Short Communication:

Initial data on adsorption of Cs and Sr to the surfaces of microplastics with biofilm

Mathew P. Johansen[a+], Emily Prentice[a,b], Tom Cresswell[a], Nick Howell[a]

[a] Australian Nuclear Science and Technology Organisation (ANSTO), Locked Bag 2001, Kirrawee DC, NSW 2232, Australia. [+]Corresponding author; Mathew.johansen@ansto.gov.au

[b] University of Technology Sydney, 15 Broadway, Ultimo, NSW 2007, Australia

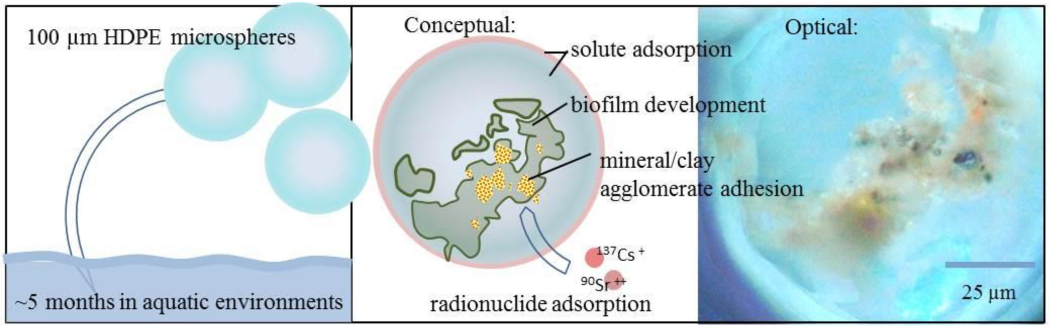
Short Communication:

Initial data on adsorption of Cs and Sr to the surfaces of microplastics with biofilm

Abstract

The adsorption of radiocesium and radiostrontium onto a range of natural materials has been well quantified, but not for the new media of environmental plastics, which may have enhanced adsorption due to surface-weathering and development of biofilms. Microplastic samples were deployed in freshwater, estuarine and marine conditions, then characterised using infrared spectroscopy to document changes to the plastic surface (vs interior). Synchrotron elemental mapping data revealed surfaces that were well-covered by accumulation of reactive water solutes and sulphur, but, in contrast, had highly discrete coverage of elements such as Fe and Ti, indicating adhered mineral/clay-associated agglomerates that may increase adsorption capacity. Plastics that had been deployed for nearly five months adsorbed radionuclides in both freshwater and estuarine conditions with highest K_d for cesium (Cs) in freshwater (80 ml g^{-1}) and lowest for strontium (Sr) in estuarine conditions (5 ml g^{-1}). The degree of Cs and Sr adsorption onto plastics appears to be approximately 2-3 orders of magnitude lower than for sediment reference values. While lower than for sediments, adsorption occurred on all samples and may indicate a significant radionuclide reservoir, given that plastics are relatively buoyant and mobile in water regimes, and are increasing in global aquatic systems.

Keywords: microplastic, adsorption, K_d, cesium, strontium, biofilm



1. Introduction

While adsorption rates of metals onto microplastics have been well documented, there is a lack of published data that quantifies adsorption of key radionuclides of concern onto environmental plastics. Approximately 950 PBq of ^{137}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). During the period of Fukushima fallout, a large influx of buoyant, tsunami-mobilised plastics entered the open ocean, and was transported eastward via the North Pacific Gyre (Carlton et al., 2017). This event highlighted an increasing abundance of plastics in global aquatic systems (Barnes et al., 2009; Wang et al., 2016), including weathered derivative “microplastics” of various sizes (Eriksen et al., 2014). In aquatic environments, plastic surfaces are relatively rapidly colonised by bacteria, algae, fungi, and protozoa (Lobelle and Cunliffe, 2011; Oberbeckmann et al., 2015; Zettler et al., 2013), and, with adherence of additional organic and inorganic suspended matter, form “biofilms” (Wetzel, 1993). Recent studies have focused on the development of biofilms on plastics, and the adsorption of metals on plastics (Ashton et al., 2010; Eich et al., 2015; Lehtola et al., 2004; Zettler et al., 2013). There are however, sparse reports on radionuclide interactions with environmental plastics. Elevated ^{137}Cs, thought to be derived from the Fukushima accident, was detected on the surfaces of plastics recovered from a contaminated freshwater lake and was associated with adsorbed clays and diatoms (Tazaki et al., 2015).

This study aims to compare the adsorption of the key fission products, radioactive Cs and Sr, onto microplastics following biofilm development in freshwater, estuarine and marine conditions. Partition coefficients (K_ds) are developed to estimate bulk adsorption, and spectroscopy and microscopy methods are applied to provide insights on surface weathering and adsorption processes. The use of highly sensitive nuclear techniques to study the role of plastics as vectors of contaminant transfer in the aquatic environment has been highlighted by Lanctôt et al. (submitted, this issue). The work reported here is from a first phase pilot effort in which nuclear techniques were developed and applied here in novel ways for determining adsorption of radiotracers onto plastics with biofilms.

2. Experimental

This study considered ~100 μm diameter microspheres of high density polyethylene (HDPE) (90-106 μm microspheres, 0.96 g cc^{-1} sourced from Cospheric LLC). The microspheres were pre-conditioned by gamma-irradiation (1.17 MeV, ^{60}Co source) to simulate the surface properties of long-term environmentally exposed plastics. The effect of gamma irradiation on the polymer surface was measured using Attenuated Total Reflection Fourier-transform Infrared Spectroscopy (ATR-FTIR). This research project also considers other plastic types, shapes, and pre-conditioning, with, however, the HDPE microsphere data being most complete and reported here in this short communication.

The plastics were deployed at freshwater, estuarine (salinity at high water of 26±3 mg L^{-1}), and marine (35 mg L^{-1} salinity) sites to encourage biofilm development. The sites were associated with the Georges River system, NSW, Australia, with a catchment containing natural bushland, residential and light industry. Less than 1.5g of plastics were deployed within 10µm nylon mesh bags, within 250ml protective polycarbonate containers, which provided protection from disturbance by large organisms but allowed circulation of water and suspended sediment via numerous 3mm circular openings.

Subsamples of the freshwater, estuarine, and marine plastics were gathered after 19 days, rinsed repeatedly to remove unattached material, mixed with OCT compound (Tissue-Tek, Sakura Finetek Europe B.V.), snap frozen in liquid nitrogen, cryosectioned into 25 µm thin sections and then thaw-mounted onto 200nm silicon nitride windows (1.5x1.5mm). These thin sections allowed interrogation of the outer weathered edges with biofilm, as well as the freshly-microtomed inner plastic material (ATR-FTIR method using a Bruker Alpha FTIR with the platinum ATR module). The degree of environmental exposure at the weathered edges was estimated by monitoring the absorbance within the carbonyl stretch (1780-1680 cm^{-1}) and comparing the surface polymer to the internal polymer. Spectra were taken from the microspheres before and after gamma irradiation, and the same IR stretch monitored until the degree of surface oxidation approximated that observed in a comparison set of environmentally-weathered plastics. The same thin sections were also analysed by X-ray Fluorescence Microscopy (XFM at 16.5 KeV), at the Australian Synchrotron, for elemental mapping of the deposits that developed on the microplastic surfaces during deployment.

Except for the subsamples discussed above, the plastic samples remained deployed for 142 days (26 February - 18 July, 2016). However, after this period, only the freshwater and estuarine samples were retrieved as the marine sample was removed by persons unknown and not available for use in the following adsorption studies. Adsorption of Cs and Sr onto the retrieved plastics, with biofilm, was measured using a standard method for determining partitioning coefficients (K_ds): *Development of the partition coefficient (K_d) test method for use in environmental risk assessments* (Environment Agency UK, 2005) with some modification, briefly described as follows. Upon retrieval, plastic particles were removed from the mesh bags and rinsed over 10 µm nylon mesh using host water from each deployment site until unattached material was removed. Each sample was split in two, then added to 0.45µm-filtered host water (pH of 8.08 for freshwater, 7.80 for estuarine) in 50ml tubes. Following a 12-hour settling period, each tube received 101µL of solution containing 10kBq ^{134}Cs (produced by the Australian Nuclear Science and Technology Organisation; ANSTO, Australia) and 9.2kBq ^{85}Sr (Eckert and Zeigler, United States) radiotracers (7µg L^{-1} and 5µg L^{-1} stable concentration of each isotope, respectively). The addition of the radiotracers to the host water did not affect the final pH. The 50 ml tubes, with tracer solution and biofilm-covered plastics, were subjected to circular agitation (50 rpm) for a 48-hour adsorption period, which was intended to achieve substantial, but not necessarily complete equilibration as most adsorption of metals on microplastics appears to occur in the first 30 hours (Holmes et al., 2012; Turner and Holmes, 2015). The solution was separated from the plastics by vacuum filtration. Subsamples from the filtrate (<0.45 μm) were analysed by gamma spectroscopy (Perkin Elmer 2480 WIZARD^2) using 300s count time against in-house matrix- and geometry-matched standards (11.7% and 15.1% absolute efficiency for Cs-134 and Sr-85 respectively). The amount adsorbed onto the plastics + biofilm was determined by subtracting the radiotracer activity in filtered solution from the mean of four control replicates, which compensated for any losses due to sorption to the walls of the 50 ml containers.

The distribution coefficients (K_ds) of the Cs and Sr radiotracers were determined using the standard equation for 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^{-1} (IAEA, 2004, 2010).

3. Results and Discussion

The ATR-FTIR data were used to compare the spectra of the external surfaces of environmentally-weathered plastics with their freshly-exposed internal surfaces. Increased absorbance within the characteristic carbonyl stretch, from 1780-1680 cm^{-1}, indicated substantial surface changes by oxidation due to environmental exposure. Evaluation of absorption at 1712 cm^{-1} also indicated that the method of using gamma irradiation of HDPE microspheres was successful in imitating a major component of the oxidation chemistry that occurs on HDPE as a result of long-term environmental weathering (e.g. UV, natural gamma). This resulted in a substantial lowering of hydrophobicity which allowed for increased water-plastic surface interactions.

The XFM data revealed the distribution of key elements on the surfaces of the 19-day deployed microplastic subsamples. Relatively complete spatial coverage occurred for pervasive reactive water solutes (e.g. Cl, Br in the estuarine sample shown in Figure 1). In contrast, highly heterogeneous, discrete coverage occurred for elements such as Fe and Ti likely associated with adhered mineral/clay agglomerates. The term agglomerates is appropriate here as the mineral-rich masses were, after drying, frangible to varying degrees, and had visually distinct components that typically included fibrous organic material. These Fe- & Ti-rich agglomerates are located at the sphere surfaces (the 25 μm thin sections imaged in Figure 1 exhibit some amount of displacement that occurred during the microtome process). Other elements (Sr and Zn) had distributions consistent with both adsorption of solutes and concentration in the same discrete agglomerates associated with Fe and Ti. The distribution of S indicates its arrival on these same surfaces during environmental deployment and suggests a pattern consistent with biomass accumulation in general including potential sulphide-oxidizing organisms in biofilm (e.g. photosynthetic sulphur bacteria, Pickering et al 2001). However, the observed S may also be explained by its association with fine non-biological deposits or solute adsorption.

From the K_d adsorption tests, the adsorption of the Cs radiotracer was greatest for freshwater conditions, averaging 6800 Bq g^{-1} on HDPE microspheres (6437 min, 7162 max). The least adsorption was for Sr in estuarine conditions, which averaged 623 Bq g^{-1} $^{(}$194 min, 1053 max). The means of Cs adsorption were higher than those of Sr in all cases. The freshwater adsorption of Cs was greater than that of estuarine conditions, while Sr adsorption was similar in freshwater and estuarine conditions.

The greater observed adsorption of Cs in freshwater vs estuarine conditions (Table 1) is consistent with known general decreases in Cs adsorption in estuarine/marine conditions due to other cations, primarily K^+, competing for adsorption sites as salinity increases (Evrard et al., 2015). Similarly, in recent studies that also used tracers to measure adsorption on plastics, higher K_ds were observed in freshwater for Cd, Co, Ni, and Pb as compared with marine conditions (Holmes et al., 2012; Turner and Holmes, 2015). Our overall results for Cs and Sr, alkali and alkaline-earth metals, (K_ds of 1-81 ml g^{-1}) are comparable to those for the range of metal adsorption on virgin and weathered plastics (K_ds <1-221 ml g^{-1}) measured by Turner and Holmes (2015) and Holmes et al. (2012) . In those studies, the authors attributed most adsorption to surface-attached matter, as well as surface modification by photooxidation. These are consistent with our XFM and FTIR observations.

Table 1. K_d values following 48-hour agitation in radiotracer solution of HDPE microspheres after 142 days of deployment.

		Mean	Min	Max
			ml g^{-1} *	
Estuarine	Cs	9.3	2.7	15.8
	Sr	5.0	1.5	8.4
Freshwater	Cs	80.3	79.2	81.4
	Sr	6.9	6.0	7.8

*The mass of the plastics + biofilm used here reflects damp (not completely dry) conditions as the algae and other living components of the biofilm were maintained as viable during the experiment.

Cs and Sr adsorption onto plastics+biofilm were measurable in all experimental cases in this study. They were, however, far lower than those for reported for sediments in most cases (Figure 2). Specifically, K_d for plastics+biofilm for Cs are 2-3 orders of magnitude lower than reference values for sediments from a large number of field and laboratory studies summarised by the IAEA (IAEA, 2004, 2010) and other published data (Børretzen and Salbu, 2002; Carpenter, 1997; Oughton et al., 1997; Saengkul et al., 2013). Likewise, for 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 field and laboratory studies. However, our results for Sr in estuarine conditions appear comparable with reference marine K_ds (IAEA 1985). This similarity may be due to the estuarine influence in our study (higher K_ds expected), but may also reflect the limits of the reference data. No data are available from estuarine conditions, and, although n=62 for reference laboratory K_d values, almost all of these came from one study (Takata et al., 2014) and therefore Sr values for a wide range of global marine sediments are not yet available.

In the above comparison, the reference field data tend to have higher apparent K_ds as they are influenced by additional processes (e.g. dilution in the water column by tidal exchange etc.) which often lead to dilution of the water component of the K_d equation. For plastics, like sediments, the oversimplified parameter K_d does not account for the dynamics of water exchange, reversible adsorption isotherms, suspended vs. bed 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).

The main point of the various comparisons above is that our limited laboratory-derived results suggest the K_ds for Cs and Sr adsorption to plastics are generally 2-3 orders of magnitude lower than those for sediments, with more data required for Sr in estuarine conditions. The low, but positive results for adsorption in estuarine conditions suggest that like sediments, aquatic microplastics provide an environmental sink for radionuclides although to a lesser degree. Plastics as an absorbing media may be of more importance in the open ocean where mobile and buoyant plastics have the potential to interact with atmospherically-deposited ^{137}Cs without competition from sediments., A question that arose following the Fukushima accident, and that has yet to be answered, is how much of the ^{137}Cs and other particle-reactive radionuclides that were deposited onto the open ocean areas of the North Pacific (Buesseler et al., 2016) adsorbed to the well-documented masses of buoyant plastics there (Barnes et al., 2009; Eriksen et al., 2014).

While the data from this initial study demonstrate radionuclide adsorption on the surfaces of the plastic+biofilm samples, the biofilm component has yet to be characterised in detail (e.g. using DNA sequencing and SEM-EDX techniques) to better understand the relative adsorption of the specific biofilm components. Visual inspection suggested the mineral-rich agglomerates were associated with underlying biofilm growth on the plastic, but this association has yet to be quantified.

A methods issue of this study was that small quantities of plastic were deployed in the field which limited the sample available for biofilm characterisation tests, and increased the error of what would be normally minor losses during filtration and rinsing. The small sample sizes also increased uncertainty in the mass measurements, which, in many of the experiment steps, were made prior to complete drying in order to maintain viability of the biofilm through subsequent experiment steps and likely resulted in a small under-prediction of the K_d values of this study. The relatively short adsorption period (48 hrs) may have also resulted in under prediction of K_ds, although the length of time used here was generally consistent with Holmes et al. (2012) who suggested 25-100 hours for equilibration of metal cation adsorption onto marine plastics. Also, under prediction of K_d values may have resulted by our rinsing of the samples retrieved after deployment, but prior to the adsorption tests. In contrast, retrieved sediments are not typically rinsed prior to laboratory K_d adsorption tests. We included the pre-rinse step in this study to imitate real-world conditions where plastics are subjected to stream currents, waves, and other hydraulic forces that dislodge weakly-attached material from biofilm. Weak vs strong adsorption is often explored in K_d studies and can be determined through use of either sequential rinsing/sonic separation and repeated gamma measurement, or multiple split samples subjected to differing degrees of agitation/rinsing. Future studies should consider using deployed plastic masses of 10 g or larger, in multiple replicates, to rectify these small-mass issues.

Despite the limitations of this initial study, its results are generally consistent with a conceptual model of plastic surfaces being altered by environmental exposure, the relatively rapid development of biofilm, and the presence of discrete, patchy mineral-rich accumulations (the adherence of which may be facilitated by microbial colonisation), and the resulting adsorption of cationic Cs and Sr radionuclides similar to that observed for metals. The degree of Cs and Sr adsorption to plastics, as indicated by K_ds, appears to be 2-3 orders of magnitude lower than for sediments, with more data required for Sr in estuarine conditions. While this study focused on key fission radionuclides, the X-ray fluorescence and radiotracer methods demonstrated here can be applied to a range of metal contaminants of concern (e.g. As, Cd, Ce, Se, Mn, Zn). Future studies need particular focus on testing the specific role of microorganisms in facilitating the adherence of water-dispersed mineral/clay particles which, on environmental plastic surfaces, likely dominate in the adsorption of cationic radionuclides.

Acknowledgements

XFM measurements were performed under the direction of Daryl Howard, XFM beamline, Australian Synchrotron, Victoria, Australia.

References

Aoyama, M., Kajino, M., Tanaka, T.Y., Sekiyama, T.T., Tsumune, D., Tsubono, T., Hamajima, Y., Inomata, Y., Gamo, T., 2016. 134Cs and 137Cs in the North Pacific Ocean derived from the March 2011 TEPCO Fukushima Dai-ichi Nuclear Power Plant accident, Japan. Part two: estimation of 134Cs and 137Cs inventories in the North Pacific Ocean. Journal of Oceanography 72, 67-76.

Ashton, K., Holmes, L., Turner, A., 2010. Association of metals with plastic production pellets in the marine environment. Mar. Pollut. Bull. 60, 2050-2055.

Barnes, D.K.A., Galgani, F., Thompson, R.C., Barlaz, M., 2009. Accumulation and fragmentation of plastic debris in global environments. Philosophical Transactions of the Royal Society B: Biological Sciences 364, 1985-1998.

Børretzen, P., Salbu, B., 2002. Fixation of Cs to marine sediments estimated by a stochastic modelling approach. J. Environ. Radioact. 61, 1-20.

Buesseler, K., Dai, M., Aoyama, M., Benitez-Nelson, C., Charmasson, S., Higley, K., Maderich, V., Masqué, P., Oughton, D., Smith, J.N., 2016. Fukushima Daiichi–Derived Radionuclides in the Ocean: Transport, Fate, and Impacts. Annual Review of Marine Science.

Buesseler, K.O., 2014. Fukushima and ocean radioactivity. Oceanography 27, 92-105.

Carlton, J.T., Chapman, J.W., Geller, J.B., Miller, J.A., Carlton, D.A., McCuller, M.I., Treneman, N.C., Steves, B.P., Ruiz, G.M., 2017. Tsunami-driven rafting: Transoceanic species dispersal and implications for marine biogeography. Science 357, 1402.

Carpenter, R., 1997. Interactions of Radionuclides with Sediments and Sustpended Particles. IAEA, Vienna.

Eich, A., Mildenberger, T., Laforsch, C., Weber, M., 2015. Biofilm and Diatom Succession on Polyethylene (PE) and Biodegradable Plastic Bags in Two Marine Habitats: Early Signs of Degradation in the Pelagic and Benthic Zone? PLoS One 10, e0137201.

Environment Agency UK, 2005. Development of the partition coefficient (Kd) test method for use in environmental risk assessments. Environment Agency, UK, Bristol, England.

Eriksen, M., Lebreton, L.C.M., Carson, H.S., Thiel, M., Moore, C.J., Borerro, J.C., Galgani, F., Ryan, P.G., Reisser, J., 2014. Plastic Pollution in the World's Oceans: More than 5 Trillion Plastic Pieces Weighing over 250,000 Tons Afloat at Sea. PLoS One 9, e111913.

Evrard, O., Laceby, J.P., Lepage, H., Onda, Y., Cerdan, O., Ayrault, S., 2015. Radiocesium transfer from hillslopes to the Pacific Ocean after the Fukushima Nuclear Power Plant accident: A review. J. Environ. Radioact. 148, 92-110.

Holmes, L.A., Turner, A., Thompson, R.C., 2012. Adsorption of trace metals to plastic resin pellets in the marine environment. Environmental Pollution 160, 42-48.

IAEA, 2004. Sediment distribution coefficients and concentration factors for biota in the marine environment (TRS 422). International Atomic Energy Agency, Vienna, AUT.

IAEA, 2010. Handbook of parameter values for the prediction of radionuclide transfer in terrestrial and freshwater environments (TRS 472). International Atomic Energy Agency, Vienna, Austria.

Lehtola, M.J., Miettinen, I.T., Keinänen, M.M., Kekki, T.K., Laine, O., Hirvonen, A., Vartiainen, T., Martikainen, P.J., 2004. Microbiology, chemistry and biofilm development in a pilot drinking water distribution system with copper and plastic pipes. Water Research 38, 3769-3779.

Lobelle, D., Cunliffe, M., 2011. Early microbial biofilm formation on marine plastic debris. Mar. Pollut. Bull. 62, 197-200.

Oberbeckmann, S., Löder, M.G.J., Labrenz, M., 2015. Marine microplastic-associated biofilms – a review. Environmental Chemistry 12, 551-562.

Oughton, D., Børretzen, P., Salbu, B., Tronstad, E., 1997. Mobilisation of 137Cs and 90Sr from sediments: Potential sources to arctic waters.

Periáñez, R., Brovchenko, I., Jung, K.T., Kim, K.O., Maderich, V., 2018. The marine kd and water/sediment interaction problem. J. Environ. Radioact.

Saengkul, C., P, P., P, S., 2013. Effect of sediment characteristics on sorption of 137Cs at the sediment-water interface.

Takata, H., Tagami, K., Aono, T., Uchida, S., 2014. Distribution coefficients (Kd) of strontium and significance of oxides and organic matter in controlling its partitioning in coastal regions of Japan. The Science of the total environment 490, 979-986.

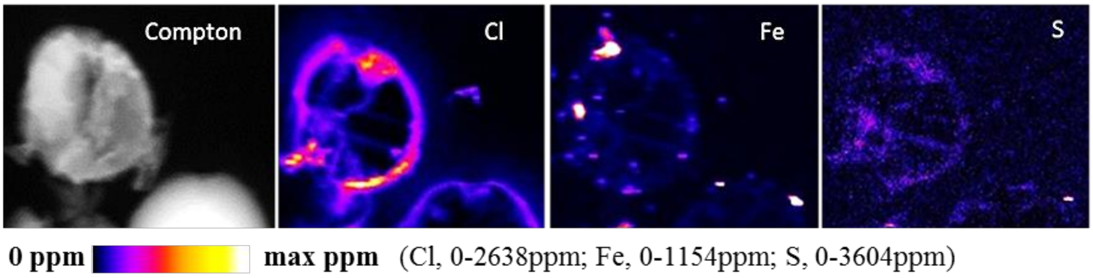
Turner, A., Holmes, L.A., 2015. Adsorption of trace metals by microplastic pellets in fresh water. Environmental Chemistry 12, 600-610.

Wang, J., Tan, Z., Peng, J., Qiu, Q., Li, M., 2016. The behaviors of microplastics in the marine environment. Marine Environmental Research 113, 7-17.

Wetzel, R.G., 1993. Microcommunities and microgradients: Linking nutrient regeneration, microbial mutualism, and high sustained aquatic primary production. Netherland Journal of Aquatic Ecology 27, 3-9.

Zettler, E.R., Mincer, T.J., Amaral-Zettler, L.A., 2013. Life in the "plastisphere": Microbial communities on plastic marine debris. Environmental Science and Technology 47, 7137-7146.

Figure 1. XFM elemental mapping data on HDPE microspheres that were thin-sectioned (25 µm) after 19 days deployment in estuarine conditions.



(Cl, 0-2638ppm; Fe, 0-1154ppm; S, 0-3604ppm)

Figure 2. Bulk Cs and Sr adsorption in freshwater (light blue) and estuarine/marine conditions (dark blue) comparing K_ds of HDPE microsphere plastics+biofilm with reference sediment K_ds from field and laboratory studies (see text). Columns represent geometric means, whiskers indicate minimum and maximum data.