Physical and chemical characterisation of sea-surface microplastics collected from coastal and inland waters of Scotland in the summer of 2017

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Summary

The contamination of the marine environment with microplastics is recognised as a widespread and pervasive problem. Although much of the focus on marine plastics pollution to date has been on the presence and impacts of larger, more immediately visible and recognisable pieces of plastic 'litter', there are growing concerns for the potential impacts of exposure of marine species to smaller microplastics (<5 mm in size), both because of direct effects of the plastics when they are ingested and because of the mixture of chemical additives and contaminants they can carry.

Surveys of microplastics floating at the sea surface have been conducted in many different areas around the world over the past few decades, but so far there is relatively little information available on the distribution of microplastics in the waters around the coast of Scotland, or of their chemical characteristics, despite the importance of these waters as breeding and foraging grounds for a range of marine species.

As a contribution to scientific understanding of the status of microplastic pollution in the region, Greenpeace undertook a survey of microplastic abundance and associated chemical constituents in coastal and inland waters around Scotland during the early summer of 2017 (May and June), with a particular focus on the waters around the islands of the Hebrides and especially those noted for basking shark aggregation and seabird foraging.

A total of 50 surface seawater debris samples, from a total of 27 different locations in Scottish waters (East and West coast, plus one location in Loch Ness), were collected between 09th May and 16th June 2017, of which 49 were subject to detailed analysis of microplastic abundance, polymer type and associated chemical additives and contaminants. Almost two thirds of the samples (31 of 49) contained at least one identifiable piece of microplastic in the size range 0.5 - 5.0 mm diameter (including 4 fibres with lengths greater than 5mm but diameters less than 1mm). 4 samples contained 10 or more pieces of microplastic, including one sample from the Firth of Forth, one from Gunna Sound (close to Tiree) and two from waters around the Shiant Islands.

Samples collected one after another from the same locations frequently yielded very different results, in some cases with microplastics found in one time/location duplicate but not in the other. Whether or not the net encountered microplastics during a sampling tow was unpredictable, just as will be the case, therefore, for basking sharks or other wildlife feeding in these waters.

Of the total of 141 pieces of plastic >0.5mm that were isolated from all of the samples, the most common material found was polyethylene (43%), followed by polypropylene and polyamide (including nylon) in roughly equal proportions (around 12% each). Whereas the microplastics found in samples from most of the locations in the study were often of a mix of plastic types, those isolated from net tow samples collected in waters off the Shiant Islands were almost exclusively fragments of polyethylene, perhaps because the relatively low density of this plastic means that it is less likely to sink than many other types of plastic.

Chemical analyses of the microplastics found in each sample, analysed as a composite of all the pieces found, revealed the presence of a total of 95 different organic compounds associated with the microplastics, though only a fraction of those were found in any one sample. Compounds included:

- 12 phthalate esters (man-made chemicals used as additives in certain plastics, inks and a range of other products),
- 4 pesticides (two insecticides, a fungicide and a herbicide),
- 3 additional organophosphorus chemicals (including two used as flame retardants,

- 2 chemicals used as UV stabilizers in plastics,
- a polycyclic musk, closely related to the human sex hormone oestradiol and
- the persistent perfluorinated chemical PFOS.

In addition, some of the samples contained significant concentrations of certain toxic metals, including lead, copper, chromium and, in one case, cadmium.

The number and mix of organic chemicals and metals associated with the microplastics varied greatly from sample to sample, but showed no clear geographical patterns, nor any apparent correlation with the numbers, sizes or total masses of microplastics isolated from the samples. Given the inevitably small size and heterogeneous nature of the composite microplastics samples analysed in this study, it has not been possible to determine concentrations for the majority of the compounds identified. Nonetheless, the confirmed presence of such complex and varied mixtures of chemical deserves further, targeted field research in order to determine their significance in terms of overall exposures.

A preliminary, purely qualitative analysis of samples for microplastics within the size range below 63 μm, too small to have been retained quantitatively by the manta net mesh, indicates that these may also be a common characteristic of the waters in these areas, including small fragments and fibres identified as nylon, polyester and polypropylene. This is an aspect that deserves further investigation as microplastics within these small size ranges are clearly of significance in relation to determination of overall levels of contamination and, therefore, potential exposure of marine species of all sizes.

Taken together, the results from this complex set of surface manta net tow samples paints a picture of high variability, and therefore low predictability, not only in the apparent abundances and types of microplastics as pollutants at different locations and different times in the waters of Scotland, but also similar unpredictability of the chemical signatures that those microplastics carry. What might appear as a 'hotspot' for floating microplastics during one hour might appear relatively clear of microplastics the next, and vice versa.

What these data do reveal is that, even in the relatively remote waters around the Hebrides on the Northwest coast of Scotland, microplastics have become an unwelcome part of the fabric of marine ecosystems. The high variability in distribution of microplastics over time and space, in the plastic types they represent and in the chemicals they carry on their surface or within their structures, illustrates the huge difficulties in preparing assessments and mapping of the risks they may pose.

As far as we are aware, this is the most detailed survey published to date of microplastic contamination in surface waters around the Hebrides, and the first study to subject the microplastics recovered from each discrete surface water manta net tow sample to such a depth of sequential analysis to determine plastic type and associated organic and inorganic chemical constituents and contaminants.

Acknowledgments

This work would not have been possible without the dedicated support, patience and hard work of the whole of the crew of the MV Beluga II. Access to the PerkinElmer Frontier FT-IR spectrometer and Spotlight 400 imaging FT-IR microscopy system was made possible under a Research Partnership Agreement between the Greenpeace Research Laboratories and PerkinElmer. Our thanks to Dr Matthew Witt for preparing the detailed maps at Annex 1 showing the locations of hotspots for basking shark abundance in relation to our sampling locations.

1. Introduction

1.1 Microplastics as contaminants of the marine environment

One of the many consequences of the unsustainable growth in production and wasteful overuse of plastics has been the proliferation of microplastics as globally distributed, pervasive and persistent pollutants in all parts of our environment, including in estuaries, coastal seas and open oceans (see reviews published by GESAMP 2015, 2016). Microplastics, commonly defined as pieces of plastic in the size range of 5mm diameter or less (Arthur *et al.* 2009), include fragments of larger plastic items that have broken up into smaller pieces under a combination of the mechanical stress of wave action and sediment abrasion, and degradation in sunlight, among other processes (Thompson 2015) as well as plastic particles deliberately manufactured to be in this size range, such as the microbeads included in cosmetics and personal care products that are increasingly coming under regulatory control. Microplastics can originate from both onshore and offshore sources, including from wastewater discharges from land and at sea, urban run-off, wind-blown litter and even loss or abandonment of fishing gear; in short, wherever there are plastics, there are sources of microplastics. While larger pieces of plastic litter are a very visible symptom of ongoing overuse and poor management of plastic, microplastics are a far less visible but perhaps no less damaging part of the same problem, and arguably even more difficult to measure and address.

Whatever their origins, microplastics are now known to be a feature of all marine areas investigated to date, including surface and deeper waters, close to the coast and far offshore (Law *et al.* 2010, Moore *et al.* 2001), and from tropical waters through temperate seas (Kanhai *et al.* 2017) to the polar oceans (Waller *et al.* 2017, Cózar *et al.* 2017). Microplastics have been reported as contaminants in beach sand (Browne *et al.* 2011, Hidalgo-Ruz *et al.* 2012) and in seabed sediments (Ling *et al.* 2017), including in deep ocean areas (Van Cauwenberghe *et al.* 2013c), as well as in the guts or other tissues of a wide range of marine species, including fish and shellfish (Jabeen *et al.* 2017, Santillo *et al.* 2017), planktivorous seabirds (Amélineau *et al.* 2016), cetaceans (Besseling *et al.* 2015, Lusher *et al.* 2015) and in planktonic organisms that form the base of marine food webs (Steer *et al.* 2017, Sun *et al.* 2017). The full nature and scale of the threats that microplastics pose to marine ecosystems remain to be determined (Ogonowski *et al.* 2018), though it is already clear that the physical presence of microplastics in seawater, and their tendency to be taken in along with food particles by filter-feeding and foraging species, among other routes, can have physiological and behavioural consequences for marine organisms (Von Moos *et al.* 2012, Besseling *et al.* 2013, Cole *et al.* 2015, Xu *et al.* 2017, Lo & Chan 2018).

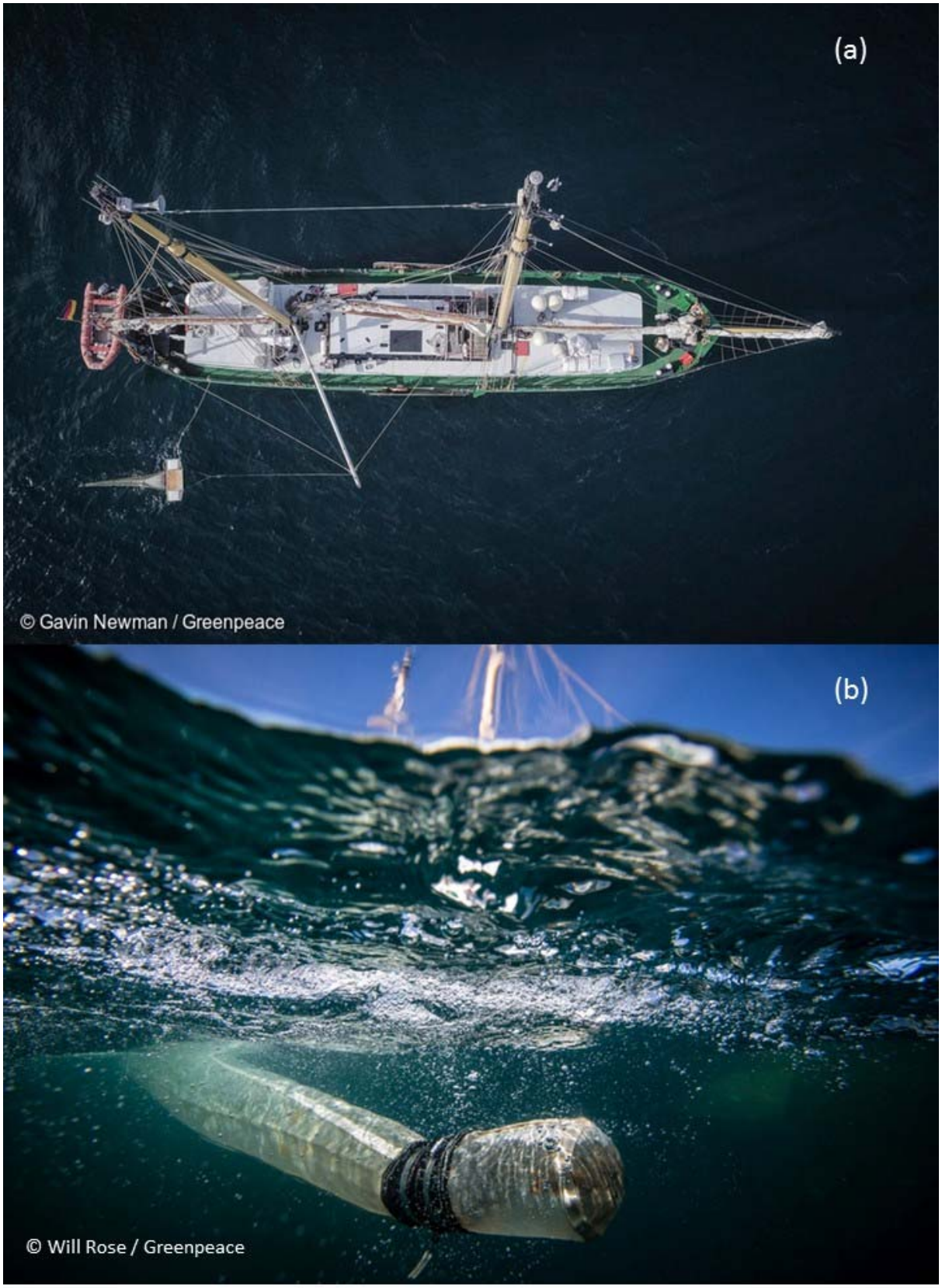


Figure 1: (a) The Greenpeace vessel MV Beluga II with the manta net deployed for sea-surface microplastics sampling in Scottish coastal waters. (b) The 'cod end' of the manta net assembly *in situ.*

It is also known that, partly because of their synthetic chemical nature and partly their propensity to adsorb chemicals from seawater on to their surfaces, microplastics can also carry a diverse array and, in some cases, substantial concentrations of a range of chemical additives and contaminants (see GESAMP 2016 for a summary). Therefore microplastics can contribute to overall exposure of marine species to a variety of hazardous chemicals (Browne et al 2013, Rochman *et al.* 2013). The wider chemical fingerprinting of microplastics sampled from the sea surface environment for non-target chemicals is an aspect that has so far received relatively little study (Andrady 2017), though non-target investigations that have been carried out to date on microplastics collected from beaches have reported the presence of a complex mix of hydrocarbons, plasticizers, flame retardants and stabilizer chemicals, among others, associated with plastic pellets (Gauquie *et al.* 2015, Rani *et al.* 2015, 2017).

Microplastics were first reported as sea surface contaminants more than 40 years ago, from net trawl samples collected in the North Pacific and North Atlantic (Carpenter & Smith 1972, Wong *et al.* 1974). Since then, many studies of their distribution and abundance have focused, understandably, on the major gyre features within the Pacific Ocean, long noted for their accumulation of larger items of plastic litter (see GESAMP 2015 for a good summary). More recently, research has extended to other regions, both offshore and in coastal and estuarine waters, in order to document the scale and diversity of the issue and, as far as is possible, to begin to trace the problem back to key land-based sources. Some recent examples include studies in the Arabian Gulf (Abayomi *et al.* 2017), in the Bohai Sea in China (Zhang *et al.* 2017a) and in the Gulf of Lion in the Western Mediterranean (Schmidt *et al.* 2017), all of which add to the overall knowledge base on the diversity and distribution of microplastics as marine pollutants.

1.2 Microplastics in UK waters

Within the North East Atlantic waters around the UK, probably the most extensive study to date of microplastics distribution in the water column was that conducted by Lusher *et al.* (2014). Their study, based on the analyses of 470 water samples collected at 3m depth, confirmed the widespread presence of microplastics (especially fibres) within the region's waters. Most of those samples were collected from offshore locations, with relatively few stations located in coastal waters, and analyses were limited to microplastics in sub-surface waters and in the size range less than 1mm. While there is a growing body of data relating to the distribution and sources of plastic litter on beaches (e.g. Unger & Harrison 2016, Watts *et al.* 2017), published surveys of microplastics in UK coastal surface waters to date appear to remain quite limited in their extent, so far focusing on a small number of locations. For example, Sadri & Thompson (2014) investigated movements of microplastics within the Tamar estuary in Southwest England in response to tidal cycles. More recently, Gallagher *et al.* (2016) prepared an assessment of floating microplastics in the estuarine waters of the Solent, near Southampton, also on the South coast of the UK. Studies of microplastic pollution in the Thames system have so far concentrated on levels associated with sediments (Horton *et al.* 2017). As far as we have been able to determine, published information on the distribution of microplastics at the sea surface in other parts of the UK's coastal and estuarine waters, including within Scottish waters, remains scarce. Data from a programme of sea surface sampling conducted by Marine Scotland since 2011 (Russell & Webster 2017) have yet to be published.

The coastal waters of Scotland are important areas for breeding and foraging of a wide range of marine species, including seabirds, cetaceans (whales and dolphins) and sharks. Indeed, the islands and coastal waters of Scotland support internationally important breeding populations of more than 20 seabirds, as well as being vital summer feeding grounds for basking sharks (*Cetorhinus maximus*),

which gather in particularly large numbers in certain 'hotspot' areas of waters of the Hebrides on the west coast (Witt *et al.* 2016). As basking sharks, as well as many seabirds, feed predominantly at or very close to the sea surface, the presence of any floating plastic debris, including microplastics, in these areas might be of particular concern.

Given the remoteness of much of Scotland's coastal sea area and generally low levels of coastal development away from the few major cities, these waters may be expected to be relatively clean in terms of plastics pollution and associated chemical contaminants. While this may well be true in comparison with more developed Southern coasts of the UK, the situation is complicated by the diversity of both land-based and sea-based sources of plastic debris, which can include fishing gear and other plastics lost from vessels, and by the influence of currents from the wider Atlantic Ocean (especially on the west coast) which may carry plastics, whether floating at the surface or in deeper water, over very large distances and deliver them to coastal waters and remote beaches (Nelms *et al.* 2017). A recent synthesis of studies on seabirds within the wider Northeast Atlantic region, including a number of records relating to Scotland, highlights the potential for species such as Atlantic puffin to ingest significant quantities of plastic debris while foraging in these waters (O'Hanlon *et al.* 2017). To date, we are unaware of any studies into the significance of ingestion of plastic debris, including microplastics, by basking sharks while feeding, though this has been suggested as a source of some of the plastic-related chemical contaminants identified in the tissues of basking sharks sampled in the Mediterranean Sea by Fossi *et al.* (2014). More recently, Germanov et al. (2018) have highlighted the urgent need for studies to address the substantial knowledge gaps surrounding the exposure to microplastics of a range of filter-feeding megafauna, including basking sharks, whale sharks and baleen whales.

Taking into account the large volumes of near surface water that can be swept by an adult basking shark while feeding, perhaps more than 800 m^3 per hour (Sims 2008), it is important to obtain greater understanding of the distribution and abundance of microplastics at the sea surface in the 'hotspot' areas in which these fish aggregate, as well as the chemical characteristics of those microplastics in terms of both the distribution of plastic types and any chemical additives or contaminants that may be associated with them. At the same time, recognising the limits to published data on abundance and characteristics of microplastics in Scottish coastal waters more generally, sea-surface sampling at other locations in the region is also justified.

1.3 Purpose of the current study

On this basis, Greenpeace undertook a survey of microplastic abundance and associated chemical constituents in coastal and inland waters around Scotland during the early summer of 2017 (May and June), with a particular focus on the waters around the islands of the Hebrides and especially those noted for basking shark aggregation and seabird foraging. This survey was not intended to provide for a specific assessment of the risk to basking sharks, seabirds or other marine species from encounters with and ingestion of microplastics, nor of the comparative importance of microplastic ingestion as sources of exposure to hazardous chemicals compared to other routes of exposure. Rather it was intended to provide a wider and higher resolution insight into the presence of sea surface microplastics in Scottish coastal waters than is currently available, including variability in their distribution over space and time, the range of plastic types present and the diversity of chemical substances associated with microplastics either as additives incorporated into the plastic matrix at the time of manufacturing or as contaminants adsorbed onto the surface of microplastic pieces once they reach the marine environment.

2. Materials & Methods

This section provides a brief description of the materials and methods employed in this study. More detailed methods for the analytical techniques employed are provided in Annex 2.

A total of 50 surface seawater debris samples, from a total of 27 different locations in Scottish waters (east and west coast, plus one location in Loch Ness), were collected between 09th May and 16th June 2017 (see Figure 2, along with more detailed maps A1 to A3 showing the individual regions sampled at Annex 1), using a towed manta net assembly (Ocean Instruments, Inc. (San Diego), net mouth dimensions 0.87m wide x 0.155m depth,) with a net mesh size of 0.33 mm (330 μm), as used in numerous previous studies (Carpenter & Smith 1972, Moore et al. 2001, Law et al. 2010, Reisser et al. 2014).

At 23 of those locations, two 'time/location duplicate' net tow samples were collected, deploying the net twice in succession and towing over similar distances (between 1.033 km and 3.655 km equivalent, depending on current flow) within a total period of under 3 hours (see Table 1). Distances towed were recorded in each case using a standard flow meter (General Oceanics, Inc., Florida) located in the mouth of the manta net. For logistical reasons, at four locations (two in the Firth of Forth on the East coast and two near the Shiant Islands on the West coast), it was not possible to collect a second net tow sample.

After each deployment of the manta net, it was retrieved on board, the material it contained rinsed down into the cod end using a seawater hose applied to the outside of the net, and that solid material (containing a mix of biological material and floating debris) transferred to a clean polyethylene self-sealing bag as a discrete surface sample. All samples were frozen on board and later returned to the Greenpeace Research Laboratories, based at the University of Exeter, for analysis.

49 samples were taken forwards for analysis[2], involving:

- the manual sorting and physical separation of possible microplastic items (fragments, film, fibres, etc., down to a size range of approximately 0.5 mm diameter) from other (biological and inorganic) material in the samples, aided by use of a large lit magnifier lens and a dissecting microscope,
- infrared analysis (FT-IR) to identify plastic type for each individual candidate microplastic item against commercial databases and to reject non-plastics from further analysis and
- a sequential forensic chemical analysis on the mix of microplastic pieces isolated from each sample to identify chemicals associated with the microplastics, including a range of common plastic additives and environmental contaminants, such as persistent organic pollutants, pesticide residues and heavy metals

The Fourier-transform infrared (FT-IR) analyses to identify plastic type were conducted using a PerkinElmer Frontier spectrometer with either a universal diamond-ATR attachment or a micro-ATR attachment linked to a PerkinElmer Spotlight 400 microscope system (supplied under a research partnership agreement with PerkinElmer). Further details are provided in Annex 2.

The forensic chemical analyses were carried out on the microplastic pieces found in each sample, to look for the presence of a range of chemical additives and contaminants. In the case of samples

[2] sample 17BU002 contained very high quantities of biological material and has not yet been analysed

containing multiple pieces of microplastic, the **chemical analysis was carried out on all those pieces combined, in the form of a composite of all the microplastic material found in that net tow sample.** This is because our key interest was in the diversity of chemicals associated with the microplastic components isolated from each unique sample, to determine if there were any discernible patterns in chemical fingerprint from one region to another.

Forensic chemical analyses were carried out using a combination of gas chromatography (GC), liquid chromatography (LC) and inductively coupled plasma (ICP) analysis, all linked to mass spectrometry (MS) in order to identify the organic and inorganic (metals and metalloids) chemical additives or contaminants present on the surface of the plastic or embedded within the plastic itself.

In the case of the organic chemicals, a new method was developed for this work in order to carry out a range of chemical extractions in sequence on the same small composite samples of microplastics, combined with mass spectrometry for both targeted analysis of a range of common environmental contaminants (including 275 pesticides, 101 pharmaceuticals and veterinary drugs and more than 70 industrial chemicals) and non-targeted 'screening' analysis to identify other, less commonly encountered chemicals.

After they had been subject to solvent extraction for the GC-MS (Agilent) and LC-MS (Thermo Q Exactive/Orbitrap) analyses described above, the same composite samples (other than four of the smallest samples for which insufficient material could be recovered from GC-MS and LC-MS analyses) were analysed for metals and metalloids using ICP-MS (Agilent) analysis, following acid digestion to release the metals from the plastic matrix. In this case, it was possible to determine absolute concentrations per unit mass of microplastic for the metals identified.

Further details of the methods employed for forensic chemical analysis are also provided at Annex 2.

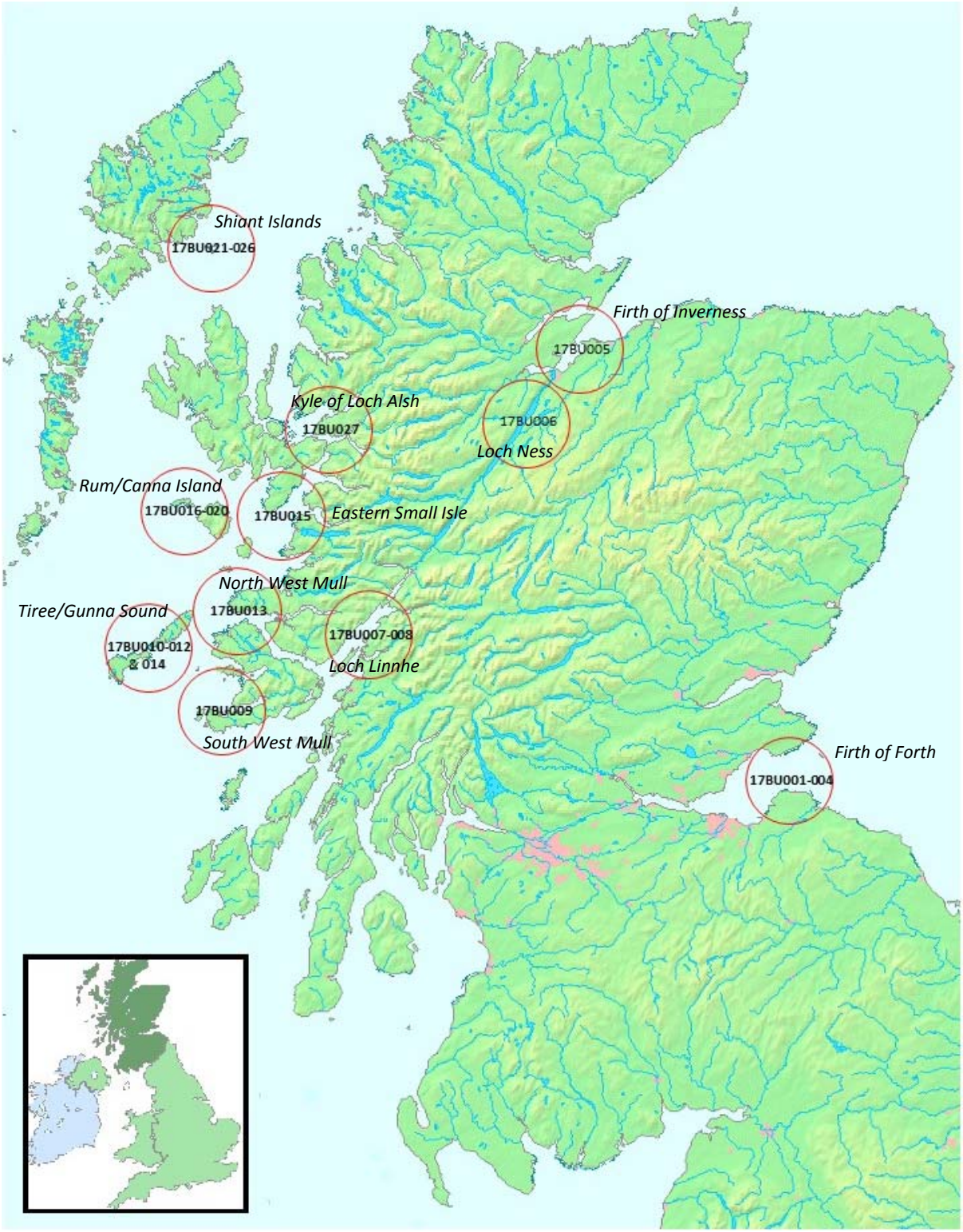


Figure 2: areas from which the 50 manta net surface tow samples were collected during May and June 2017. Higher resolution maps showing the locations at which each individual sample was collected, in relation to areas known to be important for basking shark foraging, are included as Figures A1-A3 at Annex 1.

Table 1: summary of manta net tow samples collected, along with distance and area swept by the net, numbers of plastic pieces recovered from each sample by visual inspection and estimated equivalent abundance per square kilometre of sea surface.

Location	Sample code	Location of net tow start	Date and time of net tow start	Distance towed (m)	Area swept (m^2)	Approx. volume swept (m^3)	Number of microplastic pieces found	Equivalent microplastic pieces per km^2
Firth of Forth	17BU001	N56° 11.067' W2° 53.557'	09/05/2017, 18:39	2089	1817	282	4	2201
	17BU002	N56° 04.328' W2° 38.443'	09/05/2017, 18:47	2058	1790	277	n/a	n/a
	17BU003A	N56° 10.909' W2° 43.432'	10/05/2017, 09:19	1817	1581	245	0	0
	17BU003B	N56° 10.883' W2° 39.914'	10/05/2017, 10:22	2098	1825	283	15	8218
	17BU004A	N56° 10.446' W2° 34.612'	10/05/2017, 13:39	1729	1504	233	1	665
	17BU004B	N56° 10.324' W2° 33.399'	10/05/2017, 14:37	1920	1670	259	1	599
Firth of Inverness	17BU005A	N57° 32.428' W4° 07.724'	12/05/2017, 09:37	2017	1755	272	3	1710
	17BU005B	N57° 32.427' W4° 07.724'	12/05/2017, 10:32	2033	1768	274	4	2262
Loch Ness	17BU006A	N57° 16.899' W4° 28.566'	13/05/2017, 16:30	1882	1638	254	1	611
	17BU006B	N57° 15.716' W4° 30.268'	13/05/2017, 17:20	1931	1680	260	0	0
Loch Linnhe	17BU007A	N56° 35.798' W5° 24.846'	17/05/2017, 10:49	2403	2090	324	0	0
	17BU007B	N56° 37.408' W5° 23.199'	17/05/2017, 11:44	2239	1948	302	2	1027
	17BU008A	N56° 25.941' W5° 30.203'	17/05/2017, 15:03	1733	1508	234	0	0
	17BU008B	N56° 25.407' W5° 32.415'	17/05/2017, 15:57	2390	2079	322	0	0
South West Mull	17BU009A	N56° 21.440' W6° 18.615'	19/05/2017, 16:32	1880	1636	254	3	1834
	17BU009B	N56° 21.333' W6° 16.403'	19/05/2017, 17:22	1791	1558	242	0	0
Tiree/ Gunna Sound	17BU010A	N56° 32.753' W6° 42.396'	20/05/2017, 07:45	1961	1706	264	0	0
	17BU010B	N56° 32.910' W6° 42.621'	20/05/2017, 09:16	2171	1889	293	0	0
	17BU011A	N56° 35.837' W6° 47.662'	20/05/2017, 10:56	2057	1789	277	5	2794
	17BU011B	N56° 35.279' W6° 49.080'	20/05/2017, 11:52	1982	1725	267	5	2899
	17BU012A	N56° 33.128' W6° 43.276'	20/05/2017, 13:15	1708	1486	230	0	0
	17BU012B	N56° 33.095' W6° 40.474'	20/05/2017, 13:59	3054	2657	412	12	4517
North West Mull	17BU013A	N56° 37.837' W6° 16.447'	23/05/2017, 11:48	3666	3189	494	2	627
	17BU013B	N56° 39.026' W6° 13.233'	23/05/2017, 12:51	2238	1947	302	0	0
Tiree/ Gunna Sound	17BU014A	N56° 33.950' W6° 45.001'	25/05/2017, 12:14	2162	1881	292	5	2658
	17BU014B	N56° 35.974' W6° 45.452'	25/05/2017, 13:16	1914	1665	258	4	2402

Table 1 (continued): summary of manta net tow samples collected, along with distance and area swept by the net, numbers of plastic pieces recovered from each sample by visual inspection and estimated equivalent abundance per square kilometre of sea surface

Location	Sample code	Location of net tow start	Date and time of net tow start	Distance towed (m)	Area swept (m^2)	Approx. volume swept (m^3)	Number of microplastic pieces found	Equivalent microplastic pieces per km^2
Eastern Small Isle	17BU015A	N56° 59.475' W5° 58.259'	29/05/2017, 10:46	2092	1820	282	0	0
	17BU015B	N56° 58.635' W6° 01.977'	29/05/2017, 11:50	1835	1596	247	3	1880
South West Rhum	17BU016A	N56° 56.613' W6° 23.167'	29/05/2017, 14:33	1976	1720	267	0	0
	17BU016B	N56° 57.421' W6° 25.405'	29/05/2017, 15:24	2403	2090	324	3	1435
Canna Island	17BU017A	N57° 04.878' W6° 29.458'	31/05/2017, 11:37	1905	1657	257	6	3620
	17BU017B	N57° 04.539' W6° 32.907'	31/05/2017, 12:32	1550	1348	209	4	2967
	17BU018A	N57° 00.299' W6° 36.923'	31/05/2017, 15:08	1986	1728	268	4	2315
	17BU018B	N57° 00.736' W6° 33.995'	31/05/2017, 16:04	2018	1756	272	4	2278
	17BU019A	N57° 03.345' W6° 38.399'	02/06/2017, 11:31	1793	1560	242	5	3206
	17BU019B	N57° 03.847' W6° 37.883'	02/06/2017, 13:00	1723	1499	232	0	0
	17BU020A	N57° 00.789' W6° 41.154'	02/06/2017, 14:58	1429	1243	193	2	1609
	17BU020B	N57° 00.044' W6° 42.136'	02/06/2017, 15:58	1331	1158	179	1	864
Shiant Isles	17BU021	N57° 53.532' W6° 20.676'	05/06/2017, 10:47	1500	1305	202	0	0
	17BU022A	N57° 54.456' W6° 19.410'	05/06/2017, 15:49	3523	3065	475	0	0
	17BU022B	N57° 52.635' W6° 17.301'	05/06/2017, 16:58	2759	2400	372	1	417
	17BU023A	N57° 54.574' W6° 24.137'	08/06/2017, 15:10	1591	1384	215	10	7225
	17BU023B	N57° 54.770' W6° 21.980'	08/06/2017, 16:01	1269	1104	171	17	15397
	17BU024A	N57° 53.444' W6° 24.767'	09/06/2017, 10:10	1556	1353	210	1	739
	17BU024B	N57° 52.629' W6° 22.382'	09/06/2017, 11:02	1576	1371	212	4	2918
	17BU025	N57° 59.345' W6° 23.788'	09/06/2017, 17:14	1033	899	139	1	1112
	17BU026A	N57° 54.769' W6° 20.366'	10/06/2017, 14:22	1734	1509	234	0	0
	17BU026B	N57° 54.218' W6° 23.846'	10/06/2017, 15:32	2404	2091	324	8	3826
Loch Alsh- Kyle	17BU027A	N57° 16.207' W5° 42.329'	16/06/2017, 09:55	2074	1804	280	0	0
	17BU027B	N57° 16.603' W5° 40.161'	16/06/2017, 11:00	2388	2077	322	0	0

3. Results & Discussion

3.1 Microplastic abundance

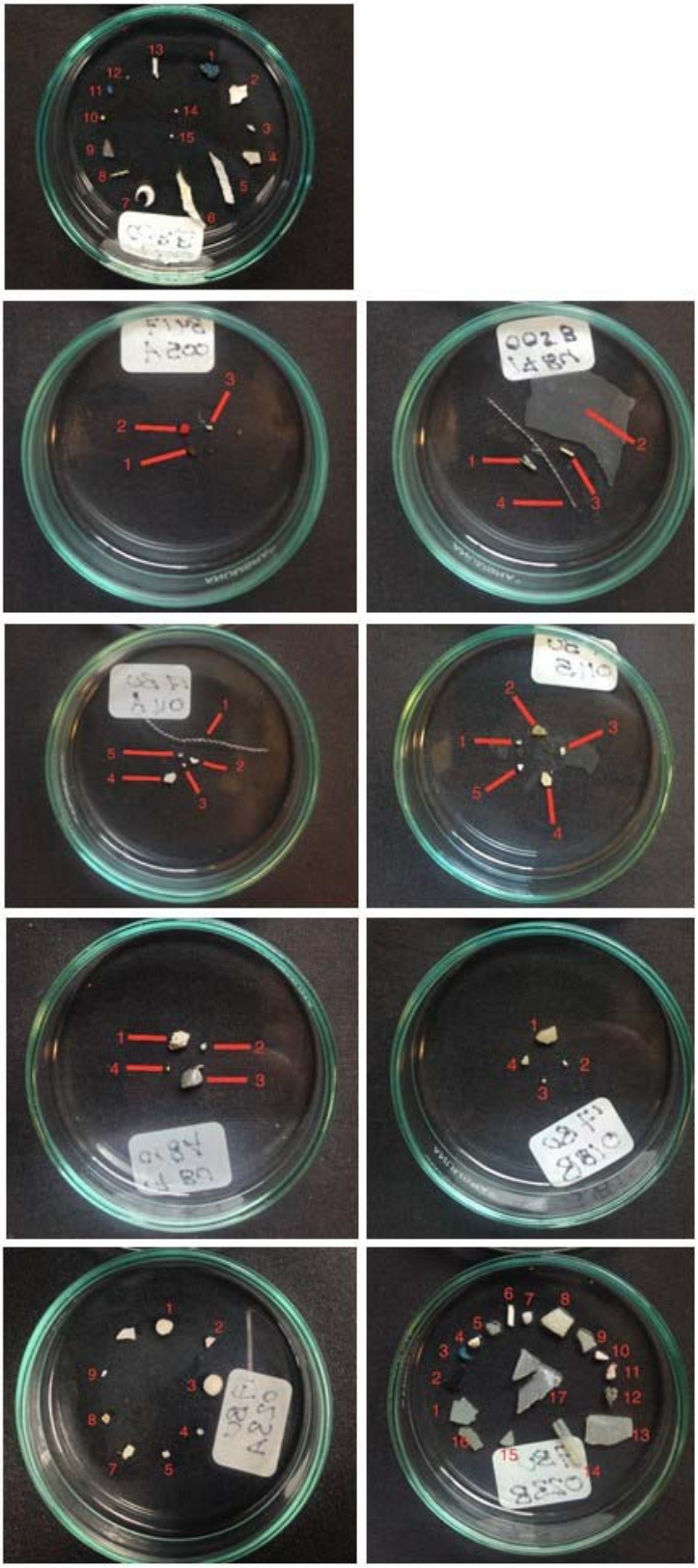
Almost two thirds of the net tow samples analysed (31 of the 49) contained at least one identifiable piece of microplastic in the size range 0.5 - 5.0 mm diameter in two dimensions. 4 samples contained 10 or more pieces of microplastic in that size range, including one sample from the Firth of Forth, one from Gunna Sound (close to Tiree) and two from waters around the Shiant Islands. Figure 3 shows examples of the range of plastic fragments and fibres recovered in samples from different locations, as an illustration of the diversity of microplastic types encountered.

Of the total of 141 items identified as plastics/polymers across all samples, 8 fragments had at least one dimension greater than 5mm (though in all but one case less than 10mm). We also found a total of 4 fibres with lengths greater than 5mm but diameters less than 0.5 mm. Although these larger fragments and fibres would strictly fall above the size range commonly used to define microplastics (<5mm in all dimensions), they were not excluded from the further analyses conducted in the current study, as it was felt to be justifiable in this case to maintain whole sample integrity given that a key objective was to characterise physical and chemical variability in the floating plastic debris that might be encountered by marine species when filter feeding or foraging at the sea surface.

Based on the specific surface area sampled in each case, the numbers of microplastics found in those 31 net tow samples in the size range from 5 mm down to 0.5 mm translate to indicative abundance estimates of between 600 and 12 600 pieces of microplastic per square km (or between 600 and 15 300/km^2, if those fragments larger than 5mm in more than one dimension were also included in the counts). Mean (average) abundance of microplastic pieces across all 49 net tows analysed (including those that yielded no visible microplastics in the size range greater than 0.5 mm) was equivalent to 1772 pieces per square km, with a median value for the same whole data set of 864/km^2.

It must be noted that these statistics are based in some cases on extrapolation from a small number of pieces actually found in the net tow samples, as has been the case in several other published studies. Nonetheless, such calculations of estimated abundances per square km do allow for some comparison with the abundance of microplastics reported for different sea areas at different times, with the caveat that detailed statistical comparisons are inevitably limited by differences in the protocols used for the collection, separation and identification of sea surface microplastics between different studies in the past (Miller *et al.* 2017).

The abundances of microplastic pieces estimated using data from our study, whether expressed as a range or as mean or median values, are (perhaps unsurprisingly) substantially lower than those reported for sea surface microplastics collected using similar sampling equipment (also with a 0.33 mm net mesh size) from the major ocean gyres in the Pacific and Atlantic Oceans that are known to accumulate floating debris (Moore *et al.* 2011, Law *et al.* 2014). Our estimates are also at the lower end of the ranges reported recently for surface waters in the Gulf of Lion (Schmidt *et al.* 2017), in the Arabian Gulf (Abayomi *et al.* 2017) and around Australia (Reisser *et al.* 2014). Nonetheless, microplastics are clearly present as widespread and complex feature of marine pollution in Scotland's coastal waters, even in areas remote from centres of human population and inputs from rivers.



(a) 17BU003B
Firth of Forth

(b) 17BU005A & B:
Firth of Inverness

(c) 17BU011A & B:
Gunna Sound, Tiree

(d) 17BU018A & B:
Canna Island

(e) 17BU023A & B:
Shiant Islands

Figure 3 (a-e): examples of microplastic pieces (fragments, fibres and microbeads) found in manta net tow samples from five different locations in Scottish coastal waters.

Results for 'time/location duplicate' samples were generally quite different, i.e. samples collected one after another from the same locations frequently yielded very different results, in some cases with microplastics found in one time/location duplicate but not in the other. For example:

- sample 17BU003B (from the Firth of Forth) yielded 15 pieces of microplastic of 0.5 mm diameter or greater, whereas sample 17BU003A collected from a similar location in the previous hour contained no identifiable pieces of microplastic in this size range.
- Likewise, 12 pieces of microplastic were found in sample 17BU012B from a location in Gunna Sound, off Tiree, whereas its 'time/location duplicate' 17BU012A yielded none.

This illustrates the fact that microplastics are not uniformly distributed in seawater, such that each net tow sample is essentially unique, even if collected from the same location one after another. **Whether or not the net encounters microplastics during a sampling tow is unpredictable, just as will be the case, therefore, for basking sharks or other wildlife feeding in these waters.**

The highest overall number of microplastic pieces recorded across two 'time/location duplicate' samples was for samples 17BU023A and B, collected off the Shiant Islands in the northern part of the Hebrides, which contained 10 and 17 pieces of microplastic of 0.5 mm diameter or greater respectively (or 10-15 pieces in the size range <5mm). 15 pieces of plastic in this size range were found in one of two time/location duplicate net tow samples from a site in the Firth of Forth (17BU003B) (or 13 pieces < 5mm), and 12 pieces in one of two duplicates at a site near Tiree in Gunna Sound (17BU012B). Given that our net tows filtered volumes of water that were, on average, only between a third and a half of the volumes that can be filtered every hour by an adult basking shark, these levels of microplastic abundance are by no means insignificant.

3.2 Identification of polymer types

Of the total of 141 pieces of plastic >0.5mm that were isolated from all of the samples, **the most common material found was polyethylene (43%), followed by polypropylene and polyamide (including nylon) in roughly equal proportions (around 12% each) (see Table 2 and Figure 4).** Polyester (including polybutylene terephthalate) (7%) and various vinyl acetate (including EVA and PVA) fragments (5%) were less frequently encountered, and polystyrene was found in only one of the samples (17BU012B, collected in Gunna Sound). A predominance of polyethylene and polypropylene in samples of microplastics collected at the sea surface is not unexpected, especially in samples collected some distance offshore. These plastics have a low density relative to seawater (Andrady 2011, 2017) and are therefore more likely to remain at the surface for extended periods than denser forms of plastic.

Typical infrared (FT-IR) spectra obtained for fragments or fibres of the three most common types of polymer identified are shown in Figure 5. The spectrum shown here for polypropylene shows additional broad peaks (at between 3500 and 3000 cm^{-1} and around 1600 cm^{-1}) that are indicative of surface oxidation and weathering of the plastic matrix following prolonged periods of exposure at the sea surface (ter Halle *et al.* 2017). Similar characteristics were also found in spectra obtained for many of the polyethylene fragments found. Some recent research has suggested that, in the case of polystyrene microplastics, the process of 'aging' (including weathering and colonisation by biofilms) that occurs over time at the sea surface may increase their attractiveness to grazing planktonic organisms which mistake them for food (Vroom *et al.* 2017), and this may also be the case for other plastic types.

Table 2: plastic types identified for individual plastic pieces found in each manta net tow sample (as summarised for all samples in Figure 3 above). Abbreviations: PVA – polyvinyl acetate, EVA – ethylene vinyl acetate copolymer, VA copoly. – other vinyl acetate copolymer, PBT – polybutylene terephthalate, PVC – polyvinyl chloride, PS – polystyrene, PEst – polyester, PVSt – polyvinyl stearate.

Location	Sample code	Number of microplastic pieces found	Polyethylene (PE)	Polypropylene (PP)	Polyamide (PA) incl. Nylon	Vinyl acetate (VA)	Acrylics	Other identified polymer	Unidentified polymer
Firth of Forth	17BU001	4							
	17BU002	n/a							
	17BU003A	0							
	17BU003B	15	8	4		1 (EVA)			2
	17BU004A	1	1						
	17BU004B	1					1		
Firth of Inverness	17BU005A	3				1 (EVA)		1 (PBT)	1 (PVC?)
	17BU005B	4	1	1	1 (Nylon)				1
Loch Ness	17BU006A	1		1					
	17BU006B	0							
Loch Linnhe	17BU007A	0							
	17BU007B	2		2					
	17BU008A	0							
	17BU008B	0							
South West Mull	17BU009A	3							3
	17BU009B	0							
Tiree/ Gunna Sound	17BU010A	0							
	17BU010B	0							
	17BU011A	5	1	1	2 (Nylon)				1
	17BU011B	5	1	1	2	1 (EVA)			
	17BU012A	0							
	17BU012B	12	4	2	2		2	2 (PS)	
North West Mull	17BU013A	2	1	1					
	17BU013B	0							
Tiree/ Gunna Sound	17BU014A	5			1 (Nylon)			3 (1xPBT, 2xPEst)	1
	17BU014B	4	1					1 (PEst)	2 (PVC?)

Table 2 (continued): plastic types identified for individual plastic pieces found in each manta net tow sample (as summarised for all samples in Figure 3 above). Abbreviations: PVA – polyvinyl acetate, EVA – ethylene vinyl acetate copolymer, VA copoly. – other vinyl acetate copolymer, PBT – polybutylene terephthalate, PVC – polyvinyl chloride, PS – polystyrene, PEst – polyester, PVSt – polyvinyl stearate

Location	Sample code	Number of microplastic pieces found	Polyethylene (PE)	Polypropylene (PP)	Polyamide (PA) incl. Nylon	Vinyl acetate (VA)	Acrylics	Other identified polymer	Unidentified polymer
Eastern Small Isle	17BU015A	0							
	17BU015B	3				1 (PVA)		1 (PVSt)	1
South West Rhum	17BU016A	0							
	17BU016B	3			1 (Nylon)			2 (PEst)	
Canna Island	17BU017A	6	1	1				2 (PEst)	2
	17BU017B	4	1		2				1
	17BU018A	4	1		1	1 (VA copoly.)			1
	17BU018B	4	1	1		1 (PVA)	1		
	17BU019A	5	4					1 (PEst)	
	17BU019B	0							
	17BU020A	2		1	1				
	17BU020B	1			1				
Shiant Isles	17BU021	0							
	17BU022A	0							
	17BU022B	1	1						
	17BU023A	10	5		1 (Nylon)	1 (PVA)			3
	17BU023B	17	15	1	1				
	17BU024A	1	1						
	17BU024B	4	4						
	17BU025	1	1						
	17BU026A	0							
	17BU026B	8	8						
Loch Alsh- Kyle	17BU027A	0							
	17BU027B	0							

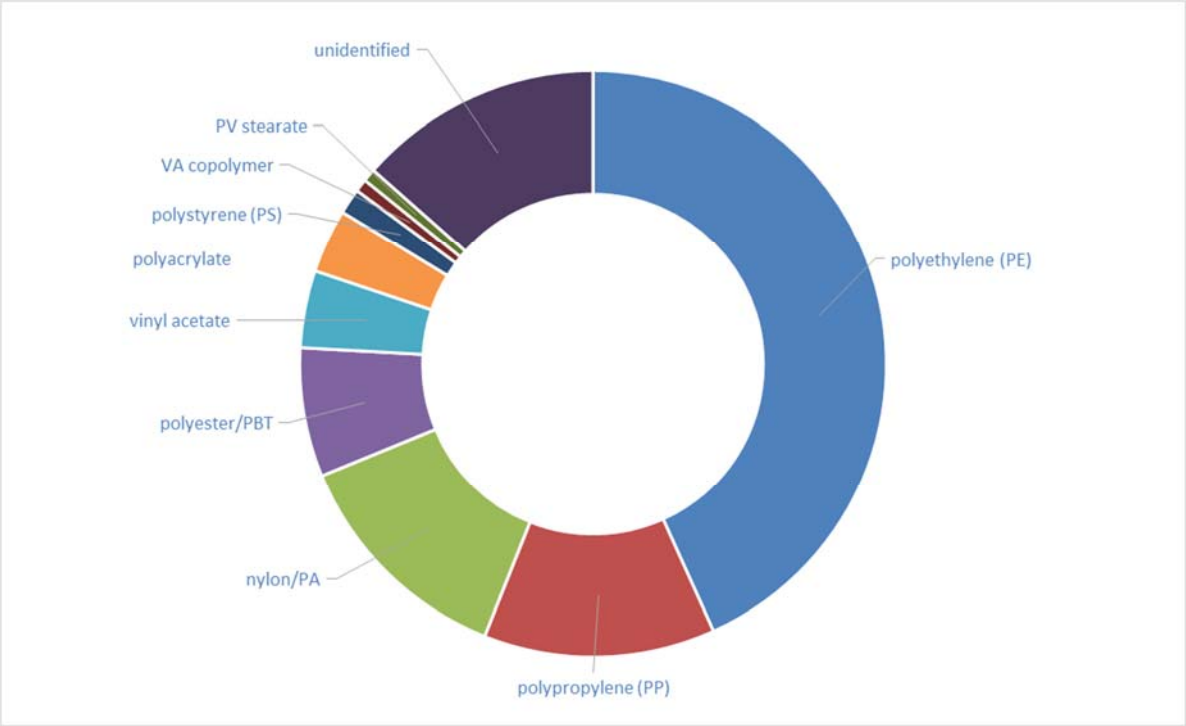
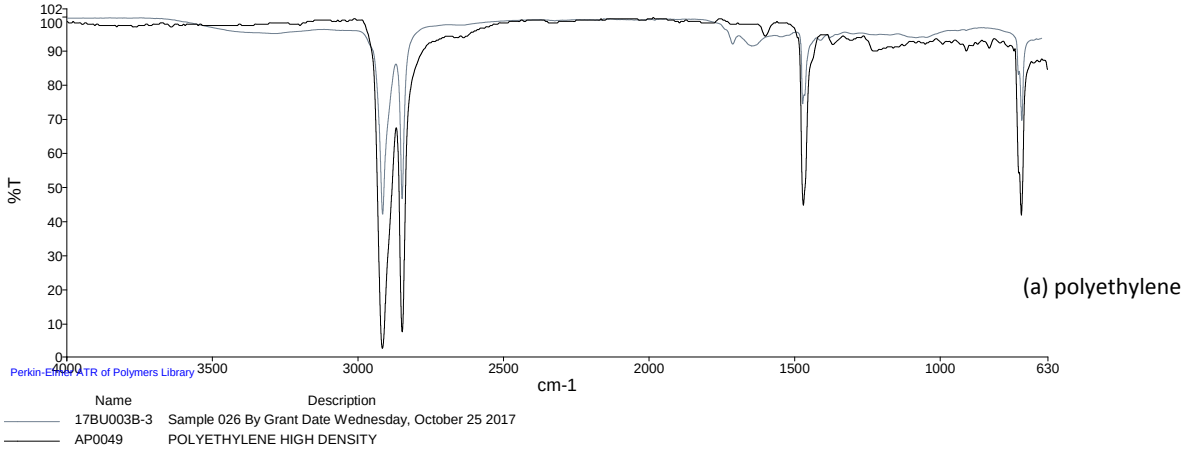


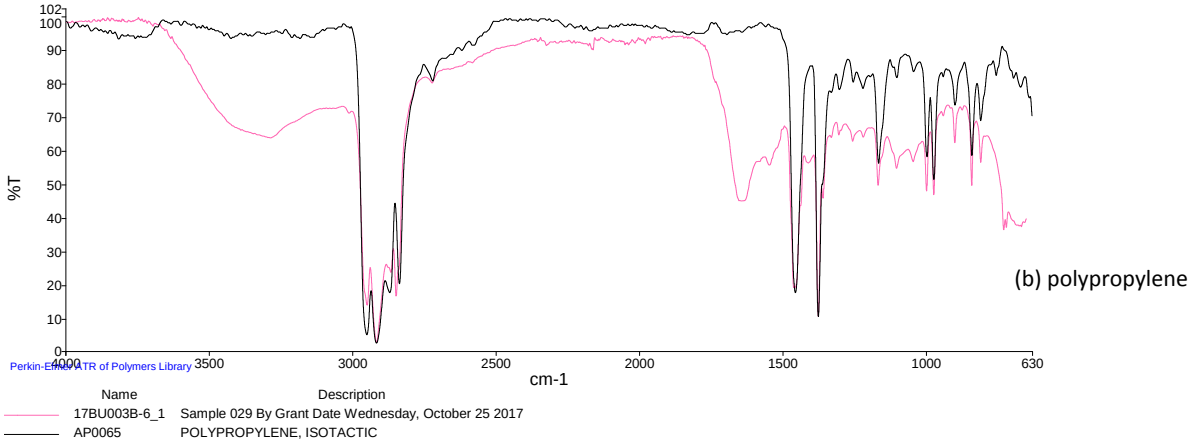
Figure 4: proportions of different plastic types for the total number of plastic pieces found in all net tow samples.

For around 13% of all of the pieces isolated, the infra-red spectra obtained did not provide for conclusive identification of polymer type, either because the signal was too weak (for particularly small or very brittle pieces) or because the spectrum was too complex, possibly as a result of interferences from high concentrations of chemical additives contained in the plastics or as a result of either partial degradation or biological colonisation of the plastic surface. In two samples, (17BU005A from the Firth of Inverness and 17BU014A from Gunna Sound), at least one of the unidentified pieces of microplastic gave an FT-IR spectrum indicative of the presence of a phthalate ester compound, of the type used as plasticiser additives to soften PVC, for example. Forensic chemical analysis of these two samples by a combination of GC-MS and LC-MS subsequently confirmed the presence of several phthalates within the plastics isolated from those two samples; this is discussed in more detail below.

Whereas the microplastics found in samples from most of the locations in the study were often of a mix of plastic types, those isolated from net tow samples collected in waters off the Shiant Islands were almost exclusively fragments of polyethylene. This could perhaps reflect both a greater diversity of land-based sources for those samples collected further south and closer to the mainland, along with the greater ability of polyethylene to accumulate at the sea surface over time, as a result of its relatively low density compared to many other plastics (Andrady 2011). It is not known whether the microplastics isolated from any of the samples in this study have predominantly local origin or have been carried to the locations sampled from more distant sources. What we can say, however, is that microplastics are a complex and diverse, but widespread and relatively common, component of Scotland's surface marine waters.

At only 3 locations were no microplastic pieces above 0.5 mm in diameter identified in either time/location duplicate net tow; one of the two sites in Loch Linne (17BU008A and B), one of four locations in Gunna Sound (17BU010A and B) and a location near the Kyle of Loch Alsh (17BU027A and B). At one further location, off the Shiant Islands (17BU021), no microplastic pieces in this size range were isolated from the single net tow sample collected but it was not possible to carry out a time/location duplicate.





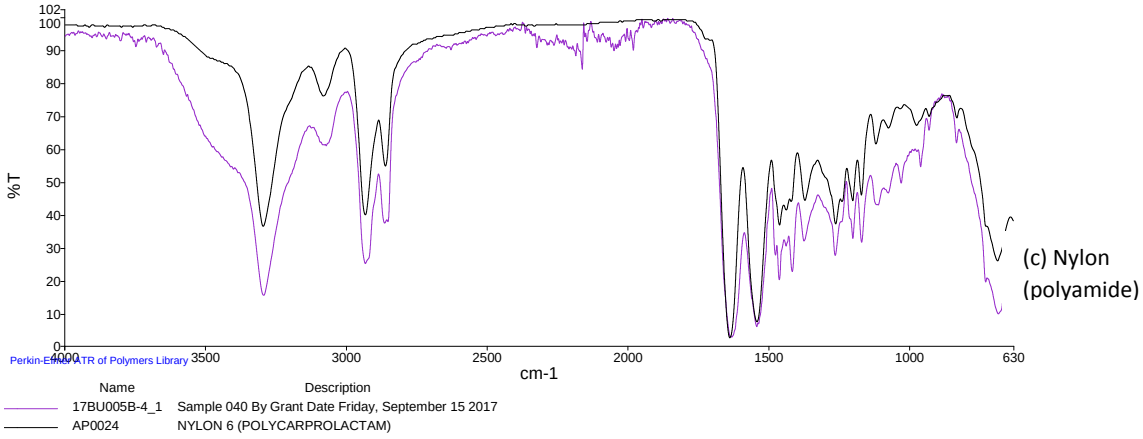


Figure 5 (a-c): typical Fourier-transformed infrared (FT-IR) spectra for the three most commonly identified plastic/polymer types among the microplastic pieces found in the manta net two samples. In each case, the black line shows the best identification match to library spectra. Differences between sample spectra and library spectra may reflect a combination of the presence of chemical additives in the plastics, partial polymer degradation and presence of residues of bacterial/fungal biofilms that had colonised the plastic surfaces over time.

It cannot be concluded from these findings, however, that these 4 locations are completely free from microplastic pollution.

- Firstly, we know from comparison of the other location replicates that the abundance of microplastics can vary greatly over short periods of time even at the same locations as currents, tides and the
  wind move different bodies of water around (Zhang 2017). Further samples collected at the same locations may have produced quite different results.
- Secondly, we cannot rule out the presence of microplastic fragments in the microscopic size ranges (significantly smaller than 0.5mm in diameter), partly because the manta net could collect only a fraction of those given the mesh size (0.33mm) and partly because the method used to isolate microplastics from the manta net tow samples relies on visual recognition and manual selection with the aid of a magnifier and dissecting microscope.

Some preliminary, non-quantitative investigations were carried out to determine if some smaller microplastic fragments and fibres were present in a subset of the net tow samples collected, i.e. microplastics that, despite being smaller than the mesh size of the net, were nonetheless retained amongst the biological material that was captured by the net. These analyses, which were qualitative and indicative only, are discussed later in this report.

3.3 Forensic analysis of microplastics for chemical additives and contaminants

3.3.1 Organic compounds

A total of 95 individual organic compounds were identified as being associated with the microplastics, though only a fraction of those were found in any one of the composite samples from an individual net tow. It is possible that the majority of those compounds identified could be natural components of microbial biofilms adhering to the surface of the plastics, including, for example, the 29 fatty acids or fatty acid derivatives found. 14 of the chemicals were linear aliphatic hydrocarbons, which may also be of natural origin but which could equally arise as contaminants from oil or fuel-oil products used at sea or on land. A complete list of the chemicals identified set out according to the samples in which they were found is provided in Annex 3.

More interesting, however, was the presence among the 95 chemicals of a number of synthetic (man-made) chemicals, either as additives in the original plastic items or as contaminants that had been absorbed from the environment (Tables 3 & 4), including:

- **12 phthalate esters** (man-made chemicals used as additives in certain plastics, inks and a range of other products), which were the most frequently found man-made chemicals associated with the microplastics,
- **4 pesticides**, including chlorpyrifos-ethyl (a highly toxic organophosphate insecticide, found in 5 samples), flufenacet (a herbicide, found in one sample), tebuconazole (a fungicide commonly used on cereal and vegetable crops, found in one sample) and buprofezin (a thiadiazine insecticide, found in one sample),
- **3 additional organophosphorus chemicals**, including triphenylphosphate and tris(2-chloroethyl)phosphate (both used as flame retardants and each found in one sample)
- 2 chemicals used as **UV stabilizers** (found in 4 and 3 samples, respectively)
- a **polycyclic musk**, closely related to the human sex hormone estradiol (found in one sample)
- the **persistent perfluorinated chemical PFOS** (found in one sample)

Table 3. Emerging contaminants found in the samples by semi-target LC-MS analysis, including CAS number, formula, ionisation polarity, pseudo-molecular ion monitored, retention time, database used for spectrum matching, product ions matched with the database, detection frequency and samples containing the compounds

Compound	CAS number	Formula	ESI mode	Precursor (Da)	Retention time (min)	Database	MS/MS ions matched	Frequency (%)	Positive samples
Poly-fluoroalkyl Surfactants									
1H,1H,2H,2H-perfluorooctane sulfonic acid	27619-97-2	C8H5F13O3S	-	426.9679	14.9	m/zCloud*	80.9637 79.9559	3%	17BU025A
Phthalate esters Plasticizers									
Benzyl butyl phthalate	85-68-7	C19H20O4	+	313.1434	17.9	m/zCloud	149.0233 91.0542 65.0386	3%	17BU024A
Di(2-ethylhexyl) phthalate	117-81-7	C24H38O4	+	391.2843	22.04	m/zCloud	167.0339 149.0233 71.0862 57.0699	10%	17BU005A 17BU006A 17BU007B
Dibutyl phthalate	84-74-2	C16H22O4	+	279.1591	17.7; 17.9	m/zCloud	149.0233 121.0284 65.0386 57.0699	21%	17BU003B 17BU014A 17BU022B 17BU024A 17BU025A 17BU026B
Dipentyl phthalate	131-18-0	C18H26O4	+	307.1904	19.5	m/zCloud	149.0233 121.0284 65.0386	10%	17BU005A 17BU006A 17BU012B
Dihexyl phthalate	84-75-3	C20H30O4	+	335.2217	20.1; 20.7	m/zCloud	149.0233 121.0284	7%	17BU005A 17BU024B
Diheptyl phthalate	3648-21-3	C22H34O4	+	363.253	21.5; 21.6	m/zCloud	149.0233 121.0284 65.0386	17%	17BU003B 17BU024A 17BU024B 17BU025A 17BU026B
Dinonyl phthalate	84-76-4	C26H42O4	+	419.316	22.7	Metlin	149.0233 127.1480 121.0284 85.1012 71.0850 57.0699	7%	17BU003B 17BU024B
Didecyl phthalate	84-77-5	C28H46O4	+	447.347	22.7	Metlin	307.1900 289.1800 149.0233 85.1012 57.0699 71.0850	7%	17BU003B 17BU024B
Di(2-methoxyethyl) phthalate	117-82-8	C14H18O6	+	283.1176	10.4	m/zCloud	149.0233 59.0491	3%	17BU017B
Organo-phosphates Plasticizers and flame retardants									
Tris (2-chloroethyl) phosphate	115-96-8	C6H12Cl3O4P	+	284.9612	11.1	m/zCloud	222.9688 186.9922 160.9766 124.9999 98.9842 62.9998	3%	17BU024A
Benzotriazoles UV stabilizer									
UV P	2440-22-4	C13H11N3O	+	226.0975	19.4	m/zCloud	183.0679 120.0555 107.0491 95.0490 79.0542 65.0386	14%	17BU009A 17BU024A 17BU024B 17BU025A
UV 326	3896-11-5	C17H18ClN3O	+	316.1211	23.3	[1] **	260.0586 107.0494	10%	17BU003B 17BU018A 17BU023A

Table 3 (continued): Emerging contaminants found in the samples by semi-target LC-MS analysis, including CAS number, formula, ionisation polarity, pseudo-molecular ion monitored, retention time, database used for spectrum matching, product ions matched with the database, detection frequency and samples containing the compounds

Compound	CAS number	Formula	ESI mode	Precursor (Da)	Retention time (min)	Database	MS/MS ions matched	Frequency (%)	Positive samples
				Poly-cyclics Musk					
Galaxolidone	1222-05-5	C18H24O2	+	273.1849	18.1	m/zCloud	255.1743 255.1274 240.1509 212.1560 197.1325 157.1012	14%	17BU003B 17BU024A 17BU024B 17BU025A
				Others					
Hexamethylenetetramine	100-97-0	C6H12N4	+	141.1132	0.8	m/zCloud	112.0869 98.0713 85.0760 71.0604 58.0651	7%	04A 24A

*identified using the fragments from PFOS
**identified with spectrum from Bignardi et al [1]

Table 4: Pesticides found in the microplastic samples using LC-MS analysis, including retention time, precursor and product ions, detection frequency and samples containing the pesticides

Pesticide	Ret time (min)	Precursor ion (Da)	Product ions (Da)	Detection Frequency (%)	Positive samples
Buprofezin	10.58	306.1635	201.1058 116.0529 106.0652 57.0702	3%	17BU014A
Chlorpyrifos-Ethyl	11.09	349.9336	293.8709 197.9276 171.0240 114.9614	14%	17BU004A 17BU005A 17BU006A 17BU007B 17BU012B
Flufenacet	9.87	364.0737	194.0977 152.0507 124.0558 109.0449	3%	17BU003B
Tebuconazole	10.22	308.1542	125.0155 70.0402	3%	17BU003B

Table 5: additional organic chemicals identified as additives or contaminants associated with the microplastics using GC-MS non-target forensic screening methods

COMPOUND	CAS #	DETECTION FREQUENCY, %	POSITIVE SAMPLES
PHTHALATE ESTERS			
Bis(2-ethylhexyl) phthalate	000117-81-7	3	17BU005a
Diethyl phthalate*	000084-66-2	7	17BU005a, 17BU024b
Dimethyl phthalate	000131-11-3	3	17BU014a
Di-n-hexyl phthalate	000084-75-3	3	17BU014a
Di-iso-nonyl phthalate*	028553-12-0	3	17BU024b
CARBOXYLIC/FATTY ACIDS AND DERIVATIVES			
13-Docosenoic acid, methyl ester	001120-34-9	3	17BU009a
2-Propenoic acid, tridecyl ester	003076-04-8	3	17BU024b
5,8,11,14,17-Eicosapentaenoic acid	002734-47-6	7	17BU009a, 17BU012b
5,8,11,14,17-Eicosapentaenoic acid, methyl ester	001191-65-7	3	17BU011b
7,10,13,16,19-Docosapentaenoic acid, methyl ester	108698-02-8	3	17BU009a
7-Hexadecenoic acid, methyl ester	056875-67-3	3	17BU026b
9,12-Octadecadienoic acid (Z,Z)-	000060-33-3	7	17BU012b, 17BU023b
9-cis-Hexadecenoic acid	000373-49-9	17	17BU003b, 17BU011b, 17BU012b, 17BU020a, 17BU023b
9-cis-Hexadecenoic acid, methyl ester, (Z)-	001120-25-8	17	17BU011b, 17BU017b, 17BU018a, 17BU018b, 17BU020a
9-Octadecenoic acid, methyl ester, (Z)-	000112-62-9	3	17BU011a
Benzoic acid	000065-85-0	3	17BU014a
Benzoic acid, 2-cyano- OR Phthalimide	003839-22-3 OR 000085-41-6	3	17BU014a
Benzoic acid, dimethyl-	000000-00-0	34	17BU003b, 17BU012b, 17BU013a, 17BU014a, 17BU018a, 17BU018b, 17BU019a, 17BU020a, 17BU023a, 17BU023b
Decanoic acid	000334-48-5	3	17BU020a
Dodecanoic acid	000143-07-7	14	17BU012b, 17BU023a, 17BU023b, 17BU024b
Dodecanoic acid, methyl ester	000111-82-0	3	17BU016b
Heptanoic acid	000111-14-8	3	17BU020a
Hexadecanoic acid	000057-10-3	52	17BU003b, 17BU004b, 17BU005a, 17BU005b, 17BU012b, 17BU013a, 17BU014a, 17BU018a, 17BU018b, 17BU019a, 17BU020a,

COMPOUND	CAS #	DETECTION FREQUENCY, %	POSITIVE SAMPLES
			17BU023a, 17BU023b, 17BU024b, 17BU026b
Hexadecanoic acid, methyl ester	000112-39-0	14	17BU003b, 17BU004a, 17BU009a, 17BU026b
Hexanoic acid	000142-62-1	3	17BU005b
Hexanoic acid, 2-ethyl-, methyl ester	000816-19-3	3	17BU016b
Nonanoic acid	000112-05-0	7	17BU020a, 17BU026b
Octadecanoic acid	000057-11-4	45	17BU003b, 17BU004a, 17BU004b, 17BU012b, 17BU017b, 17BU018a, 17BU020a, 17BU023a, 17BU023b, 17BU024b, 17BU026b
Octadecanoic acid, methyl ester	000112-61-8	3	17BU023a
Octanoic acid	000124-07-2	3	17BU020a
Oxiraneoctanoic acid, 3-octyl-, methyl ester	002500-59-6	3	17BU004b
Pentadecanoic acid	001002-84-2	3	17BU023a
Tetradecanoic acid	000544-63-8	41	17BU003b, 17BU004b, 17BU005b, 17BU011b, 17BU012b, 17BU013a, 17BU018a, 17BU020a, 17BU023a, 17BU023b, 17BU024b, 17BU026b
Tetradecanoic acid, methyl ester	000124-10-7	3	17BU009a
LINEAR ALIPHATIC HYDROCARBONS			
1-Decene	000872-05-9	24	17BU004a, 17BU016b, 17BU018b, 17BU024a, 17BU024b, 17BU025a, 17BU026b
1-Pentadecene	013360-61-7	3	17BU023b
1-Tetradecene	001120-36-1	3	17BU023b
Cyclodecane	000293-96-9	10	17BU005a, 17BU018b, 17BU023b
Cyclododecane	000294-62-2	17	17BU003b, 17BU004b, 17BU023a, 17BU023b, 17BU024b
Cyclotetradecane	000295-17-0	3	17BU012b
Dodecane	000112-40-3	21	17BU018b, 17BU023a, 17BU023b, 17BU024b,

COMPOUND	CAS #	DETECTION FREQUENCY, %	POSITIVE SAMPLES
			17BU025a, 17BU026b
Eicosene	074685-33-9	3	17BU026b
Heptadecane	000629-78-7	14	17BU020b, 17BU025a, 17BU026b
Octadecane	000593-45-3	10	17BU016b, 17BU024a, 17BU025a
Pentadecane	000629-62-9	10	17BU023b, 17BU025a, 17BU026b
Pentadecane, 2,6,10,14-tetramethyl-	001921-70-6	21	17BU003b, 17BU009a, 17BU013a, 17BU020a, 17BU023a, 17BU023b
Tetradecane	000629-59-4	3	17BU026b
Tridecane	000629-50-5	10	17BU023b, 17BU025a, 17BU026b
ORGANOSULPHUR COMPONDS			
Dimethyl sulfone	000067-71-0	7	17BU005b, 17BU024b
Dimethyl sulfoxide	000067-68-5	21	17BU005b, 17BU012b, 17BU013a, 17BU023b, 17BU024b, 17BU026b
ORGANOPHOSPHORUS COMPOUNDS			
Phosphine oxide, triphenyl-	000791-28-6	3	17BU005a
Phosphoric acid, triphenyl ester	000115-86-6	3	17BU016b
OTHERS			
1,2-Dimethyl-4-(dimethoxymethyl)benzene	000000-00-0	66	17BU003b, 17BU004b, 17BU007b, 17BU009a, 17BU011a, 17BU011b, 17BU013a, 17BU014a, 17BU016b, 17BU018a, 17BU018b, 17BU019a, 17BU020a, 17BU020b, 17BU023a, 17BU023b, 17BU024a, 17BU025a, 17BU026b
1,19-Eicosadiene	014811-95-1	14	17BU009a, 17BU011a, 17BU013a, 17BU024b
1,21-Docosadiene	053057-53-7	3	17BU013a
1,3-Cyclooctadiene, (Z,Z)-	003806-59-5	3	17BU012b
1,3-Propanediol, 2,2-dimethyl-	000126-30-7	7	17BU005a, 17BU016b
1-Heptadecanol	001454-85-9	3	17BU024b

COMPOUND	CAS #	DETECTION FREQUENCY, %	POSITIVE SAMPLES
1-Hexadecanol	036653-82-4	7	17BU013a, 17BU023b
2,5-Hexanedione	000110-13-4	10	17BU005b, 17BU017b, 17BU018b
2-Furan-carboxaldehyde	000098-01-1	3	17BU023a
Benzaldehyde, 3,5-dimethyl-	005779-95-3	3	17BU024b
Benzene, (dimethoxymethyl)-	001125-88-8	7	17BU014a, 17BU016b
Benzene, 1,4-bis(1,1-dimethylethyl)-	000064-16-3	3	17BU018b
Bicyclo[10.8.0]eicosane, cis-	000448-95-7	3	17BU009a,
Cholesterol	000057-88-5	14	17BU023a, 17BU023b, 17BU024b, 17BU026b
Cyclohexanone	000108-94-1	3	17BU023b
Cyclopropane, nonyl-	074663-85-7	3	17BU026b
Ethanone, 1-(1,3-dimethyl-1H-pyrazol-4-yl)-	052773-23-6	7	17BU014a, 17BU015b
Ethanone, 1-(2,4-dimethyl-furan-3-yl)-	032933-07-6	10	17BU016b, 17BU019a, 17BU026b
Methenamine	000100-97-0	3	17BU018b
Oxime-, methoxy-phenyl-	000000-00-0	31	17BU011a, 17BU016b, 17BU017b, 17BU018b, 17BU019a, 17BU020b, 17BU023a, 17BU024b, 17BU025a
Phenanthrene*	000085-01-8	3	17BU014a
Phthalic anhydride	000085-44-9	3	17BU014a
Pyridine, 2,4,6-trimethyl-	000108-75-8	3	17BU012b
Spiro[5-fluorobenzo[5,6-b]furan-2,5-dione-3,1'-1',4'-dihydro-6'-methoxynaphthalene]	000000-00-0	3	17BU014a
Squalene	000111-02-4	3	17BU023a
Tinuvin (R) 292**	041556-26-7	3	17BU014a

* - compound detected at trace levels only using selected ion monitoring mode (SIM)

** - mixture of two compounds, from which Bis(1,2,2,6,6-pentamethyl-4-piperiinyl) sebacate (CAS: 41556-26-7) was reliably identified, while the second compound, methyl 1,2,2,6,6-pentamethyl-4-piperidyl sebacate (CAS No.82919-37-7), was only suggested due to a similar pattern of fragmentation to the that of the first one. This putative identification was subsequently confirmed through LC-MS analysis.

No residues of any the pharmaceutical compounds screened for were found to be associated with the microplastics from any location.

The range of chemical groups identified in this analysis, as well as their overall diversity and complexity, show some considerable overlap and similarity to those chemicals previously reported to be associated with plastic and microplastic items retrieved from beaches in Belgium (Gauquie *et al.* 2015) and in South Korea (Rani *et al.* 2015). For example, in addition to the mix of hydrocarbons, fatty acids and phthalate esters, we identified an organophosphate flame retardant and a benzotriazole UV stabiliser that were also reported by Rani *et al.* (2015) as components of beached plastic waste. More

recently, Zhang *et al.* (2018) also reported the presence of organophosphorus esters and phthalates in samples of beached microplastics from beaches in Northern China.

Given the diverse range of organic chemicals included in this screening analysis, combined with very limited masses of the microplastic samples, it was not possible to determine extraction recoveries or, therefore, absolute concentrations for these chemical additives and contaminants. The analyses conducted do, nonetheless, give high confidence that these additives and contaminants were present and could therefore be ingested along with the microplastic particles. **The number and mix of chemicals associated with the microplastics varied greatly from sample to sample, but showed no clear geographical patterns, nor any apparent correlation with the numbers, sizes or total masses of microplastics isolated from the samples (see Figure 6).** Rather, just as was the case for exposure to the microplastics themselves, the potential for a foraging or filter-feeding organism to encounter any of these particular chemicals contained within, or concentrated onto the surface of, a piece of microplastic appears to be impossible to predict under real world conditions. Furthermore, as noted by Andrady (2017), the presence of chemical additives may well also influence the environmental fate of microplastics in ways that cannot currently be predicted.

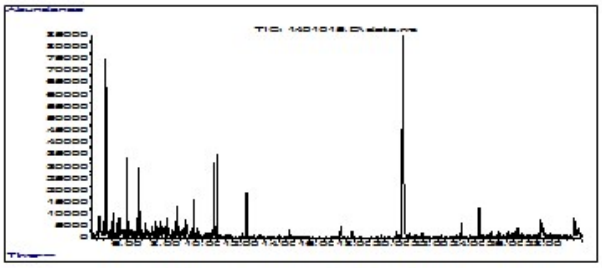
3.3.2 Metals

Several of the composite microplastics samples contained concentrations of heavy metals that were also particularly notable (Table 6), including:

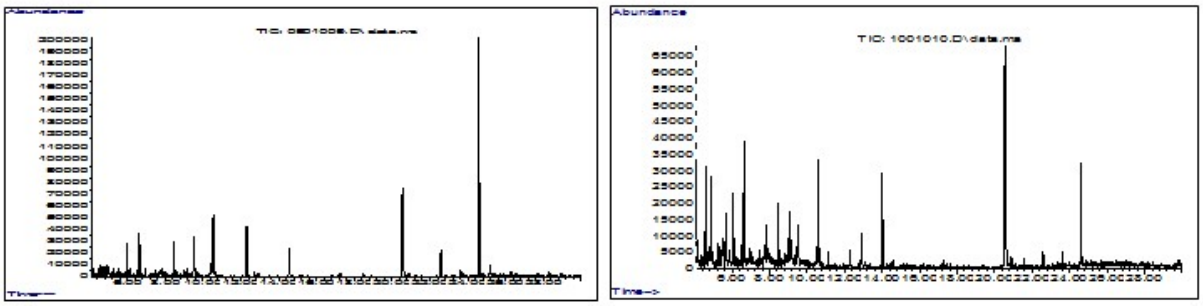
- Sample 17BU003B from the Firth of Forth, which contained **lead** (171 mg/kg), **copper** (73.2 mg/kg) and **chromium** (35.9 mg/kg)
- Sample 17BU012B from Gunna Sound, which contained **lead** (686 mg/kg), **chromium** (129 mg/kg) and **manganese** (141 mg/kg)
- Sample 17BU017B from close to Canna Island, which contained **lead** (205 mg/kg) and **chromium** (49.6 mg/kg) and
- Sample 17BU026B from waters around the Shiant Islands, which contained **cadmium** (195 mg/kg)

As was the case for the organic chemicals identified in the GC-MS and LC-MS analyses, **there were no apparent geographical patterns in the distribution of heavy metals associated with the microplastics recovered from these manta net tows, nor any noticeable correspondence between location replicates, nor correlation with total number, size or mass of microplastics in each sample.** There is also no apparent relationship between the types of organic chemicals (pesticides, industrial chemicals, etc.) found to be associated with the microplastics in the net tow samples and the metals associated with the same microplastics.

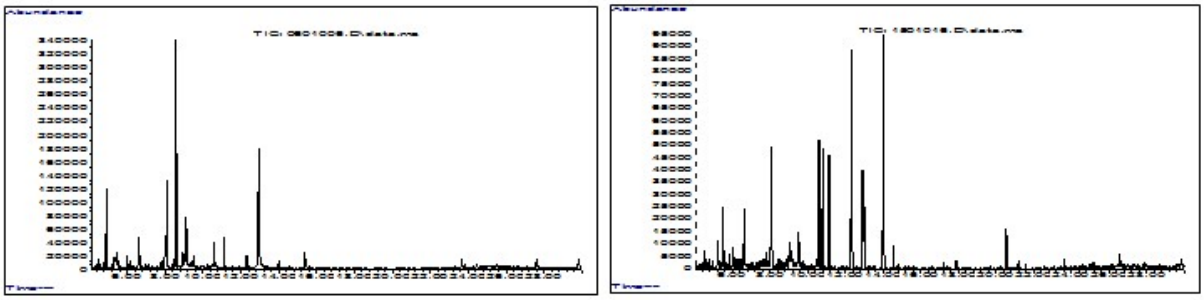
In addition, we cannot be certain of the origin of each of the contaminants found, i.e. whether they are predominantly associated with the microplastics at source or rather have been adsorbed from the surrounding seawater over time. The potential for microplastics to adsorb metals from surrounding seawater has been evidenced in a number of studies (e.g. Rochman *et al.* 2014, Brennecke *et al.* 2016), though to date there appear to be few data relating to the concentrations of metals associated with microplastics recovered from the environment in net tows at the sea surface. Those studies that are available have tended to focus on the metals associated with beached microplastics, with an emphasis on pre-production pellets. For example, Vedolin *et al.* (2017) analysed beached pellets from the shoreline around Sao Paolo, Brazil, reporting concentrations of iron, copper and manganese that are, in the majority of cases, similar to those recorded from our samples, though we measured substantially higher levels of these metals in some samples. In a study of plastic pellets from beaches in SW England, Massos & Turner (2017) report finding a small proportion (7%) of samples containing particularly high concentrations of lead and cadmium, exceeding 1000 mg/kg. Such high levels



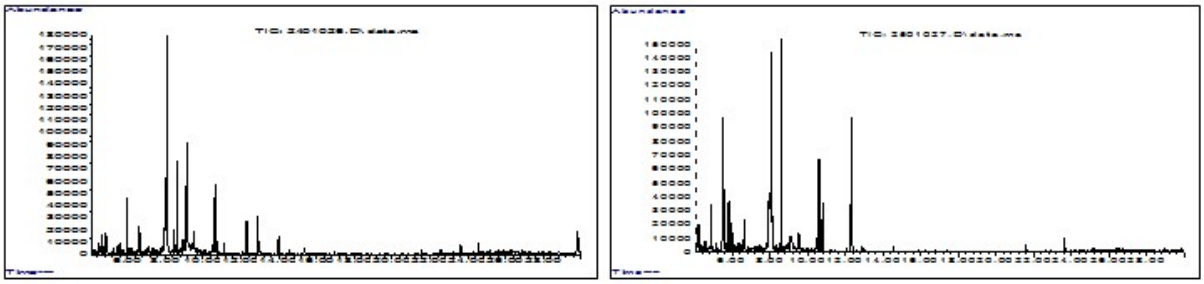
(a) 17BU003B: Firth of Forth



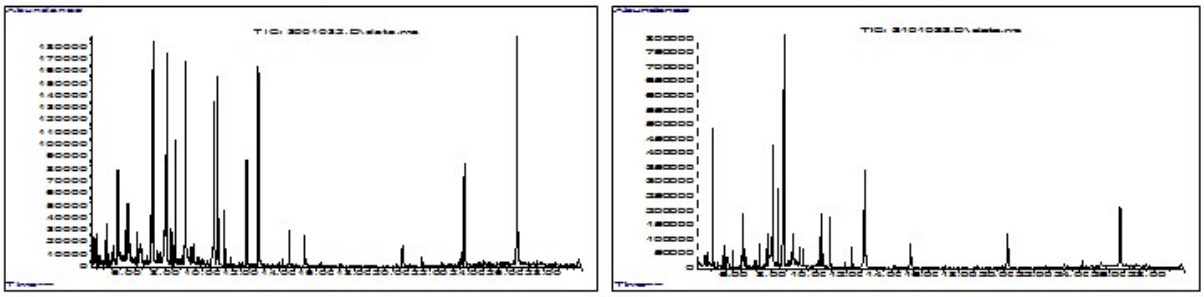
(b) 17BU005A & B: Firth of Inverness



(c) 17BU011A & B: Gunna Sound, Tiree



(d) 17BU018A & B: Canna Island



(e) 17BU023A & B: Shiant Islands

Figure 6 (a-e): total ion chromatographs arising from the forensic screening for chemical additives and contaminants of the microplastic pieces found in the nine samples illustrated in Figure 3 (a-e) using GC-MS techniques, illustrating the complexity and variability in chemical mixtures associated with different microplastic samples, even when collected consecutively from the same locations.

Table 6: Concentrations of metals and metalloids in plastic samples (mg/kg), No data are available for four samples for which there was insufficient material to carry out analysis for metals/metalloids; 17BU004a, 17BU004B, 17BU015B, 17BU016B.

	Firth of Forth	Firth of Inverness	Firth of Inverness	Loch Ness	Loch Linnhe	South West Mull	Tiree/ Gunna Sound	Tiree/ Gunna Sound	Tiree/ Gunna Sound	North West Mull	Tiree/ Gunna Sound	Tiree/ Gunna Sound
Metal/ metalloid	17BU003B	17BU005A	17BU005B	17BU006A	17BU007B	17BU009A	17BU011A	17BU011B	17BU012B	17BU013A	17BU014A	17BU014B
Antimony	<0.04	2.5	0.04	<1	<2	3.8	<0.3	<0.4	0.31	1.3	3.9	<0.4
Arsenic	0.58	6.8	0.16	<1	0.75	<2	<0.3	4.7	1.28	0.32	2.2	0.83
Barium	3.0	66300	1.2	<10	2	52	3	6	52.6	20.4	56400	45
Cadmium	0.24	<0.6	<0.01	<1	<0.1	2	<0.2	<0.3	0.06	0.1	0.7	0.6
Chromium	35.9	120	2.3	<6	<1	<20	<2	4	129	2.2	22	<2
Cobalt	0.11	18.6	0.04	<0.4	<0.1	<0.6	<0.1	<0.2	0.56	0.32	146	2.1
Copper	73.2	42	0.52	<4	2	<6	<1	5	2.0	61.6	447	74
Iron	1030	234000	180	<200	700	500	<60	1200	380	910	51200	300
Lead	171	9	0.92	<2	9.4	15	<0.6	3	715	4.1	16	3
Manganese	7.9	1150	1.8	<4	5.5	12	1.2	17	141	30.7	252	8.7
Mercury	<0.5	<7	0.2	<10	<2	<20	<3	<4	<2	<1	<5	<4
Molybdenum	0.5	4	0.05	<2	0.3	<3	<0.6	<0.8	0.1	0.2	6	0.8
Nickel	<2	<30	<0.5	<40	<7	<60	<10	<20	<1	<3	<20	<20
Selenium	<0.5	<7	<0.1	<10	<2	<20	<3	<4	<0.2	<0.8	<5	<4
Strontium	9.15	1890	0.66	<4	7.6	42	4	21	8.1	24.9	983	28
Tin	1.2	64	0.46	<2	0.7	10	<0.6	1	0.4	1	25	5
Titanium	27.0	110	7.40	<8	4.0	<10	<2	25	7.51	37.8	57	7
Vanadium	1.6	6	0.70	<2	2	<4	<0.6	5	1.6	2.6	1650	1
Zinc	32	1850	134	<80	320	<100	<2	<30	182	110	1330	410

	Canna Island	Canna Island	Canna Island	Canna Island	Canna Island	Canna Island	Canna Island	Shinat Isles	Shinat Isles	Shinat Isles	Shinat Isles	Shinat Isles	Shinat Isles	Shinat Isles
Metal/ metalloid	17BU017A	17BU017B	17BU018A	17BU018B	17BU019A	17BU020A	17BU020B	17BU022B	17BU023A	17BU023B	17BU024A	17BU024B	17BU025A	17BU026B
Antimony	<0.2	0.07	<0.03	<0.1	0.05	0.12	0.68	<0.9	<0.07	0.44	0.2	<0.02	<0.06	<0.03
Arsenic	<0.2	0.08	0.11	<0.1	0.12	0.25	0.1	<0.9	2.21	0.14	2.0	0.18	<0.06	1.56
Barium	2	121	1.8	91.5	61.7	220	0.9	<9	0.8	0.4	17	2.0	<0.6	25.0
Cadmium	<0.2	0.04	0.1	<0.1	0.18	<0.04	<0.1	<0.7	0.1	0.01	<0.1	0.03	<0.1	195
Chromium	<1	49.6	17.9	0.8	4.2	<0.3	<0.5	<5	3.7	1.70	42.1	0.92	<0.4	2.6
Cobalt	0.72	0.05	0.03	0.65	0.30	<0.02	<0.03	<0.4	0.35	0.01	0.2	<0.01	<0.03	<0.01
Copper	<0.8	0.2	1.2	<0.4	1.5	3.4	<0.3	20	1	2.07	6.9	0.1	<0.3	5.7
Iron	<40	140	130	50	120	50	210	<200	2230	35	540	20	20	50
Lead	<0.4	205	2.3	0.3	12.3	0.4	0.3	<2	2.3	2.55	2.2	1.2	<0.1	0.2
Manganese	<0.8	3.0	3.4	8.9	2.3	2.3	9.5	<4	103	0.56	33.6	0.64	0.6	0.7
Mercury	3	<0.3	<0.3	<1	<0.1	<0.5	0.9	<9	<0.7	<0.05	<1	<0.2	<0.6	<0.3
Molybdenum	<0.4	0.3	<0.1	<0.2	0.26	<0.1	<0.2	<2	0.6	0.1	<0.2	<0.04	<0.1	<0.1
Nickel	<8	<1	<1	<4	<0.3	<2	<3	<40	<3	<0.2	<4	<1	<3	<1
Selenium	<2	<0.3	<0.3	<1	<0.1	<0.5	<0.8	<9	<0.7	<0.1	<1	<0.2	<0.6	<0.3
Strontium	1	5.8	3.0	7.7	2.69	156	10	<4	13	1.89	19	1.7	1.7	14.3
Tin	2	0.4	0.2	0.4	0.76	0.4	1	<2	19.7	1.54	2.9	1.3	0.4	1.1
Titanium	<2	3.6	35.1	3.9	11.3	2.6	3.5	20	7.0	8.04	205	26.1	5.4	10.3
Vanadium	<0.4	0.3	0.2	<0.2	0.21	0.1	0.4	<2	2.4	0.1	0.9	0.1	0.6	<0.1
Zinc	<20	59	65	38	192	67	9	<80	21	9.4	58	42.5	26	23

are more likely to arise from the presence of metal salts as plastic additives (as stabilisers or colourants, for example), rather than simply from adsorption from the water column, and this may also be the case for those samples in our study that yielded the highest concentrations of metals such as lead, chromium and cadmium.

3.4 Qualitative investigation of the presence of microplastics smaller than 0.5 mm in a subset of the manta tow net samples

In order to determine whether any microplastic fragments and fibres smaller than 0.5mm had been retained by the manta net, as a qualitative indication of their presence to inform future studies, a subset of 10 of the manta net tow samples (3 from Gunna Sound off Tiree, 3 off Canna Island, 3 off the Shiant Islands and one from Loch Ness) were also subjected to analysis using infrared (FT-IR) microscopy (PerkinElmer Spotlight 400 FT-IR Imaging System), following pre-screening through 250 μm and 63 μm stainless steel mesh to remove biological material and filtration on to a 5 μm silver filter. Further details of the method employed are provided in Annex 2.

Examination of the filters indicated that microplastics in these smaller size ranges, especially fibres, can be found in all 10 of this randomly selected subset of samples (see Figure 7). Although it is often difficult to obtain high quality infrared spectra from fibres with diameters in the range of only 20-30 μm is difficult, especially when they are partially degraded and have a circular cross section rather than presenting a flat surface, it was nevertheless possible to identify fibres and fragments of nylon, polyester and polypropylene, among other materials found. Although only a preliminary analysis has been possible to date, this suggests that microplastics within the size range below 63 μm, too small to have been retained quantitatively by the manta net mesh, may therefore be a common characteristic of the waters in these areas. This is an aspect that deserves further investigation as microplastics within these small size ranges are clearly of significance in relation to determination of overall levels of contamination and, therefore, potential exposure of marine species of all sizes.

4. Conclusions

Taken together, the data available to date for this complex set of surface manta net tow samples paints a picture of high variability, and therefore low predictability, not only in the apparent abundances and types of microplastics as pollutants at different locations and different times in the waters of Scotland, but also similar unpredictability of the chemical signatures that those microplastics carry. A basking shark or other marine organism filter-feeding or even foraging at the surface of the sea might encounter few or no microplastics in the size range from 1mm and above within any particular feeding period, or may unwittingly encounter many – just as was the case with our manta net tows, it really is just the luck of the draw. Even though the abundance of microplastics found in this study are very far from the highest reported for other sea areas around the world, they nonetheless represent an uncontrollable symptom of historic and ongoing overuse, misuse and careless disposal of plastics.

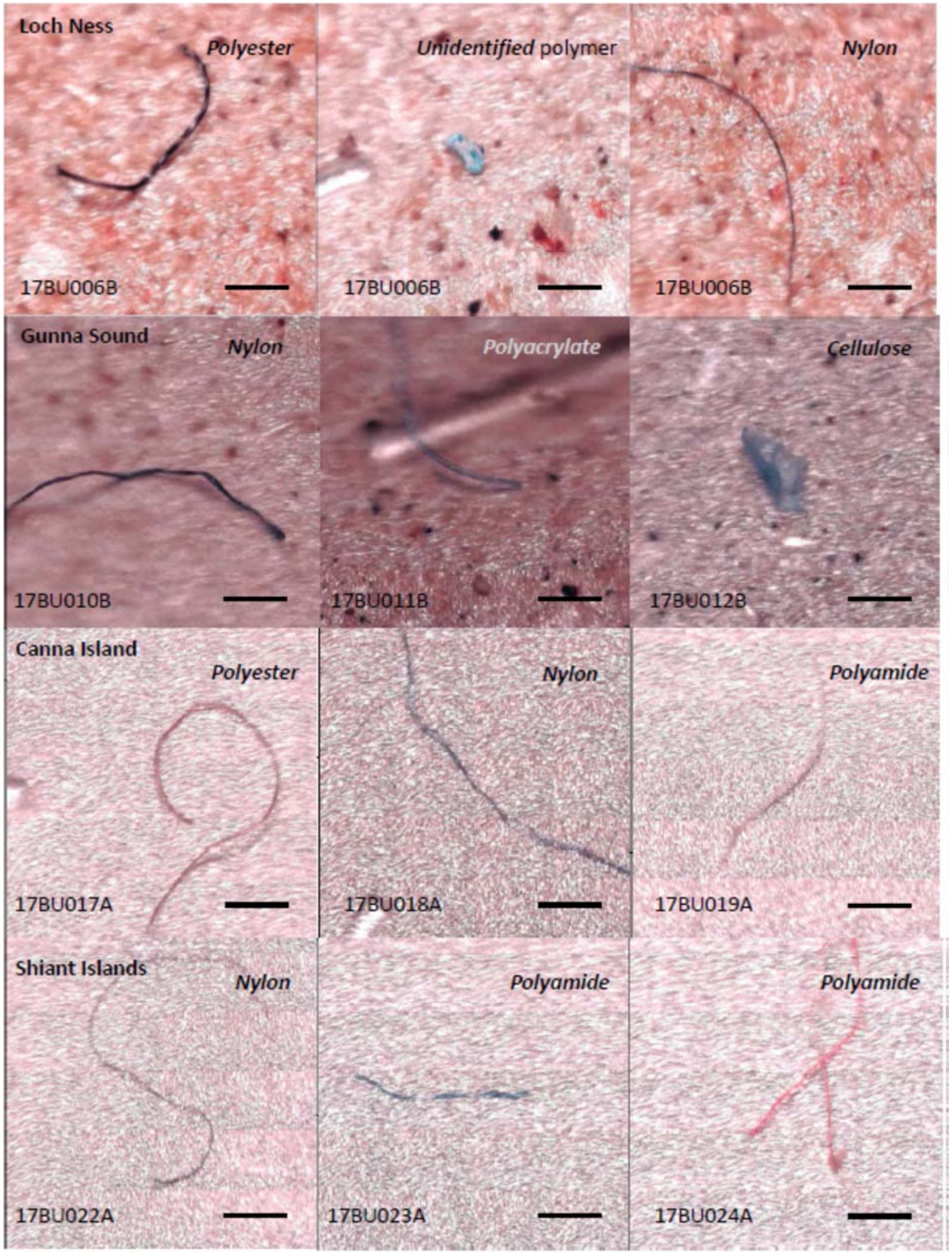


Figure 7: a selection of the plastic fragments and fibres found during qualitative screening of the <63 µm fraction of net tow samples from 9 locations (one sample in Loch Ness and three separate samples each from Gunna Sound, near Canna Island and close to the Shiant Islands). These are not intended to be representative of the locations listed, but simply to illustrate an additional component of the overall diversity of microplastic contamination at all four locations that would otherwise not reflected in regular manta net tow sample analyses.

From our research, it is not possible to identify particular pollution hotspots in Scottish waters, not least because the water masses are constantly in motion – **what might appear as a hotspot during one hour might appear relatively clear of microplastics the next, and vice versa.** Nor is it possible to use these data to estimate the scale of risk posed by the presence of microplastics in surface waters, either to marine species or to humans through the consumption of seafood, nor how far they may contribute to overall exposures of marine life to harmful chemical contaminants.

What the data do reveal, however, is that **even in the relatively remote waters around the Hebrides on the Northwest coast of Scotland, microplastics have become an unwelcome part of the fabric of marine ecosystems.** The high variability in distribution of microplastics over time and space, in the plastic types they represent and in the chemicals they carry on their surface or within their structures, illustrates the huge difficulties in preparing any sort of assessment and mapping of the risks they may pose.

As far as we are aware, this is the most detailed survey published to date of microplastic contamination in surface waters around the Hebrides, and the first study to subject the microplastics recovered from each discrete surface water manta net tow sample to such a depth of sequential analysis to determine plastic type and associated organic and inorganic chemical constituents and contaminants.

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Annex 1: higher resolution maps showing the locations of the start positions of all individual trawl samples, in relation to areas know to be important foraging areas for basking sharks.

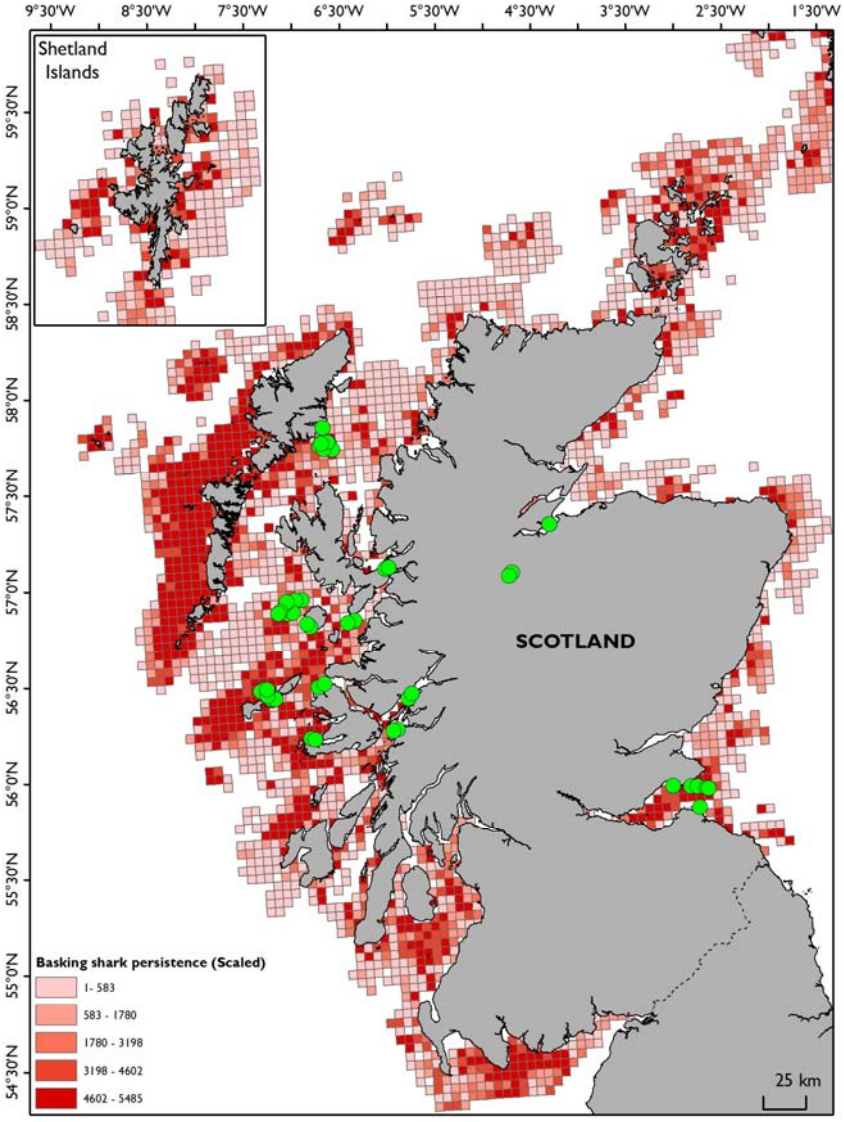
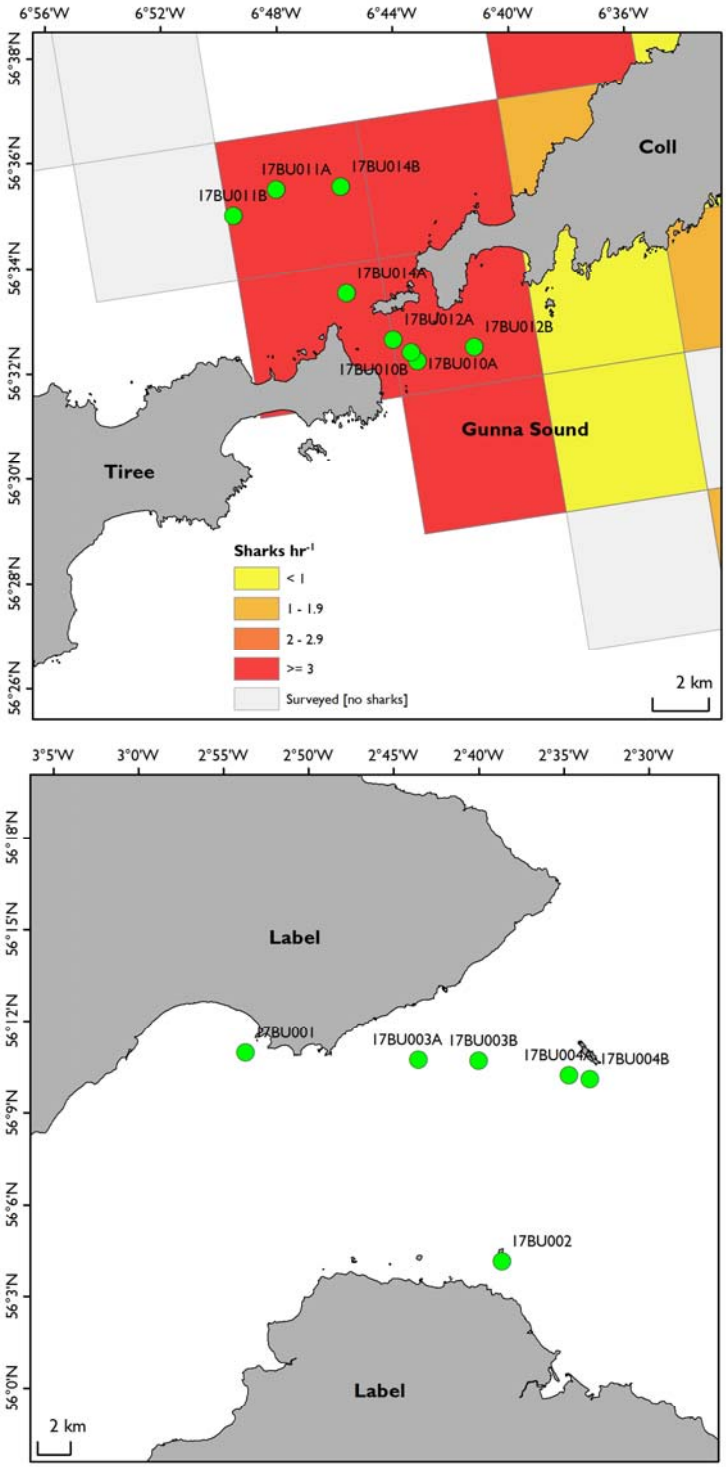


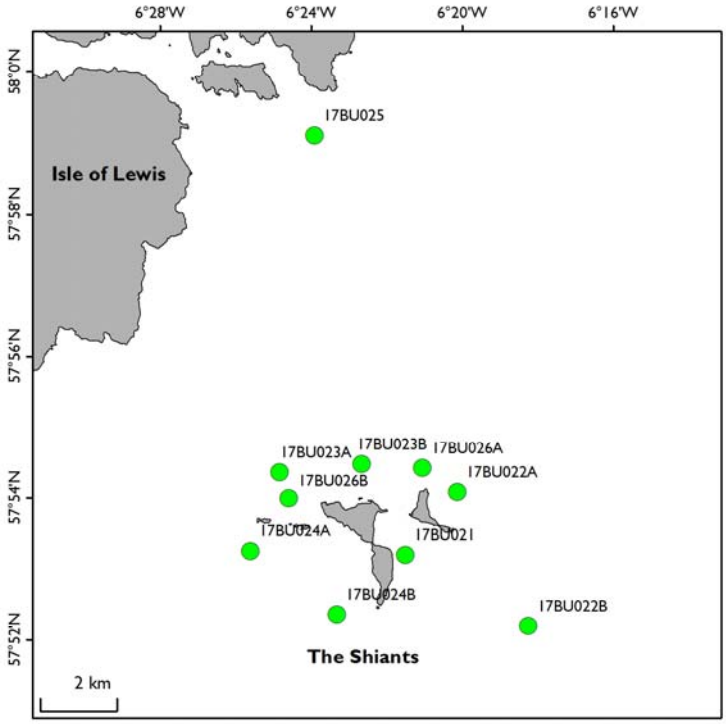
Figure A1: All samples (prepared by Matthew Witt)



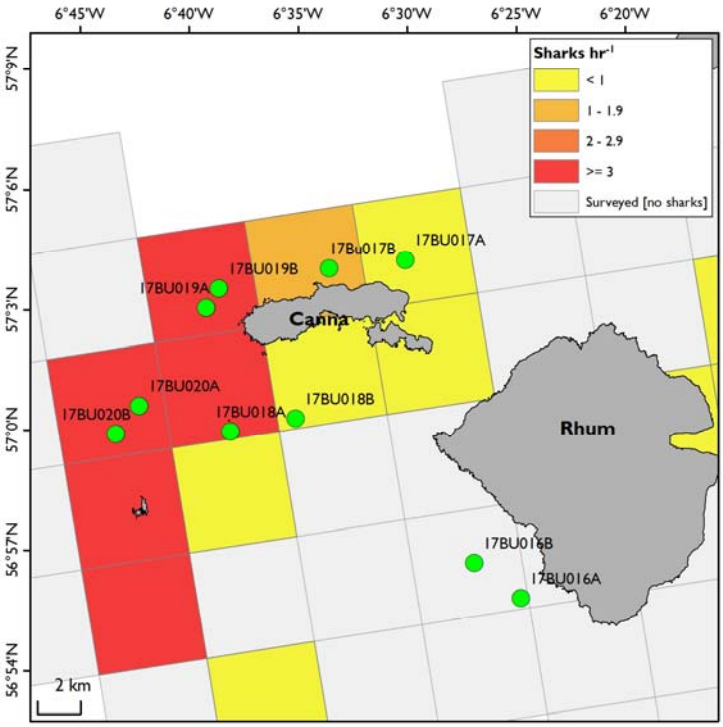
a)

b)

Figure A2: a) Tiree/Gunna Sound (samples 17BU010-012 & 014) & b) Firth of Forth (samples 17BU001-004) (prepared by Matthew Witt)



a)



b)

Figure A3: Shiant Islands (samples 17BU021-026) & Rhum/Canna Island (samples 17BU016-20) (prepared by Matthew Witt)

Annex 2: details of analytical methods employed

A 2.1 Manual separation of microplastics from manta net trawl samples

Each discrete time/location duplicate sample was resuspended in 3% saline prepared in MilliQ deionised water, left to thaw completely at room temperature and then observed under a combination of a large backlit magnifying lens and high powered dissecting microscope in order to identify visually all candidate microplastic pieces (fragments, fibres, films, beads, etc.). When identified, each microplastic item was manually separated from the sample using fine forceps and a dissecting needle and transferred to a pre-cleaned (acid-washed and solvent-rinsed) small glass petri dish (5cm diameter) for storage and onward analysis. Once all identifiable microplastics had been retrieved in this way from a sample, both the petri dish containing the candidate microplastics and the remaining resuspended sample (following transfer to a screw-cap glass Duran bottle) were returned to the freezer for storage and subsequent analysis.

A 2.2 Identification of microplastic fragments and fibres using FT-IR (diamond-ATR)

All of the candidate microplastic pieces retrieved from each discreet sample were subsequently subjected to analysis using a PerkinElmer Frontier Fourier-transform infrared (FT-IR) spectrometer. For those pieces that could be easily handled, FT-IR analysis was carried out using a universal diamond –ATR attachment, placing each fragment or fibre onto the diamond surface (after precleaning the surface with analytical grade ethanol) and applying a consistent force using the sample clamp. For microplastic pieces too small to analyse reliably in this way, FT-IR spectra were obtained instead using a PerkinElmer Spotlight 400 microscopy system linked to the same Frontier spectrometer, using a micro ('drop down')-ATR accessory to contact the sample.

In both cases, FT-IR spectra (near infrared) were obtained for each candidate microplastic piece by scanning in the wave number range between 4000 and 650 cm^{-1}, at a resolution of 4 cm^{-1}, and acquiring a minimum of 4 scans per item (up to a maximum of 16 scans per item for some micro-ATR analyses in order to obtain clearer spectra). All spectra obtained were processed using PerkinElmer's Spectrum software (version 10.5.4), enabling post-acquisition background subtraction and normalisation of the data and subsequent comparison against a number of commercially available spectral databases, including PerkinElmer's standard Polymers Library, as well as against a custom built database prepared in our own laboratory through analysis of a range of analytical standards of common plastics.

The PerkinElmer FT-IR spectrometer and microscopy system and all accessories and FT-IR spectral libraries used in this study were supplied by and purchased from PerkinElmer under a research partnership agreement with Greenpeace.

A 2.3 Qualitative and indicative screening of selection of manta trawl samples for presence of fragments and fibres in the <63 um size range

A subsample of the material remaining in the sample after manual removal of the microplastics down to 0.5 mm size range was homogenised in a heated sonic bath for two hours, sieved through 250 μm and 63 μm stainless steel meshes and then filtered onto a silver filter (pore size 5 μm), before being rinsed with filtered deionised water and pentane, dried and inspected under a high power dissecting microscope to identify candidate materials for micro-FT-IR analyses. For each sample, material captured in the 250 μm and 63 μm sieves was also inspected under a dissecting microscope to identify any larger candidate microplastics, though none were found.

For each sample, individual candidate materials (fibres and fragments) retained on the silver filters were examined using a PerkinElmer Spotlight 400 FT-IR Imaging System (MCT detector, KBr window) operating in reflectance mode and with a wavenumber resolution of 4 cm^{-1}. A total of 16 scans were collected for at least two sections of each candidate fibre or fragment, across a wavenumber range from 4000 to 750 cm^{-1}. The infrared spectra were acquired, processed and analysed using PerkinElmer

Spectrum software (version 10.5.4.738), with polymers being identified by automated matching combined with expert judgment against commercially available spectral libraries (including polymers, additives, solvents, etc.) and an additional custom spectral library prepared in our laboratory using a range of polymer standards and potential contaminating materials (e.g. tissues, gloves, laboratory coats). Only match qualities greater than 70% were accepted for identification purposes.

A 2.3 Forensic chemical analysis of microplastics (target and non-target screening)

A 2.3.1 Sample preparation

Following completion of FT-IR analysis, all composite microplastic samples were subjected to ultra-sound assisted extraction (USAE) to release organic chemical additives and contaminants. In brief, microplastic pieces, weighing from 0.02 to 104.05 mg, were introduced in pre-cleaned 2 mL glass vials with the help of forceps and spatula. Afterwards, 1 mL of methanol was added into each vial, which were capped and placed into a water bath thermostatically controlled at 40° C. Then, sonication was applied for 30 minutes, after what extracts were filtered through 0.45 µm pore size PES membranes and transferred to a pre-cleaned amber analytical vial. Extracts were immediately analysed by different instrumental techniques, GC-MS and LC-MS, and stored at -20° C for future further analysis.

Three procedural blank extracts were obtained after applying the whole protocol to empty vials.
Following methanol extraction, the remaining sample material were digested independently for ICP-MS metals analysis. For each sample, any residue methanol was evaporated at 30°C, the solid material weighed into a microwave digestion vessel, and concentrated nitric acid (1.0 ml, ultra purity grade) together with concentrated hydrochloric acid (0.1 ml, super purity grade) were added to each sample. For four samples there was not sufficient material to carry out analysis for metals/metalloids; 17BU004a and 17BU004B (Firth of Forth), 17BU015B (Eastern Small Isle), 17BU016B (South West Rhum).

Three blanks and two certified reference samples were prepared in an identical manner; EC681k, low density polyethylene, certified by the Institute for Reference Materials and Measurements (IRMM) and FLX-PVC2, trace elements in PVC, certified by FLUXANA GmbH & Co.KG, Germany.

The sealed vessels were heated using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 110°C over 10 minutes, held for 10 minutes, ramped to 170°C over 10 minutes, held for 10 minutes, ramped to 220°C over 10 minutes and held for 10 minutes . Cooled digests were filtered and made up to 10 ml with deionised water.

A 2.3.2 LC-Orbitrap-MS analysis

Pesticides screening

Microplastic sample extracts, pesticides standards and procedural blanks were analysed by liquid chromatography - mass spectrometry (LC-MS) with an Orbitrap Q Exactive Focus (Thermo Fisher Scientific). The LC instrument was a Dionex Ultimate 3000 and the high-resolution Orbitrap mass spectrometer was furnished with a HESI-II electrospray ionisation source (ESI), a quadrupole mass filter and an HCD collision cell. A total of 275 pesticides were screened in the samples (full list available in **Table S1** in **Annex 4**).

The next parameters were applied in the ESI source: sheath gas flow 40 a.u., auxiliary gas flow 10 a.u. and 350° C, spray voltage 3.3 V and capillary temperature 325° C. Samples were run twice, one in each polarity mode.

Pesticides were separated in an Accucore aQ C18 column (100 x 2.1 mm, 2.6 µm), provided by Thermo Fisher Scientific, at 25° C. The mobile phase consisted of a gradient mixture of two solutions: A, water containing 2% methanol, 0.1% formic acid and 5 mM ammonium formate and B, methanol containing

2% water, 0.1% formic acid and 5 mM ammonium formate. The gradient applied was: 0 - 0.5 min 2% B, 7 min 70% B, 9 - 12 min 100% B; at a flow of 300 µL min^{-1}.

The instrument acquired full-scan data at a resolution of 70,000 (FWHM at 200 Da) within the 80 – 1000 Da m/z range, with a maximum injection time of 200 ms, AGC target 1.0E6. Simultaneously, the system acquired 17,500 resolution data-dependent MS/MS (dd-MS^2) spectra from the precursor ions of the pesticides at a stepped collision energy of 15, 30 and 45 eV, with a maximum injection time of 100 ms, AGC target 5.0E4. The high resolution full-scan data combined with the dd-MS^2 spectra permitted the unambiguous identification of the pesticides.

The TraceFinder 4.1 software (Thermo fisher Scientific) was used to control the LC-Orbitrap-MS instrument and to process the results.

Antimicrobials and other veterinary drugs

Samples were screened for a group of 101 veterinary drugs, including antibiotics, following a protocol equivalent to the pesticides screening method. The complete list of targets can be seen in **Table S2** in the **Annex 4**.

Semi-target screening

An inventory of 75 substances of environmental interest, with chances of being present in the microplastic samples, was created. This list included emerging contaminants frequently found in water and other environmental matrices, such as alkyl-phenols, poly-fluoro alkyl carboxylic and sulfonic acids, phthalate esters and benzotriazoles, and pharmaceuticals and personal care product ingredients, among them hormones, biocides and antimycotic drugs. **Table S3** in **Annex** 4 shows the full list together with the theoretical masses of their pseudo-molecular ions.

The chromatographic separation of the compounds involved the same column and mobile phases used before with the following gradient: 0 - 0.5 min 2% B, 2 min 15% B, 20 - 30 min 100% B.
A first injection of all the extracts and blanks was done, acquiring full-scan high-resolution (70,000) data in the 100-1000 Da m/z range, with ionisation polarity switching. Then, chromatograms were searched for the ions contained in **Table S3** and an inclusion list was created with the masses and the retention times found. In a second injection, a dd-MS^2 experiment was conducted, using the inclusion list to trigger the MS/MS experiments, at a resolution of 17,500 and with stepped collision energy: 15, 30 and 45 eV.

The FreeStyle 1.3 software (Thermo fisher Scientific) was used for data visualization and database searching. The m/zCloud (www.mzcloud.org), MassBank (www.massbank.jp) and Metlin (metlin.scripps.edu) databases were employed to tentatively identify the substances.

A 2.3.3 GC/MS forensic organic screen analysis

For the total organic compounds screening, samples were analysed using an Agilent 6890 Series II GC with Restek Rxi-17Sil column (30m, 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5975B MSD operated in EI mode and interfaced with an Agilent Enhanced Chem Station data system. The GC oven temperature program employed was as follows: an initial temperature of 70^0C, held for 2 minutes, raised to 160^0C at 20^0C/min, then to 220^0C at 5^0C/min, held for 2 minutes, then to 300^0C at 15^0C/min, held for 8min, and finally raised to 330^0C at 50^0C/min, held for 26min. The carrier gas was helium, supplied initially at 1ml/min for 10 min and then raised to 5ml/min for the rest of the run. Extracts (5 ul) were injected automatically by means of an Agilent 6890 autosampler in pulsed splitless mode (pulse pressure 33 psig, pulse time 1 min). The MS was operating in both total (SCAN) and selective ion monitoring (SIM) modes simultaneously. Identification of compounds was carried out by matching spectra against both the Wiley 10 and Pesticides Libraries, using expert judgment as necessary in order to avoid misidentifications. Additionally, both the spectra and retention times of compounds isolated from the samples were matched against those obtained during GC-MS analysis of standard mixtures containing a range of chlorinated benzenes, chlorinated pesticides,

polybrominated diphenyl ethers (PBDEs), phthalates, polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons. The list of key target compounds and ions monitored in SIM mode are presented in **Table A4** in the **Annex**.

A 2.3.4 Metals/metalloids analysis using ICP-MS analysis

Prepared sample digests were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using an Agilent 7900 Spectrometer utilizing a collision cell with helium as the collision gas to minimize polyatomic interferences. Multi-element standards, matrix matched to the samples, at concentrations of 1, 10, 100 and 1000 μg/l respectively, other than for mercury (1, 2, 5, 20 μg/l respectively) were used for instrument calibration. Analysis employed in-line addition of an internal standard mix at 1000 μg/l (scandium, germanium, yttrium, indium, terbium and bismuth). Calibration of the ICP-MS was validated by the use of quality control standards at 80 μg/l and 800 μg/l (4 μg/l and 16 μg/l for mercury) prepared in an identical manner but from different reagent stocks to the instrument calibration standards.

Annex 3: detailed results from forensic screening analysis of microplastic samples for organic contaminants (LC-MS and GC-MS data combined). X indicates compounds identified using GC-MS forensic screening techniques. L indicates compounds identified using LC-MS targeted screening techniques. B indicates that the compounds was identified using both techniques

COMPOUND	CAS #	17BU003B	17BU004A	17BU004B	17BU005A	17BU005B	17BU006A	17BU007B	17BU009A	17BU011A	17BU011B	17BU012B	17BU013A	17BU014A	17BU014B	17BU015B	17BU016B	17BU017A	17BU017B	17BU018A	17BU018B	17BU019A	17BU020A	17BU020B	17BU022B	17BU023A	17BU023B	17BU024A	17BU024B	17BU025A	17BU026B
		Firth of Forth	Firth of Forth	Firth of Forth	Firth of Inverness	Firth of Inverness	Loch Ness	Loch Linnhe	South West Mull	Tiree/ Gunna	Tiree/ Gunna	Tiree/ Gunna	North West Mull	Tiree/ Gunna	Tiree/ Gunna	Easten Small Isle	South West Rhum	Canna Island	Canna Island	Canna Island	Canna Island	Canna Island	Canna Island	Canna Island	Shiant Isles	Shiant Isles	Shiant Isles	Shiant Isles	Shiant Isles	Shiant Isles	Shiant Isles
PHTHALATE ESTERS																															
Bis(2-ethylhexyl) phthalate	000117-81-7				B		L	L																							
Diethyl phthalate*	000084-66-2																												X		
Dimethyl phthalate	000131-11-3													X																	
Di-n-hexyl phthalate	000084-75-3				L									X															L		
Benzyl butyl phthalate	85-68-7																											L			
Dibutyl phthalate	84-74-2	L			X									L											L			L		L	L
Dipentyl phthalate	131-18-0				L		L					L																			
Diheptyl phthalate	3648-21-3	L																										L	L	L	L
Di-iso-nonyl phthalate*	028553-12-0																												X		
Dinonyl phthalate	84-76-4	L																											L		
Didecyl phthalate	84-77-5	L																											L		
Di(2-methoxyethyl) phthalate	117-82-8																		L												
CARBOXYLIC/FATTY ACIDS AND DERIVATIVES																															
13-Docosenoic acid, methyl ester	001120-34-9								X																						
2-Propenoic acid, tridecyl ester	003076-04-8																												X		
5,8,11,14,17-Eicosapentaenoic acid	002734-47-6								X			X																			
5,8,11,14,17-Eicosapentaenoic acid, methyl ester	001191-65-7										X																				
7,10,13,16,19-Docosapentaenoic acid, methyl ester	108698-02-8								X																						
7-Hexadecenoic acid, methyl ester	056875-67-3																														X
9,12-Octadecadienoic acid (Z,Z)-	000060-33-3											X															X				
9-cis-Hexadecenoic acid	000373-49-9	X									X	X											X				X				
9-cis-Hexadecenoic acid, methyl ester, (Z)-	001120-25-8										X								X	X	X		X								

COMPOUND	CAS #	17BU003B	17BU004A	17BU004B	17BU005A	17BU005B	17BU006A	17BU007B	17BU009A	17BU011A	17BU011B	17BU012B	17BU013A	17BU014A	17BU014B	17BU015B	17BU016B	17BU017A	17BU017B	17BU018A	17BU018B	17BU019A	17BU020A	17BU020B	17BU022B	17BU023A	17BU023B	17BU024A	17BU024B	17BU025A	17BU026B
		Firth of Forth	Firth of Forth	Firth of Forth	Firth of Inverness	Firth of Inverness	Loch Ness	Loch Linnhe	South West Mull	Tiree/ Gunna	Tiree/ Gunna	Tiree/ Gunna	North West Mull	Tiree/ Gunna	Tiree/ Gunna	Easten Small Isle	South West Rhum	Canna Island	Canna Island	Canna Island	Canna Island	Canna Island	Canna Island	Canna Island	Shiant Isles	Shiant Isles	Shiant Isles	Shiant Isles	Shiant Isles	Shiant Isles	Shiant Isles
9-Octadecenoic acid, methyl ester, (Z)-	000112-62-9									X																					
Benzoic acid	000065-85-0													X																	
Benzoic acid, 2-cyano-, or Phthalimide	003839-22-3 or 000085-41-6													X																	
Benzoic acid, dimethyl-	000000-00-0	X										X	X	X						X	X	X	X			X	X				
Decanoic acid	000334-48-5																						X								
Dodecanoic acid	000143-07-7											X														X	X		X		
Dodecanoic acid, methyl ester	000111-82-0																X														
Heptanoic acid	000111-14-8																						X								
Hexadecanoic acid	000057-10-3	X	X		X	X						X	X	X						X	X	X	X			X	X		X		X
Hexadecanoic acid, methyl ester	000112-39-0	X	X						X																						X
Hexanoic acid	000142-62-1					X																									
Hexanoic acid, 2-ethyl-, methyl ester	000816-19-3																X														
Nonanoic acid	000112-05-0																						X								X
Octadecanoic acid	000057-11-4	X	X	X								X							X	X			X			X	X		X		X
Octadecanoic acid, methyl ester	000112-61-8																									X					
Octanoic acid	000124-07-2																						X								
Oxiraneoctanoic acid, 3-octyl-, methyl ester	002500-59-6			X																											
Pentadecanoic acid	001002-84-2																									X					
Tetradecanoic acid	000544-63-8	X		X		X					X	X	X							X			X			X	X		X		X
Tetradecanoic acid, methyl ester	000124-10-7								X																						
LINEAR ALIPHATIC HYDROCARBONS																															
1-Decene	000872-05-9		X														X				X							X	X	X	X
1-Pentadecene	013360-61-7																										X				
1-Tetradecene	001120-36-1																										X				
Cyclodecane	000293-96-9				X																X						X				
Cyclododecane	000294-62-2	X		X																						X	X		X		
Cyclotetradecane	000295-17-0											X																			
Dodecane	000112-40-3																				X					X	X		X	X	X
Eicosene	074685-33-9																														X
Heptadecane	000629-78-7																							X						X	X
Octadecane	000593-45-3																X											X		X	

COMPOUND	CAS #	17BU003B	17BU004A	17BU004B	17BU005A	17BU005B	17BU006A	17BU007B	17BU009A	17BU011A	17BU011B	17BU012B	17BU013A	17BU014A	17BU014B	17BU015B	17BU016B	17BU017A	17BU017B	17BU018A	17BU018B	17BU019A	17BU020A	17BU020B	17BU022B	17BU023A	17BU023B	17BU024A	17BU024B	17BU025A	17BU026B
		Firth of Forth	Firth of Forth	Firth of Forth	Firth of Inverness	Firth of Inverness	Loch Ness	Loch Linnhe	South West Mull	Tiree/ Gunna	Tiree/ Gunna	Tiree/ Gunna	North West Mull	Tiree/ Gunna	Tiree/ Gunna	Easten Small Isle	South West Rhum	Canna Island	Canna Island	Canna Island	Canna Island	Canna Island	Canna Island	Canna Island	Shiant Isles	Shiant Isles	Shiant Isles	Shiant Isles	Shiant Isles	Shiant Isles	Shiant Isles
Pentadecane	000629-62-9																										X			X	X
Pentadecane, 2,6,10,14-tetramethyl-	001921-70-6	X							X				X										X			X	X				
Tetradecane	000629-59-4																														X
Tridecane	000629-50-5																										X			X	X
ORGANOSULPHUR COMPONDS																															
Dimethyl sulfone	000067-71-0					X																						X			
Dimethyl sulfoxide	000067-68-5					X						X	X														X		X		X
ORGANOPHOSPHORUS COMPOUNDS																															
Phosphine oxide, triphenyl-	000791-28-6				X																										
Phosphoric acid, triphenyl ester	000115-86-6																X														
Tris (2-chloroethyl) phosphate	115-96-8																											L			
PESTICIDES																															
Buprofezin														L																	
Chlorpyrifos-Ethyl			L		L		L	L				L																			
Flufenacet		L																													
Tebuconazole		L																													
BENZOTRIAZOLES UV STABILIZER																															
UV P	2440-22-4								L																			L	L	L	
UV 326	3896-11-5	L																		L						L					
POLY-CYCLICS MUSK																															
Galaxolidone	1222-05-5	L																										L	L	L	
POLY FLUORINATED COMPOUNDS																															
1H,1H,2H,2H-perfluorooctane sulfonic acid (PFOS)	27619-97-2																													L	
OTHERS																															
Hexamethylenetetramine	100-97-0		L																									L			
1,2-Dimethyl-4-(dimethoxymethyl)benzene	000000-00-0	X		X				X	X	X	X		X	X			X			X	X	X	X	X		X	X	X		X	X
1,19-Eicosadiene	014811-95-1								X	X			X																X		
1,21-Docosadiene	053057-53-7												X																		
1,3-Cyclooctadiene, (Z,Z)-	003806-59-5											X																			
1,3-Propanediol, 2,2-dimethyl-	000126-30-7				X												X														
1-Heptadecanol	001454-85-9																												X		
1-Hexadecanol	036653-82-4												X																X		

COMPOUND	CAS #	17BU003B	17BU004A	17BU004B	17BU005A	17BU005B	17BU006A	17BU007B	17BU009A	17BU011A	17BU011B	17BU012B	17BU013A	17BU014A	17BU014B	17BU015B	17BU016B	17BU017A	17BU017B	17BU018A	17BU018B	17BU019A	17BU020A	17BU020B	17BU022B	17BU023A	17BU023B	17BU024A	17BU024B	17BU025A	17BU026B
		Firth of Forth	Firth of Forth	Firth of Forth	Firth of Inverness	Firth of Inverness	Loch Ness	Loch Linnhe	South West Mull	Tiree/ Gunna	Tiree/ Gunna	Tiree/ Gunna	North West Mull	Tiree/ Gunna	Tiree/ Gunna	Easten Small Isle	South West Rhum	Canna Island	Canna Island	Canna Island	Canna Island	Canna Island	Canna Island	Canna Island	Shiant Isles	Shiant Isles	Shiant Isles	Shiant Isles	Shiant Isles	Shiant Isles	Shiant Isles
2,5-Hexanedione	000110-13-4					X													X		X										
2-Furan-carboxaldehyde	000098-01-1																									X					
Benzaldehyde, 3,5-dimethyl-	005779-95-3																												X		
Benzene, (dimethoxymethyl)-	001125-88-8													X			X														
Benzene, 1,4-bis(1,1-dimethylethyl)-	000064-16-3																				X										
Bicyclo[10.8.0]eicosane, cis-	000448-95-7								X																						
Cholesterol	000057-88-5																									X	X		X		X
Cyclohexanone	000108-94-1																										X				
Cyclopropane, nonyl-	074663-85-7																														X
Ethanone, 1-(1,3-dimethyl-1H-pyrazol-4-yl)-	052773-23-6													X		X															
Ethanone, 1-(2,4-dimethyl-furan-3-yl)-	032933-07-6																X					X									X
Methenamine	000100-97-0																				X										
Oxime-, methoxy-phenyl-	000000-00-0									X							X		X		X	X		X		X			X	X	
Phenanthrene*	000085-01-8													X																	
Phthalic anhydride	000085-44-9													X																	
Pyridine, 2,4,6-trimethyl-	000108-75-8												X																		
Spiro[5-fluorobenzo[5,6-b]furan-2,5-dione-3,1'-1',4'-dihydro-6'-methoxynaphthalene]	000000-00-0													X																	
Squalene	000111-02-4																									X					
Tinuvin (R) 292**	041556-26-7													X																	

Annex 4: supplementary information

Table S1. Pesticides screened in the samples, including retention time, formula adduct and monitored ions

Compound	Retention time (min)	Formula	Adduct	Ion (Da)
2,4-D	8.9	C8H6Cl2O3	M-H	218.9621
Acephate	2.91	C4H10NO3PS	M+H	184.0192
Acetamiprid	6.6	C10H11ClN4	M+H	223.0745
Acibenzolar-S-methyl	9.98	C8H6N2OS2	M+H	210.9994
Alachlor	11.06	C14H20ClNO2	M+H	270.1255
Aldicarb-sulfone	4.7	C7H14N2O4S	M+H	223.0747
Allethrin	10.97	C19H26O3	M+H	303.1955
Ametryn	8.39	C9H17N5S	M+H	228.1277
Aminocarb	3.94	C11H16N2O2	M+H	209.1285
Ancymidol	8.11	C15H16N2O2	M+H	257.1285
Anilofos	10.34	C13H19ClNO3PS2	M+H	368.0305
Aramite	10.96	C15H23ClO4S	M+NH4	352.1344
Atrazine	8.8	C8H14ClN5	M+H	216.1011
Avermectin B1a	11.41	C48H72O14	M+Na	895.4814
Azaconazole	9.12	C12H11Cl2N3O2	M+H	300.0301
Azamethiphos	7.78	C9H10ClN2O5PS	M+H	324.9809
Azinphos-ethyl	10.02	C12H16N3O3PS2	M+H	346.0444
Azinphos-methyl	9.34	C10H12N3O3PS2	M+H	318.0131
Azoxystrobin	9.37	C22H17N3O5	M+H	404.1241
Bendiocarb	7.99	C11H13NO4	M+H	224.0917
Benodanil	8.79	C13H10INO	M+H	323.988
Benoxacor	9.29	C11H11Cl2NO2	M+H	260.024
Bensulfuron-methyl	9.3	C16H18N4O7S	M+H	411.0969
Bentazone	8.13	C10H12N2O3S	M-H	239.0496
Benzoximate	10.51	C18H18ClNO5	M+H	364.0946
Benzoylprop-ethyl	10.4	C18H17Cl2NO3	M+H	366.0658
Bifenazate	9.86	C17H20N2O3	M+H	301.1547
Bitertanol	10.47	C20H23N3O2	M+H	338.1863
Boscalid	9.6	C18H12Cl2N2O	M+H	343.0399
Brodifacoum	11.71	C31H23BrO3	M+H	523.0903
Bromacil	7.94	C9H13BrN2O2	M+H	261.0233
Bromoxynil	8.82	C7H3Br2NO	M-H	273.8509
Bromuconazole	9.85	C13H12BrCl2N3O	M+H	375.9614
Bupirimate	9.74	C13H24N4O3S	M+H	317.1642
Buprofezin	10.83	C16H23N3OS	M+H	306.1635
Butachlor	11	C17H26ClNO2	M+H	312.1725
Butafenacil	9.85	C20H18ClF3N2O6	M+NH4	492.1144
Butocarboxim-sulfoxide	4.12	C7H14N2O3S	M+H	207.0798
Butoxycarboxim	4.6	C7H14N2O4S	M+H	223.0747
Carbaryl	8.38	C12H11NO2	M-C2H2NO	145.0648
Carbendazim	5.23	C9H9N3O2	M+H	192.0768
Carbetamide	7.62	C12H16N2O3	M+H	237.1234
Carbofuran	7.94	C12H15NO3	M+H	222.1125

Carbofuran,3OH-	6.35	C12H15NO4	M+H	238.1074
Carfentrazone-ethyl	10.21	C15H14Cl2F3N3O3	M+H	412.0437
Carpropamid	10.41	C15H18Cl3NO	M+H	334.0527
Chlorantraniliprole	9.14	C18H14BrCl2N5O2	M+H	481.9781
Chlorbromuron	9.73	C9H10BrClN2O2	M+H	292.9687
Chlorfenvinphos	10.35	C12H14Cl3O4P	M+H	358.9768
Chlorfluazuron	11.3	C20H9Cl3F5N3O3	M+H	539.9702
Chloridazon	6.5	C10H8ClN3O	M+H	222.0429
Chlormequat	0.82	C5H12ClN	M-Cl	122.0731
Chloroxuron	9.93	C15H15ClN2O2	M+H	291.0895
Chlorpyrifos-Ethyl	11.16	C9H11Cl3NO3PS	M+H	349.9336
Chlortoluron	8.75	C10H13ClN2O	M+H	213.0789
Cinosulfuron	7.79	C15H19N5O7S	M+H	414.1078
Clethodim	10.76	C17H26ClNO3S	M+H	360.1395
Clomazone	9.28	C12H14ClNO2	M+H	240.0786
Clothianidin	6.13	C6H8ClN5O2S	M+H	250.016
Coumaphos	10.47	C14H16ClO5PS	M+H	363.0217
Crotoxyphos	9.55	C14H19O6P	M+NH4	332.1258
Cumyluron	9.84	C17H19ClN2O	M+H	303.1259
Cyanazine	7.69	C9H13ClN6	M+H	241.0963
Cyazofamid	10.11	C13H13ClN4O2S	M+H	325.0521
Cycloate	10.69	C11H21NOS	M+H	216.1417
Cycluron	9.04	C11H22N2O	M+H	199.1805
Cyflufenamid	10.45	C20H17F5N2O2	M+H	413.1283
Cyromazine	2.07	C6H10N6	M+H	167.104
Demeton-S-Methyl-Sulfone	5.27	C6H15O5PS2	M+H	263.0171
Desmedipham	9.13	C16H16N2O4	M+NH4	318.1449
Desmethyl-pirimicarb	5.5	C10H16N4O2	M+H	225.1346
Desmetryn	7.7	C8H15N5S	M+H	214.1121
Diclobutrazol	10.24	C15H19Cl2N3O	M+H	328.0978
Dicrotophos	5.81	C8H16NO5P	M+H	238.0839
Diethofencarb	9.31	C14H21NO4	M+H	268.1543
Difenacoum	11.39	C31H24O3	M+H	445.1798
Difenoconazole	10.64	C19H17Cl2N3O3	M+H	406.072
Diflubenzuron	10.23	C14H9ClF2N2O2	M+H	311.0393
Dimefuron	9.17	C15H19ClN4O3	M+H	339.1218
Dimethametryn	9.8	C11H21N5S	M+H	256.159
Dimethenamid	9.48	C12H18ClNO2S	M+H	276.082
Dimethoate	6.39	C5H12NO3PS2	M+H	230.0069
Dimethomorph	9.55	C21H22ClNO4	M+H	388.131
Dimoxystrobin	10.21	C19H22N2O3	M+H	327.1703
Diniconazole	10.63	C15H17Cl2N3O	M+H	326.0821
Dinotefuran	4.41	C7H14N4O3	M+H	203.1139
Dithiopyr	10.73	C15H16F5NO2S2	M+H	402.0615
Diuron	9.14	C9H10Cl2N2O	M+H	233.0243
DNOC	8.84	C7H6N2O5	M-H	197.0204
Dodemorph	9.12	C18H35NO	M+H	282.2791
Epoxiconazole	10.04	C17H13ClFN3O	M+H	330.0804

Esprocarb	10.92	C15H23NOS	M+H	266.1573
Etaconazol	10.06	C14H15Cl2N3O2	M+H	328.0614
Ethiofencarb	8.42	C11H15NO2S	M+H	226.0896
Ethiofencarb sulfone	5.83	C11H15NO4S	M+H	258.0795
Ethiofencarb sulfoxide	5.95	C11H15NO3S	M+H	242.0845
Ethiprole	9.51	C13H9Cl2F3N4OS	M+H	396.9899
Ethirimol	6.95	C11H19N3O	M+H	210.1601
Ethofumesate	9.42	C13H18O5S	M+H	287.0948
Ethoxyquin	8.37	C14H19NO	M+H	218.1539
Etofenprox	11.78	C25H28O3	M+NH4	394.2377
Etoxazole	11.18	C21H23F2NO2	M+H	360.177
Etrimfos	10.34	C10H17N2O4PS	M+H	293.0719
Fenamidone	9.47	C17H17N3OS	M+H	312.1165
Fenamiphos	10.12	C13H22NO3PS	M+H	304.1131
Fenarimol	9.94	C17H12Cl2N2O	M+H	331.0399
Fenazaquin	11.71	C20H22N2O	M+H	307.1805
Fenbuconazole	10.1	C19H17ClN4	M+H	337.1215
Fenhexamid	9.86	C14H17Cl2NO2	M+H	302.0709
Fenobucarb	9.34	C12H17NO2	M+H	208.1332
Fenoxanil	10.13	C15H18Cl2N2O2	M+H	329.0818
Fenoxycarb	10.19	C17H19NO4	M+H	302.1387
Fenpyroximate	11.32	C24H27N3O4	M+H	422.2074
Fensulfothion	8.95	C11H17O4PS2	M+H	309.0379
Fenthion	10.44	C10H15O3PS2	M+H	279.0273
Fenthion-sulfoxide	8.33	C10H15O4PS2	M+H	295.0222
Fenuron	6.2	C9H12N2O	M+H	165.1022
Flazasulfuron	9.26	C13H12F3N5O5S	M+H	408.0584
Florasulam	7.22	C12H8F3N5O3S	M+H	360.0373
Fluazifop	9.52	C15H12F3NO4	M+H	328.0791
Fluazinam	10.94	C13H4Cl2F6N4O4	M-H	462.9441
Flubendiamide	10.17	C23H22F7IN2O4S	M-H	681.016
Flufenacet	9.96	C14H13F4N3O2S	M+H	364.0737
Flufenoxuron	11.15	C21H11ClF6N2O3	M+H	489.0435
Flumetsulam	6.32	C12H9F2N5O2S	M+H	326.0518
Fluometuron	8.6	C10H11F3N2O	M+H	233.0896
Fluopicolide	9.67	C14H8Cl3F3N2O	M+H	382.9727
Fluopyram	9.86	C16H11ClF6N2O	M+H	397.0537
Fluoxastrobin	9.86	C21H16ClFN4O5	M+H	459.0866
Fluquinconazole	9.92	C16H8Cl2FN5O	M+H	376.0163
Flurochloridone	9.87	C12H10Cl2F3NO	M+H	312.0164
Flusilazole	10.16	C16H15F2N3Si	M+H	316.1076
Flutriafol	8.78	C16H13F2N3O	M+H	302.11
Forchlorfenuron	9.11	C12H10ClN3O	M+H	248.0585
Formetanate	4.08	C11H15N3O2	M+H	222.1237
Formothion	7.59	C6H12NO4PS2	M+H	258.0018
Fosthiazate	8.5	C9H18NO3PS2	M+H	284.0539
Fuberidazole	6.13	C11H8N2O	M+H	185.0709
Furathiocarb	10.83	C18H26N2O5S	M+H	383.1635

Griseofulvin	8.81	C17H17ClO6	M+H	353.0786
Halofenozide	9.52	C18H19ClN2O2	M+H	331.1208
Haloxyfop	10.22	C15H11ClF3NO4	M+H	362.0402
Haloxyfop-methyl	10.6	C16H13ClF3NO4	M+H	376.0558
Heptenophos	9.04	C9H12ClO4P	M+H	251.0235
Hexaconazole	10.46	C14H17Cl2N3O	M+H	314.0821
Hexaflumuron	10.72	C16H8Cl2F6N2O3	M-H	458.9743
Hexazinone	8.01	C12H20N4O2	M+H	253.1659
Hexythiazox	11.12	C17H21ClN2O2S	M+H	353.1085
Imazalil	8.75	C14H14Cl2N2O	M+H	297.0556
Imazaquin	8.07	C17H17N3O3	M+H	312.1343
Imazethapyr	7.54	C15H19N3O3	M+H	290.1499
Imibenconazole	10.99	C17H13Cl3N4S	M+H	410.9999
Imidacloprid	6.1	C9H10ClN5O2	M+H	256.0596
Indoxacarb	10.6	C22H17ClF3N3O7	M+H	528.078
Ioxynil	9.32	C7H3I2NO	M-H	369.8231
Iprovalicarb	9.86	C18H28N2O3	M+H	321.2173
Isocarbophos	8.97	C11H16NO4PS	M-C3H8N	230.9875
Isoprocarb	8.75	C11H15NO2	M+H	194.1176
Isoprothiolane	9.69	C12H18O4S2	M+H	291.0719
Isoproturon	8.94	C12H18N2O	M+H	207.1492
Isoxaben	9.6	C18H24N2O4	M+H	333.1809
Isoxadifen-ethyl	10.24	C18H17NO3	M+H	296.1281
Kresoxim-methyl	10.24	C18H19NO4	M+H	314.1387
Lenacil	8.83	C13H18N2O2	M+H	235.1441
Malaoxon (Malathion-oxon)	8.05	C10H19O7PS	M+H	315.0662
Mandipropamid	9.59	C23H22ClNO4	M+H	412.131
MCPA	9.1	C9H9ClO3	M-H	199.0168
Mefenacet	9.84	C16H14N2O2S	M+H	299.0849
Mepiquat	0.86	C7H15N	M+H	114.1277
Mepronil	9.72	C17H19NO2	M+H	270.1489
Metamitron	6.33	C10H10N4O	M+H	203.0927
Metazachlor	8.81	C14H16ClN3O	M+H	278.1055
Metconazole	10.47	C17H22ClN3O	M+H	320.1524
Methabenzthiazuron	9.03	C10H11N3OS	M+H	222.0696
Methamidophos	1.7	C2H8NO2PS	M+H	142.0086
Methiocarb	9.52	C11H15NO2S	M+H	226.0896
Methiocarb-sulfone	6.73	C11H15NO4S	M+H	258.0795
Methiocarb-sulfoxide	6.28	C11H15NO3S	M+H	242.0845
Methomyl	4.99	C5H10N2O2S	M+H	163.0536
Methoprotryne	8.63	C11H21N5OS	M+H	272.154
Methoxyfenozide	9.74	C22H28N2O3	M+H	369.2173
Metobromuron	8.85	C9H11BrN2O2	M+H	259.0077
Metolachlor	10.04	C15H22ClNO2	M+H	284.1412
Metolcarb	7.59	C9H11NO2	M+H	166.0863
Metosulam	8.24	C14H13Cl2N5O4S	M+H	418.0138
Metoxuron	7.4	C10H13ClN2O2	M+H	229.0738
Metrafenone	10.58	C19H21BrO5	M+H	409.0645

Metsulfuron-methyl	8.14	C14H15N5O6S	M+H	382.0816
Mevinphos	7	C7H13O6P	M+H	225.0523
Mexacarbate	5.18	C12H18N2O2	M+H	223.1441
Monocrotophos	5.55	C7H14NO5P	M+H	224.0682
Monolinuron	8.6	C9H11ClN2O2	M+H	215.0582
Napropamide	10.02	C17H21NO2	M+H	272.1645
Neburon	10.28	C12H16Cl2N2O	M+H	275.0713
Nicosulfuron	8.01	C15H18N6O6S	M+H	411.1081
Nuarimol	9.45	C17H12ClFN2O	M+H	315.0695
Ofurace	8.04	C14H16ClNO3	M+H	282.0892
Omethoate	3.82	C5H12NO4PS	M+H	214.0297
Oxadixyl	7.51	C14H18N2O4	M+H	279.134
Oxamyl	4.82	C7H13N3O3S	M+NH4	237.1016
Paclobutrazol	9.64	C15H20ClN3O	M+H	294.1368
Penconazole	10.33	C13H15Cl2N3	M+H	284.0716
Pencycuron	10.59	C19H21ClN2O	M+H	329.1415
Phenmedipham	9.2	C16H16N2O4	M+H	301.1183
Phenthoate	10.24	C12H17O4PS2	M+H	321.0379
Phoxim	10.51	C12H15N2O3PS	M+H	299.0614
Picoxystrobin	10.16	C18H16F3NO4	M+H	368.1104
Piperonyl-butoxide	10.96	C19H30O5	M+NH4	356.2432
Piperophos	10.65	C14H28NO3PS2	M+H	354.1321
Pirimicarb	6.57	C11H18N4O2	M+H	239.1503
Pirimiphos-methyl	10.43	C11H20N3O3PS	M+H	306.1036
Primisulfuron-methyl	9.79	C15H12F4N4O7S	M+H	469.0436
Prochloraz	10.42	C15H16Cl3N3O2	M+H	376.0381
Profenofos	10.85	C11H15BrClO3PS	M+H	372.9424
Promecarb	9.59	C12H17NO2	M+H	208.1332
Prometon	8.09	C10H19N5O	M+H	226.1662
Prometryn	9.34	C10H19N5S	M+H	242.1434
Propamocarb	3.99	C9H20N2O2	M+H	189.1598
Propazine	9.38	C9H16ClN5	M+H	230.1167
Propetamphos	9.79	C10H20NO4PS	M+H	282.0923
Propiconazole	10.42	C15H17Cl2N3O2	M+H	342.0771
Propoxur	7.89	C11H15NO3	M+H	210.1125
Propyzamide	9.75	C12H11Cl2NO	M+H	256.0291
Prosulfocarb	10.79	C14H21NOS	M+H	252.1417
Pymetrozine	3.96	C10H11N5O	M+H	218.1036
Pyraclostrobin	10.49	C19H18ClN3O4	M+H	388.1059
Pyrimethanil	9.11	C12H13N3	M+H	200.1182
Pyroxsulam	8.04	C14H13F3N6O5S	M+H	435.0693
Quinoxyfen	11.25	C15H8Cl2FNO	M+H	308.004
Quizalofop P	10.19	C17H13ClN2O4	M+H	345.0637
Quizalofop-ethyl	10.87	C19H17ClN2O4	M+H	373.095
Resmethrin	11.51	C22H26O3	M+H	339.1955
Rimsulfuron	8.55	C14H17N5O7S2	M+H	432.0642
Rotenone	10.16	C23H22O6	M+H	395.1489
Schradan	6.72	C8H24N4O3P2	M+H	287.1396

Sethoxydim	10.91	C17H29NO3S	M+H	328.1941
Simeconazole	9.95	C14H20FN3OSi	M+H	294.1432
Simetryn	7.86	C8H15N5S	M+H	214.1121
Spinosad A	10.47	C41H65NO10	M+H	732.4681
Spinosad D	10.66	C42H67NO10	M+H	746.4838
Spiromesifen	11.14	C23H30O4	M+H	371.2217
Spirotetramat	9.85	C21H27NO5	M+H	374.1962
Spiroxamine	9.65	C18H35NO2	M+H	298.2741
Sulfotep	10.3	C8H20O5P2S2	M+H	323.03
Sulprofos	11.18	C12H19O2PS3	M+H	323.0358
Tebuconazole	10.31	C16H22ClN3O	M+H	308.1524
Tebufenozide	10.16	C22H28N2O2	M+H	353.2224
Tebufenpyrad	10.87	C18H24ClN3O	M+H	334.1681
Tebuthiuron	8.09	C9H16N4OS	M+H	229.1118
Teflubenzuron	11.09	C14H6Cl2F4N2O2	M+H	380.9815
Tepraloxydim	9.89	C17H24ClNO4	M-H	340.1322
Terbumeton	8.16	C10H19N5O	M+H	226.1662
Terbuthylazine	9.62	C9H16ClN5	M+H	230.1167
Terbutryn	9.35	C10H19N5S	M+H	242.1434
Tetraconazole	9.99	C13H11Cl2F4N3O	M+H	372.0288
Tetramethrin	10.87	C19H25NO4	M+H	332.1856
Thiabendazole	5.91	C10H7N3S	M+H	202.0433
Thiacloprid	7.13	C10H9ClN4S	M+H	253.0309
Thiamethoxam	5.38	C8H10ClN5O3S	M+H	292.0266
Thidiazuron	8.17	C9H8N4OS	M+H	221.0492
Thiobencarb	10.6	C12H16ClNOS	M+H	258.0714
Thiophanate-methyl	7.91	C12H14N4O4S2	M+H	343.0529
Tolfenpyrad	10.96	C21H22ClN3O2	M+H	384.1473
Tralkoxydim	11.12	C20H27NO3	M+H	330.2064
Triadimefon	9.76	C14H16ClN3O2	M+H	294.1004
Triadimenol	9.84	C14H18ClN3O2	M+H	296.116
Triazophos	9.89	C12H16N3O3PS	M+H	314.0723
Trichlorfon	6.14	C4H8Cl3O4P	M+H	256.9299
Tricyclazole	7.48	C9H7N3S	M+H	190.0433
Tridemorph	10.38	C19H39NO	M+H	298.3104
Trietazine	10	C9H16ClN5	M+H	230.1167
Trifloxystrobin	10.61	C20H19F3N2O4	M+H	409.137
Triflumizole	10.75	C15H15ClF3N3O	M+H	346.0929
Vamidothion	6.35	C8H18NO4PS2	M+H	288.0488
Zoxamide	10.45	C14H16Cl3NO2	M+H	336.0319

Table S2. Antimicrobials and other veterinary drugs screened in the samples, including retention time, formula adduct and monitored ions

Compound	Retention time (min)	Formula	Adduct	m/z
2-NP-AOZ	6.64	C10H9N3O4	[M+H]+	236.0666
Furaltadone	4.02	C13H16N4O6	[M+H]+	325.1143
Furazolidone	5.35	C8H7N3O5	[M+H]+	226.0458
Nitrofurantoin	5.27	C8H6N4O5	[M+H]+	239.0411
Nitrofurazone	5.21, 5.36	C6H6N4O4	[M+H]+	199.0462
Chlortetracycline	6.29, 6.75	C22H23ClN2O8	[M+H]+	479.1216
Doxycycline	7.63	C22H24N2O8	[M+H]+	445.1605
Minocycline	5.15, 5.4	C23H27N3O7	[M+H]+	458.1922
Oxytetracycline	5.74	C22H24N2O9	[M+H]+	461.1555
Tetracycline	5.24, 5.68	C22H24N2O8	[M+H]+	445.1605
Ciprofloxacin	6.06	C17H18FN3O3	[M+H]+	332.1405
Danofloxacin	6.13	C19H20FN3O3	[M+H]+	358.1561
Difloxacin	6.29	C21H19F2N3O3	[M+H]+	400.1467
Enoxacin	5.8	C15H17FN4O3	[M+H]+	321.1357
Enrofloxacin	6.1	C19H22FN3O3	[M+H]+	360.1718
Flumequine	8.48	C14H12FNO3	[M+H]+	262.0874
Lomefloxacin	6.15	C17H19F2N3O3	[M+H]+	352.1467
Marbofloxacin	5.54	C17H19FN4O4	[M+H]+	363.1463
Nalidixic acid	8.16	C12H12N2O3	[M+H]+	233.0921
Ofloxacin	5.79	C18H20FN3O4	[M+H]+	362.1511
Orbifloxacin	6.17	C19H20F3N3O3	[M+H]+	396.153
Pipemidic acid	5.38	C14H17N5O3	[M+H]+	304.1404
Sarafloxacin	6.41	C20H17F2N3O3	[M+H]+	386.1311
Sulfabenzamide	6.41	C13H12N2O3S	[M+H]+	277.0641
Sulfadimethoxine	6.97	C12H14N4O4S	[M+H]+	311.0809
Sulfadoxine	6.05	C12H14N4O4S	[M+H]+	311.0809
Sulfamethoxypyridazine	5.58	C11H12N4O3S	[M+H]+	281.0703
Sulfanilamide	1.32	C6H8N2O2S	[M+H]+	173.0379
Sulfaphenazole	6.71	C15H14N4O2S	[M+H]+	315.091
Sulfaquinoxaline	7.2	C14H12N4O2S	[M+H]+	301.0754
Amoxicillin	5.75	C16H19N3O5S	[M+H]+	366.1118
Ampicillin	6	C16H19N3O4S	[M+H]+	350.1169
Cloxacillin	8.86	C19H18ClN3O5S	[M+H]+	436.0728
Dicloxacillin	9.19	C19H17Cl2N3O5S	[M+H]+	470.0339
Nafcillin	9.22	C21H22N2O5S	[M+H]+	415.1322
Oxacillin	8.68	C19H19N3O5S	[M+H]+	402.1118
Penicillin G	8.15	C16H18N2O4S	[M+H]+	335.106
Penicillin V	8.68	C16H18N2O5S	[M+H]+	351.1009
Maduramicin	11.85	C47H83NO17	[M+H]+	934.5734
Monensin	11.67	C36H62O11	[M+NH4]+	688.463
Salinomycin	11.93	C42H70O11	[M+NH4]+	768.5256
Aminophenazone	4.38	C13H17N3O	[M+H]+	232.1444
Carprofen	10.26	C15H12ClNO2	[M-H]-	272.0484
Diclofenac	10.28	C14H11Cl2NO2	[M+H]+	296.024
Etodolac	10.19	C17H21NO3	[M+H]+	288.1594

Flunixin	9.86	C14H11F3N2O2	[M+H]+	297.0845
Ibuprofen	10.39	C13H18O2	[M+NH4]+	224.1646
Ketoprofen	9.22	C16H14O3	[M+H]+	255.1016
Meloxicam	9.32	C14H13N3O4S2	[M+H]+	352.042
Naproxen	9.46	C14H14O3	[M+H]+	231.1016
Paracetamol	3.97	C8H9NO2	[M+H]+	152.0706
Phenylbutazone	9.91	C19H20N2O2	[M+H]+	309.1598
Tolfenamic acid	10.99	C14H12ClNO2	[M+H]+	262.0629
Sulfacetamide	3.12	C8H10N2O3S	[M+H]+	215.0485
Sulfameter	5.33	C11H12N4O3S	[M+H]+	281.0703
Sulfamethizole	5.4	C9H10N4O2S2	[M+H]+	271.0318
Sulfanitran	8.23	C14H13N3O5S	[M-H]-	334.0503
Sulfapyridine	4.62	C11H11N3O2S	[M+H]+	250.0645
Sulfathiazole	4.57	C9H9N3O2S2	[M+H]+	256.0209
Flubendazole	8.81	C16H12FN3O3	[M+H]+	314.0932
Mebendazole	8.54	C16H13N3O3	[M+H]+	296.103
Albendazole	8.68	C12H15N3O2S	[M+H]+	266.0958
Dimetridazole	4.57	C5H7N3O2	[M+H]+	142.0611
Ipronidazole	5.55	C7H11N3O2	[M+H]+	170.0924
Metronidazole	3.68	C6H9N3O3	[M+H]+	172.0717
Oxibendazole	7.61	C12H15N3O3	[M+H]+	250.1186
Ronidazole	4.03	C6H8N4O4	[M+H]+	201.0618
Thiabendazole	5.71	C10H7N3S	[M+H]+	202.0433
Tinidazole	4.88	C8H13N3O4S	[M+H]+	248.07
Triclabendazole	10.75	C14H9Cl3N2OS	[M+H]+	358.9574
Cinoxacin	7.1	C12H10N2O5	[M+H]+	263.0662
Norfloxacin	5.94	C16H18FN3O3	[M+H]+	320.1405
Oxolinic acid	7.44	C13H11NO5	[M+H]+	262.071
Clarithromycin	9.46	C38H69NO13	[M+H]+	748.4842
Erythromycin	8.77	C37H67NO13	[M+H]+	734.4685
Josamycin	9.4	C42H69NO15	[M+H]+	828.474
Oleandomycin	8.09	C35H61NO12	[M+H]+	688.4267
Spiramycin	6.95	C43H74N2O14	[M+2H]2+	422.2643
Tilmicosin	7.7	C46H80N2O13	[M+2H]2+	435.2903
Tylosin	8.61	C46H77NO17	[M+H]+	916.5264
Beclomethasone dipropionate	10.65	C28H37ClO7	[M+H]+	521.2301
Betamethasone dipropionate	10.48	C28H37FO7	[M+H]+	505.2596
Dexamethasone	8.98	C22H29FO5	[M+H]+	393.2072
Fludrocortisone acetate	9.12	C23H31FO6	[M+H]+	423.2177
Flumethasone	8.85	C22H28F2O5	[M+H]+	411.1978
Hydrocortisone	8.49	C21H30O5	[M+H]+	363.2166
Methylprednisolone	9.07	C22H30O5	[M+H]+	375.2166
Mometasone furoate	10.22	C27H30Cl2O6	[M+H]+	521.1492
Prednicarbate	10.27	C27H36O8	[M+H]+	489.2483
Prednisolone	8.48	C21H28O5	[M+H]+	361.201
Triamcinolone	7.59	C21H27FO6	[M+H]+	395.1864
Triamcinolone acetonide	9.13	C24H31FO6	[M+H]+	435.2177
Sulfachloropyridazine	5.78	C10H9ClN4O2S	[M+H]+	285.0208

Sulfadiazine	4.15	C10H10N4O2S	[M+H]+	251.0597
Sulfaguanidine	1.17	C7H10N4O2S	[M+H]+	215.0597
Sulfamerazine	4.84	C11H12N4O2S	[M+H]+	265.0754
Sulfamethazine	5.32	C12H14N4O2S	[M+H]+	279.091
Sulfamethoxazol	5.89	C10H11N3O3S	[M+H]+	254.0594
Sulfamonomethoxine	6	C11H12N4O3S	[M+H]+	281.0703
Sulfisoxazole	6.15	C11H13N3O3S	[M+H]+	268.075

Table S3. Active substances included in the semi-target screening, classified by families and including the monitored [M+H]+ and [M-H]- ions in Da

Group	Substance	[M-H]-	[M+H]+
Alkyl-phenols	Bisphenol A	227.1078	
	Bisphenol B	241.1234	
	Bisphenol AP	289.1234	
	Bisphenol S		251.0368
	Bisphenol F		201.0910
	4-n-Nonylphenol	219.1754	
	4-n-octylphenol	205.1598	
	4-t-octylphenol	205.1598	
Poly-fluoroalkyls	Trifluoroacetic acid	112.9856	
	Perfluoro butanoic acid	212.9792	
	Perfluoro pentanoic acid	262.9760	
	Perfluoro hexanoic acid	312.9728	
	Perfluoro heptanoic acid	362.9696	
	Perfluoro octanoic acid	412.9664	
	Perfluoro nonanoic acid	462.9632	
	Perfluoro decanoic acid	512.9600	
	Perfluoro undecanoic acid	562.9714	
	Perfluoro dodecanoic acid	612.9536	
	Perfluoro tridecanoic acid	662.9504	
	Perfluoro tetradecanoic acid	712.9472	
	Perfluoro hexadecanoic acid	812.9409	
	Perfluoro octadecanoic acid	912.9345	
	Trifluoro methane sulfonic acid	148.9526	
	Perfluoro butane sulfonic acid	298.9430	
	Perfluoro hexane sulfonic acid	398.9366	
	Perfluoro heptane sulfonic acid	448.9334	
	Perfluoro octane sulfonic acid	498.9302	
	Perfluoro decane sulfonic acid	598.9238	
	7H-Perfluoro heptanoic acid	344.9790	
	2H,2H-Perfluoro decane acid	476.9789	
	2H,2H,3H,3H-Perfluoro undecanoic acid	490.9945	
	Perfluoro-3H-4,8-dioxa nonanoic acid	476.9625	
	Perfluoro-3,7-dimethyl octanoic acid	512.9600	
	1H,1H,2H,2H Perfluoro octane sulfonic acid	426.9679	
	1H,1H,2H,2H-Perfluoro decane sulfonic acid	526.9615	
	Perfluoro octane sulfonamide	497.9462	
Phtalate esters	Benzyl butyl phthalate		313.1434
	Di(2-ethylhexyl) phthalate		391.2843
	Di(2-methoxyethyl) phthalate		283.1176
	Tri(2- chloroethyl)phosphate		284.9612
	Dibutyl phthalate		279.1591
	Dipentyl phthalate		307.1904
	Dihexyl phthalate		335.2217
	Diheptyl phthalate		363.2530
	Dioctyl phthalate		391.2843
	Dinonyl phthalate		419.3160

	Didecyl phthalate		447.3470
Benzotriazoles	Benzotriazol		120.0556
	4-Toliltriazol		134.0713
	5-Toliltriazol		134.0713
	5,6-dimetilbenzotriazol		148.0869
	5-clorobenzotriazol		154.0167
Benzotriazole UV stabilizers	UV P		226.0975
	UV 326		316.1211
	UV 327		358.1681
Hormones	Estrone	269.1548	271.1693
	Estradiol	271.1705	273.1849
	Ethynylestradiol		319.1669
Biocides	Triclosan	286.9439	
	Triclocarban	312.9297	314.9853
	Dichlorocarbanilide	279.0086	
	Bis(tributyltin) oxide		291.1129
Antimycotic drugs	Fluconazole		307.1113
	Etaconazole		328.0614
	Ketoconazole		531.1560
	Clotrimazole		277.0788
	Econazole		383.0293
	Miconazole		416.9904
Other pharmaceuticals	Terbinafine		292.2060
	Climbazole		293.1108
	Amitryptiline		278.1909
	Sertraline		306.0811
	Amiodarone		646.0310
	N-Desethylamiodarone		617.9997

Table S4. The list of key target compounds and ions monitored in SIM mode during GC/MS organoscreen analysis

#	Ret Time, min	Compound Name	Ions monitored	Group #
1	4.778	Benzene, 1,3-dichloro-	146, 148, 111	1
2	4.952	Benzene, 1,4-dichloro-	146, 148, 111	
3	5.246	Benzene, chloromethyl-	91, 125.9, 127.9	
4	5.288	Benzene, 1,2-dichloro-	146, 148, 111	
5	5.374	Ethane, hexachloro-	117, 119, 201	2
6	6.054	Benzene, 1,3,5-trichloro-	180, 182, 184	3
7	6.540	Butadiene, hexachloro-	225, 227, 223	
8	6.679	Benzene, 1,2,4-trichloro-	180, 182, 184	4
9	7.068	Naphthalene	128, 129, 127	
10	7.136	Benzene, 1,2,3-trichloro-	180, 182, 184	
11	7.189	Benzene, trichloromethyl-	159, 161, 89	5
12	7.718	Hexachlorcyclopentadiene	237, 239, 235	
13	8.124	Benzene, 1,2,3,5-tetrachloro-	216, 214, 218	6
14	8.168	Benzene, 1,2,4,5-tetrachloro-	216, 214, 218	
15	8.460	Acenaphthene	153, 154, 152	
16	8.921	Benzene, 1,2,3,4-tetrachloro-	216, 214, 218	
17	9.200	Naphthalene, 1-chloro-	162, 127, 164	7
18	10.456	Acenaphthylene	152, 151, 153	
19	10.502	Dimethyl phthalate	163, 164, 77	8
20	10.534	Benzene, pentachloro-	250, 252, 215	
21	10.720	4-tert-octyl phenol	135.1, 136.1, 134	9
22	11.280	Diethyl phthalate	149, 150, 177	10
23	11.296	Fluorene	166, 165, 163	
24	11.32 - 11.93	Nonylphenol, isomeric	135, 121, 149, 107, 163.1	11
25	12.025	Benzene, hexachloro-	284, 286, 282	12
26	13.542	Di-iso-butyl phthalate	149, 150 223	
27	13.713	Phenanthrene	178, 176, 179	13
28	13.81	Anthracene	178, 176, 179	
29	13.899	gamma-HCH	181, 183, 219	
30	13.921	Heptachlor	272, 274, 270	14
31	14.983	Di-n-butyl phthalate	149, 150, 223	
32	15.681	Bis(4-methyl-2-pentyl) phthalate isom. 1	149, 167, 150	
33	15.743	Bis(4-methyl-2-pentyl) phthalate isom. 2	149, 167, 150	15
34	16.549	Heptachlor epoxide	353, 355, 351	
35	16.907	Bis(2-methoxyethyl) phthalate	59, 58, 149	16
36	17.182	cis-Chlordane	373, 375, 377	
37	17.537	Di-n-pentyl phthalate	149, 150, 237	17
38	17.58	trans-Chlordane	373, 375, 377	
39	17.693	Endosulfan I	241, 195, 239	18
40	18.041	Fluoranthene	202, 200, 101	
41	18.202	Bis(2-ethoxyethyl) phthalate	72, 45, 149	19
42	18.615	p,p'-DDE	246, 248, 318	

#	Ret Time, min	Compound Name	Ions monitored	Group #
43	18.715	Dieldrin	79, 81, 263	20
44	19.213	Pyrene	202, 200, 101	
45	19.997	Endrin	81, 263, 265	21
46	20.466	Di-n-hexyl phthalate	149, 150, 251	
47	21.036	p,p'-DDD	235, 237, 165	22
48	21.059	BDE-28	246, 248, 405.8	
49	21.175	Endosulfan II	195, 237, 241	23
50	21.929	p,p'-DDT	235, 237, 165	
51	22.126	Endrin aldehyde	250, 345, 347	24
52	22.389	Butyl benzyl phthalate	149, 91, 150	
53	22.580	Endosulfan sulfate	272, 274, 387	25
54	22.649	Bis(2-ethylhexyl)phthalate	149, 167, 150	
55	22.998	Bis(2-butoxyethyl) phthalate	149, 85, 193	26
56	23.747	Bis(2-ethylhexyl) terephthalate	70, 149, 167	
57	23.863	Dicyclohexyl phthalate	149, 167, 150	27
58	23.976	Benz[a]Anthracene	228, 226, 114	
59	24.047	Endrin ketone	317, 315, 319	28
60	24.178	BDE-47	325.9, 485.7, 483.7	
61	24.181	Chrysene	228, 226, 113	29
62	24.335	Di-n-octyl phthalate	149, 150, 279	
63	25.454	Di-n-nonyl phthalate	149, 150, 167	
64	25.662	BDE-99	403.8, 405.8, 563.7	30
65	26.039	BDE-100	405.8, 403.8, 563.7	
66	26.375	Benzo[b]Fluoranthene	252, 250, 253	
67	26.432	Benzo[k]Fluoranthene	252, 250, 253	
68	27.300	BDE-154	483.7, 481.6, 643.6	31
69	27.312	Benzo[a]Pyrene	252, 250, 126	
70	28.000	BDE-153	483.7, 481.6, 643.6	32
71	30.719	Indeno[123-cd]pyrene	276, 277	
72	30.761	Dibenzo[a,h]anthracene	278, 279	
73	31.706	BDE-183	563.6, 561.6, 721.6	33
74	32.128	Benzo[ghi]Perylene	276, 277	
75	36.763	BDE-197	320.7, 321.7, 641.5	34
76	43.781	BDE-207	359.6, 360.6, 721.5	
77	57.984	BDE-209	399.6, 398.5, 799.3	35

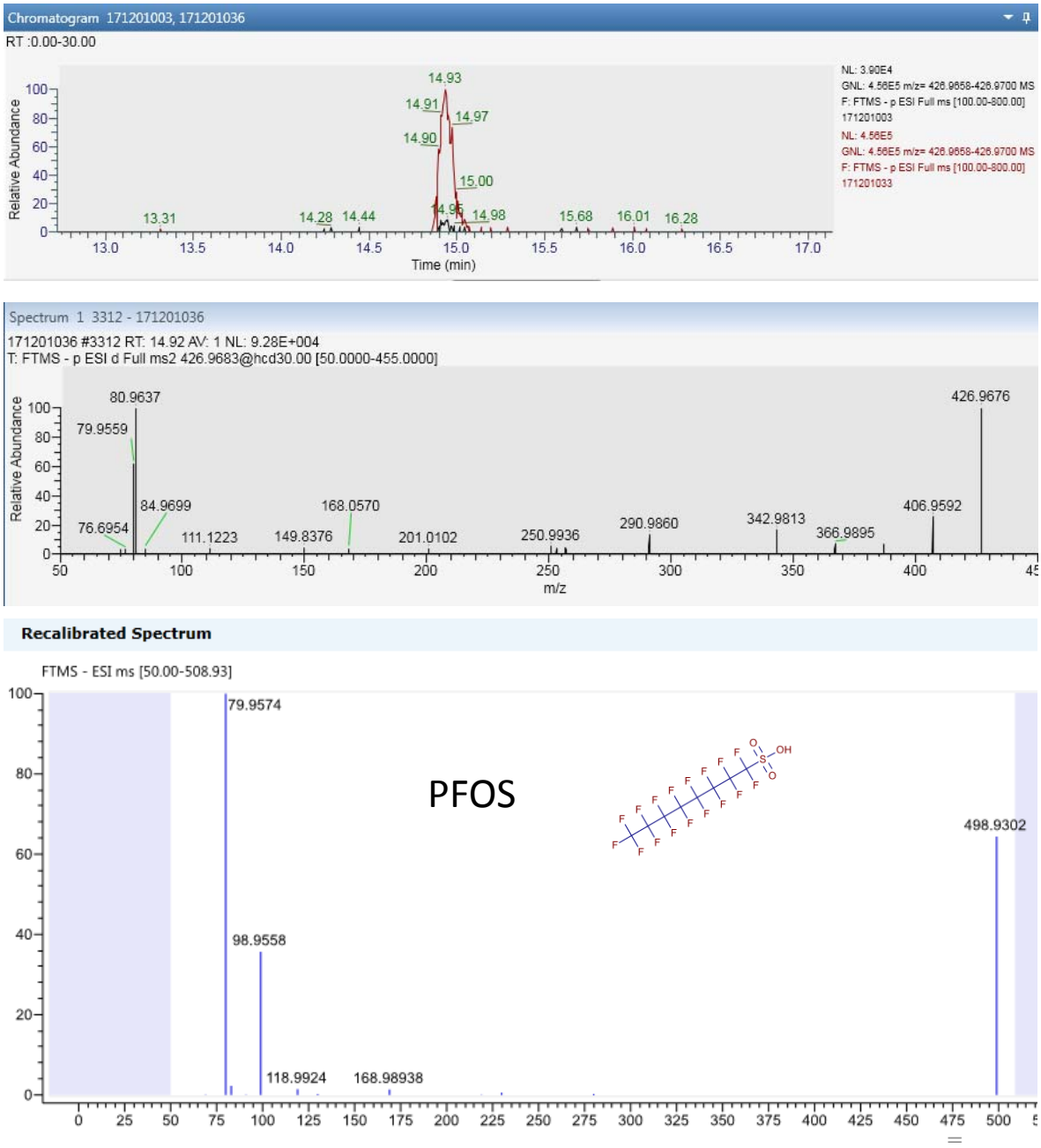


Figure S1. Upper panel: overlapped chromatograms of the trace for 426.9679 Da (C8H4F13O3S-) in sample 17BU025A (in red) and a procedural blank (in black). Middle panel: MS/MS spectrum obtained for the chromatographic peak in the sample. Lower panel: experimental MS/MS spectrum for PFOS

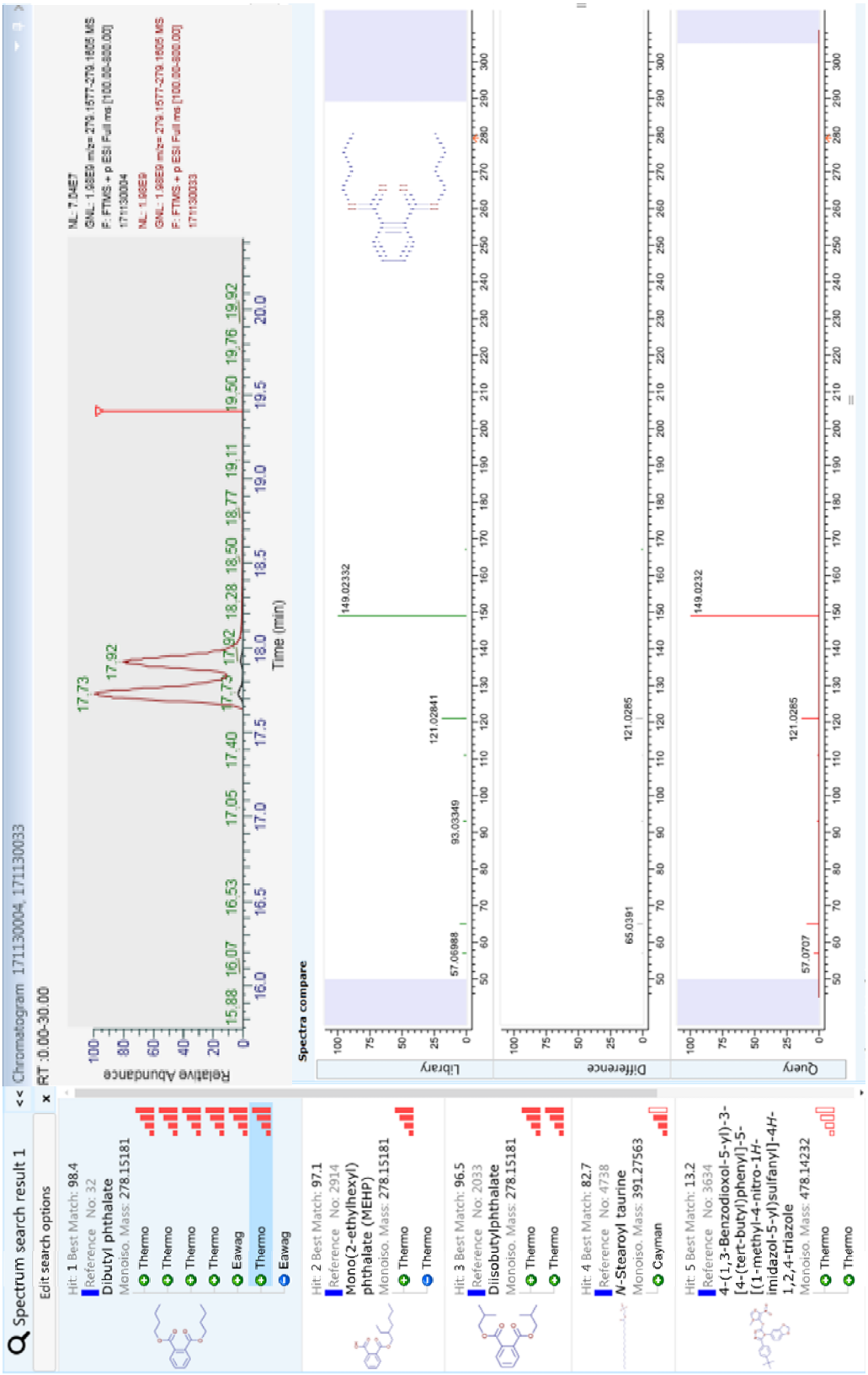


Figure S2. Upper panel: overlapped chromatograms of the trace for 307.1904 Da (C16H23O4+) in sample 17BU024A (in red) and a procedural blank (in black). Lower panel: comparison between the MS/MS spectrum for dibutyl phthalate in the library and the one obtained from the sample.