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Validation of density separation for the rapid recovery of microplastics from sediment.

Brian Quinn*, Fionn Murphy, Ciaran Ewins

Address:

Institute of Biomedical and Environmental Health Research (IBEHR), School of Science & Sport, University of the West of Scotland, Paisley, PA1 2BE, Scotland.

*Corresponding author:

Email: brian.quinn@uws.ac.uk

Abstract:

Several density separation techniques using numerous brine solutions have been developed for the separation of microplastics from sediment. The aim of this study was to validate the use of various brine solutions in a relatively rapid, reproducible, low cost single stage method that can deliver consistently high recoveries for different microplastic polymers <1 mm appropriate for monitoring programmes. The recovery of environmentally relevant microplastics (200 – 400 µm and 800 – 1000 µm) from post-consumer products was tested against tap water and brine solutions of varying density including sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI) and zinc bromide ($ZnBr_2$). As expected general trend of increasing microplastic recovery with increasing solution density was observed, with NaI and $ZnBr_2$ having significantly ($p=<0.001$) higher rates of microplastic recovery. Microplastic size was found to influence recovery rates and needs to be taken into consideration when choosing a brine solution. From this work it is evident that density separation recovery tests are needed to validate the use of brine solutions for microplastic recovery and that $ZnBr_2$ is a novel and appropriate brine solution for microplastic extraction. This study represents the most in depth validation of brine solutions for the density separation of microplastic from sediments undertaken to date.

Keywords:

Density separation; brine solution; microplastic; sediment; validation

1. Introduction

Microplastics are commonly found throughout the environment and have been isolated from water, sediment and biological samples throughout the world (for review see[1]). Much of this research has concentrated on marine sediments which are seen as the ultimate sink for all microplastic[2] and where microplastics can represent 3.3% of the sediment by weight on heavily polluted beaches.[3] Following sediment sample collection for microplastic analysis the potential plastic fragments need to be separated from other organic and inorganic material for identification and quantification. In some cases the sample may be reduced in the field by filtration or density separation,[4] but in most cases a bulk sample will be taken back to the laboratory for microplastic analysis. There are several laboratory techniques commonly used for the separation of microplastics from sediment including visual sorting, filtration, sieving, density separation, elutriation, flotation and chemical digestion.[5-7] As with most aspects of microplastic research, the rapid development of the field and the lack of standardised techniques have led to an inconsistency in the extraction methods used to quantify microplastics, particularly from sediments.[1, 8] However, guidelines and protocols have been produced by regulatory bodies in an attempt to standardise the separation of microplastics from environmental samples[6, 9, 10]. In this study we compare and validate the use of several brine solutions for the density separation of microplastics from sediment.

The method used for the separation of microplastics from sediment is influenced by the physical characteristics (size, density, shape) of both the sediment and the microplastics. The separation of larger microplastics from fine sediments (mud or silt) by visual sorting, sieving or filtration is relatively simple and commonly practiced[5, 11, 12]. However the separation of small microplastics can be more difficult, particularly from finer sediments with microplastic shape influencing the separation ability. Several techniques have been developed to overcome these issues including elutriation (separated based on size, shape and density by a stream of gas or liquid flowing in an opposite direction to sedimentation) and flotation (separation based on relative buoyancy and hydrophobic nature) that have been successfully used for the separation of microplastics from sediments.[13-17] However, density separation is the most reliable and common method for the separation of microplastics from sediment or sand.

In density separation, materials of different densities are placed in a liquid of intermediate density, where the less dense material floats and separates out from the more dense sinking material. Changing the density of the liquid, commonly a brine solution (a solution of a salt in water) allows

for the floating of particles of different density, relative to the density of the solution. This technique has been applied in 65% of the studies where microplastics were separated from sediments.[5] The most common brine solution is saturated sodium chloride (NaCl) with a specific gravity of 1.2 g/cm^3, separating only items lighter than this from the more dense sinking sediment, with a typical density of 2.65 g/cm^3. Density separation is normally achieved by agitating the sediment in saturated NaCl solution as described by Thompson et al.[18]. NaCl has the advantage of being cheap, widely available and environmentally benign. However although many microplastics have a density <1.2 g/cm^3 including polypropylene (PP), polyethylene (PE), polystyrene (PS) and polyamide more commonly known as nylon (see table 1) and may be floated by this solution, several others will not include the more dense polyvinyl chloride (PVC) and polyethylene terephthalate (PET) which make up >17% of global plastic demand[19]. This is of particular importance as these more dense plastics will be the first to settle and be incorporated into marine sediments [1] and will therefore be under represented in sediment analysis. Despite this the Marine Strategy Framework Directive (MSFD) technical sub-group on marine litter recommend NaCl solution for the separation of microplastics from sediments by density separation [9].

To address this issue brine solutions with a higher density have been used for microplastic sediment extraction including sodium polytungstate (1.4 g/cm^3) [20, 21], zinc chloride (1.5-1.7 g/cm^3) [15, 22], Calcium chloride (1.30 – 1.35 g/cm^3) [17] and sodium iodine (1.8 g/cm^3) [13, 14, 23]. Recently, NOAA recommended the use of 5.4 M lithium metatungstate (1.62 g/cm^3) for density separation [10]. To ensure the separation of all plastic polymers from sediment brine solutions of a density of >1.45 g/cm^3 have been recommended [1, 15]. However these higher density solutions are often very expensive and toxic to the environment, reducing their practical use in larger scale studies and in many cases their ability to recover microplastics from sediments has not been investigate.

Despite the use of several different brine solutions in the density separation of microplastics from sediments, only limited validation has been undertaken on their effectiveness. Several publications use larger (>1 mm) spherical microplastics in relatively course sediments that although provide good microplastics recoveries, may not be environmentally realistic [24-26]. Using density separation microplastic recoveries of 91-99 % have been recorded for microplastics ~1 mm, [14] but with recovery rates reducing to 40% for smaller (40-309 µm) particles [15]. The current work focuses on validating the efficiency of four brine solutions and water for the separation of environmentally relevant post-consumer microplastics from two different size ranges (200 – 400 µm and 800 – 1000 µm) based on the original density separation method by Thompson et al.[18] and further developed by Claessens et

al.[27] . The aim of this work was to validate a relatively rapid, robust technique that would include separation of high and low density plastics in a one stage process for use in monitoring by regulatory agencies.

2. Materials and Methods

2.1 Brine solution preparation:

The density separation of tap water and four brine solutions (sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI) and zinc bromide ($ZnBr_2$)) with various densities (Table 1) was tested. Fully saturated solutions of NaCl, NaBr and NaI were made by dissolving the relevant salt into a volume of distilled water (1L) on a magnetic stirring plate until a small excess formed at the bottom of the beaker and no more salt would dissolve into solution. At this stage the density of the solution was tested to ensure saturation using the equation:

$$Density = \frac{(Weight\ of\ flask\ and\ brine\ (g) - \ Weight\ of\ flask\ (g))}{Volume\ of\ flask\ (cm^3)}$$

As saturated $ZnBr_2$ has a density of 4.2 g/cm^3, a 25% saturated solution was made to obtain the desired density of 1.7 g/cm^3. For this the appropriate amount of salt (1125 g L^{-1}) was slowly added to distilled water using a stirring plate with the density checked at regular intervals using the equation above.

The same brine solutions were reused throughout the series of density separation tests and were filtered twice through Whatman Grade 540 ashless filters and a thin layer of Celite® 512 medium (Sigma) between tests. The density of the solution was checked after each use as described above and adjusted where necessary. The microplastic separation efficiency of these reused solutions was checked regularly using a reference plastic (polyethylene (180 µm) Sigma) and was found to be consistently within 2% of the reference results presented in Figure 1.

2.2 Microplastic preparation

Eight different types of plastic polymer were taken from 11 different post-consumer products (listed in Table 2) that were broken down to secondary microplastics by various physical methods including a coffee grinder, food processor and in some cases with the use of liquid nitrogen. The colour and reference density was noted for each plastic sample and Fourier Transform Infrared Spectroscopy (FTIR) analysis was undertaken to confirm the correct sample identification as per the Resin

Identification Code (RIC). Following mechanical breakdown the plastics were passed through a series of sieves on a mechanical shaker and divided into size classes with the 200 - 400 µm and 800 - 1000 µm fraction being investigated. Although of varying shape, these secondary microplastics could be considered as fragments. Commercially obtained polyethylene spheres (180 µm) were obtained from Sigma. The nylon sample (thread) was cut into small pieces using a scissors with the average size (340 µm, ±174 Std Dev) calculated by observation using a graticule under a light microscope.

2.3 Marine sediment preparation

A sample of marine sediment was collected from a beach along the Firth of Clyde in the west of Scotland. This beach and its sediment were representative of the area and of beaches commonly found throughout the UK. A subsample was passed through a series of sieves on a mechanical shaker with the 200 - 400 µm particle size fraction collected and cleaned by repeated (x 3) washing with 25% $ZnBr_2$ brine solution using the technique described below to remove all floating debris and any traces of environmental microplastic contamination, verified by microscopic examination. This sediment was stored in a glass container and kept clean following the strict contamination prevention outlined below. The sediment was cleaned between each density separation using 25% ZnBr2 brine solution to remove all floating debris and ensure no contamination between each test.

2.4 Density separation

The percentage recovery of tap water and the four brine solutions was investigated using a series of spiking experiments, where 66.66 g of clean sediment and 0.066g of microplastic was added to a 400 ml glass beaker. A volume of 200 ml of the solution to be investigated was added following the ratio of 3:1 described by Claessens et al.[28] and the mixture was stirred using an overhead stirrer at 300 rpm for 3 minutes. The stirrer was lifted from the solution and the paddle rinsed with the relevant solution. The solution was left to settle for 10 minutes, allowing the lighter plastic particles to float or stay in suspension as the heavier sediment particles sank. The particles that accumulated on the surface of the solution were recovered by vacuum suction. A glass tube connected to a vacuum system by a rubber tube was moved around the surface of the solution and particles would be collected into a three necked flask which acted as a trap, the rubber and glass tubing was thoroughly rinsed with the relevant solution to ensure no microplastics were lost. A small amount of soap was occasionally touched to the liquid surface causing the plastics to accumulate on one side of the beaker and making it easier for them to be collected by suction. This top layer of solution containing the plastic that was collected in the trap was filtered through a clean filter paper (Whatman No 1,

cellulose) using a Buchner funnel. Once filtration was complete the flask was thoroughly washed to ensure no loss of sample and the filter paper transferred to a watch glass and placed in an oven (70 °C) for 10 min. Once dry the microplastics were transferred to a pre-weighted filter paper, weighed using an analytical scale and the percentage recovery calculated following the equation:

% Recovery = (final weight of plastic / initial weight of plastic) x 100

The lower density solutions (water, NaCl and NaBr) required 3 washes for microplastics extraction as per Thompson et al. [18] with the more dense NaI and $ZnBr_2$ brine solutions only requiring a single wash. This protocol was used to test the separation efficiency of water and four brine solutions on selected microplastics from two size ranges (200 – 400 µm and 800 – 1000 µm). The microplastics were tested for each solution individually and as a mixture made from an equal mass of each polymer (200 – 400 µm only).

2.5 Contamination mitigation

To prevent microplastic contamination a strict contamination mitigation protocol was adhered at every step of the procedure. This protocol was outlined in detail in Murphy et al. [29] and is summarised below. Clean cotton white lab coats were worn at all times with no synthetic fibres underneath. The protocol involves three steps: 1) all surfaces and equipment were cleaned three times with 70% ethanol and distilled H_2O and equipment examined under a dissection microscope for microplastic contamination before use. 2) All laboratory benches were examined for particle contamination using the taping technique used in forensic science. This was undertaken before and after all procedures with the tapings being examined microscopically and by FTIR where necessary. 3) Atmospheric microplastic contamination was investigated using the taping technique and by leaving clean filter papers in petri dishes for the duration of the lab work that were later checked for contamination.

Care was taken to limit the amount of time a sample was exposed to air both during the density separation protocol and after the microplastics had been recovered. Filter papers containing microplastics were kept in sealed petri dishes to prevent contamination. Blank runs were undertaken to ensure glassware was properly clean, using the density separation protocol with no sediment sample, allowing the determination of potential microplastic particles remaining from previous runs.

2.6 FTIR polymer identification

Before being broken down into secondary microplastics each item was positively identified by Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) using a Perkin Elmer Spectrum One FTIR. This was also randomly undertaken on microplastic samples to ensure no contamination. Infrared radiation from 600–4000 cm^{-1} was used with a spectral resolution of 4 cm^{-1} with 4 scans taken to produce the specific spectra, which was compared to reference spectra present on the Thermo Scientific™ OMNIC™ software to identify the plastic polymers. FTIR allows for the identification of chemical bonds present in the samples and gives a characteristic signal in the "fingerprint" region.

2.7 Statistical analysis

Microplastic recovery data (%) was expressed as the mean ± the standard deviation. Sample numbers of n=9 and n=3 were used for the 200 – 400 µm and 800-1000 µm fractions respectively giving a total number of 450 and 105 density separations for each size fraction respectively. Data normality and distribution (homogeneity of variances) were tested using the Shapiro-Wilks and Levene`s tests respectively. Where normality and equal variance was demonstrated analysis of variance was performed and critical differences between groups appraised using the Bonferroni t-test. Following transformation if data were found to fail one or other of these tests nonparametric analysis of variance was performed using Kruskal-Wallis one way ANOVA on ranks. All statistics were undertaken using Statistica (Version 6).

3. Results and Discussion

Although various degrees of validation of the different methods for separating microplastics from sediment (flotation, elutriation and density separation) have been undertaken,[13-15, 28] it has been mentioned that validation tests on recovery rates for microplastic extraction from sediments are rarely reported.[14] The results from the series of 200 – 400 µm microplastic experiments clearly show a general trend of increasing microplastic recovery with increasing solution density, with NaI and $ZnBr_2$ having significantly ($p=<0.001$) higher rates of recovery for all polymers (except PVC (P) with $ZnBr_2$) (Figure 1). Tap water consistently had the lowest microplastic recovery rates, as would be expected being the least dense solution. This was particularly true for the denser PET samples and a low recovery rate (~70%) was found for the microplastics mixture. Despite this recovery rates of

>95% were found for nylon fibres. These results are in accordance with data recently published by Alomar et al.[12] who most commonly found microplastic fibres when using distilled water for density separation of marine sediments. It would appear that density separation with water would actively select fibres as they have a large surface to volume ratio and given their shape they are easily trapped in the surface tension film.

Of the four brine solutions investigated, NaCl showed the lowest recovery rates (85-95% and <90% for mixed microplastics) and largest error bars (indicating greater variability) for the 200 – 400 µm microplastics (Figure 1). Interestingly only four of the tested twelve samples (nylon, PVC (UP) and both HDPEs) showed significantly higher recover rates than water. This is particularly relevant as although they have similar densities (Table 1), NaCl is the most popular brine solution for microplastic density separation and is recommended for use by the Marine Strategy Framework Directive (MSFD) Technical Sub- group on Marine Litter[9] since it is low cost, abundant and environmentally benign. NaCl was the original brine solution used for microplastic density separation by Thompson et al.[18] and is still commonly used throughout the world.[30-33] These recovery rates are similar to the 68.8-97.5% recoveries found by Claessens et al.[28] using the Thompson protocol, but in this work no details were provided on the recovery rates for specific polymers. Interestingly, low recovery rates were found for PET 1 using both NaCl and water, particularly compared against the PET 2 sample. Although having the same resin identification code (RIC) these samples were taken from a carbonated soft drink bottle (PET 1) and a water bottle (PET 2) and are indicative of how the same polymer can contain different additives or wetting agents that can impact on their density and subsequent separation. This has been observed by Wang et al.[16] who found the addition of various wetting agents to a polymer can significantly decrease its floatability.

To the authors knowledge this is the first time NaBr has been used as a brine solution for the density separation of microplastics. Having a medium density (1.37 g/cm^3) it consistently showed better microplastic recoveries than both NaCl and water, with significantly higher recoveries than water for nine of the twelve tested microplastics, with the lighter PE samples and PET 2 being the exception (Figure 1). However it showed no significant differences in recovery rates compared to NaCl, with the exception of nylon fibres. Therefore for microplastic of the 200 – 400 µm size range, NaBr does not hold any significant advantage for the replacement of the commonly used NaCl solution. A brine solution of sodium polytungstate with a similar density (1.4 g/cm^3) has been used to separate out microplastics from marine sediments,[20, 34] but to our knowledge no recovery test for this solution

have been undertaken. Another brine solution of calcium chloride, with a similar density (1.30 – 1.35 g/cm^3) showed recovery rates of ~55% for PE (100 – 1000 µm) enriched sediment using an air venting separation technique.[17] From these results it would appear that a brine solution of >1.4 g/cm^3 is needed to ensure effective microplastic separation, as previously recommended by several authors.[1, 15]

The NaI brine solution was particularly effective for the separation of the 200 – 400 µm microplastics, showing significantly higher recovery rates than water and for nine and three of the twelve microplastics compared to NaCl and NaBr respectively (Figure 1). NaI also showed higher recovery rates than $ZnBr_2$ for four of the tested microplastics, being significantly higher for PVC (P). NaI has previously been used for the density separation of microplastics from sediments.[13, 14, 23] In recovery experiments using 1mm microplastics (PE, PP, PVC, PET, PS and polyurethane (PUR)) recovery rates of between 91-99% were obtained.[14] This paper represents one of the few in depth studies to investigate microplastic recovery rates. However comparison is difficult as they used a 2 step method to extract microplastics from sediments involving air-induced overflow (AIO) based on fluidisation in a NaCl solution to reduce the material volume, followed by flotation using NaI solution. As saturated NaI solution has sufficient density (1.6 g/cm^3) to separate the heavier additive containing polymers it has been recommended as a suitable brine solution above NaCl for microplastic separation.[35]

This study is the first to report the use of $ZnBr_2$ for the density separation of microplastics from sediments. A 25% saturated solution (density of 1.71 g/cm^3) was used, as when fully saturated $ZnBr_2$ has a density of 4.5 g/cm^3, dense enough to cause sediment floatation. $ZnBr_2$ gave the highest recovery rates for eight of the twelve microplastics in the 200 – 400 µm size range, being significantly higher than both water and NaCl for all but PVC (P) and HDPE (gum) (NaCl only). Despite having the highest recovery rates, these were not significantly higher than NaI. $ZnBr_2$ showed particularly good recoveries (99%) for the mixed microplastic sample that most closely represents environmental samples. This brine solution also provided relatively tight error bars indicating a good level of reproducibility for all polymers investigated. $ZnBr_2$ has a similar density to zinc chloride ($ZnCl_2$, 1.7 g/cm^3) which has been previously used for microplastic separation.[15, 22] In recovery experiments $ZnCl_2$ brine solution was found to have a 100% and 95% recovery rate for large (1-5 mm) and small (<1 mm) microplastics (respectively) from seven environmentally relevant plastic types (PA, PE, PVC, PC, HDPE, PET, PP).[15] However comparison with the present data is difficult as a Munich Plastic Sediment Separator (MPSS) device was used for density separation on mostly virgin

plastic pellets. Using the classic Thompson[18] technique, recovery rates of ~40% were found for the small microplastics. This is considerably lower than the current study, but was thought to be due to the significant loss of microplastics during handling as they stuck to the wall of the apparatus. Due to their similar densities, both $ZnBr_2$ and $ZnCl_2$ brine solutions are good candidates for microplastic density separation.

The density separation of the larger microplastic size class (800 - 1000 µm) showed a similar but more pronounced trend of increasing recovery rates with increasing brine solution density. Interestingly the recovery rates for both water and NaCl are lower for the larger microplastic size compared to the smaller particles of the same polymer, being below 80% and 85% respectively (Figure 2). These recovery rates fell to ~60% for the heavier PVC and PET samples indicating that neither NaCl nor water are suitable for the extraction of these heavier plastic fragments. Although this decrease in recovery rates is substantial (Figure 2), due to the non-parametric statistical methods used, it was not significant. The results for the remaining brine solutions show a clear stepwise increase in recovery with increasing density from NaBr, NaI to $ZnBr_2$. This increase is significant for the lighter microplastics (PP, HDPE and both PS samples), but not for the heavier PVC and PET, again most likely due to the non-parametric statistical methods used. For these polymers only $ZnBr_2$ shows significantly higher recoveries than water. It is evident from these results that for larger microplastics class $ZnBr_2$ shows the best recoveries with rates consistently >95%, higher than those obtained for the smaller (200 - 400 µm) particles. In contrast, although not significant NaBr and NaI solutions show higher recovery levels for the smaller rather than larger microplastics.

Although not always reported in the literature, the size of the microplastics used in recovery tests can impact on their recovery rates. As microplastics include particle up to 5 mm and separating them from sediments can often become more difficult at smaller sizes, most authors only include plastics >1 mm for both environmental sampling[16, 24-26, 34, 36] and recovery experiments[14, 34, 37]. More attention needs to be paid to influence of brine solution on particle size as small microplastics (<1 mm) represent 35-90% of all microplastics in the marine environment[26, 38-41] and therefore need to be included in environmental sampling to avoid a serious underestimation of microplastic contamination in sediments.

In this work we focused on making the validation method as realistic as possible to field sampling conditions by using post-consumer plastics commonly found in the environment in non-uniform shapes and sizes and sediment (cleaned and graded to 200-400 µm to help standardisation) taken

from the environment. The technique used closely resembled that by Thompson et al.[18] and further developed by Claessens et al.[28] and was kept as simple as possible to help reduce contamination and allow a relatively rapid process time that is needed by regulatory agencies for monitoring programmes involving large numbers of samples. Although there have been several published techniques that produce high microplastic recovery rates such as elutriation,[13] MPSS[15] and a two-step air-induced overflow (AIO) followed by NaI density separation,[14] our aim was to validate a relatively rapid, reproducible, low tech, low cost approach that can deliver consistently high recoveries for different polymers <1 mm appropriate for monitoring programmes. Both NaI and $ZnBr_2$ also have the advantage of only needing a single wash of the sediment for microplastic removal, as opposed to the three washes needed for NaCl solution, making the process more efficient. NaI showed similar recovery rates to $ZnBr_2$ and is cheaper and less environmentally dangerous, but when used on sediment samples from the environment it turned the filter paper black, making it very difficult to isolate the microplastics. This was thought to result from the excess sodium iodide creating free iodine which reacts with starch in the paper. Although these tests indicate $ZnBr_2$ is the most suitable brine solution for the extraction of microplastics from sediment it is expensive and severely hazardous to the environment.[14] However these issues are overcome by the successful reuse of this brine solution following careful filtration and clean up. Although the solution can change to a light brown colour and needs the density checked and adjusted where necessary, this is simple process and will allow the solution to be used indefinitely offering a relatively cheap and environmentally responsible method for density separation of microplastics from sediment.

4. Conclusion

There are numerous brine solutions that are potentially suitable for the density separation of microplastics from sediment samples. However, before they can be used for monitoring purposes their ability to separate out a wide range of environmentally relevant polymers with the appropriate shape and sizes that are commonly found in the environment needs to be investigated. Although the recovery tests outlined in the present work are relatively simple and indeed are designed to be so, this validation step is essential to ensure that a proper representative microplastic sample is obtained to prevent an underrepresentation of microplastics (particularly <1 mm) in the environment. Given the wide range of techniques and brine solutions currently used to separate microplastics from sediment it is increasingly difficult to compare the results generated from various

studies undertaken around the world to get a true representative picture of the scale of microplastic pollution. Only through the use of standardised, validated protocols can we ascertain the most suitable methods and get a true picture of the scale of microplastic contamination.

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References

1. L. Van Cauwenberghe, L. Devriese, F. Galgani, J. Robbens and C. R. Janssen, *Marine Environmental Research*, 2015, **111**, 5-17.
2. A. Cózar, F. Echevarría, J. I. González-Gordillo, X. Irigoien, B. Úbeda, S. Hernández-León, Á. T. Palma, S. Navarro, J. García-de-Lomas, A. Ruiz, M. L. Fernández-de-Puelles and C. M. Duarte, *Proceedings of the National Academy of Sciences*, 2014, **111**, 10239-10244.
3. H. S. Carson, S. L. Colbert, M. J. Kaylor and K. J. McDermid, *Marine Pollution Bulletin*, 2011, **62**, 1708-1713.
4. L. Fok and P. K. Cheung, *Marine Pollution Bulletin*, 2015, **99**, 112-118.
5. V. Hidalgo-Ruz, L. Gutow, R. C. Thompson and M. Thiel, *Environmental Science & Technology*, 2012, **46**, 3060-3075.
6. GESAMP, *Sources, fate and effects of microplastics in the marine environment: a global assessment*, Rep. Stud. GESAMP, 2015.
7. K. Duis and A. Coors, *Environmental Sciences Europe*, 2016, **28**, 1-25.
8. C. Wesch, A.-K. Barthel, U. Braun, R. Klein and M. Paulus, *Environmental Research*, 2016, **148**, 36-38.
9. JRC, *MSFD GES Technical Subgroup on Marine Litter, Marine Litter and Technical Recommendations for the Implementation of MSFD Requirements*, Luxembourg 2011.
10. J. Masura, J. Baker, G. Foster and C. Arthur, *NOAA Technical Memorandum*, 2015, **NOS-OR&R-48**, 1-39.
11. W. Zhang, X. Ma, Z. Zhang, Y. Wang, J. Wang, J. Wang and D. Ma, *Marine Pollution Bulletin*, 2015, **99**, 28-34.
12. C. Alomar, F. Estarellas and S. Deudero, *Marine Environmental Research*, 2016, **115**, 1-10.
13. M. Claessens, L. Van Cauwenberghe, M. B. Vandegehuchte and C. R. Janssen, *Mar Pollut Bull*, 2013, **70**, 227-233.
14. M.-T. Nuelle, J. H. Dekiff, D. Remy and E. Fries, *Environmental Pollution*, 2014, **184**, 161-169.
15. H. Imhof, J. JSchmid, R. Niessner, N. P. Ivleva and C. Laforsch, *Limnology and Oceanography: Methods*, 2012, **10** 524-537.
16. H. Wang, C.-q. Wang, J.-g. Fu and G.-h. Gu, *Waste Management*, 2014, **34**, 309-315.
17. A. Stolte, S. Forster, G. Gerdts and H. Schubert, *Marine Pollution Bulletin*, 2015, **99**, 216-229.
18. R. C. Thompson, Y. Olsen, R. P. Mitchell, A. Davis, S. J. Rowland, A. W. G. John, D. McGonigle and A. E. Russell, *Science*, 2004, **304**, 838.

19. PlasticsEurope, *Plastics - the Facts 2013. An analysis of European latest plastics production, demand and waste data.* , Plastics Europe: Association of Plastic Manufacturers, Brussels, 2013.
20. P. L. Corcoran, M. C. Biesinger and M. Grifi, *Marine Pollution Bulletin*, 2009, **58**, 80-84.
21. S. Zhao, L. Zhu and D. Li, *Environmental Pollution*, 2015, **206**, 597-604.
22. G. Liebezeit and F. Dubaish, *Bull Environ Contam Toxicol*, 2012, **89**, 213-217.
23. J. H. Dekiff, D. Remy, J. Klasmeier and E. Fries, *Environmental Pollution*, 2014, **186**, 248-256.
24. J. Baztan, A. Carrasco, O. Chouinard, M. Cleaud, J. E. Gabaldon, T. Huck, L. Jaffrès, B. Jorgensen, A. Miguelez, C. Paillard and J.-P. Vanderlinden, *Marine Pollution Bulletin*, 2014, **80**, 302-311.
25. H. B. Jayasiri, C. S. Purushothaman and A. Vennila, *Environmental Monitoring and Assessment*, 2013, **185**, 7709-7719.
26. K. J. McDermid and T. L. McMullen, *Marine Pollution Bulletin*, 2004, **48**, 790-794.
27. M. Claessens, S. D. Meester, L. V. Landuyt, K. D. Clerck and C. R. Janssen, *Marine Pollution Bulletin*, 2011, **62**, 2199-2204.
28. M. Claessens, S. De Meester, L. Van Landuyt, K. De Clerck and C. R. Janssen, *Mar Pollut Bull*, 2011, **62**, 2199-2204.
29. F. Murphy, C. Ewins, F. Carbonnier and B. Quinn, *Environmental Science & Technology*, 2016, **50**, 5800-5808.
30. J. P. G. L. Frias, J. Gago, V. Otero and P. Sobral, *Marine Environmental Research*, 2016, **114**, 24-30.
31. Q. Qiu, J. Peng, X. Yu, F. Chen, J. Wang and F. Dong, *Marine Pollution Bulletin*, 2015, **98**, 274-280.
32. H. A. Nel and P. W. Froneman, *Marine Pollution Bulletin*, 2015, **101**, 274-279.
33. S. Klein, E. Worch and T. P. Knepper, *Environmental Science & Technology*, 2015, **49**, 6070-6076.
34. S. Zhao, L. Zhu and D. Li, *Regional Studies in Marine Science*, 2015, **1**, 55-62.
35. T. Rocha-Santos and A. C. Duarte, *TrAC Trends in Analytical Chemistry*, 2015, **65**, 47-53.
36. N. W. Heo, S. H. Hong, G. M. Han, S. Hong, J. Lee, Y. K. Song, M. Jang and W. J. Shim, *Ocean Science Journal*, 2013, **48**, 225-233.
37. X. Zhu, *Marine Pollution Bulletin*, 2015, **92**, 69-72.
38. M. A. Browne, T. S. Galloway and R. C. Thompson, *Environ Sci Technol*, 2010, **44**, 3404-3409.
39. M. Eriksen, S. Mason, S. Wilson, C. Box, A. Zellers, W. Edwards, H. Farley and S. Amato, *Marine Pollution Bulletin*, 2013, **77**, 177-182.
40. Y. K. Song, S. H. Hong, M. Jang, J.-H. Kang, O. Y. Kwon, G. M. Han and W. J. Shim, *Environmental Science & Technology*, 2014, **48**, 9014-9021.
41. S. Zhao, L. Zhu, T. Wang and D. Li, *Marine Pollution Bulletin*, 2014, **86**, 562-568.

Figures & Tables

Table 1. The density of the different brine solutions and water tested for microplastic recovery by density separation in the study.

Solution	Density (g/cm^{-3})
Water (H_2O)	1.0032
Sodium Chloride (NaCl)	1.1708
Sodium Bromide (NaBr)	1.37
Sodium iodide (NaI)	1.566
Zinc bromide ($ZnBr_2$) 25%	1.71

Table 2. The polymer type, source, resin identification code (RIC) used for recycling, colour and density of the microplastics used in the density separation validation studies.

Plastic	Source	RIC	Colour	Density
Polypropylene (PP)	Plastic Container*	5	Clear	0.855 – 0.946 g/cm^3
Low density Polyethylene (LDPE)	Face wash	4	Blue	0.915 – 0.925 g/cm^3
Polyethylene (PE 180µm)	Sigma	4	White	0.926 – 0.940 g/cm^3
Polyethylene (PE)	Supermarket Bag	4	Clear	0.926 – 0.940 g/cm^3
High density Polyethylene (HDPE)	Milk carton Chewing gum box*	2	White black	0.94 to 0.97 g/cm3
Polystyrene (PS)	Plastic Fork* Coffee cup lid*	6	White	0.96 – 1.04 g/cm^3
Polyamide (nylon)	Thread	7	Green	1.13-1.15
Plasticised Polyvinyl Chloride (PVC P)	Electrical cable*	3	Black	1.1 – 1.35 g/cm^3
Un-plasticised Polyvinyl Chloride (PVC UP)	Window frame*	3	White	1.35 – 1.45 g/cm^3
Polyethylene terephthalate (PET)	Soft drink bottle 1 Water bottle 2*	1	Clear	1.38 g/cm^3

*Also used for the larger microplastics (800 – 1000 µm) recovery tests.

Figure 1.

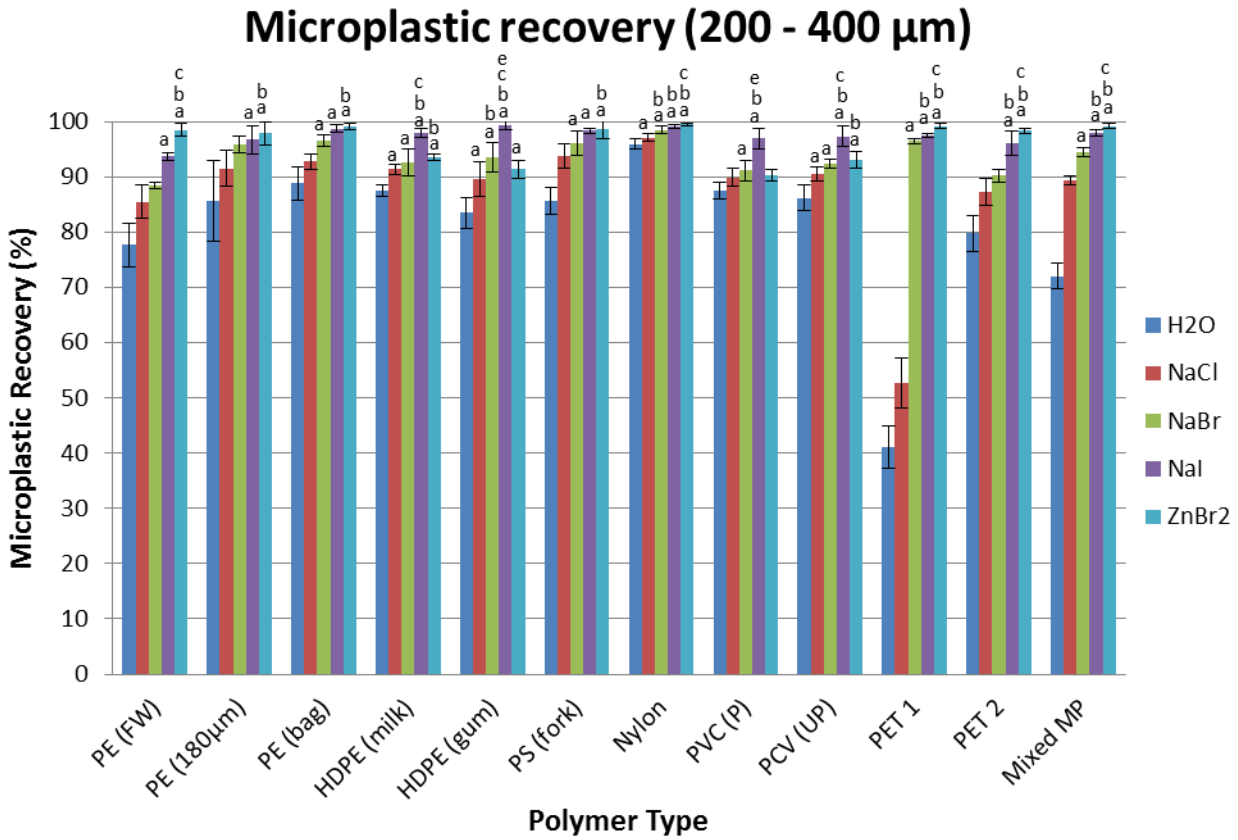

Figure 1. Microplastic recovery (% mean (n=9) ±Std Dev) for various polymers sized 200 – 400 µm tested individually using water and sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI) and zinc bromide ($ZnBr_2$) brine solutions. Polymer type abreviations are provided in Table 1. Letters indicate significantly higher recovery compared to H_2O (a), NaCl (b), NaBr (c), NaI (d) and $ZnBr_2$ (e).

Figure 2.

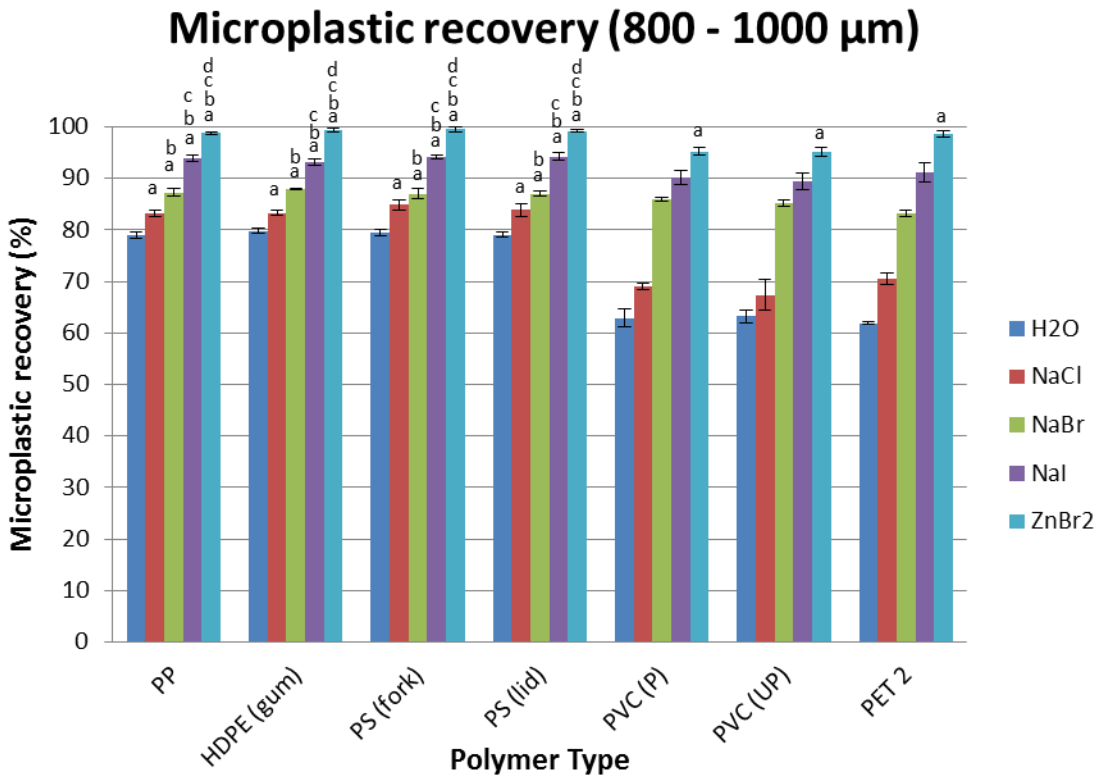

Figure 2. Microplastic recovery (% mean (n=3) ±Std Dev) for various polymers sized 800 – 1000 µm tested individually using water and sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI) and zinc bromide ($ZnBr_2$) brine solutions. Polymer type abreviations are provided in Table 1. Letters indicate significantly higher recovery compared to H_2O (a), NaCl (b), NaBr (c) and NaI (d).