



# Biofilm-enhanced adsorption of strong and weak cations onto different microplastic sample types: Use of spectroscopy, microscopy and radiotracer methods

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## ABSTRACT

The adsorption of metals and other elements onto environmental plastics has been previously quantified and is known to be enhanced by surface-weathering and development of biofilms. However, further biofilm-adsorption characterisation is needed with respect to the fate of radionuclides. This study uses spectroscopy, microscopy and radiotracer methods to investigate the adsorption capacity of relatively strong and weak cations onto different microplastic sample types that were conditioned in freshwater, estuarine and marine conditions although marine data were limited. Fourier-transform infrared spectroscopy confirmed that surface oxidation chemistry changes induced by gamma irradiation were similar to those resulting from environmental exposures. Microscopy elemental mapping revealed patchy biofilm development, which contained Si, Al, and O, consistent with microbial-facilitated capture of clays. The plastics+biofilm of all sample types had measurable adsorption for Cs and Sr radiotracers, suggesting environmental plastics act broadly as a sink for the key pervasive environmental radionuclides of <sup>137</sup>Cs and <sup>90</sup>Sr associated with releases from nuclear activities. Adsorption onto high-density polyethylene plastic types was greater than that on polypropylene. However, in most cases, the adsorption rates of all types of plastic+biofilm were much lower than those of reference sediments and roughly consistent with their relative exchangeable surface areas.

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## 1. Introduction

The increasing abundance of plastics in global aquatic systems (Barnes et al., 2009; Turner and Holmes, 2015), including weathered derivative fragments of various sizes and chemical composition (Cole et al., 2011; Gregory, 2009), has led to consideration of plastics as a pervasive media that influences the fate and behaviour of aquatic contamination (Ivar do Sul and Costa, 2014; Wang et al., 2016). Similar to other particulate media, plastics are of interest as vectors for transfer of contaminants among ecosystem compartments including living organisms (Browne et al., 2007; Farrell and Nelson, 2013; Rochman et al., 2013; Tanaka et al., 2013) although the flux to organisms from this pathway may be low relative to that

from water and food uptake (Bakir et al., 2016; Koelmans et al., 2016; Ziccardi et al., 2016). Such transfer is often facilitated or influenced by contaminant-to-particulate adsorption and understanding the role of plastics as an agent of transfer requires basic data collection on such adsorption as well as insights into the abiotic and biotic processes influencing adsorption capacities.

Upon entry into the aquatic environment, bacteria, algae, fungi, and protozoa colonise plastic surfaces relatively rapidly (Lobelle and Cunliffe, 2011). Microorganism colonisation on plastics differs from that of autochthonous substrates (Zettler et al., 2013) and also differs among plastic types (Eich et al., 2015). This colonisation forms a basis for adherence of additional organic and inorganic suspended matter to form biofilms (Mora-Gómez et al., 2017; Wetzel, 1993), which are known to accumulate metals (Dranguet et al., 2017; Eich et al., 2015; Lavoie et al., 2012; Lehtola et al., 2004; Zettler et al., 2013) typically more so than the underlying plastics (Ashton et al., 2010).

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Radionuclides released into aquatic systems are among a suite of contaminants of concern some of which are anthropogenically-sourced and pervasive such as plutonium isotopes,  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  (Fisher and Chen, 2011; Stark et al., 2017; Whicker, 1982). Approximately 950 PBq of  $^{137}\text{Cs}$  was deposited in world oceans in past decades from nuclear weapons testing (Buesseler, 2014), with additions of ~85–100 PBq from the Chernobyl, and ~12–15 PBq from the Fukushima accidents (Aoyama et al., 2016; Johansen et al., 2015). Because radioactive and stable isotopes of the same element tend to behave chemically similarly in environmental and biological processes (Whicker, 1982), it is probable that radionuclides are adsorbing to, and being transported by microplastics on a global scale. There are, however, sparse investigations of radionuclide interactions with environmental plastics. Tazaki et al. (2015) detected elevated  $^{137}\text{Cs}$  on the surfaces of plastics recovered from a freshwater lake contaminated by fallout from the Fukushima accident. Some limited data on adsorption of radionuclides on one type of microplastic was provided in a precursor to this paper (Johansen et al., 2018). Lacking are basic studies on the adsorption of key radionuclides on various environmental plastic types and data that relates such adsorption to surface weathering and biofilm development.

The objective of this study was to quantify the adsorption onto differing types of environmentally-conditioned aquatic microplastics of relatively strong (Cs) and weak (Sr) cations representing common radioactive contaminants ( $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  isotopes). We varied plastic composition (high-density polyethylene, HDPE and polypropylene, PP), physical form (microspheres and 50  $\mu\text{m}$  thick strips), as well as aquatic ecosystem type (freshwater, estuarine and marine). The study also aims to develop the use of radiotracers for estimating bulk adsorption along with the application of multiple spectroscopy and microscopy methods to provide insights on surface weathering and biofilm development. Such nuclear techniques that have been identified as valuable tools in environmental microplastics research (Lanctôt et al., 2018).

## 2. Materials and methods

Three plastic sample types were considered: HDPE 100  $\mu\text{m}$  microspheres (90–106  $\mu\text{m}$  diameter, 0.96  $\text{g cc}^{-1}$  density, sourced from Cospheric LLC), and 50  $\mu\text{m}$  thick strips that were microtomed from field-collected HDPE and PP samples. The nominal surface area per gram of the spheres and strips were approximately 625 and 440  $\text{cm}^2 \text{g}^{-1}$  respectively, neglecting surface topography. The ~100  $\mu\text{m}$  HDPE microspheres may provide for a standardised basis of plastic type and size to which future studies may compare. Some limited data on the HDPE microspheres were reported in Johansen et al. (2018). The 50  $\mu\text{m}$  “microstrips,” of HDPE and PP plastic types, were added to the present study as many plastics appear in fibrous forms. As the previous studies showed biofilm-enhanced adsorption is complex, it was desired to study the microspheres and microstrips of varying plastic forms and types using multiple radiotracer adsorption, spectroscopy and microscopy methods.

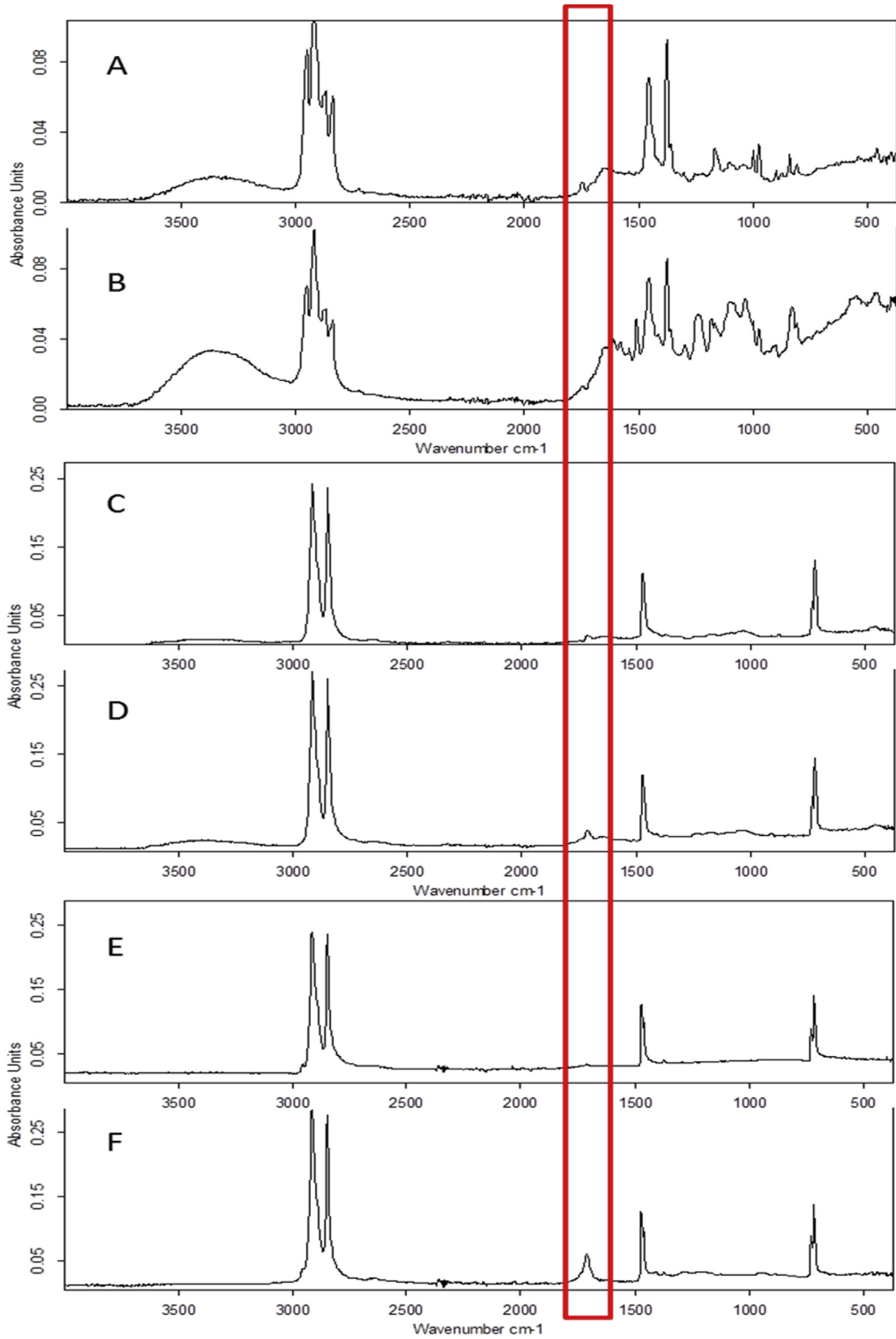
The study design sought to gain information on freshly manufactured plastic surfaces vs those weathered through environmental exposure. The freshly-manufactured HDPE microspheres were pre-conditioned by gamma-irradiation (1.17 MeV,  $^{60}\text{Co}$  source) to simulate the surface properties of environmentally exposed plastics. Attenuated Total Reflectance Fourier-transform Infrared Spectroscopy (ATR-FTIR) spectra were collected using a Bruker Alpha FTIR with the platinum ATR module. Measurements on the microspheres, taken before and after irradiation, showed an increase in absorbance at 1712  $\text{cm}^{-1}$  (Fig. 1). This peak, within the characteristic carbonyl stretch (1780–1680  $\text{cm}^{-1}$ ), was also manifest on the external surfaces of comparative HDPE environmentally-

weathered field samples. In contrast, the peak is absent in the spectra from freshly-exposed (no environmental weathering) internal surfaces of the same plastics (Fig. 1). Our results are similar to those achieved by Martinez-Romo et al. (2015) in that an irradiation protocol was successful in imitating a major component of the oxidation chemistry that occurs on HDPE as a result of long-term environmental exposure.

In order to develop biofilms over a range of aquatic environments, plastics were deployed at sites in freshwater ( $\text{Cs} < 0.1$ ,  $\text{Sr} = 91 \mu\text{g L}^{-1}$ ), estuarine ( $\text{Cs} = 0.65$ ,  $\text{Sr} = 4190 \mu\text{g L}^{-1}$ , salinity measured at high water of  $23 \pm 3 \text{ mg L}^{-1}$ ), and marine ( $35 \text{ mg L}^{-1}$  salinity). These sites were associated with the Georges River system, which has a catchment containing natural bushland, residential and light industry, and flows to the southern Pacific Ocean on the eastern coast of New South Wales, Australia. At each site, duplicates of <1.5 g (dry weight) of plastics were deployed within nylon mesh bags with 10  $\mu\text{m}$  apertures. The mesh bags were housed within 250 ml polycarbonate centrifuge tubes, which provided protection from disturbance by large organisms while allowing circulation of water and suspended sediment via numerous 3 mm circular openings.

Subsamples of the deployed plastics were gathered after 19 days, rinsed to remove unattached material, visually inspected to confirm the absence of inadvertently-captured material, and mixed with OCT compound (Tissue-Tek, Sakura Finetek Europe B.V.). The compound with plastics was frozen in liquid nitrogen, cryosectioned into 25–50  $\mu\text{m}$  thin sections and then mounted onto 200 nm silicon nitride windows ( $1.5 \times 1.5 \text{ mm}$ ). These thin sections allowed interrogation of the freshly-microtomed inner plastic material as well as the outer edges that had been exposed to sunlight and water in conditions conducive to the development of biofilms. Subsamples of these plastics were analysed by ATR-FTIR as described above. The sectioned plastics were also imaged using X-ray Fluorescence Microscopy (XFM at 16.5 KeV) at the Australian Synchrotron (Paterson et al., 2011), to create elemental maps of the deposits that had developed on the outer microplastic surfaces during deployment. Whole microspheres, with surface biofilm intact, were analysed using scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDS) coupled with electron backscattered imaging to determine elemental composition and surface characteristics. Approximately 50 Å of carbon was evaporated onto the surfaces under vacuum to prevent charging. SEM analysis was performed using a Zeiss Ultra Plus with an attached Oxford Instruments X-Max 80  $\text{mm}^2$  silicon drift detector (SDD) X-ray microanalysis system at an accelerating voltage of 15 kV. Oxford Aztec software was used to perform the semi-quantitative elemental analysis on the particles after quant optimisation using copper. All results are in weight percent using processing option “all elements analysed (Normalised),” and are relative to the elements detectable by SEM-EDS.

The adsorption capacity of two different cations was accomplished using  $^{134}\text{Cs}$  and  $^{85}\text{Sr}$  radiotracers and the remaining plastic samples which were environmentally-conditioned for a total of 142 days (26 February - 18 July 2016). The Cs and Sr radiotracers differ in their relative adsorption strengths (freshwater-sediment partitioning coefficient geometric means of  $>1\text{E}04$  and  $<1\text{E}03$  respectively and referred to as relatively strong and weak for the purposes of this paper). After the 142-day deployment period, the freshwater and estuarine samples were retrieved for radiotracer testing. While the marine plastics had been sub-sampled at 19 days and used for FTIR and XFM testing, they had subsequently been removed from the field by persons unknown and were not available for the adsorption experiment. Approximately 10 kBq of  $^{134}\text{Cs}$  and  $^{85}\text{Sr}$  were added to duplicate 50 ml polycarbonate tubes with filtered (0.45  $\mu\text{m}$ ) host water from each deployment site and known masses



of each plastic type. As most adsorption of metals on microplastics appears to occur in the approximate first 30 h (Holmes et al., 2012; Turner and Holmes, 2015), the experimental tubes were gently agitated for 48 h, after which the solution was separated from plastics via vacuum filtration (0.45 µm glass fibre). Subsamples of the filtrate were analysed via gamma spectrometry, and the activity concentration for each radionuclide was compared with that from four control treatments that did not contain plastics.

Calculations of the distribution coefficients ( $K_d$ s) provided the ratio of the mass activity density of the solid phase to the volumetric activity density of the liquid phase, expressed in units of ml g<sup>-1</sup> (Environment Agency UK, 2005; IAEA, 2010). Additional details on materials and methods can be found in the Supplementary information.

### 3. Results and discussion

#### 3.1. Retention of radiotracers on differing types of plastics+biofilm

The adsorption of <sup>134</sup>Cs and <sup>85</sup>Sr radiotracers onto the environmentally-conditioned plastics+biofilm was measurable for all plastic types. Our adsorption data for Cs and Sr, alkali and alkaline-earth metals, ( $K_d$ s of 1–81 ml g<sup>-1</sup>) are comparable to those for the range of transition metal adsorption on virgin and weathered plastics ( $K_d$ s <1–221 ml g<sup>-1</sup>) determined previously (Holmes et al., 2012; Turner and Holmes, 2015). The greatest observed adsorption value was for <sup>134</sup>Cs on HDPE microspheres in freshwater conditions (Table 1), and <sup>134</sup>Cs adsorption in freshwater was significantly greater than for estuarine conditions for all plastic types, ( $p$ -value = 0.03, Mann-Whitney  $U$  test, one-tailed). <sup>134</sup>Cs adsorption in estuarine/marine conditions is known to be inhibited by other cations, primarily K<sup>+</sup>, competing for adsorption sites (Evrard et al., 2015). Similar to our results, greater adsorption in freshwater, as compared with marine conditions, was observed in recent studies with Cd, Co, Ni, and Pb, which also used tracer-adsorption testing methods (Holmes et al., 2012; Turner and Holmes, 2015).

The mean Sr  $K_d$ s ranged from 1.0 to 14.0 mg L<sup>-1</sup> in contrast to the higher Cs range of 3.6–80.3 mg L<sup>-1</sup>. While the <sup>85</sup>Sr adsorption was typically less than that of <sup>134</sup>Cs, it was, however, measurable for all conditions and plastic types (Table 1). Sr was not markedly different between freshwater and estuarine conditions. The least of the observed mean adsorption values was for Sr associated with PP 50 µm strips in freshwater conditions (129 Bq g<sup>-1</sup>,  $K_d$  of 1.0 mg L<sup>-1</sup>). A single non-detect value for one of the PP subsample replicates, in freshwater, is reported in Table 1 (minimum for the Freshwater-PP-<sup>85</sup>Sr combination). It indicates the adsorption of <sup>85</sup>Sr onto microplastics in that particular subsample was small and generally within the same range as the variation that occurred in adsorption to study-container walls. However, the non-detect was for only one subsample, and the mean of that sample type/condition indicated positive adsorption.

Among plastic types, mean adsorption on PP strips was less than that of HDPE samples by factors of 2–9. Rochman et al. (2014) measured adsorption of a range of metals onto environmental PP that was both lower and higher than that of HDPE depending on conditions. However, no directly comparable previous data for adsorption of radionuclides onto different types of plastic were available. As a comparative baseline, we estimated adsorption on unweathered, non-biofilm PP surfaces to be approximately

**Table 1**

Retention of <sup>134</sup>Cs and <sup>85</sup>Sr tracers on plastics with biofilm after 48 h of exposure to radiotracers following 142 days of deployment in freshwater and estuarine conditions.

		Retained tracer (Bq g <sup>-1</sup> ) <sup>a</sup>			$K_d$ (mg L <sup>-1</sup> )			
		mean	min	max	mean	SD	min	max
<b>Freshwater</b>								
HDPE microspheres <sup>b</sup>	<sup>134</sup> Cs	6800	6437	7163	80.3	1.6	79.2	81.4
	<sup>85</sup> Sr	829	730	928	6.9	1.3	6.0	7.8
HDPE strips	<sup>134</sup> Cs	5689	4786	6592	41.9	16.3	30.4	53.4
	<sup>85</sup> Sr	748	375	1122	6.1	4.5	2.9	9.3
PP strips	<sup>134</sup> Cs	1502	1201	1802	8.4	2.5	6.6	10.2
	<sup>85</sup> Sr	129	ND <sup>3</sup>	343	1.6	1.5	ND <sup>3</sup>	2.7
<b>Estuarine</b>								
HDPE microspheres <sup>b</sup>	<sup>134</sup> Cs	1644	512	2776	9.3	9.2	2.7	15.8
	<sup>85</sup> Sr	623	194	1053	5.0	4.9	1.5	8.4
HDPE strips	<sup>134</sup> Cs	2433	1892	2975	14.0	5.5	10.1	17.9
	<sup>85</sup> Sr	1619	1227	2012	14.0	5.9	9.8	18.2
PP strips	<sup>134</sup> Cs	647	593	702	3.6	0.5	3.2	3.9
	<sup>85</sup> Sr	355	291	420	2.9	0.8	2.3	3.5

<sup>a</sup> The mass of the plastics+biofilm used here reflects damp (not completely dry) conditions in order to maintain algae and other living components of the biofilm as viable during the experiment.

<sup>b</sup>  $K_d$  data for HDPE microspheres from Johansen et al. (2018). ND refers to non-detection (see text).

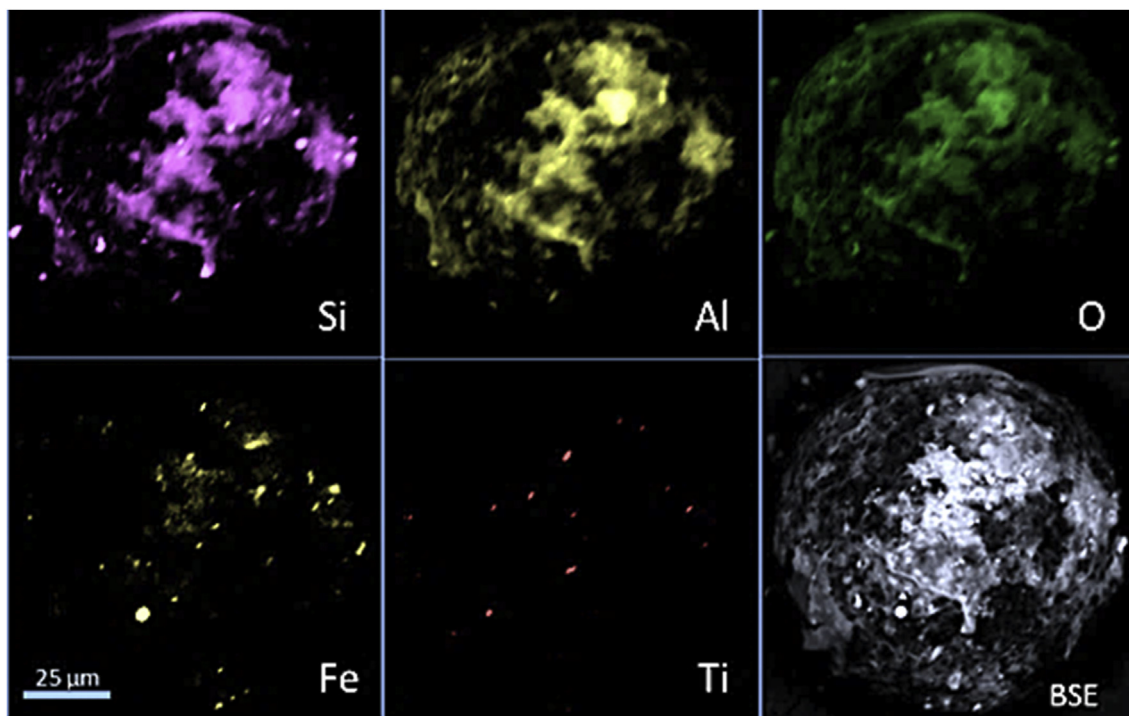
1.0–1.6% that of the weathered+biofilm conditioned plastics (using the experimental range of solution activity concentrations and nominal area cm<sup>-2</sup> of our PP ~50 µm of this study along with a 6E-04% solution cm<sup>-2</sup> adsorption rate of <sup>137</sup>Cs onto clean PP slides at neutral pH reported in Eichholz et al. (1965)).

#### 3.2. Biofilm coverage and composition on plastic surfaces

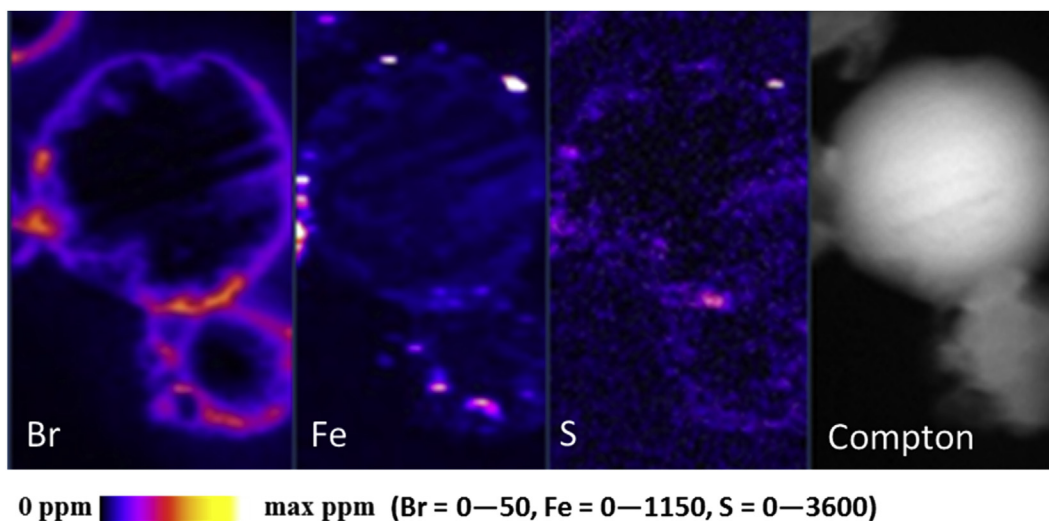
In several previous studies, the authors attributed most adsorption of cationic metals to surface-attached matter, as well as surface modification by photooxidation (Ashton et al., 2010; Holmes et al., 2012; Turner and Holmes, 2015). The microscopy data of this study revealed higher proportions of Si, Al, and O co-located in heterogeneous patches consistent with the accumulation in biologically-facilitated deposits (Fig. 2). These patchy areas were interspersed with mostly bare, or sparsely-colonised areas that still had adsorbed mineral components, but at much lower concentrations (e.g. Al reduced from 24% to 12% in freshwater and 21%–13% in estuarine conditions for biofilm-dominated vs mostly bare areas, see supplemental). Using a SEM-EDS summary long-count (12 h) on an estuarine-conditioned plastic+biofilm surface, O was most abundant (~47%, which was in part due to plastic) followed by Si (~21%), Al (~14%) Fe (~9%) with <2% of Ca, Cl, K, Mg, Mn, Na, P, S, and Ti. This element-abundance profile is consistent generally with that of clays, most of which are dominated by SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> with lesser amounts of Fe<sub>2</sub>O<sub>3</sub>, and often include trace elements such as Ti (IAEA, 2013). Fe and Ti were present in surface deposits of the study samples, primarily in discrete concentrations that were typically located within the same deposits containing Si–Al–O (SEM-EDS and XFM data, Figs. 2 and 3).

Visual inspection confirmed these patches included

**Fig. 1.** Characteristic Infrared Spectroscopy spectra obtained from the internal (A) and external (B) polymer of the PP environmental sample; the internal (C) and external (D) polymer of the HDPE environmental sample; the microspheres before (E) and after (F) the irradiation protocol. The characteristic carbonyl stretch is highlighted in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 2.** SEM-EDS elemental mapping on the curved surface of a single 100 µm HDPE microsphere with biofilm and adhered mineral elements after deployment in estuarine conditions. Colours are artificial to help distinguish among different elements. BSE refers to backscattered electron image which provides an overall rendering of the sample surface. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 3.** Bromine, iron, sulphur and Compton scatter XFM maps of thin-sectioned (25–50 µm) multiple 100 µm HDPE microspheres after deployment in estuarine conditions.

agglomerated masses dominated by frangible weakly bound fine-grained material (consistent with clays) along with occasional crystalline-structured grains and fibrous organic material. Some adhered discrete particles had variable elemental makeup that suggests anthropogenic origin. The results provide insights into the elemental composition of the biofilms, however quantification of the total surface area added by the biofilm among plastic types and deployment conditions has yet to be achieved as it requires a systematic method of measuring biofilm composition along with three dimensional structure at <math>< \mu\text{m}</math> scales, the development of which will be desirable in future studies. It may be possible to develop techniques of analysing the inorganic chemical fingerprint of the

biofilm associated with the plastic to infer the presence and type of plastic in a given water body. However, a great deal of further work, conducted initially in the laboratory then translated to the field, would need to be undertaken to determine the differences in chemical fingerprint among biofilms with differing organism communities and differing adsorbed inorganic particles that are associated with different plastic types and ages.

The adsorption patterns of other elements such as Cl and Br did not align with the discrete patchy Si–Al–O deposits but exhibited more continuous spatial coverage generally consistent with that expected from non-particulate, pervasive reactive water solutes (Fig. 3) with greater Cl and Br adsorption on marine samples which

also had some discrete Fe and Zn concentrations (Fig. S2; the striation patterns resulted from the sectioning process in which surface material was pulled into the cross section face by the microtome blade). The Compton scatter image indicates where the incident photon beam encountered electrons within the solid material target and is used here as an indicator of the size and location of the microtomed plastic thin section. The presence of S on the surface of the particles suggests organic proteinaceous materials and possibly sulphide-oxidising biofilm, such as photosynthetic sulphur bacteria (Pickering et al., 2001), but may also be explained by solute adsorption, or association with fine non-biological deposits.

Overall, the microscopy data of individual microplastic particles that were analysed post-rinsing in filtered ( $<0.45\ \mu\text{m}$ ) host water, are consistent with the capture and incorporation of clays (micro and nano-sized), as well as a range of discrete mineral grains and other materials, in discontinuous biofilm structures on the surfaces of the plastics.

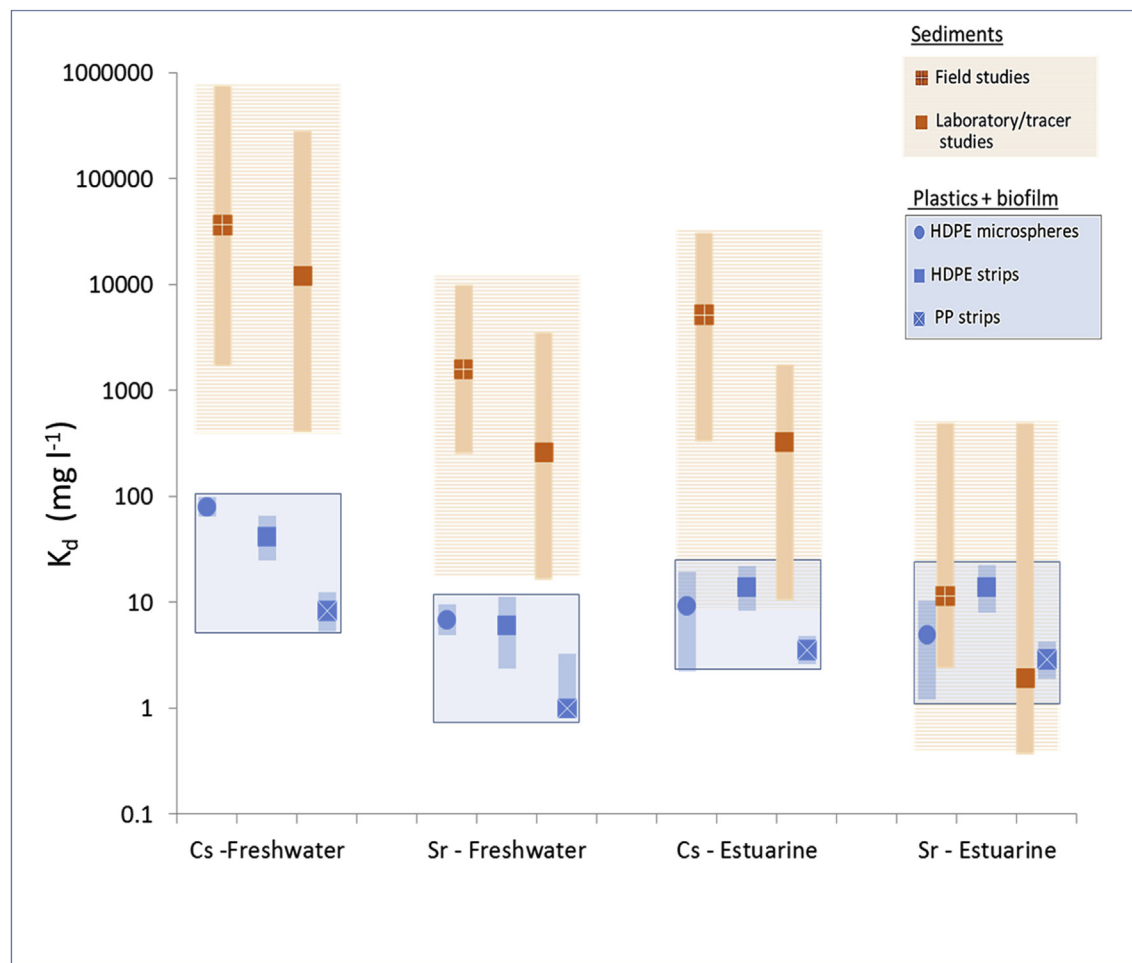
### 3.3. Comparison with sediment $K_d$ s

Our measured  $K_d$  values for HDPE and PP types of plastics+biofilm are substantially lower than those reported for sediments from both field and laboratory studies in most cases (Fig. 4). Specifically,  $K_d$  for plastics+biofilm for  $^{134}\text{Cs}$  from the current study

are 2–3 orders of magnitude lower than reference values for sediments from a large number of studies (field and laboratory) as summarised by the International Atomic Energy Agency (IAEA, 2004, 2010) and other published data (Børretzen and Salbu, 2002; Carpenter, 1997; Oughton et al., 1997; Saengkul et al., 2013). Similarly, for  $^{85}\text{Sr}$  in freshwater, our results suggest that the  $K_d$  for plastics+biofilm, are 2–3 orders of magnitude lower than reference values for sediments from other studies, while  $^{85}\text{Sr}$  in estuarine conditions did not appear to be different (discussed below).

The orders of magnitude greater adsorption for sediments in most study cases (Fig. 4) is consistent with their greater relative surface areas. Adsorption is, in part, a function of the surface area of the adsorbent, which generally reflects available binding sites and the electrochemical characteristics of those sites. Clays have exchangeable surface areas typically in the  $1 \times 10^5 - 1 \times 10^6\ \text{cm}^2\ \text{g}^{-1}$  range (Macht et al., 2011) as compared with the nominal  $<1 \times 10^4\ \text{cm}^2\ \text{g}^{-1}$  for the plastics used in this study. Our results here are consistent with other studies (Ashton et al., 2010; Turner and Holmes, 2015) that found biofilm development on plastic surfaces substantially raised their overall adsorption capacity but does not approach that of relatively high-surface area sediments (IAEA, 2010).

The  $K_d$  experimental results, along with the microscopy data, are consistent with a conceptual model that biofilm, with captured



**Fig. 4.**  $^{134}\text{Cs}$  and  $^{85}\text{Sr}$  adsorption ( $\text{mg l}^{-1}$ ) onto plastics+biofilm types of this study (blue box) compared with reference  $K_d$ s from field and laboratory sediment studies (geometric means, whiskers are minimum and maximum values where available; see supplemental for values). Marine  $K_d$  reference values are shown here in the estuarine Sr column due to lack of estuarine data. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

clays, increases the overall adsorption rates onto plastics, but at lower rates compared with native sediments as the biofilm was manifest as variable patchy deposits on the otherwise relatively smooth and low-reactive surfaces of the plastics. However, the relative surface area per mass changes with scale. Typical aqueously-dispersed clays range from 0.001 to 0.009  $\mu\text{m}$  in thickness (Nadeau, 1985). In comparison, the plastic shapes of this study were relatively large (50–100  $\mu\text{m}$ ), and at these scales much of the plastic is within, not at the surface of the particle, and thus limits sites available for biofilm development and adsorption. Experimental constraints determined the size of the plastics we used in this study. In nature, plastics may fragment or weather into smaller sizes (Bond et al., 2018; Cole et al., 2011). Dawson et al. (2018) demonstrated that Antarctic krill fed microplastic pieces (31.5  $\mu\text{m}$ ), egest fragmented particles <1  $\mu\text{m}$  in diameter likely due to mechanical grinding in the krill's gastric mill. When plastics weather to smaller, < $\mu\text{m}$  scales, their overall nominal surface area increases on a per gram basis. However, the overall availability of binding sites, the extent and nature of biofilm community structure and the ecocorona (Lynch et al., 2009), will also depend on the plastic's surface composition, topography and the environmental setting and these factors should be further studied to determine their relative influence on adsorbing molecules (Rummel et al., 2017).

While the plastics+biofilm adsorption was generally much less than that of sediments, the exception in this study was the combination of  $^{85}\text{Sr}$  in estuarine conditions in which the adsorption  $K_d$ s of microplastics+biofilm appear to be comparable with those reported for reference marine sediments (IAEA, 2004). This similarity may be due to the weaker salinity in the estuarine conditions of our study where, for many metals, adsorption depends on the salinity gradient (Holmes et al., 2014), but may also reflect the limits of the reference data. No reference sediment  $K_d$  data were available for Sr in estuarine conditions, and, although  $n = 62$  for reference laboratory  $K_d$  values in simulated marine conditions, the vast majority of these came from a single study (Takata et al., 2014) and therefore Sr values for a wide range of field marine sediments are not yet available for comparison.

The  $K_d$  parameter is used here mainly as a bulk means of comparing plastic adsorption of Cs and Sr to that of sediments. For both of these media, the  $K_d$  concept has limitations as it is a parameter that combines numerous processes, and has an underlying assumption of equilibrium conditions that are rarely, if ever, found in nature. The reference field  $K_d$  data tend to be higher than laboratory-derived data as they are influenced by additional processes (e.g. tidal exchange) which often lead to dilution of the water component of the  $K_d$  equation. The presence of biological material in field conditions also likely increases the adsorption onto the solid phase, therefore increasing  $K_d$ s of the field data. Whether for plastics or sediments, the oversimplified parameter  $K_d$  does not account for dynamic environments found in field conditions such as water exchange, reversible adsorption isotherms, exchange between suspended vs. sedimentary material, and especially the dynamic mixing and dilution that occurs to radionuclides in the water column over time and distance following acute releases into aquatic environments (Periáñez et al., 2018).

Our results suggest Cs and Sr radionuclide adsorption onto microplastics should be considered in fate and transport assessments as the more buoyant plastics may mobilise released radionuclides along pathways that sediments would not. One such release occurred during the period of days to weeks succeeding the March 2011 tsunami that led to the Fukushima accident, when a large influx of tsunami-mobilised plastics entered the open ocean and was transported eastward via the North Pacific Gyre (Murray et al., 2018; Therriault et al., 2018). It is not yet understood how

much of the  $^{137}\text{Cs}$  and other particle-reactive radionuclides that were released from the Fukushima accident have adsorbed to the well-documented masses of buoyant plastics in the open waters of the Pacific (Barnes et al., 2009; Eriksen et al., 2014), or to less buoyant plastics (Bond et al., 2018) associated with the freshwater, estuarine and coastal sediments of eastern Japan that are receiving ongoing radionuclides via surface erosion and runoff (Buesseler et al., 2017).

While our results suggest plastics, as potential sinks and transport vectors, should be considered among the fate pathways of released radionuclides, the relatively weak adsorption rates do not suggest plastics as a principle vector for transfer of radionuclides to living organisms. Such potential transfer should be investigated. However, recent re-evaluation of past studies has suggested that in aquatic systems, the overall flux of HOCs bioaccumulated from the ingestion of natural diet overwhelms the flux associated with ingested microplastics (Koelmans et al., 2016; Ziccardi et al., 2016). Even when gut surfactants or the influence of gut pH or temperature were considered for HOC desorption (hence leading to bioaccumulation), modelling by Bakir et al. (2016) suggested that ingestion of microplastic does not provide a quantitatively important additional pathway for the transfer of adsorbed HOCs from seawater to biota.

Although this study focused on key radionuclides associated with accidents and other releases, the X-ray fluorescence, SEM-EDS and radiotracer methods used here can be applied to a range of metal contaminants of concern (e.g. As, Cd, Ce, Se, Mn, Zn) associated with micro-particles of differing types. The gamma irradiation used here was shown to be a useful tool for rapidly simulating some of the surface photooxidation seen on environmentally exposed plastics that may be important for micro-organism colonisation and aggregation. Future studies in this area should focus on assessing the specific role of microorganisms in facilitating the accretion of mineral/clay particles which aggregate on the surfaces of environmental plastic and the plastic degradation pathways that lead to microbial colonisation, including focus on systematic means of relating biofilm composition, physicochemical characteristics and microstructure coverage to overall adsorption rates.

#### 4. Conclusions

Our results indicate that HDPE and PP type aquatic microplastics+biofilm provide an environmental sink for pervasive reactive radionuclides, similar to sediments albeit to a lesser degree. Microscopy elemental mapping revealed patchy biofilm development, that, compared with relatively bare plastic surfaces was enriched with Si, Al, and O, consistent with microbial-facilitated capture of clays. When subjected to radiotracers, the resulting  $^{134}\text{Cs}$  and  $^{85}\text{Sr}$  adsorption onto the 50–100  $\mu\text{m}$  size range of microplastics+biofilm were generally 2–3 orders of magnitude less than those for sediments (although more data for Sr in estuarine field conditions are required). As the difference between sediments vs microplastics+biofilm adsorption appears roughly in line with their respective surface areas, our results suggest that smaller microplastics+biofilm (smaller than studied here) may exhibit increased adsorption rates as surface area per mass increases. However, there may be other mechanisms that drive the adsorption of monovalent and divalent cations onto microplastics+biofilm that we have not identified (e.g. biofilm community and ecocorona composition), and further work in this area is required.

Overall, the results of this study are generally consistent with a conceptual model of plastic surfaces altered by environmental exposure, the rapid development of discrete biofilm patches that include accretion of Al–Si–O and other elements (the adherence of which may be facilitated by microbial colonisation), and the

resulting adsorption of the cationic alkali and alkaline earth metals Cs and Sr similar to that observed for transition metals. Future work should focus on understanding the surface state of the plastic particles in relation to physical and chemical properties (e.g. roughness, chemical composition, surface charge of the plastics as well as the pH and DOC of the host water) and biological properties (e.g. microbial community and ecocorona composition) under differing environmental exposures and how these factors influence contaminant adsorption.

### Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2019.04.029>.

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