, W, Sr, Su	38	Medium	ABC	4
2-Hydroxyterbuthylazine	A, W, Sr, Su	A, W, Sr, Su	A, W, Sr, Su	44	Medium	ABC	4
Dimethenamid		A, W, Sr, Su	A, W, Sr, Su	20	Medium	BC	4
Flufenacet	A, W, Sr	A, W, Sr	A, W, Sr	52	Medium	ABC	5
Cyproconazole Peak 1	A, W, Sr	A, W, Sr	A, W, Sr	42	Medium	ABC	5
Tebuconazole	A, W, Sr	A, W, Sr	A, W, Sr	52	Medium	ABC	5
Cyproconazole Peak 2	A, W, Sr	A, W, Sr	A, W, Sr	41	Medium	ABC	5
Uniconazole	A, W, Sr	A, W, Sr	A, W, Sr	36	Medium	ABC	5
Quinmerac	A, W, Sr	A, W, Sr	A, W, Sr	34	Medium	ABC	5
Clomazone (Command)	W, Sr	W, Sr	A, W, Sr	38	Medium	ABC	6
BTS 44595 (metabolite Prochloraz)	W, Sr	W, Sr	A, W, Sr	25	Medium	ABC	6
Terbuthylazine	W, Sr	W, Sr	A, W, Sr	29	Medium	ABC	6
Metolachlor		Sr	Sr	11	Low	BC	2
Prometryn (Caparol)	Su		Su	31	Low	ABC	3
Pyrethrins: Cinerin I	A, W	A, W	A, W	22	Low	ABC	4
BTS 40348 (metabolite Prochloraz)			A, W	6	Low	C	4
Chlorotoluron		A, W	A, W	10	Low	BC	4
Flurtamone	A, W	A, W	A, W	27	Low	ABC	5
Fluopyram	W, Sr	W, Sr	W, Sr	42	Low	ABC	6
Penthiopyrad		W, Sr	W, Sr	14	Low	BC	6
Boscalid	W, Sr	W, Sr	W, Sr	12	Low	ABC	6
Atrazine		Su	Su	9	vLow	BC	1
Carbetamide Fragm 192		Sr	Sr	7	vLow	BC	1
Fenpyrazamine			A	2	vLow	C	1
Atrazine-desethyl			Su	1	vLow	C	1

Napropamide		W	W	2	vLow	BC	1
Pyrimethanil			A	1	vLow	C	1
Simazine	Sr	Sr	Sr	6	vLow	ABC	2
Linuron	Sr	Sr	Sr	6	vLow	ABC	2
Pyrethrins: Jasmolin I	Sr	Sr	Sr	8	vLow	ABC	2
Dimethomorph Peak 2		Su	Su	5	vLow	BC	3
Methothrin	Su	Su	Su	8	vLow	ABC	3
Metobromuron		Su	Su	3	vLow	C	3
Thiacloprid	Su		Su	3	vLow	AC	3
Warfarin	Su	Su	Su	23	vLow	ABC	3
Dimethomorph Peak 1		Su	Su	2	vLow	BC	3
Fenamidone			Su	1	vLow	C	3
Pyracarbolid			Su	1	vLow	C	3
Silthiofam	A	A	A	13	vLow	ABC	4
Cycluron	Su	Su	Su	12	vLow	ABC	4
Dichlorvos		A, W	A, W	4	vLow	BC	4
CGA 321113 (Trifloxystrobin Metabolite)	W	W	W	16	vLow	ABC	6
Fluopicolide			Su	4	vLow	C	6
Isopyrazam	W,Sr	W,Sr	W,Sr	11	vLow	ABC	6
Mesosulfuron-methyl	Sr	Sr	Sr	9	vLow	ABC	6
Metrafenone			W	3	vLow	C	6
Bixafen	Sr	Sr	Sr	6	vLow	ABC	6
Carbofuran 3-keto-			A	3	vLow	ABC	6
Imazamox		Sr	Sr	2	vLow	BC	6
Metconazole	Sr		Sr	4	vLow	AC	6

*ABC: present site 1,2 and 3, BC: present site 2 and 3, CA: present site 1 and 3, C: present site 3 only.