




## Suspended clay and surfactants enhance buoyant microplastic settling

Bruce R. Sutherland<sup>1,2</sup>, Maninderpal S. Dhaliwal<sup>1</sup>, Dennis Thai<sup>1</sup>, Yuhao Li<sup>2</sup>, Murray Gingras<sup>2</sup> & Kurt Konhauser<sup>2</sup>

Most of the plastic waste that enters rivers and the oceans is unaccounted for. Approximately half of the world's produced plastics are buoyant in water, meaning that processes must take place that effectively increase their density, causing them to settle out of solution. One such mechanism is biofouling, in which organic matter grows on the surface of plastics, making them denser. Here we present a new mechanism supported by laboratory experiments for buoyant plastic settling in which particles of clay adhere to the surface of the plastic, mediated by the presence of surfactants. Although the plastic particles in our experiments were a hundred times larger than the micrometer-sized clay particles, we show that clay can adhere to the plastic with sufficient mass to cause the plastic to sink. This occurs even though the plastic is electrically neutral. It is hypothesized that the hydrophobic tails of the surfactant molecules are attracted to the plastic while the hydrophilic heads attract the clay. A greater fraction of plastic sinks if the surfactant concentration is larger. Our findings suggest that microplastic settling is enhanced in muddy rivers due to interactions with naturally occurring or discharged surfactants, even in the absence of biofouling.

<sup>1</sup>Department of Physics, University of Alberta, Edmonton T6G 2E1 AB, Canada. <sup>2</sup>Department of Earth & Atmospheric Sciences, University of Alberta, Edmonton T6G 2E3 AB, Canada. ✉email: [bruce.sutherland@ualberta.ca](mailto:bruce.sutherland@ualberta.ca)

Of the hundreds of millions of tonnes of plastic waste that are produced each year, ~10 million tonnes of municipal plastic waste enters the ocean, largely via rivers<sup>1,2</sup>. Surprisingly, the total amount of floating plastic in the ocean is estimated to be only 0.3 million tonnes<sup>3</sup>. This revelation is particularly concerning in light of the fact that about half of all plastics produced are less dense than sea water<sup>4</sup> and many other plastic items (e.g., discarded water bottles) contain trapped air and so likewise should float on the ocean. This raises the question: where is all the missing plastic? Of particular concern is the fate of microplastics, having sizes ranging from millimeters to nanometers. Lighter microplastics accumulate in marine life near the surface, while denser microplastics can settle through the water column and be taken up by benthic organisms. Microplastics can be harmful to marine life and, when consumed by fish and bivalves, they can eventually bioaccumulate in humans, presenting long-term physical and chemical hazards. Although substantial research has been conducted on plastic waste's impact on aquatic ecosystems, less is known about the pathways through which microplastics travel within estuaries to the coastal ocean and beyond<sup>5</sup>.

Sedimentary microplastics have been found in many depositional settings, including lacustrine<sup>6</sup>, fluvial<sup>7</sup>, deltaic<sup>8</sup>, intertidal flats<sup>9</sup>, shoreface<sup>10</sup>, offshore marine<sup>11</sup> and in sea ice<sup>12</sup>. It is evident that the distribution of microplastics in sediment is pervasive. This is owing to its transportability by water. For example a study of the Rhine River surface waters showed that microplastics were found in all samples taken from 11 locations along 820 km of the Rhine, averaging 892,777 particles per square kilometer, with a peak of 3.9 million in the Rhine-Ruhr area<sup>13</sup>.

All plastic waste ultimately settles, though this process can take days, months, years, or even centuries depending, in part, upon the density and size of the plastics. The mechanisms involving the transport, break-up, and settling of plastic waste in rivers and the ocean remain poorly understood<sup>14</sup>. Floating plastics, with a density less than that of water, can become more brittle due to exposure to ultraviolet light from the sun<sup>15</sup> and then broken up into smaller pieces over time due to turbulence and waves<sup>16,17</sup>. One mechanism for the ultimate settling of buoyant plastics is through biofouling, in which microbes grow on the surface of plastic particles, increasing their density<sup>18–23</sup>.

In this laboratory study, we demonstrate a different, inorganic, mechanism for accelerating the settling of plastics by means of surfactant-mediated clay accumulation on their surfaces. Although, as we demonstrate, the plastic particles we use are electrically neutral, recent studies have shown that surfactants can interact with hydrophobic plastics making them hydrophilic<sup>24,25</sup>. Thus, surfactants act as an intermediary through which clay can attach to buoyant microplastics making them more dense than their surroundings. Surfactants are naturally produced by marine organisms such as phytoplankton<sup>26</sup> as well as being released into rivers and the coastal ocean from municipal wastewater treatment plants<sup>27</sup>. Circumstances are thus prevalent where microplastics released in muddy rivers and estuaries interact with both suspended clay and surfactants.

In our experiments, we used “Pliolite”, a plastic used globally in paints and other consumer products. This relatively soft plastic is easily ground and passed through sieves in order to study settling of plastic particles in narrow size range. As Pliolite has a density of  $1.023 \text{ g cm}^{-3}$ , the experiments were conducted in water mixed with NaCl that has an ionic strength typical of seawater ( $\approx 1.03 \text{ g cm}^{-3}$ ). We used two common clay minerals, kaolinite and montmorillonite, as well as two types of surfactants, sodium dodecyl sulfate (SDS) and Triton X-100 (TritonX). Dilute concentrations of the plastic, clay and surfactant were used in all experiments. The surfactant concentrations were comparable to those measured for urban wastewater entering in rivers (20–70 mg/L)<sup>28</sup>. The clay

concentrations were relatively conservative compared to natural clay concentrations found in modern estuaries (e.g.,<sup>29</sup>). The concentration of Pliolite was chosen so that its mass could be accurately measured before and after each experiment. Though larger than found in most natural settings, the concentration of plastic was small enough in most experiments that there was sufficient clay to allow the plastics to settle. (Of course, in a natural setting, smaller plastic concentrations would be more prone to settling given the relatively larger concentration of suspended clay.)

Details of the experiment set-up and measurement procedures are given in the Methods section. In Supplementary Material, we provide two tables listing the input parameters and results for “good” experiments with no clay, with kaolinite and with montmorillonite clays (Supplementary Tables 1 and 2). Each experiment was performed in a 600 mL glass beaker (see methods) to which 500 mL of saline water was combined with a measured mass of plastic, one of the two types of clay and one of the two types of surfactants. Some experiments were performed with clay and plastic and no surfactant, and some with plastic and surfactant and no clay. In all cases the beaker contents were vigorously mixed over 10 seconds. In some cases, a magnetic stirrer performed additional mixing for up to 1 h. After mixing, the beaker was covered and left overnight. The following day, the particles floating on the surface and those settled on the bottom were carefully extracted and put onto different filter paper lying on separate Buchner funnels. The samples were rinsed and then allowed to air-dry overnight. On the second day, the two dried samples were weighed. Knowing the masses of the filter papers, we thus determined the mass of floating particles and the mass of settled particles. An experiment was considered “good” if the sum of these masses was within 10% of the sum of the initially added masses of plastic and clay. Below we also include results from “acceptable” experiments for which the sum of dried masses was within 20% of the initial sum. For some experiments, after the settled and floating particles were dried they were subjected to analysis under a scanning electron microscope (SEM) using energy-dispersive X-ray spectroscopy.

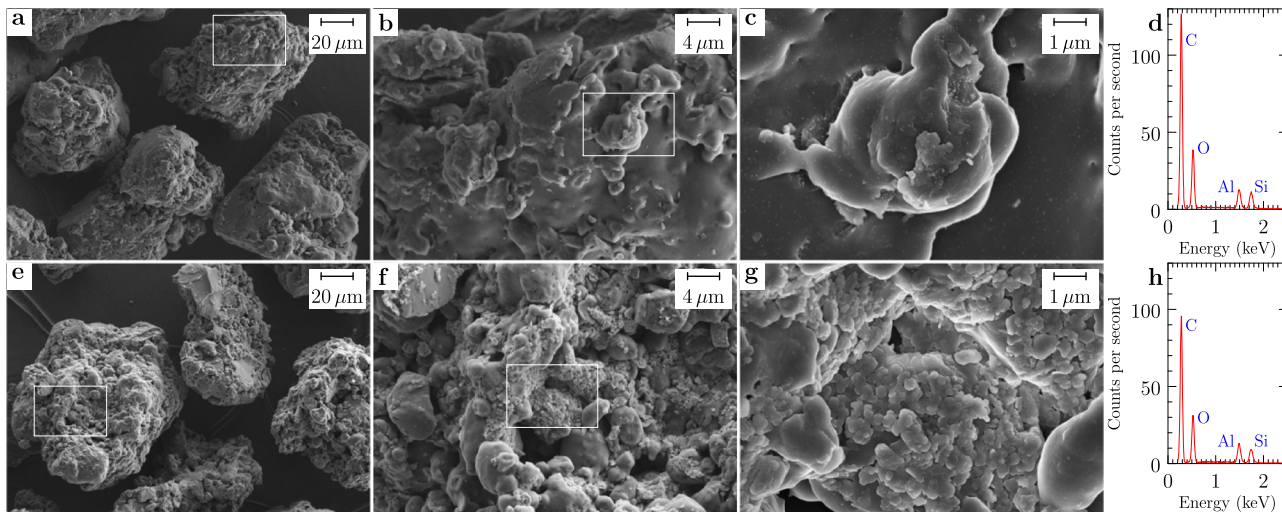
Our results are given in terms of  $f_s$ , which is the difference between the measured mass of settled particles and the mass of added clay, all divided by the mass of added plastic. If no clay adhered to the floating particles,  $f_s$  would represent the fraction of settled plastic particles. Should some clay be attached to the floating particles, the actual fraction of settled plastic particles would be larger.

The results below clearly show that clay adhered to the plastic particles and that the mass of settled plastic generally increased with increasing mass of added surfactant and clay.

## Results and discussion

**Qualitative results.** As shown in Fig. 1, SEM images revealed that the floating settled particles, after being filtered and dried, comprised plastic particles of sizes consistent with what was added for that specific experiment. Upon further magnification, it was observed that micron-sized clay particles were attached to the plastic surfaces. The presence of clay was additionally confirmed through energy-dispersive X-ray spectroscopy, which showed energy peaks corresponding to the presence of aluminum and silicon, which are elements in kaolinite.

Table 1 lists the parameters and values of  $f_s$  for a subset of the 77 good experiments performed. This subset was chosen for illustrative purposes, with supplementary material giving values for all good experiments in Supplementary Tables 1 and 2. Plastic settling was only observed in experiments having both clay and surfactant; no settling occurred in the absence of either clay or surfactant. In general, experiments that used larger amounts of surfactant and larger relative concentration of clay resulted in a



**Fig. 1 Scanning electron microscope analysis of plastics and clay.** SEM images of particles recovered from the top (a–c) and bottom (e–g) of a beaker after filtering and drying. In the experiment, 0.40 g of Pliolite particles of mean size  $d_p \approx 83 (\pm 8) \mu\text{m}$  were mixed with 0.1 g kaolinite and 0.04 g SDS in 500 mL of a salt water solution with density  $1.031 \text{ g cm}^{-3}$ . The white box in (a) and (e) indicates the windows in (b) and (f), respectively, and the white box in (b) and (g) indicates the windows in (c) and (g), respectively. The scale for each image is indicated at the top left. The energy-dispersive X-ray spectroscopy analysis of the images in (b) and (f) are shown in (d) and (h), respectively.

**Table 1 Measurements for selected experiments.**

Exp.	$d_p$ ( $\mu\text{m}$ )	$m_p$ (g)	clay type	$m_c$ (g)	$m_s$ (g)	$f_s$ (%)
1	106–125	0.40	kaolinite	0.10	0.004	8 ( $\pm 3$ )
2	106–125	0.40	kaolinite	0.10	0.022	38 ( $\pm 4$ )
3	90–106	0.20	kaolinite	0.10	0.020	45 ( $\pm 2$ )
4	90–106	0.10	kaolinite	0.20	0.020	40 ( $\pm 4$ )
5	90–106	0.10	kaolinite	0.10	0.044	60 ( $\pm 4$ )
6	90–106	0.10	kaolinite	0.10	0.082	95 ( $\pm 5$ )
7	90–106	0.40	kaolinite	0.10	0.040	53 ( $\pm 5$ )
8	75–90	0.40	kaolinite	0.10	0.026	38 ( $\pm 3$ )
9	45–53	0.40	kaolinite	0.10	0.020	33 ( $\pm 2$ )
10	106–125	0.40	montmorillonite	0.10	0.004	5 ( $\pm 3$ )
11	106–125	0.40	montmorillonite	0.10	0.020	20 ( $\pm 2$ )
12	90–106	0.40	montmorillonite	0.10	0.020	48 ( $\pm 3$ )
13	63–75	0.40	montmorillonite	0.10	0.020	53 ( $\pm 3$ )
14	45–53	0.40	montmorillonite	0.10	0.020	43 ( $\pm 2$ )

Results for a subset of experiments showing plastic particle size ranges ( $d_p$ , in  $\mu\text{m}$ ) and added plastic mass ( $m_p$ , in g), clay type and added clay mass ( $m_c$ , in g), added mass of SDS surfactant ( $m_s$ , in g) and the excess of measured bottom mass to added clay mass relative to the added plastic mass,  $f_s$  (errors in parentheses).

greater mass of settled plastic. By comparison, the fraction of added plastic that settled exhibited a weaker dependence on the plastic size, the plastic mass relative to clay, the type of clay used, and the type of surfactant.

**Influence of clay and surfactant concentration.** The importance of clay and surfactant concentration on plastic settling is further demonstrated in Fig. 2. The plot includes data for all experiments that were deemed good (plotted as red symbols) or acceptable (plotted as blue symbols).

The minimum volume of clay necessary to attach to a plastic particle to make the agglomerate more dense than its surroundings is (see Methods)

$$\phi_{c,crit} \approx \frac{\rho_f - \rho_p}{\rho_c - \rho_f}, \tag{1}$$

in which  $\rho_f$ ,  $\rho_c$  and  $\rho_p$  are the densities, respectively, of the ambient fluid density, clay and plastic. Given the initial volume concentration of clay in a beaker of volume  $V_f$  we estimate the

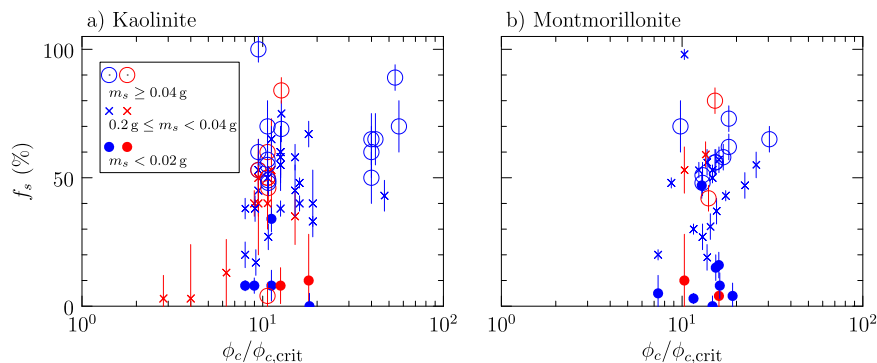
volume of clay that interacts with a plastic particle over the fluid column to be (see Methods)

$$\phi_c \approx \frac{V_c H}{V_f d_p}, \tag{2}$$

in which  $V_c = m_c/\rho_c$  is the volume of added clay,  $H$  is the fluid depth and  $d_p$  is the plastic particle diameter. Thus, we expect that few plastic particles will settle if  $\phi_c \lesssim \phi_{c,crit}$  and that more settling will occur for larger  $\phi_c/\phi_{c,crit}$ .

Despite the scatter of the data in Fig. 2, the results generally show little settling of plastic particles for  $\phi_c/\phi_{c,crit} \lesssim 7$  and more settling (at fixed surfactant concentration) for larger relative  $\phi_c$ . The scatter is expected due to the random nature of the initial turbulent mixing by the hand blending, bringing plastic and clay particles together. Additionally mixing by the magnetic stirrer resulted in no significant difference in  $f_s$  with other parameters being kept fixed (see Supplementary Tables 1 and 2).

The different symbols in Fig. 2 indicate different ranges in the concentration of added surfactant. Despite the scatter, generally



**Fig. 2 Measurements of settled plastic mass.** For experiments with (a) kaolinite and (b) montmorillonite, approximate relative mass of settled plastic,  $f_s$ , as it depends on the prediction of clay concentration (Eq. (2)) relative to the minimum concentration required for settling (Eq. (1)). The latter ratio is plotted on a log axis. Blue symbols are good and red symbols are acceptable (see text), with error bars drawn as vertical lines. In both plots, different symbols correspond to the mass of added surfactant as indicated in the legend in (a):  $m_s < 0.02$  g (solid circles),  $0.02 \leq m_s < 0.04$  g (open squares),  $m_s \geq 0.04$  g (open circles). Vertical bars on each symbol denote errors associated with measurement of masses of particles and filters.

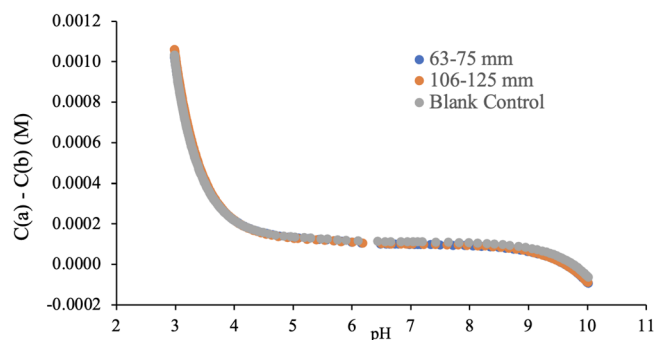
more plastic settling occurs if more surfactant is added, at least in the ranges explored up to  $0.2 \text{ g L}^{-1}$  of surfactant in solution. For kaolinite (montmorillonite) with  $7 \leq \phi_c/\phi_{c,\text{crit}} \leq 20$ , the mean settled fraction is  $\bar{f}_s = 11\%$  ( $12\%$ ) for  $m_s < 0.2$  g,  $\bar{f}_s = 47\%$  ( $44\%$ ) for  $0.2 \leq m_s < 0.4$  g, and  $\bar{f}_s = 67\%$  ( $59\%$ ) for  $m_s \geq 0.4$  g.

In these plots,  $f_s$  would represent the fraction of added plastic that settles only if no clay is attached to the floating plastic particles. Because SEM images show that some clay is also attached to the floating plastic,  $f_s$  is actually a lower bound on the relative mass of plastic that settles. We can estimate an upper bound on the relative mass of settled plastic,  $f_{sp,\text{max}}$ , by supposing the maximum relative volume of clay,  $\phi_{c,\text{crit}}$ , is attached to each floating particle, rendering each neutrally buoyant. In this case, the relative mass of settled particles is given in terms of  $f_s$  by (see Methods)

$$f_{sp,\text{max}} = \frac{f_s + \phi_{c,\text{crit}} \rho_c / \rho_p}{1 + \phi_{c,\text{crit}} \rho_c / \rho_p}. \quad (3)$$

In our experiments,  $\phi_{c,\text{crit}}$  is on the order of 1%. And so  $f_{sp,\text{max}}$  is no larger than 1% of  $f_s$ . That is, within the errors of our experiments,  $f_s$  is a good estimate of the fraction of added plastic that settles.

**Electric neutrality of plastic.** Potentiometric acid-base titration<sup>30</sup> and cadmium (Cd) adsorption experiments<sup>31,32</sup> were performed to confirm that Pliolite is an electrically neutral plastic. The two methods are generally used to measure the surface electric properties of particles. In titration experiments, successive quantities of acid and base were added to a solution of salt water with and without particles and the resultant pH was measured. In the Cd adsorption experiments, the change in the concentration of dissolved  $\text{Cd}^{2+}$  was measured over time. (See Methods.) In the titration experiments, the presence of plastics exhibited negligible change to the variation of pH with added acid and base, as shown in Fig. 3. The saltwater weakly buffered the addition of acid and base, as indicated by the plateau in the difference of acid and base concentration as the pH varied from  $\approx 5$  to 9. However, the measured curve with and without plastics was the same, to within errors. This indicated that the plastics had no surface charge, which would have changed the structure of the plateau. In contrast, we show the titration results for solutions with montmorillonite clay and with cyanobacteria, whose surface reactivities were previously well-characterized in other studies<sup>29,33</sup> (see Supplementary Fig. 1). In comparison to experiments without clay or bacteria, the experiments clearly



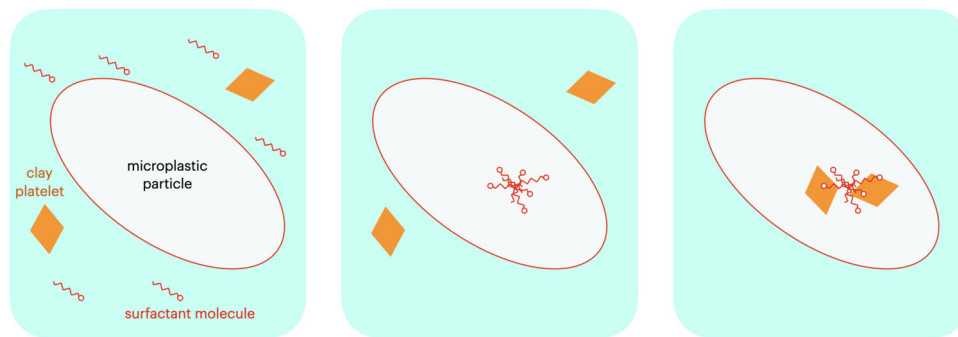
**Fig. 3 Titration experiments.** Representative results from each of the three triplicate potentiometric acid-base titration experiments. Vertical axis represents the concentration difference in molar between acid added during the initial down titration to pH 3 and base added during the subsequent forward titration from pH 3 to pH 10. Horizontal axis represents real time pH values during the respective forward titration. The titration curve from both sizes of microplastic particles show identical buffering capacity compared to the blank, which indicates that both samples have little to non-reactive sites on their surfaces.

show a different response to the pH of the solution as the concentration of acid and base is varied. Likewise, a continuously mixed solution of  $\text{Cd}^{2+}$  and plastic particles showed no significant difference in the Cd concentration over two and a half days. Therefore, it is concluded that Cd did not adsorb onto microplastic particles studied here, further indicating their non-reactive nature.

Because these experiments show that the surface of Pliolite particles are electrically neutral and non-reactive, the mechanism by which electrically charged clay particles might attach to the plastic requires an additional ingredient. We hypothesize a conceptual model in which surfactant acts as an intermediary that draws clay to the surface of plastic.

**Conceptual model.** We propose a mechanism for how the presence of surfactant enhances the attraction of clay to plastic (Fig. 4). Surfactants have hydrophobic tails that avoid water and tend to collect near solid surfaces or intertwine as micelles<sup>34</sup>. Consequently, even though plastics are electrically neutral, the hydrophobic tails of surfactants naturally accumulate onto their surfaces to avoid being surrounded by water. By contrast, the hydrophilic heads of surfactants are attracted to ionic molecules, and hence, naturally attract dipolar-charged clay particles. Thus,





**Fig. 4 Schematic showing proposed mechanism for clay accretion onto plastic.** The hydrophobic tails of surfactant molecules accumulate onto the plastic surface to avoid immersion in water. Platelets of clay are then attracted to the hydrophilic heads of the surfactant molecules.

surfactants serve as an intermediary mechanism, facilitating the attraction of clays to the surface of plastics, or any other submerged particle that is electrically neutral.

It has previously been shown that clay flocculation is enhanced in the presence of dissolved salts<sup>35</sup>. Thus, the accumulation of clay onto plastics is further enhanced in saline water through the formation of flocs, as is evident in Fig. 1, which shows stacks of clay particles on the surface.

## Conclusions

We have shown that surfactants (SDS and Triton X) can cause clays (kaolinite and montmorillonite) to accumulate on the surface of the plastic Pliolite. The accumulation of clay can increase the bulk density of the plastic to make it sink through the ambient fluid. As opposed to the process of biofouling, our study indicates what, to the best of our knowledge, is a new inorganic process through which buoyant plastics may ultimately sink, and dense plastics may settle more rapidly.

Surfactants are commonly mixed with synthetic plastic fibers in clothing, some of which are released in tandem into municipal wastewater when laundered. Natural surfactants, such as phospholipids—originating from cell membranes, are also present in rivers and estuaries. These may interact with fibers from clothing, tires, or plastics from other consumer products to increase the density and settling rate of microplastics.

Our study has focused on Pliolite, a type of plastic which is more dense than fresh water, but buoyant in sea water. We hypothesized that the specific type of plastic used has little influence on clay accumulation as it only serves as an electrically neutral solid surface. This hypothesis is supported by separate ongoing research showing that glass particles are attracted to a plastic that is lighter than fresh water. The presence of saltwater in our experiments can increase clay flocculation, resulting in larger masses of clay on their surface. To what degree this may enhance plastic particle settling in estuaries and coastal regions has yet to be investigated.

## Methods

**Plastic, clays, and surfactants.** Pliolite is a polymerized styrene produced by Goodyear Chemical. Being relatively soft, it is readily ground to small size using a mortar and pestle. After grinding, the particles were put into a stack of sieves that were then shaken to produce batches of particles in different sizes with mean diameters,  $d_p$ , in the following ranges: 49 ( $\pm 4$ )  $\mu\text{m}$ , 58 ( $\pm 5$ )  $\mu\text{m}$ , 69 ( $\pm 6$ )  $\mu\text{m}$ , 83 ( $\pm 7$ )  $\mu\text{m}$ , 98 ( $\pm 8$ )  $\mu\text{m}$  and 116 ( $\pm 10$ )  $\mu\text{m}$ .

Our experiments used two types of clays: kaolinite (aluminum silicate,  $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) was provided by Thermo Fisher Scientific Chemicals; montmorillonite, originating from Saskatchewan, Canada, was provided by Plainsman Pottery Supply.

The two types of surfactants used (SDS and TritonX) were both provided by Fisher Scientific.

**Experiment set-up.** A stock NaCl saline solution was prepared and its density measured to 5-digit accuracy with an Anton Paar DMA 4500 densitometer. Typical fluid densities were  $\rho_f \approx 1.03 \text{ g cm}^{-3}$  (0.56 M), set to be about 1 percent larger than the density of the Pliolite plastic. A measured mass (between 0.02 and 0.41 g) of Pliolite of a given size range was put in a petri dish along with a measured mass of clay (between 0.10 and 0.40 g). Separately, a measured mass of surfactant (0.004–0.42 g) was put into a 600 mL glass beaker. The beaker was then filled to  $\sim 200$  mL with the stock saline solution and the plastic and clay were added. The contents were vigorously mixed with a Braun hand mixer in a series of pulses for 10 s. This uniformly combined the particles in solution, overcoming any effects of surface tension. The mixer was pulled out of the solution, hovering over the surface while and more of the stock saline solution was poured over the mixer to rinse any clinging particles into the beaker. The beaker was then topped off with more of the saline solution until the mixture had a volume of 500 mL. In most experiments, the beaker was then covered and then left to rest until particles settled on the bottom or floated to the top, the latter initially mingling with the surfactant-induced foam floating on the surface as a consequence of the mixing. In some experiments, the beaker was placed on a magnetic stirrer with a stir bar that continued to mix the contents of the beaker for a set amount of time between 5 and 60 min. Afterwards, the magnet was removed and clinging particles rinsed off with saline solution into the beaker. The beaker was then covered and left to rest. Although most of the settling occurred within tens of minutes after mixing, the beaker was typically left to rest overnight allowing all the particles either to rise to the surface or settle on the bottom.

**Particle extraction and measurement.** After resting overnight, the settled particles lay consolidated at the bottom of the beaker in a sediment layer less than 1 mm deep. At the surface, any bubbles that formed during the previous day's mixing had dissipated and the floating particles were confined to the surface. The ambient fluid was perfectly clear between the bottom-settled and surface-floating particles.

The particles floating on the surface were carefully extracted onto Whatman (10312644) filter paper (pore size  $< 2 \mu\text{m}$ ) lying on a Buchner funnel. Particles that settled on the bottom were extracted onto Filtrafine PTFE filter paper (pore size  $0.1 \mu\text{m}$ ) lying on a separate Buchner funnel. These extracted samples from the surface and bottom were then air-dried overnight, and the dry samples were weighed. Knowing the masses of the filter papers, we determined the mass of floating particles,  $m_{\text{top}}$ , and the mass of settled particles,  $m_{\text{bottom}}$ . An experiment was considered good (acceptable) if the sum of these masses was within 10% (20%) of the sum of the initially added masses of plastic and clay. The fraction of added plastic that settled was estimated from the

measured mass of settled particles minus the mass of added clay:  
 $f_s = (m_{\text{bottom}} - m_c)/m_p$ .

**Titration experiments.** Two sizes of microplastic particles (63–75 mm; and 106–125 mm) were examined for their surface charges via potentiometric acid-base titrations on a Metrohm Titrando 905 titrator. Each titration started with 250 mL of 0.56 M NaCl solution at a density of  $1.032 \text{ g cm}^{-3}$  in a titration vessel with a stir bar continuously stirring the solution to create a vortex. Subsequently, 0.2 g of sample was slowly added into the vortex to assure that the majority of plastic particles remained in the background solution throughout the experiment. The titration vessel was then carefully sealed and the mixture was purged with  $\text{N}_2$  gas for 30 min to create an anoxic environment. From nearly circumneutral pH 7, the pH of each sample was first titrated down to 3 by incremental additions of 0.1 M  $\text{HNO}_3$ . This was followed by increasing the pH of the mixture to 10 with incremental additions of 0.1 M NaOH. Finally, to test the reversibility, the pH was again titrated down to pH 3 using the same acid. The real-time experimental data including pH values, and the corresponding amounts of acid and base added into the mixture was recorded. Titrations were conducted in triplicates for both sizes of microplastics plus a blank control without microplastics. The results are shown in Fig. 3.

We also conducted Cd adsorption experiments in seawater with pH 8 to confirm and characterize the surface reactive sites on the sample of interest if they were present on the samples. Cd was chosen as the model cation because it is commonly used in metal adsorption experiments (e.g., to bacteria, clays, organic polymers) and thus the plastic reactivity can be compared to other substrata<sup>31,32,36</sup>. An aliquot of microplastic particles in the range of 63–75 mm was added and suspended in a 50 mL falcon tube with 0.56 M NaCl and Cd-spiked solution at an initial Cd concentration of 0.8 ppm. Immediately afterwards, the pH of the mixture solution was adjusted to 8. The mixture solution was then vigorously stirred overnight followed by another pH adjustment to 8 and put on a rotator for constant mixing for up to 60 h, during which pH of the mixture was carefully monitored and re-adjusted when needed. A total of 4 samples were extracted from the original mixture solution at the following four stages: 1) beginning of the experiment right after the first pH adjustment; 2) 24 h after mixing; 3) 48 h after mixing; and 4) 60 hours after mixing. Each sample was filtered through a 0.22  $\mu\text{m}$  filter membrane and subsequently diluted with a 2%  $\text{HNO}_3$  and 0.5% HCl solution, and lastly measured for dissolved Cd concentration on an Agilent 8800 Triple Quadrupole ICP-MS. The result is shown in Table 2.

During the 60 h incubation and four different time points, the concentrations of free Cd cations that stayed in solution remained at the same level with the initial concentration of 0.8 ppm [Table 2]. The most pronounced difference in dissolved Cd concentration in solution came from the last sampling time point, where the Cd concentration was only 4.41% higher compared to the initial value. The 4.41% discrepancy in Cd concentration is well below the manufacturer-specified level of instrumental error of 5 to 10%. Therefore, it is concluded that Cd did not adsorb onto microplastic particles studied here, further indicating their non-reactive nature.

**Table 2 Cadmium adsorption experiment results.**

Hours	0	24	48	60
Concentration (ppm)	0.8090	0.8155	0.8155	0.8447

The concentrations of dissolved Cd that remained in solution during the course of 60 h incubation of Cd adsorption onto the microplastic particles (63–75 mm range).

**Model for critical clay concentration.** Consider a plastic particle of volume  $V_{p1}$  and density  $\rho_p$  in fluid of density  $\rho_f > \rho_p$ . Suppose a volume  $V_c$  of clay, with density  $\rho_c$ , adheres to the plastic particle. The effective density of the plastic with attached clay is

$$\rho_{pc} = (\rho_p V_{p1} + \rho_c V_c)/(V_{p1} + V_c),$$

and the difference between this and the fluid density is

$$\rho_{pc} - \rho_f = [(\rho_p - \rho_f)V_{p1} + (\rho_c - \rho_f)V_c]/(V_{p1} + V_c).$$

We seek the critical volume of clay,  $V_{c,\text{crit}}$  such that this density difference is zero, meaning that any larger volume of attached clay would make the particle settle. Assuming the density of plastic is much closer to the fluid than the density of clay, we may assume  $V_{c,\text{crit}}$  is much less than  $V_{p1}$ . And so the critical volume of clay relative to the volume of plastic is

$$V_{c,\text{crit}}/V_{p1} \simeq \phi_{c,\text{crit}} \simeq \frac{\rho_f - \rho_p}{\rho_c - \rho_f}.$$

This is the quantity defined as  $\phi_{c,\text{crit}}$  in Eq. (1). For typical density values for the experiments presented here, we have  $\phi_{c,\text{crit}} \sim 0.01$ .

The question is whether in our experiments, a single plastic particle initially mixed in solution can interact with a sufficient volume of clay particles before rising to the surface so that it becomes more dense and sinks. Let  $V_{c1}$  be the (mean) volume of single clay particle. If a mass,  $m_c$ , of clay is added to a volume,  $V_f$ , of fluid, the number concentration of clay particles is  $n_c = [m_c/(\rho_c V_{p1})]/V_f$ . Suppose the plastic particle has (mean) diameter  $d_p$  and that it traverses a distance  $H$  before reaching the surface. An estimate of the number of clay particles with which it interacts over this distance is  $N \simeq n_c(d_p^2 H)$ . So the volume ratio of clay particles that interact with a plastic particle is

$$\frac{NV_{c1}}{V_{p1}} \sim \frac{m_c/\rho_c H}{V_f d_p}.$$

This is the quantity defined as  $\phi_c$  in (2). Taking  $H = 9.3 \text{ cm}$  as the depth of fluid in the beaker, we find  $\phi_c \sim 0.1$ . In reality, this is an under-estimate since the initial mixing would cause the particle to sample a longer distance before reaching the surface. Even using the beaker depth for  $H$ ,  $\phi_c$  is an order of magnitude larger than  $\phi_{c,\text{crit}}$ . This indicates that it, in most experiments is reasonable to assume a plastic particle will interact with a sufficient number of clay particles before rising to the surface to reverse its buoyancy, causing it to settle should all the clay attach to the plastic. In Fig. 2, the percent of settled plastic is plotted against  $\phi_c/\phi_{c,\text{crit}}$ . In all cases, this ratio is larger than unity

**Model for maximum settled plastic.** Generally, the mass of settled and floating clay and plastic can be written as  $m_b = \alpha m_c + \beta m_p$  and  $m_t = (1 - \alpha)m_c + (1 - \beta)m_p$ , respectively. Here  $\alpha$  and  $\beta$  represent the fraction of added clay and plastic, respectively, that settle. If all the clay settles (none being attached to floating plastic) then  $\alpha = 1$  and  $\beta = (m_b - m_c)/m_p = f_{sp,\text{min}}$  is the minimum relative mass of settled plastic.

Now, suppose the maximum volume of clay is attached to the floating plastic, such that any more clay would make at least some floating particles more dense than their surroundings, causing them to sink. This volume of clay at the surface is  $(1 - \alpha^*)V_c = V_{c,\text{crit}}N_{pf}$  in which  $V_c = m_c/\rho_c$  is the volume of clay added and  $N_{pf}$  is the number of floating plastic particles. Using  $N_{pf} = (1 - \beta)V_p/V_{p1}$  and (1), we find  $(1 - \alpha^*)V_c = (1 - \beta)\phi_{c,\text{crit}}V_p$  and, therefore,

$$\alpha^*V_c = V_c - (1 - \beta)\phi_{c,\text{crit}}V_p. \quad (4)$$

Replacing  $\alpha$  with  $\alpha^*$  in the expression for  $m_b$  thus gives an expression for the settled mass in terms of the maximum fraction,

$\beta^*$ , of settled plastic particles:

$$m_b^* = m_c + \left( \beta^* - (1 - \beta^*) \phi_{c,crit} \rho_c / \rho_p \right) m_p, \quad (5)$$

in which  $\beta^*$  is the corresponding relative mass of settled plastic.

We define  $f_s = (m_b^* - m_c) / m_p$  as the relative difference of the measured settled mass and added clay. the maximum mass of clay is attached to floating plastic particles. Using (5), we have  $f_s = - (1 - \beta^*) \phi_{c,crit} \rho_c / \rho_p + \beta^*$ . Rearranging gives the expression for the maximum relative settled plastic mass  $f_{sp,max} \equiv \beta^*$ , which is given by (3).

### Data availability

The datasets generated and analyzed during the current study are available in the Supplementary Material. They are also available at <https://doi.org/10.5281/zenodo.8429163>.

Received: 31 May 2023; Accepted: 13 October 2023;

Published online: 26 October 2023

### References

- Jambeck, J. R. et al. Plastic waste inputs from land into the ocean. *Science*. **347**, 768–771 (2015).
- Siegfried, M., Koelmans, A. A., Besseling, E. & Kroeze, C. Export of microplastics from land to sea. A modelling approach. *Water Res.* **127**, 249–257 (2017).
- van Sebille, E. et al. A global inventory of small floating plastic debris. *Environ. Res. Lett.* **10**, 124006 (2015).
- Geyer, R., Jambeck, J. R. & Law, K. L. Production, use, and fate of all plastics ever made. *Sci. Adv.* **3**, e1700782 (2017).
- van Sebille, E. et al. The physical oceanography of the transport of floating marine debris. *Environ. Res. Lett.* **15**, 023003 (2020).
- Dong, H. et al. Microplastics in a Remote Lake Basin of the Tibetan Plateau: impacts of atmospheric transport and glacial melting. *Environ. Sci. Technol.* **55**, 12951–12960 (2021).
- He, B., Goonetilleke, A., Ayoko, G. A. & Rintoul, L. Abundance, distribution patterns, and identification of microplastics in Brisbane River sediments, Australia. *Sci. Total Environ.* **700**, 134467 (2020).
- Leslie, H. A., Brandsma, S. H., Velzen, M. J. M. V. & Vethaak, A. D. Microplastics en route: field measurements in the Dutch river delta and Amsterdam canals, wastewater treatment plants, North Sea sediments and biota. *Environ. Int.* **101**, 133–142 (2017).
- Blumenröder, J., Sechet, P., Kakkonen, J. E. & Hartl, M. G. Microplastic contamination of intertidal sediments of Scapa Flow, Orkney: a first assessment. *Mar. Poll. Bull.* **124**, 112–120 (2017).
- Chubarenko, I. & Stepanova, N. Microplastics in sea coastal zone: lessons learned from the Baltic amber. *Environ. Pollut.* **224**, 243–254 (2017).
- Daana, K. K. L. et al. Microplastics in sub-surface waters of the Arctic Central Basin. *Mar. Pollut. Bull.* **130**, 8–18 (2018).
- Kanhai, L.D.K., Gøardfeldt, K., Krumpfen, T., Thompson, R.C., O'Connor, I. Microplastics in sea ice and seawater beneath ice floes from the Arctic Ocean. *Sci Rep.* **10**(1):5004 (2020).
- Mani, T., Hauk, A., Walter, U. & Burkhardt-Holm, P. Microplastics profile along the Rhine River. *Sci. Rep.* **5**, 17988 (2015).
- Sutherland, B. R., DiBenedetto, M., Kaminski, A. & van den Bremer, T. Fluid dynamics challenges in predicting plastic pollution transport in the ocean: a perspective. *Phys. Rev. Fluids* **8**, 070701 (2023).
- Hebner, T. S. & Maurer-Jones, M. A. Characterizing microplastic size and morphology of photodegraded polymers placed in simulated moving water conditions. *Environ. Sci. Process. Impacts* **22**, 398–407 (2020).
- Ward, C. P. & Reddy, C. M. We need better data about the environmental persistence of plastic goods. *PNAS* **117**, 14618–14621 (2020).
- Efimova, I., Bagaeva, M., Bagaeva, A., Kileso, A. & Chubarenko, I. P. Secondary microplastics generation in the sea swash zone with coarse bottom sediments: laboratory experiments. *Front. Mar. Sci.* **5**, 313 (2018).
- Fazey, F. M. C. & Ryan, P. G. Biofouling on buoyant marine plastics: an experimental study into the effect of size on surface longevity. *Environ. Pollut.* **210**, 354–360 (2016).
- Kooi, M., van Nes, E. H., Scheffer, M. & Koelmans, A. A. Ups and downs in the ocean: effects of biofouling on vertical transport of microplastics. *Environ. Sci. Technol.* **51**, 7963–7971 (2017).
- Kaiser, D., Kowalski, N. & Waniek, J. J. Effects of biofouling on the sinking behaviour of microplastics. *Environ. Sci. Technol.* **51**, 7963–7971 (2017).
- Weinstein, J. H., Crocker, B. K. & Gray, A. D. From macroplastic to microplastic: degradation of high-density polyethylene, polypropylene, and polystyrene in a salt marsh habitat. *Environ. Toxicol. Chem.* **35**, 1632–1640 (2016).
- Semcesen, P. O. & Wells, M. G. Biofilm growth on buoyant microplastics leads to changes in settling rates: Implications for microplastic retention in the Great Lakes. *Mar. Pollut. Bull.* **170**, 112573 (2021).
- Liu, S. et al. Integrated effects of polymer type, size and shape on the sinking dynamics of biofouled microplastics. *Water Res.* **220**, 118656 (2022).
- Xia, Y., Zhou, J. J., Gong, Y. Y., Li, Z. J. & Zeng, E. Y. Strong influence of surfactants on virgin hydrophobic microplastics adsorbing ionic organic pollutants. *Environ. Pollut.* **265**, 115061 (2020).
- Jiang, Y. et al. Effect of surfactants on the transport of polyethylene and polypropylene microplastics in porous media. *Water Res.* **196**, 117016 (2021).
- Žutic, V., Čosović, B., Marčenko, E., Bihari, N. & Kršinić, F. Surfactant production by marine phytoplankton. *Mar. Chem.* **10**, 505–520 (1981).
- Jackson, M. et al. Comprehensive review of several surfactants in marine environments: fate and ecotoxicity. *Environ. Toxicol. Chem.* **35**, 1077–1086 (2016).
- Kume, G., Gallotti, M. & Nunes, G. Review on anionic/cationic surfactant mixtures. *J. Surfact. Deterg.* **11**, 1–11 (2008).
- Playter, T. et al. Microbe-Clay interactions as a mechanism for the preservation of organic matter and trace metal biosignatures in black shales. *Chem. Geol.* **459**, 75–90 (2017).
- Hao, W., Flynn, S., Alessi, D. S. & Konhauser, K. O. Change of the point of zero net proton charge (pHPZNPC) of clay minerals with ionic strength. *Chem. Geol.* **493**, 458–467 (2018).
- Petrash, D. P., Raudsepp, M., Lalonde, S. V. & Konhauser, K. O. Assessing the importance of matrix materials in biofilm chemical reactivity: Insights from proton and cadmium adsorption onto the commercially-available biopolymer alginate. *Geomicrobiol. J.* **28**, 266–273 (2011).
- Liu, Y. et al. Acid-base properties of kaolinite, montmorillonite, and illite. *Chem. Geol.* **483**, 191–200 (2018).
- Swaren, L. et al. Surface reactivity of the cyanobacterium *Synechocystis* sp. PCC 6803-Implications for trace metals transport to the oceans. *Chem. Geol.* **592**, 120045 (2021).
- Chassagne, C. Introduction to Colloid Science: Applications to Sediment Characterization. Delft: TU Delft Open; 2019.
- Sutherland, B. R., Barrett, K. J. & Gingras, M. K. Clay settling in fresh and salt water. *Environ. Fluid Mech.* **15**, 147–160 (2015).
- Koretsky, C. The significance of surface complexation reactions in hydrologic systems: a geochemist's perspective. *J. Hydrol.* **230**, 127–171 (2000).

### Acknowledgements

The authors are grateful to Nathan Gerein for his assistance in taking SEM images and to Paolo Luzzatto-Fegiz, UC Santa Barbara, for helpful advice. This research was made possible through financial support provided by the Natural Sciences and Engineering Research Council (NSERC) of Canada.

### Author contributions

B.R.S. designed the study and led writing of the paper. M.S.D. and D.T. performed and analyzed the beaker experiments. Y.L. performed the titration experiments. Y.L., M.G., and K.K. contributed to the editing and discussion of the paper.

### Competing interests

The authors declare no competing interests.

### Additional information

**Supplementary information** The online version contains supplementary material available at <https://doi.org/10.1038/s43247-023-01055-2>.

**Correspondence** and requests for materials should be addressed to Bruce R. Sutherland.

**Peer review information** *Communications Earth & Environment* thanks Roberto Fernández and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. Primary Handling Editors: Ilka Peeken, Clare Davis. A peer review file is available.

**Reprints and permission information** is available at <http://www.nature.com/reprints>

**Publisher's note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2023