Rapid extraction of high- and low-density microplastics from soil using high-gradient magnetic separation.

RAMAGE, S.J.F.F., PAGALING, E., HAGHI, R.K., DAWSON, L.A., YATES, K., PRABHU, R., HILLIER, S. and DEVALLA, S.

2022

This file contains supplementary materials at the end of the main text.

Rapid extraction of high- and low-density microplastics from soil using high-gradient magnetic separation

Stuart J. F. F. Ramage[a,b], Eulyn Pagaling[a], Reza K. Haghi[a], Lorna A. Dawson[a,b], Kyari Yates[b], Radhakrishna Prabhu[b], Stephen Hillier[a,c], Sandhya Devalla[a]

[a] The James Hutton Institute, Craigiebuckler Aberdeen, AB15 8QH, United Kingdom

[b] Robert Gordon University, Aberdeen, AB10 7GJ, United Kingdom

[c] Department of Soil and Environment, Swedish University of Agricultural Sciences (SLU), SE-75007 Uppsala, Sweden

ABSTRACT

Microplastics (MPs) are present in all environments, and concerns over their possible detrimental effects on flora and fauna have arisen. Density separation (DS) is commonly used to separate MPs from soils to allow MP quantification; however, it frequently fails to extract high-density MPs sufficiently, resulting in under-estimation of MP abundances. In this proof-of-concept study, a novel three-stage extraction method was developed, involving high-gradient magnetic separation and removal of magnetic soil (Stage 1), magnetic tagging of MPs using surface modified iron nanoparticles (Stage 2), and high-gradient magnetic recovery of surface-modified MPs (Stage 3). The method was optimised for four different soil types (loam, high-carbon loamy sand, sandy loam and high-clay sandy loam) spiked with different MP types (polyethylene, polyethylene terephthalate, and polytetrafluoroethylene) of different particle sizes (63 µm to 2 mm) as well as polyethylene fibres (2-4 mm). The optimised method achieved average recoveries of 96% for fibres and 92% for particles in loam, 91% for fibres and 87% for particles in high-carbon loamy sand, 96% for fibres and 89% for particles in sandy loam, and 97% for fibres and 94% for particles in high-clay sandy loam. These were significantly higher than recoveries achieved by DS, particularly for fibres and high-density MPs ($p <$

0.05). To demonstrate the practical application of the HGMS method, it was applied to a farm soil sample, and high-density MP particles were only recovered by HGMS. Furthermore, this study showed that HGMS can recover fibre-aggregate complexes. This improved extraction method will provide better estimates of MP quantities in future studies focused on monitoring the prevalence of MPs in soils.

Key Words: Microplastics; Fibres; Soil; HGMS; Rapid extraction; Electromagnetic

1. INTRODUCTION

1.1. Microplastic (MP) particles and fibres are emerging contaminants which are ubiquitous in the natural environment, found in all ecological niches including aquatic (Koelmans et al., 2019; Prata et al., 2019a) and terrestrial environments (Bläsing and Amelung, 2018). Consequently, MPs have been found within organisms (e.g. earthworms) (Chae and An, 2018; Prendergast-Miller et al., 2019; Rodríguez-Seijo et al., 2018), where they have the potential to induce adverse effects such as disruption to endocrine systems (de Souza Machado et al., 2018a) and therefore, have been referred to as long-term anthropogenic terrestrial ecosystem stressors (de Souza Machado et al., 2018b). MPs have also been found within the human body, but current literature on the health consequences of this is limited (Prata et al., 2020; Yan et al., 2022).

1.2. To accurately assess MP contamination, it is important to extract both high- and low-density MPs. This is a complicated task for soils as they are a complex solid matrix, with broad inter- and intra-sample density and particle size ranges (de Souza Machado et al., 2018a). Additionally, soils often contain high concentrations of organic material that form aggregates

around MPs making them difficult to extract (Bläsing and Amelung, 2018; Thomas et al., 2020; Zhang and Liu, 2018).

1.3. There are several methods that can be employed to extract MPs from soil. Methods that do not rely on plastic density include electrostatic separation (Felsing et al., 2018; Enders et al., 2020) and elutriation (Claessens et al., 2013), however, they have mainly been tested on sediments. Electrostatic separation achieved MP recoveries near 100% when applied to sediments (Felsing et al., 2018), however, MP recoveries were significantly reduced when the method was applied to mineral-rich soils (Enders et al., 2020). Moreover, there was great variability in recovery because it was dependent on MP particle size (Enders et al., 2020). Elutriation is extremely effective for MP removal in sediments (Claessens et al., 2013), however, Grause et al. (2022) reported that the method was not effective for MP extraction from soils due to the wider variability in particle size distributions within soils (Grause et al., 2022). The method also requires large amounts of liquid to fill the column which is impractical if solutions of higher density than water are desired. Another technique which involves the circulation of salt solutions through an enclosed system containing soil has proven highly effective at recovering MPs (Liu et al., 2019).

1.4. Density separation (DS) takes advantage of the difference in density between plastics and soil particles (Zhang et al., 2019), and is a simple method that has become the most common approach for MP extraction from soil. The density range of most plastics is relatively low at 0.9-2.3 g/mL, while the density of most soil particles are higher, averaging around 2.6-2.7 g/mL (Prata et al., 2020). DS uses high-density salt solutions such as zinc bromide to resuspend soil, allowing MPs to float while soil particles sink (Han et al., 2019; He at al., 2018; Liu et al., 2018; Masura et al., 2015; Scheurer and Bigalke, 2018; Zhang et al., 2018). While

this method has high recovery rates for low-density MPs (Han et al., 2019; Liu et al., 2018; Scheurer and Bigalke, 2018; Zhang et al., 2018), high-density MPs, such as polytetrafluoroethylene and polyvinyl chloride, are not easily recovered due to their densities being similar to bulk soil particles (Liu et al., 2018; Zhang et al., 2018). Moreover, DS suffers from co-extraction of organic matter (making enumeration difficult) (Hurley et al., 2018; Prata et al., 2019b; Wang et al., 2018), long sample processing times (Liu et al., 2018; Scheurer and Bigalke, 2018; Zhang et al., 2018), and issues surrounding the salt solutions' environmental toxicity (Thomas et al., 2020). Since high-density MPs represent > 20% of the global plastic demand (Plastics Europe, 2019), it is important to extract these MPs to accurately determine the levels of terrestrial plastic pollution.

1.5. Grbic et al. (2019) developed an alternative method to extract MPs involving magnetic separation using surface modified iron nanoparticles, extracting both high- and low-density MPs. Their proof-of-concept work involved the surface modification (hydrophobisation) of iron nanoparticles with hexadecyltrimethoxysilane to enable them to bind to MPs in environmental samples which were subsequently extracted using a neodymium magnet. Their work did not include testing the recovery of MPs from a terrestrial soil matrix. Instead, the method was tested using freshwater, seawater and sediment; however, MP recovery in the sediment was lower with this method compared to that achieved through DS (Grbic et al., 2019). Moreover, damage to the MPs due to removal from the magnet was observed. The principle of magnetic separation using iron nanoparticles was further studied by Shi et al. (2022) for MP removal in water samples, though no details of the type of magnetic extraction system were supplied, and particles were removed from a simple water matrix rather than sediment or soil.

1.6. A technique known as high-gradient magnetic separation (HGMS) has the potential to improve recovery of MPs from soil, and bypass the methodological issues associated with the previous magnetic extraction method (Grbic et al., 2019). HGMS is widely used to separate micro- and nano-scale particles in aqueous suspensions (Alves et al., 2019; Gerber and Birss, 1983; Hillier and Hodson, 1997; Mullins, 1977; Rikers et al., 1998; Watson, 1973; Yavuz et al., 2009), and is widely applied to various matrix separation processes including those in the medical (Bhakdi et al., 2010) and mining industries (Chun, 1995; Dahe, 2000; Ignjatović et al., 1995), and for water purification (Yavuz et al., 2006). Soils contain a vast array of minerals that, even if not ordinarily considered magnetic, are rendered magnetic in the HGMS system, and HGMS is often used to separate these 'paramagnetic' minerals from soils (Mullins, 1977). It has also been used to remediate soils from heavy metal contamination and radioactive wastes (Ebner et al., 1999; Rikers et al., 1998). HGMS systems typically consist of a column housing magnetically susceptible wires placed in an electromagnetic field. These wires dehomogenise the field, generating steep gradients that vary across the volume of any particles of appropriate size in the vicinity of the wires, thereby producing a net force on the particles. Particles are separated by the competition between magnetic forces on the one hand, and fluid drag or gravitational forces on the other. The use of an electromagnet is a useful component of the system as it allows the strength of the magnetic field to be adjusted for optimal separation of a wide range of particles with varying complexities, sizes and magnetic susceptibilities. The use of an electromagnetic also allows MPs to be subsequently retrieved after extraction without damaging them by avoiding physical contact with the magnetic source.

1.7. In this proof-of-concept study, a novel alternative method for extracting MPs from soil was developed, which uses the HGMS technique (Hillier and Hodson, 1997) in combination with

the use of hydrophobised iron nanoparticles (Grbic et al., 2019) for binding to the surface of MPs to facilitate high-gradient magnetic separation and subsequent recovery. The three-staged method involves: Stage 1 – initial removal of magnetic soil particles; Stage 2 – tagging of MPs with modified iron nanoparticles to render them magnetic; and Stage 3 – recovery of surface modified MPs. In this method, the MPs do not come into direct contact with the magnet, which avoids damage to the MPs as had been observed in the previous permanent magnetic extraction method developed by Grbic et al. (2019). This novel HGMS method recovered both high- and low-density MPs and fibres from soil, and recovered fibres that were partially embedded in soil aggregates. Furthermore, the developed method was less time-consuming, more cost-effective, and avoided the use of environmentally hazardous chemicals.

2. MATERIALS & METHODS

2.1. Soil Sampling and Soil Chemistry

2.1.1. Four soil types were used to test and optimise the method: loam (Forfar, Angus), high-carbon loamy sand (Dunmaglass, Inverness), sandy loam (Boyndie, Aberdeenshire), and high-clay sandy loam (Hartwood, North Lanarkshire). All soils were air dried and sieved to < 2 mm particles. The optimised method was then tested on a farm soil sample from the Glensaugh Farm Research Facility (Laurencekirk, Aberdeenshire). A composite surface sample (0-10 cm) was collected from the farm (20 kg) using an auger from 50 locations in a field (1,144 m^2), air dried and sieved to < 2 mm particles. Surface samples were collected because they are more likely to contain MPs. The field was used for livestock grazing. Within the field were several plots experimenting with the application of farmyard manure, compost, sludge pellets and inorganic fertiliser. Samples were not collected from these plots, but were taken elsewhere in the field.

2.1.2. Glassware and metal tools were used throughout to avoid contamination from plastic utensils, with glassware heated in a muffle oven (450 °C) before use (Dris et al., 2018). Soil clay, silt and sand content were determined by laser diffraction (British Standards Institution, 2009) using a Mastersizer 3000 particle analyser with Hydro LV sample dispersion unit (Malvern Panalytical). Total carbon content was determined by an automated Dumas combustion procedure (Pella and Colombo, 1973) using a Flash 2000 Elemental Analyser. Soil chemistry data is given in Table 1. Particle size distribution and carbon content analyses were conducted in this study to accurately determine soil types derived from the soil texture triangle. However, simple hand texturing procedures (Arshad et al., 1997) can be used effectively for determination of the likely experimental conditions required for the soil type concerned.

2.2. **High-Gradient Magnetic Separation (HGMS) System**

2.2.1. The HGMS arrangement was an in-house, custom-built unit, essentially the same as used by Hillier and Hodson (1997). A 35 cm long magnetic steel collector wire (magnetic matrix; 1.6 mm diameter) was housed within glass tubing (2.5 mm i.d. and 40 cm long) and held using a clamp stand within a magnetic field generated with an electromagnet. The magnetic poles were 40 cm long and 3 cm apart to accommodate the glass tube and the magnetic flux density was set by adjusting the applied current from customised constant current power supplies derived from electrophoresis units (Figure 1). The maximum magnetic flux density achievable in this system with this pole gap was 0.53 Tesla. Rubber tubing (Nalgene™; 3/4 in i.d. x 25 cm long) was attached to the bottom of the glass tube and a lock-grip clamp was used here to allow the glass tube to be filled with HPLC grade ethanol (Rathburn, UK) and a separate clamp was used to separate the

magnetic material from the non-magnetic material. Samples were added to the glass tubing via a glass funnel.

2.3. **Stage 1: Removal of Magnetic Soil Particles**

2.3.1. Four grams of soil were spiked with 30 MP particles or fibres and mixed thoroughly. Each MP type and MP size was tested with each soil type individually, giving a total of 196 individual tests. The MPs tested were 63-75, 106-125, 300-355 and 600-710 µm polyethylene (PE) microbeads (Cospheric LLC, USA), 2-4 mm PE fibres, 2.0 x 2.0 x 0.4 mm polyethylene terephthalate (PET) flakes and 650-850 µm polytetrafluoroethylene (PTFE) fragments, which were prepared in the laboratory. Spiking reached a concentration of 1% (w/w) or less, which is a similar concentration to those found in the environment (de Souza Machado et al., 2018b). The soil samples were resuspended in 20 mL of ethanol (Figure 2). The magnetic flux densities were adjusted to locate the optimal conditions for magnetic soil particle removal for each soil (Figure 3; 0.29 Tesla for loam, 0.35 Tesla for high-carbon loamy sand, 0.53 Tesla for sandy loam, and 0.16 Tesla for high-clay sandy loam). Each spiked soil sample was introduced to the magnetic field to allow magnetic soil particles to adhere to the collector wire (3 min settling time). The glass tube was agitated to dislodge any loosely adhered MPs from the wire. The non-magnetic fraction (containing the MPs) that had settled past the collector wire was separated from the magnetic material by a lock grip clamp attached to a flexible Nalgene™ tube and retained for Stages 2 and 3. The magnetic field was switched off and the magnetic soil fraction flushed out and discarded. This was repeated a second time. The collector wire was cleaned for Stage 3.

2.4. **Stage 2: Magnetisation of MPs**

2.4.1. Modified iron nanoparticles were prepared according to Grbic et al. (2019). Briefly, 0.16 g of iron nanoparticles (25 nm; Sigma-Aldrich) were mixed with 80 mL ethanol and 800 µL hexadecyltrimethoxysilane for 12 h on a Gallenkamp orbital shaker at 140 rev/min. The liquid was then decanted using a magnet to retain the iron nanoparticles at the bottom of the container, and the modified iron nanoparticles were then re-suspended in 20 mL deionised water for storage. Approximately 10 mg of modified iron nanoparticles were added to the non-magnetic soil fraction retained from Stage 1 using a microspatula and incubated at room temperature for 10 min (with frequent stirring by hand with a glass rod) to allow binding of the iron nanoparticles to the MPs (Figure 2).

2.5. **Stage 3: Extraction of Microplastic Particles**

2.5.1. The magnetic flux densities were adjusted to the optimal conditions for MP recovery for each soil (Figure 3) - 0.39 Tesla for loam, 0.39 Tesla for high-carbon loamy sand, 0.53 Tesla for sandy loam, and 0.39 for high-clay sandy loam. The sample was introduced to the HGMS system and the magnetic fraction retained. The process was repeated for a second cycle with the non-magnetic fraction (adding another ~10 mg of modified iron nanoparticles). The retained fractions containing MPs were filtered onto 1.2 µm Whatman GF/C glass microfibre membrane filters (Figure 2).

2.6. **Density Separation (DS)**

2.6.1. Four grams of the test soils were spiked with MPs and fibres as described above, resuspended in 50 mL of saturated zinc bromide solution (density ≈ 2.4 g/mL^3) and placed on an IKA® KS 260 basic rotary shaker at 300 rpm for 5 min and allowed to settle overnight. As with the HGMS method, a total of 196 individual spiked soil tests were processed by DS.

225

226 2.6.2. Eight grams of soil from the Glensaugh Research Facility was used directly (i.e. without
227 spiking) and processed in the same way as the test soils prior to extraction. Previously
228 published studies using DS as the extraction method used sample sizes of 5-10 g of soil
229 (Corradini et al., 2019; Radford et al., 2021; Zhang et al., 2018), so the 8 g used in this
230 study aligns with this practice. Moreover, previously published studies tested soils in
231 triplicate (Corradini et al., 2019; Han et al., 2019; Liu et al., 2018; Radford et al., 2021;
232 Scheurer and Bigalke, 2018; Zhang et al., 2018), but for improved statistics, 7 replicates
233 was used in this study.

234

235 2.6.3. Zinc bromide is a common salt solution and was used in this study as it has the potential
236 to extract both high- and low-density MPs (He et al., 2018; Liu et al., 2018; Scheurer and
237 Bigalke, 2018; Zhang et al., 2018). The deionised water used to make the saturated salt
238 solution was filtered before preparation to minimise the possibility of any MP
239 contamination. The solution was decanted and rinsed with excess solution using a glass
240 pasture pipette while carefully inverting the beaker to reduce the potential loss of
241 microplastics through their adhesion to the walls of the beaker. The decanted and rinsed
242 solution was filtered as described above, and the process repeated a second time.

243

244 2.7. **Quantification and Identification of Microplastics**

245 2.7.1. Recovered material was treated with 10 mL 30% hydrogen peroxide (Sigma-Aldrich) for
246 1 h at 60 °C to remove organic matter from the MPs, and then re-filtered. MPs were
247 counted directly on the filter papers using a Nikon SMZ1500 stereo microscope (10x
248 magnification). Both HGMS-recovered MPs and DS-recovered MPs were quantified from

7 replicates per test soil type and MPs extracted from the Glensaugh sample by HGMS and DS were also quantified from 7 replicates. A blank measurement was also performed with all reagents only. Attenuated Total Reflection - Fourier-Transform Infrared (ATR-FTIR) measurements of MPs that were > 70 µm were carried out using a Bruker Vertex 70 FTIR spectrometer. To generate an IR spectrum, a Diamond Attenuated Total Reflectance (DATR) crystal with a single reflectance system was used. Data points in the range of 4000-400 cm^{-1} were recorded with a resolution of 4 cm^{-1} and an average of 200 scans. An air blank spectrum, with the same number of scans and resolution was recorded as the background spectrum before each measurement. Interpretation of the IR spectra was achieved using searchable in-house and commercial libraries of reference IR spectra.

2.8. **Statistical Analysis**

2.8.1. Recovery of MPs was calculated as a percentage of the total number of spiked MPs. T-tests were performed to find the significance associated with the differences in MP recovery between the two methods (Welch, 1938). This is an appropriate statistical test to use when n is as small as 2 and the within-pair correlation is high (> 0.8) (de Winter, 2013). ANOVA was performed to find the significance associated with the differences in recovery of each MP particle type and fibres within each soil type for HGMS (Sthle and Wold, 1989). Both tests were performed using R (version i386 4.0.0).

3. RESULTS AND DISCUSSION

3.1. **Optimisation of MP recovery using the HGMS system**

3.1.1. Stage 1 of the HGMS method was implemented to remove naturally paramagnetic minerals (Mullins, 1977) and prevent them coating the collector wire and blocking

adherence of the MPs. Stage 2 magnetically tagged MPs by binding modified iron nanoparticles to their surface. Stage 3 recovered the MPs that were hydrophobically attached to modified iron nanoparticles, which rendered them magnetic in the HGMS system.

3.1.2. Magnetic flux densities for Stages 1 and 3 were optimised for each soil type (Figure 3). Particle capture in an axial HGMS system, configured as herein, depends on the competition between gravity settling forces and magnetic forces (Watson, 1973), with the latter a function of both the magnetic susceptibility of any given particle (or aggregate) and its radius. This means that polymer type would not affect magnetic recovery using HGMS - this is determined only by particle size and the ability of the modified iron nanoparticles to bind to the MP's surface. Plastics are diamagnetic (Keyser and Jefferts, 1989) and would ordinarily be repelled from the HGMS filter, but tagging with iron nanoparticles effectively renders them paramagnetic in the HGMS system. Grbic et al. (2019) reported that the iron nanoparticles bound to PE, PET, polypropylene, polyvinyl chloride, polystyrene and polyurethane, and this study has further demonstrated that iron nanoparticles also bound to both PTFE particles and PE fibres (Figure 4). The MPs selected in this work encompassed various chemical and physical properties, such as polar (PET) and non-polar (PE and PTFE) plastics, low-density (PE) and high-density (PET and PTFE) plastics, and different shapes (fibres, spheres, flakes, fragments) and sizes (63 µm to 2 mm) to demonstrate the ability of HGMS to extract plastics with different properties without significant reductions in their recovery.

3.1.3. Shi et al. (2022) reported that the hydrophobicity and crystallinity of MPs affected the adsorption efficiency of the modified iron nanoparticles. The lower the hydrophobicity

and crystallinity of the polymer, the lower the adsorption capacity of the iron nanoparticles, however, the polarity and pH of the background solution can influence this. Ethanol molecules are amphiphilic so have hydrophobic and hydrophilic properties. No significant differences in recovery of the plastic types were observed ($p > 0.05$), therefore, it was concluded that these physicochemical properties did not play a significant role in MP recovery in the HGMS system.

3.1.4. Differences in optimal conditions can be ascribed to factors such as different particle size distributions (Table 1), and differences in mineralogy and carbon content insomuch as this determines the magnetic susceptibility of the particles or aggregates present.

3.1.5. Both loam and high-carbon loamy sand had similar relationships between magnetic flux density and MP recovery (Figures 3A and 3B). In Stage 1, magnetic flux densities > 0.35 Tesla removed the most magnetic soil material, but this also removed > 40% of untreated MPs. Studies have reported that MPs bind to the surface of clay particles in soil (Pathan et al., 2020). This may account for the loss of some MPs in Stage 1, particularly for the loam soil (10.07% clay; Table 1), due to paramagnetic clay particles being attracted to the collector wire. Some types of organic matter may also behave paramagnetically and become attracted to the collector wire, and at stronger magnetic flux densities, organic matter behaving diamagnetically may also be attracted to parts of the collector wire (Sokolowska et al., 2016). MPs have been found to adhere to the surface of vegetation/organic matter (Mateos-Cárdenas et al., 2021), therefore, any MPs adhered to the surface of organic matter in the HGMS system has the potential to be removed through para- or diamagnetic attraction of the organic matter to the collector wire in Stage 1, particularly in soils containing a higher organic matter content

such as the high-carbon loamy sand (14.4% carbon; Table 1) used in this study. At 0.10-0.35 Tesla, a maximum of only 9% of untreated MPs were removed. Therefore, an appropriate magnetic flux density was selected that allowed maximum removal of magnetic soil material, without causing significant losses of untreated MPs. This was 0.29 and 0.35 Tesla for loam and high-carbon loamy sand, respectively.

3.1.6. High-clay sandy loam displayed a similar pattern of behaviour to loam and high-carbon loamy sand for MP removal in Stage 1, however, the removal of untreated MPs was higher at magnetic flux densities > 0.20 Tesla (Figure 3C). This was expected for this soil type as there was a higher proportion of clay particles (21.00% clay; Table 1) that could adhere to the surface of MPs, and so MPs may have been removed at lower magnetic flux densities due to this clay-MP interaction. Therefore, a suitable magnetic flux density of 0.16 Tesla was selected for high-clay sandy loam.

3.1.7. By contrast, MP removal from sandy loam during Stage 1 remained constant across the range (Figure 3D) due to its low carbon and clay content, so 0.53 Tesla was selected for this soil type.

3.1.8. In Stage 3, MP recovery decreased at electromagnetic strengths > 0.4 Tesla for loam, high-carbon loamy sand and high-clay sandy loam soils due to larger volumes of soil particles (that were not removed in Stage 1) adhering to the collector wire, likely because the resultant deposit effectively blocked the attraction of iron-bound MPs. Therefore, to achieve optimum recovery of MPs, a uniform 0.39 Tesla was selected for Stage 3 in the loam, high-carbon loamy sand and high-clay sandy loam soils (Figures 3A-

C). For the sandy loam, optimal MP recovery occurred at the highest magnetic flux density (0.53 Tesla; Figure 1D) because most magnetic soil particles were removed during Stage 1.

3.2. **Performance of HGMS method**

3.2.1. HGMS achieved significantly higher recoveries for both high- and low-density MPs in all the test soil types compared to DS ($p < 0.01$; Figure 4). The exception was recovery of PE (300-355 µm) in high-carbon loamy sand and sandy loam, and PE (600-710 µm) in high-clay sandy loam, which showed no statistical difference between the two methods ($p > 0.05$). A global t-test (i.e. a t-test performed on all 392 tests for MP recovery by DS and HGMS) showed that overall, HGMS gave significantly higher MP recoveries than DS ($p < 0.01$).

3.2.2. The average recovery of PE (63-75 µm) was 89±5% using DS and 98±2% using HGMS. The recovery of PE (106-125 µm) was 90±4% using DS and 96±3% using HGMS. The higher recoveries of these very small MPs achieved by HGMS is important because small MPs have greater detrimental impacts on organisms (Huerta-Lwanga et al., 2016; Ng et al., 2018) so it will allow future studies to consider impacts on soil biota. Moreover, small MPs are usually difficult to handle in the laboratory so they often get missed. Recovery of PE (300-355 µm) was 90±4% using DS but 94±4% using HGMS. The recovery of PE (600-710 µm) was 89±6% using HGMS, but only 75±7% using DS. PET had a recovery of 56±7% using DS and 88±5% using HGMS. A significant improvement in recovery for the highest density polymer tested, PTFE, was observed using HGMS. PTFE was not recovered at all using DS, but recoveries of 90±5% were achieved with HGMS. DS is often incapable of extracting high-density MPs due to their density being similar to that of soil

particles (Scopetani et al., 2020). High-density polymers are manufactured to be resistant to environmental, chemical and thermal degradation. This can be achieved through their polymeric structures (e.g. the high bonding energy of C-F covalent bonds in PTFE (485 kJ/mol) renders the structure chemically inert), or through the addition of additives to improve their functionality. Due to their resistance to degradation in the environment, they will likely accumulate over time. Until recently, there has been a lack of attention to the presence of high-density MPs in the environment despite their low degradability as well as their contribution of more than 20% of the global plastic demand (PlasticsEurope, 2019). Therefore, the recovery of high-density MPs using HGMS is an important aspect as it will allow a more accurate determination of MP prevalence in soil.

3.2.3. HGMS also showed improved recovery for fibres (95±3%) compared to DS (78±9%). Fibres are one of the most commonly occurring MPs in the environment (Corradini et al., 2019; Henry et al., 2019), therefore, it was important that the HGMS method was capable of extracting fibres.

3.2.4. Most HGMS recoveries had smaller standard deviations than DS, (the exception was PE (300-355 µm) where they were the same), indicating that HGMS has better reproducibility compared to both DS and to the previous magnetic extraction method developed by Grbic et al. (2019) (±6-47%). There was no significant difference in recovery of small-sized MPs (63-75 µm PE and 2-4 mm PE fibres), medium-sized MPs (106-125 µm PE and 300-355 µm PE) or large-sized MPs (600-710 µm PE, 2.0 x 2.0 x 0.4 mm PET and 650-850 µm PTFE) between the replicates in all 4 soil types ($p > 0.05$), indicating that the HGMS method is highly reproducible when extracting fibres and MPs from these soil types. The exception was in the high-carbon loamy sand where there was

a significant difference between replicates when recovering the small-sized MPs, likely as a result of their removal in Stage 1 ($p < 0.05$) (Mateos-Cárdenas et al., 2021).

3.2.5. Background levels of MP particles and fibres in the test soils were determined by HGMS and optical microscopy (at 10x magnification) to allow accurate measurements of MP recovery from the test soils used for both HGMS and DS. Only fibres were detected in all test soils except for the high-carbon loamy sand. No MP particles were detected in the test soils. These contaminant fibres were bright and long so they were easily distinguished from the spiked fibres, and were discounted from the recovery calculations. Blank control measurements showed that no MP particle or fibre contaminants were detected in any of the reagents (zinc bromide or ethanol containing modified iron nanoparticles) after filtration. All glassware was regularly heated in a muffle oven at 450 °C to reduce the potential for MP contamination (Dris et al., 2018). Therefore, we are confident that the difference in recovery rates obtained from HGMS and DS, respectively, were not a result of differences in background levels of MP particles or fibres in the test soils or reagents.

3.2.6. Taken together, HGMS achieved good MP recoveries irrespective of density, size or shape of the MP under the conditions set using the optimal magnetic flux densities selected for each soil type. However, reproducibility may be compromised for small-sized MPs (63-75 µm PE and 2-4 mm PE fibres) in high-carbon loamy sand. Several studies found high-density MPs to be either low in quantity or absent in soil (Liu et al., 2018; Scheurer and Bigalke, 2018). This may reflect inefficient extraction methods, which subsequently under-estimated the true abundance of high-density MPs.

Implementation of the HGMS method in future studies has the potential to provide more accurate quantifications of MPs and fibres.

3.2.7. The use of an electromagnet prevented fragmentation of MPs. This is an improvement on the previous magnetic extraction method developed by Grbic et al. (2019), which reported fragmentation and damage of MPs during their removal from the permanent magnet, which could result in over-estimation of MP particle abundance in real environmental samples.

3.3. **Practical application of the HGMS method to a farm soil sample**

3.3.1. The performance of the HGMS method was additionally tested against DS using a sandy loam soil sample from the Glensaugh Farm Research Facility (Table 1). Agricultural soils have been identified as being a major 'hot-spot' for MP pollution due to land management practices such as sewage sludge amendment and the use of mulching film (Guo et al, 2020). Seven replicates of 8 g of soil were used for analysis, with the sample being split into two 4 g subsamples for HGMS. The magnetic flux densities selected were based on the parameters prescribed to the test soil types. The main factors considered in determining the magnetic flux densities for Stages 1 and 3 were the clay and carbon content. Since the rate of MP recovery was sensitive to these soil factors (Section 3.1), and the Glensaugh sample contained a higher carbon content (Table 1), weaker magnetic flux densities were used compared to the sandy loam test soil. Based on these factors, 0.35 and 0.39 Tesla for Stage 1 and 3, respectively, were selected for the Glensaugh sample and the extraction was carried out as described (Section 2.3-2.6; Figure 2). HGMS extracted an average of 14±4 fibres and 3±1 MP particles per 8 g sample while DS recovered an average of 8±3 fibres and 1±1 MP particle (Figure 5). Particles

were predominantly film fragments (potentially originating from the use of silage and haylage plastic wrapping) with the other particles being fragments and flakes. Fibres and MP particles may also have originated from MP pollution that drifted onto the field by wind transportation from nearby experimental soil amendment plots which are known to contain MPs (Corradini et al., 2019; Gui et al., 2021; Rolsky et al, 2020; Vithanage et al., 2021).

3.3.2. The within-pair correlation between the MP recoveries with HGMS and DS was high (> 0.8), which meant that Welch's t-test was an appropriate test to use when looking for significant differences in recoveries. This showed that there was a significant difference in MP recovery between the two methods ($p < 0.05$), likely due to MPs becoming trapped by settling soil aggregates, reducing extraction efficiency during DS (Zhang and Liu, 2018). Fibres recovered from the Glensaugh sample ranged from approximately 2 to 15 mm in length, while the dimensions of the particles ranged from approximately 90 to 450 µm, and the PE films were an average of approximately 3 x 1.5 x 0.1 mm. The MP particles and fibres recovered were of a different size, colour, and shape to those used during the method development stage, ruling out any possibility of cross-contamination. Fibres that were partially entrapped in soil aggregates were successfully recovered using HGMS (Figure S1), possibly due to the combined effects of the bound iron nanoparticles to the fibre's surface and the magnetically susceptible soil minerals within the aggregate. No such observation was seen with DS. DS often fails to extract fibres or MP particles entrapped within aggregates (Bläsing and Amelung, 2018) due to their overall higher density. Disaggregation steps such as ultrasonication can be undertaken to improve MP recovery during DS, however, the extent of ultrasonication is dependent on soil type and the aggregate's stability, and care must be taken to minimise further

interference of the flotation of low-density soil organic matter caused during disaggregation (Thomas et al., 2020). Ultrasonication also has the potential to damage or fragment MPs. This means that the developed HGMS method has the potential to offer extraction of these commonly observed fibre-aggregate complexes resulting in higher recoveries and a more accurate quantification of terrestrial fibre and MP pollution.

3.3.3. ATR-FTIR was used to confirm the compositions of the MPs recovered from the Glensaugh soil samples (Figure 6), where MP particles were ≥ 70 µm. As a control, FTIR analysis was also performed on the pristine MPs (selected from the stock containers) used to spike the soils. This was done to ensure the presence of the bound modified iron nanoparticles on subsequently recovered MPs did not interfere with FTIR measurements (Figure S2 and 6). Spectral interpretation identified predominantly PE, PET-glycol and polyester, or blends of these plastic types for recovered fibres, PE for film fragments, and PE and PTFE for particles (Figure 6). This demonstrated that other plastic types could be recovered using HGMS other than those tested during the method optimisation stage of this work. FTIR also confirmed that HGMS recovered both high- and low-density MPs.

3.3.4. The application of HGMS to the Glensaugh farm sample demonstrated the effectiveness of the method to extract MPs from soils. The higher recovery of MP particles and fibres by HGMS from soil will enable researchers and practitioners in the agricultural and food industries to understand the true impact of agricultural films and soil amendments on soil quality and health. It has been reported that the consumption of macroplastics (> 5 mm) and MPs by sheep through grazing can occur (Beroit et al., 2021). MPs can also affect crop growth and yield (Khalid et al., 2020) or have the potential to be incorporated

into crops, fruits or vegetables (Conti et al., 2020; Dong et al., 2021; Li et al., 2020). Therefore, the developed HGMS method could potentially help with soil monitoring and subsequently inform the agriculture and food industries.

3.4. **Evaluation of the HGMS method**

3.4.1. HGMS was a significantly faster method, taking ~30 min to process one sample, compared to 2-3 days for DS. In this HGMS method, ethanol was used, which is readily biodegradable and non-toxic (Thomas et al., 2020), whereas, DS uses salt solutions that are toxic and have long lasting environmental effects (Thomas et al., 2020). Ethanol is also substantially cheaper than the salts used in DS. Ethanol was used because it has a low specific density, which resulted in better dispersion of lighter MPs into solution, improving both settling times, and contact times with the collector wire during Stages 1 and 3. Water was considered during development of the HGMS method, but this caused the flotation of lighter MPs and fibres preventing them from reaching the collector wire within the electromagnetic field for high-gradient magnetic extraction in Stage 3 (data not shown). Ethanol also has minimal impacts on MPs (Dawson et al., 2020).

3.4.2. This proof-of-concept study was intended to show the potential of HGMS to extract MPs from soil. The HGMS system can be easily adapted by other researchers who wish to build on this concept. Various filter designs are available commercially (or are easy to make) to accommodate a range of separation requirements, from large to small sample volumes to ones designed for specific sizes or quantities of target components or types of matrices. Since HGMS works as a function of magnetic forces and magnetic susceptibility and radius of the MP, a scaled-up system would simply require the quantity of modified iron nanoparticles and the capacity/throughput of the HGMS set-

522 up to be adjusted appropriately. Larger HGMS systems have indeed been used in the
523 mining industry (Chun, 1995; Dahe, 2000; Ignjatović et al., 1995) and laboratory HGMS
524 systems of various sizes are available.

525

526 3.4.3. In summary, HGMS is a faster, safer and cheaper extraction method; it is also a mature
527 industrial technology (Alves et al., 2019; Gerber and Birss, 1983; Hillier and Hodson,
528 1997; Mullins, 1977; Rikers et al., 1998; Watson, 1973; Yavuz et al., 2009) that may be
529 further optimised for MP separation on a larger scale.

530

531 3.4.4. A potential drawback of the novel HGMS method is that some knowledge of the soil
532 composition and particle size may be required prior to MP extraction as this influences
533 the parameters required for separation. However, it is possible to identify broad soil
534 types relatively easily by hand texturing (Arshad et al., 1997). In this study, laser
535 diffraction particle size analysis and Dumas combustion procedures were carried out to
536 accurately determine soil particle size and carbon content, respectively. However, hand
537 texturing would allow these extra analysis steps to be by-passed. This proof-of-concept
538 work has already optimised HGMS conditions for four soil types (loam, high-carbon
539 loamy sand, sandy loam and high-clay sandy loam), and so it likely that similar
540 experimental conditions can be used for similar soil types by other researchers wishing
541 to replicate this experimental set-up. Moreover, the conditions prescribed to the four
542 test soil types were used as a benchmark for assigning magnetic flux densities to the
543 Glensaugh farm sample, where the soil parameters differed to those in the test samples.
544 Therefore, optimising a particular soil sample for recovery is not a time-consuming task.
545 A further drawback is that some MPs may be lost during Stage 1. Any untreated MPs
546 adhered to the collector wire or physically trapped in the magnetic deposit that

accumulated on the wire in Stage 1 were discarded along with the magnetic soil particles, which likely accounted for the losses observed. Despite this, the novel HGMS method still out-performed the commonly used DS method and previous magnetic extraction method (Grbic et al., 2019) with recoveries ranging between 87-100% for all the MPs and fibres in this study.

4. CONCLUSION

4.1. The novel HGMS extraction method achieved high recoveries for both high- and low-density MPs and fibres across a range of soil types. It is a fast and inexpensive method of extraction avoiding the use of expensive and toxic chemicals as used by the DS method. This method was also capable of recovering fibre-aggregate complexes enabling more accurate enumeration of MP pollution in soils. Further work will be required to streamline the process (e.g. calibrate the set up to accommodate more soil types, larger sample volumes and optimise the design of the HGMS filter (collector wire)). However, even in a simple configuration, such as that used in the present investigation, this improved extraction method will provide an alternative quicker and more accurate method of quantifying and monitoring MP contamination in environmental samples in future studies and would be beneficial for the food, agricultural and environmental sectors.

ACKNOWLEDGEMENTS

This work was funded by the Macaulay Development Trust. EP, RH, LD and SH are supported by the Scottish Government's Rural and Environmental Science and Analytical Services (RESAS) Division. SD is supported by James Hutton Limited. The authors would like to thank Dr Allan Lilly and Pat Cooper for providing test soils and the Glensaugh soil, respectively. They would also like to thank the James

Hutton Analytical Services for determination of soil chemistry, and Graham Gaskin for providing support with the HGMS set-up.

REFERENCES

Alves MN, Miró M, Breadmore MC, Macka M. Trends in analytical separations of magnetic (nano)particles. *Trends in Analytical Chemistry*. 2019; 114: 89-97. DOI: http://dx.doi.org/10.1016/j.trac.2019.02.026

Arshad MA, Lowery B and Grossman B. Physical tests for monitoring soil quality. *Methods for assessing soil quality*. 1997; 49, 123-141. DOI: https://doi.org/10.2136/sssaspecpub49.c7

Beriot N, Peek J, Zornoza R, Geissen V, Huerta Lwanga E. Low density-microplastics detected in sheep faeces and soil: A case study from the intensive vegetable farming in Southeast Spain. *Science of The Total Environment*. 2021; 755, 142653. DOI: https://doi.org/10.1016/j.scitotenv.2020.142653

Bhakdi SC, Ottinger A, Somsri S, Sratongno P, Pannadaporn P, Chimma P, Malasit P, Pattanapanyasat K, Neumann HPH. Optimized high gradient magnetic separation for isolation of Plasmodium-infected red blood cells. *Malaria Journal*. 2010; 9(38). DOI: https://doi.org/10.1186/1475-2875-9-38

Bläsing M & Amelung W. Plastics in soil: Analytical methods and possible sources. *Science of the Total Environment*. 2018; 612, 422-435. DOI: http://dx.doi.org/10.1016/j.scitotenv.2017.08.086

British Standards Institution (2009) *BS EN ISO 13320:2009: Particle size analysis – Laser diffraction methods*. Available at: https://www.iso.org/standard/44929.html (Accessed: 02 February 2021).

Chae Y & An Y-J. Current research trends on plastic pollution and ecological impacts on the soil ecosystem: A review. *Environmental Pollution*. 2018; 240, 387-395. DOI: https://doi.org/10.1016/j.envpol.2018.05.008

593 Chun YK. The removal of iron from hard pulverised kaolin by dry high-gradient magnetic separation.
594 *Magnetic and Electrical Separation*. 1995; 6, 171-177.

595 Claessens M, Van Cauwenberghe L, Vandeghucte MB, Janssen CR. New techniques for the detection
596 of microplastics in sediments and field collected organisms. *Marine Pollution Bulletin*. 2013; 70, 227-
597 233. DOI: http://dx.doi.org/10.1016/j.marpolbul.2013.03.009

598 Conti GO, Ferrane M, Banni M, Favara C, Nicolosi I, Cristaldi A, Fiore M, Zuccarello P. Micro- and nano-
599 plastics in edible fruit and vegetables. The first diet risks assessment for the general population.
600 *Environmental Research*. 2020; 187, 109677. DOI: https://doi.org/10.1016/j.envres.2020.109677

601 Corradini F, Meza P, Eguiluz R, Casado F, Huerta-Lwanga E & Geissen V. Evidence of microplastic
602 accumulation in agricultural soils from sewage sludge disposal. *Science of the Total Environment*. 2019;
603 671, 411-420. DOI: https://doi.org/10.1016/j.scitotenv.2019.03.368

604 Dahe X. A large scale application of SLon magnetic separator in Meishan iron ore mine. *Magnetic and*
605 *Electrical Separation*. 2000; 11, 1-8. DOI: https://doi.org/10.1080/10556910211967

606 Dawson AL, Motti CA and Kroon FJ. Solving a Sticky Situation: Microplastic Analysis of Lipid-Rich Tissue.
607 *Frontiers in Environmental Science*. 2020; 8:563565. DOI: https://doi.org/10.3389/fenvs.2020.563565

608 de Souza Machado AA, Kloas W, Zarfl C, Hempel S, Rillig MC. Microplastics as an emerging threat to
609 terrestrial ecosystems. Global Change Biology. 2018a; 24, 1405-1416. DOI:
610 https://doi.org/10.1111/gcb.14020

611 de Souza Machado AA, Lau CW, Till J, Kloas W, Lehmann A, Becker R, Rillig MC. Impacts of Microplastics
612 on the Soil Biophysical Environment. *Environmental Science & Technology*. 2018b; 52, 9656-9665. DOI:
613 https://doi.org/10.1021/acs.est.8b02212

614 de Winter JCF. Using the Student's t-test with extremely small sample sizes. *Practical Assessment,*
615 *Research and Evaluation*. 2013; 18, Article 10. DOI: https://doi.org/10.7275/e4r6-dj05

Dong Y, Gao M, Qiu W, Song Z. Uptake of microplastics by carrots in presence of As (III): Combined toxic effects. *Journal of Hazardous Materials*. 2021; 411, 125055. DOI: https://doi.org/10.1016/j.jhazmat.2021.125055

Dris R, Gasperi J, Rocher V, Tassin B. Synthetic and non-synthetic anthropogenic fibers in a river under the impact of Paris Megacity: Sampling methodological aspects and flux estimations. *Science of the Total Environment*. 2018; 618, 157-164. DOI: https://doi.org/10.1016/j.scitotenv.2017.11.009

Ebner AD, Ritter JA, Nuñez L. High-gradient magnetic separation for the treatment of high-level radioactive wastes. *Separation Science and Technology*. 1999; 34, 1333-1350. DOI: https://doi.org/10.1080/01496399908951096

Enders K, Tagg AS, Labrenz M. Evaluation of Electrostatic Separation of Microplastics From Mineral-Rich Environmental Samples. Frontiers in Environmental Science. 2020; 8, 122. DOI: https://doi.org/10.3389/fenvs.2020.00112

Felsing S, Kochleus C, Buchinger S, Brennholt, Stock F, Reifferscheid G. A new approach in separating microplastics from environmental samples based on their electrostatic behavior. *Environmental Pollution*. 2018; 234, 20-28. DOI: https://doi.org/10.1016/j.envpol.2017.11.013

Gerber R, and Birss RR, 1983, High Gradient Magnetic Separation: Chichester, U.K., John Wiley and Sons, 208 p.

Grause G, Kuniyasu Y, Chien M-F, IInoue C. Separation of microplastic from soil by centrifugation and its application to agricultural soil. *Chemosphere*. 2022; 132654. DOI: https://doi.org/10.1016/j.chemosphere.2021.132654

Grbic J, Nguyen B, Guo E, You JB, Sinton DL, Rochman CM. Magnetic Extraction of Microplastics from Environmental Samples. *Environmental Science and Technology Letters*. 2019; 6: 68-72. DOI: https://doi.org/10.1021/acs.estlett.8b00671

639 Gui J, Sun Y, Wang J, Chen X, Zhang S, Wu D. Microplastics in composting of rural domestic waste:
640 abundance, characteristics, and release from the surface of macroplastics. Environmental Pollution.
641 2021; 274, 116553. DOI: https://doi.org/10.1016/j.envpol.2021.116553

642 Guo J-J, Huang X-P, Xiang L, Wang Y-Z, Li Y-W, Li H, Cai Q-Y, MO c-h, Wong M-H. Source, migration
643 and toxicology of microplastics in soil. *Environmental International*. 2020; 137, 105263. DOI:
644 https://doi.org/10.1016/j.envint.2019.105263

645 Han X, Lu X & Vogt RD. An optimized density-based approach for extracting microplastics from soil and
646 sediment samples. *Environmental Pollution*. 2019; 254, 113009. DOI:
647 https://doi.org/10.1016/j.envpol.2019.113009

648 He D, Luo Y, Lu S, Liu M, Song Y, Lei L. Microplastics in soils: Analytical methods, pollution
649 characteristics and ecological risks. *Trends in Analytical Chemistry*. 2018; 109, 163-172. DOI:
650 https://doi.org/10.1016/j.trac.2018.10.006

651 Henry B, Laitala K & Klepp IG. Microfibres from apparel and home textiles: Prospects for including
652 microplastics in environmental sustainability assessment. *Science of the Total Environment*. 2019; 652,
653 483-494. DOI: https://doi.org/10.1016/j.scitotenv.2018.10.166

654 Hillier S, Hodson ME. High-gradient magnetic separation applied to sand-size particles: An example of
655 feldspar separation from mafic minerals. *Journal of Sedimentary Research*. 1997; 67: 975-977. DOI:
656 http://dx.doi.org/10.2110/jsr.67.975

657 Huerta Lwanga E, Gertsen H, Gooren H, Peters P, Salánki T, van der Ploeg M, Besseling E, Koelmans AA
658 and Geissen V. Microplastics in the Terrestrial Ecosystem: Implications for *Lumbricus terrestris*
659 (Oligochaeta, Lumbricidae). *Environmental Science and Technology*. 2016; 50, 2685-2691. DOI:
660 https://doi.org/10.1021/acs.est.5b05478

Hurly RR, Lusher AL, Olsen M, Nizzetto L. Validation of a Method for Extracting Microplastics from Complex, Organic-Rich, Environmental Matrices. *Environmental Science & Technology*. 2018; 52, 7409-7417. DOI: https://doi.org/10.1021/acs.est.8b01517

Ignjatović MR, Ćalić N, Marković ZS, Ignjatović R. Development of a combined gravity-magnbetic separation process for magnetite ore using HGMS. *Magnetic and Electrical Separation*. 1995; 6, 161-170.

Keyser PT and Jefferts SR. Magnetic susceptibility of some materials used for apparatus construction (at 295 K). Review of Scientific Instruments. 1989; 60, 2711-2714. DOI: http://dx.doi.org/10.1063/1.1140646

Khalid N, Aqeel M, Noman A. Microplastics could be a threat to plants in terrestrial systems directly or indirectly. *Environmental Pollution*. 2020; 267, 115653. DOI: https://doi.org/10.1016/j.envpol.2020.115653

Koelmans AA, Nor NHM, Hermsen E, Kooi M, Mintenig SM, De France J. Microplastics in freshwaters and drinking water: Critical review and assessment of data quality. *Water Research*. 2019; 155, 410-422. DOI: https://doi.org/10.1016/j.watres.2019.02.054

Li L, Luo Y, Li R, Zhou Q, Peijnenburg WJGM, Yin N, Yang J, Tu C, Zhang Y. Effective uptake of submicrometre plastics by crop plants via a crack-entry mode. *Nature Sustainability*. 2020; 3, 929-937. DOI: https://doi.org/10.1038/s41893-020-0567-9

Liu M, Lu S, Song Y, Lei L, Hu J, Lv W et al. Microplastic and mesoplastic pollution in farmland soils in suburbs of Shanghai, China. *Environmental Pollution*. 2018; 242, 855-862. DOI: https://doi.org/10.1016/j.envpol.2018.07.051

Liu M, Song Y, Lu S, Qiu R, Hu J, Li X, Bigalke M, Shi H, He D. A method for extracting soil microplastics through circulation of sodium bromide solutions. *Science of the Total Environment*. 2019; 691, 341-347. DOI: https://doi.org/10.1016/j.scitotenv.2019.07.144

685 Masura J, Baker J, Foster G, Arthur C, Herring C. 2015. Laboratory methods for the analysis of
686 microplastics in the marine environment: recommendations for quantifying synthetic particles in
687 waters and sediments. NOAA Technical Memorandum NOS-OR&R-48.

688 Mateos-Cárdenas A, van Pelt FNAM, O'Halloran J and Jansen MAK. Adsorption, uptake and toxicity of
689 micro- and nanoplastics: Effects on terrestrial plants and aquatic macrophytes. *Environmental*
690 *Pollution*. 2021; 284, 117183. DOI: https://doi.org/10.1016/j.envpol.2021.117183

691 Mullins CE. Magnetic Susceptibility of the Soil and its Significance in Soil Science – A Review. *Journal*
692 *of Soil Science*. 1977; 28(2), 223-246. DOI: https://doi.org/10.1111/j.1365-2389.1977.tb02232.x

693 Ng E, Huerta Lwanga E, Eldridge SM, Jonshton P, Hu H, Geissen V and Chen D. An overview of
694 microplastic and nanoplastic pollution in agroecosystems. *Science of the Total Environment*. 2018;
695 627, 1377-1388. DOI: https://doi.org/10.1016/j.scitotenv.2018.01.341

696 Pathan SI, Arfaioli P, Bardelli T, Ceccherini MT, Nannipieri P and Pietramellara G. Soil Pollution from
697 Micro- and Nanoplastic Debris: A Hidden and Unknown Biohazard. *Sustainability*. 2020; 12, 7255. DOI:
698 https://doi.org/10.3390/su12187255

699 Pella E and Colombo B. Study of carbon, hydrogen and nitrogen by combustion gas-chromatography.
700 *Mikrochim Acta*. 1973; 1973, 697-719. DOI: https://doi.org/10.1007/BF01218130

701 PlasticsEurope, 2019. Plastics – the Facts 2019. An Analysis of European Plastics Production, Demand
702 and Waste Data. Association of Plastics Manufactures, Brussels. Plastics Europe. Available online at:
703 https://www.plasticseurope.org/en/resources/publications/1804-plastics-facts-2019 (Accessed 02
704 February 2021).

705 Prata JC, da Costa JP, Duarte AC, Rocha-Santos T. Methods for sampling and detection of microplastics
706 in water and sediment: A critical review. *Trends in Analytical Chemistry*. 2019a; 110, 150-159. DOI:
707 https://doi.org/10.1016/j.trac.2018.10.029

Prata JC, da Costa JP, Girão AV, Lopes I, Duarte AC, Rocha-Santos T. Identifying a quick and efficient method of removing organic matter without damaging microplastic samples. *Science of the Total Environment*. 2019b; 686, 131-139. DOI: https://doi.org/10.1016/j.scitotenv.2019.05.456

Prata JC, da Costa JP, Lopes I, Duarte AC, Rocha-Santos T. Environmental exposure to microplastics: An overview on possible human health effects. *Science of the Total Environment*. 2020; 702, 134455. DOI: https://doi.org/10.1016/j.scitotenv.2019.134455

Prendergast-Miller MT, Katsiamides A, Abbass M, Sturzenbaum SR, Thorpe KL, Hodosn ME. Polyester-derived microfibre impacts on the soil-dwelling earthworm *Lumbricus terrestris*. *Environmental Pollution*. 2019; 251, 453-459. DOI: https://doi.org/10.1016/j.envpol.2019.05.037

Radford F, Zapata-Restrepo LM, Horton AA, Hudson MD, Shaw PJ, Williams ID. Developing a systematic method for extraction of microplastics in soils. Analytical Methods. 2021; 13, 1695-1705. DOI: https://doi.org/10.1039/D0AY02086A

Rikers RA, Rem P, Dalmijn WL & Honders A. Characterization of Heavy Metals in Soil by High Gradient Magnetic Separation. *Journal of Soil Contamination*. 1998; 7(2): 163-190. DOI: https://doi.org/10.5402/2011/402647

Rodríguez-Seijo A, da Costa JP, Rocha-Santos T, Duarte AC, Pereira R. Oxidative stress, energy metabolism and molecular responses of earthworms (*Eisenia fetida*) exposed to low-density polyethylene microplastics. *Environmental Science and Pollution Research*. 2018; 25, 33599-33610. DOI: https://doi.org/10.1007/s11356-018-3317-z

Rolsky C, Kelkar V, Driver E, Halden RU. Municipal sewage sludge as a source of microplastics in the environment. *Current Opinion in Environmental Science & Health*. 2020; 14, 16-22. DOI: https://doi.org/10.1016/j.coesh.2019.12.001

Scheurer M & Bigalke M. Microplastics in Swiss Floodplain Soils. *Environmental Science & Technology*. 2018; 52, 3591-3598. DOI: https://doi.org/10.1021/acs.est.7b06003

732 Scopetani C, Chelazzi D,Mikola J, Leiniö V, Heikkinen R, Cincinelli A, Pellinen J. Olive oil-based method
733 for the extraction, quantification and identification of microplastics in soil and compost samples.
734 *Science of the Total Environment*. 2020; 733, 139338. DOI:
735 https://doi.org/10.1016/j.scitotenv.2020.139338

736 Shi X, Zhang X, Gao W, Zhang Y, He D. Removal of microplastics from water by magnetic nano-Fe_3O_4.
737 *Science of the Total Environment*. 2022; 802, 149838. DOI:
738 https://doi.org/10.1016/j.scitotenv.2021.149838

739 Sokolowska Z, Alekseev A, Skic K and Brzenzińska M. Impact of wastewater application on magnetic
740 susceptibility in Terric Histosol soil. *International Agrophysics*. 2016; 30, 89-94. DOI:
741 https://doi.org/10.1515/intag-2015-0064

742 Sthle L and Wold S. Analysis of variance (ANOVA). *Chemometrics and Intelligent Laboratory Systems*.
743 1989; 6, 259-272. DOI: https://doi.org/10.1016/0169-7439(89)80095-4

744 Thomas D, Schütze B, Heinze WM and Steinmetz Z. Sample Preparation Techniques for the Analysis of
745 Microplastics in Soil—A Review. *Sustainability*. 2020; 12, 9074. DOI:
746 https://doi.org/10.3390/su12219074

747 Vithanage M, Ramanayaka S, Hasinthara S, Navaratne A. Compost as a carrier for microplastics and
748 plastic-bound toxic metals into agroecosystems. Current Opinion in Environmental Science & Health.
749 2021; 24, 100297. DOI: https://doi.org/10.1016/j.coesh.2021.100297

750 Wang Z, Taylor SE, Sharma P, Flury M. Poor extraction efficiencies of polystyrene nano- and
751 microplastics from biosolids and soil. *PLoS ONE*. 2018; 13, e0208009. DOI:
752 https://doi.org/10.1371/journal.pone.0208009

753 Watson JHP. Magnetic filtration. *Journal of Applied Physics*. 1973; 44, 4209-4213. DOI:
754 https://doi.org/10.1063/1.1662920

Welch BL. The Significance of the Difference Between Two Means when the Population Variances are Unequal. *Biometrika*. 1938; 29, pp. 350–362. DOI: https://doi.org/10.1093/biomet/29.3-4.350

Yan Z, Liu Y, Zhang T, Zhang F, Ren H, Zhang Y. Analysis of Microplastics in Human Feces Reveals a Correlation between Fecal Microplastics and Inflammatory Bowel Disease Status. *Environmental Science and Technology*. 2022; 56, 414-421. DOI: https://doi.org/10.1021/acs.est.1c03924

Yavuz CT, Mayo JT, Yu WW, Prakash A, Falkner JC, Yean S, Cong L, Shipley HJ, Kan A, Tomson M, Natelson D, Colvin VL. Low-Field Magnetic Separation of Monodisperse Fe_3O_4 Nanocrystals. *Science*. 2006; 314, 964-967. DOI: https://doi.org/10.1126/science.1131475

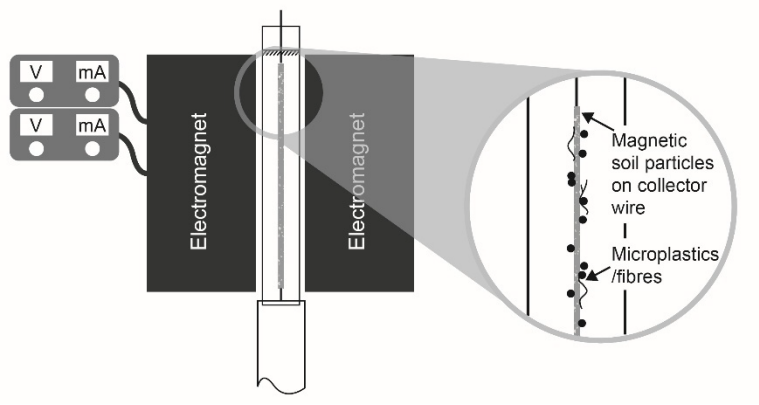
Yavuz CT, Prakash A, Mayo JT, Colvin VL. Magnetic separations: From steel plants to biotechnology. *Chemical Engineering Science*. 2009; 64, 2510-2521. DOI: https://doi.org/10.1016/J.CES.2008.11.018

Zhang GS & Liu TF. The distribution of microplastics in soil aggregate fractions in southwestern China. *Science of the Total Environment*. 2018; 642, 12-20. DOI: https://doi.org/10.1016/j.scitotenv.2018.06.004

Zhang S, Wang J, Liu X, Qu F, Wang X, Wang X et al. Microplastics in the environment: A review of analytical methods, distribution, and biological effects. *Trends in Analytical Chemistry*. 2019; 111: 62-72. DOI: https://doi.org/10.1016/j.trac.2018.12.002

Zhang S, Yang X, Gertsen H, Peters P, Salánki T, Geissen V. A simple method for the extraction and identification of light density microplastics from soil. *Science of the Total Environment*. 2018; 616-617, 1056-1065. DOI: https://doi.org/10.1016/j.scitotenv.2017.10.213

775 **Table and Figures**

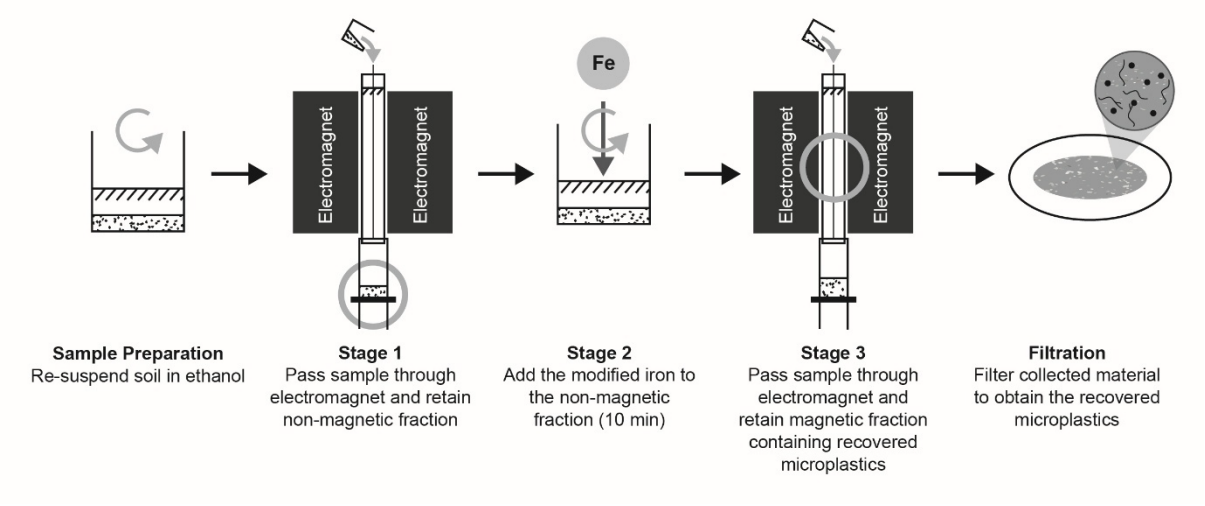


776

777 **Figure 1**. Schematic of the HGMS system showing the current suppliers, the electromagnet poles and

778 column containing the collector wire and ethanol where there are MPs adhered to the wire.

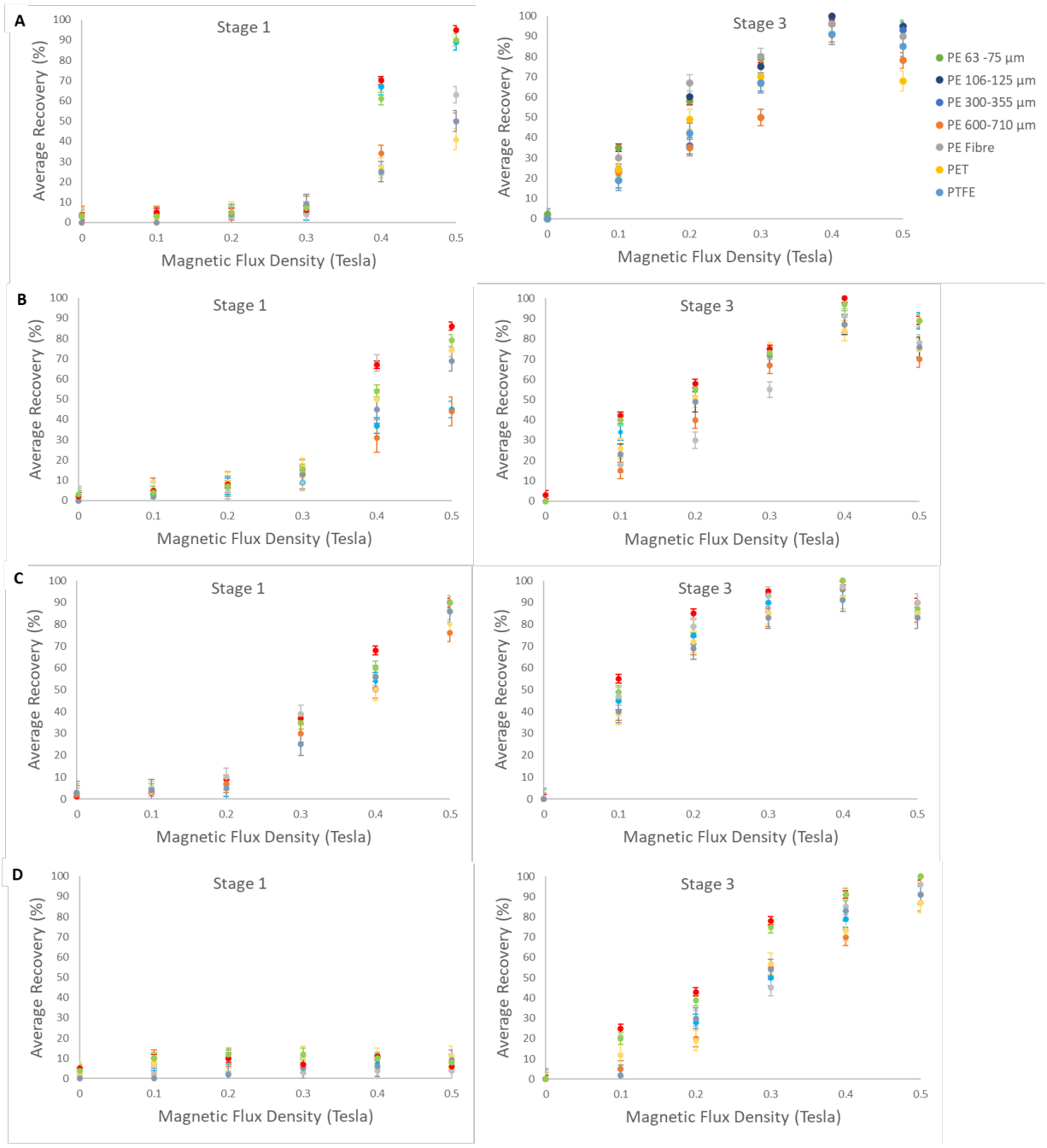
779



780

781 **Figure 2**. Schematic of the three-staged HGMS method.

782



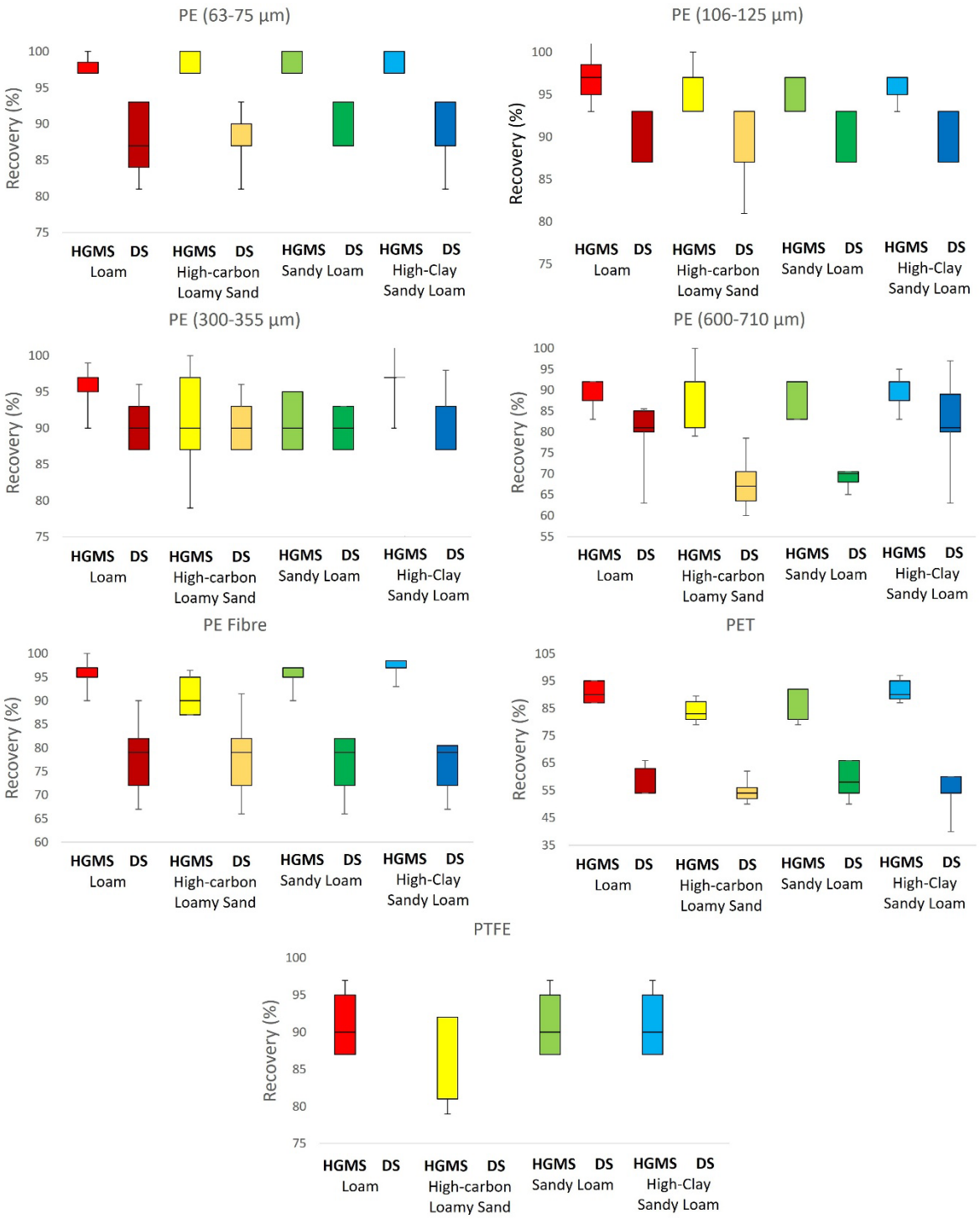
783

784 **Figure 3**. Influence of magnetic flux density on average MP recovery in (A) loam, (B) high-carbon loamy

785 sand, (C) high-clay sandy loam, and (D) sandy loam for Stage 1 and Stage 3 of HGMS. Error bars indicate

786 standard deviation.

787



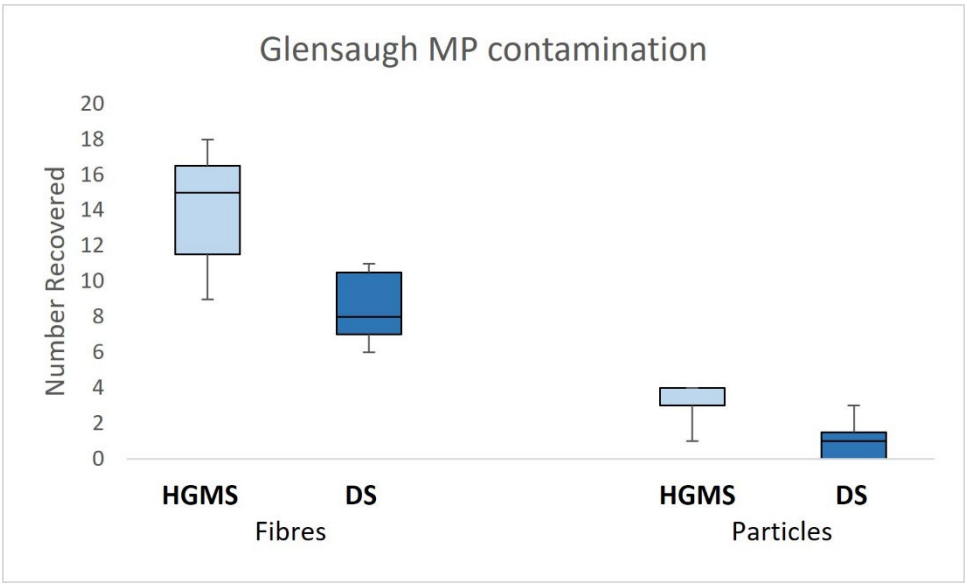
788

789 **Figure 4.** Box plots showing MP recovery using HGMS in each soil type (loam, high-carbon loamy sand,

790 sandy loam and high-clay sandy loam) compared to DS. Colours indicate soil type. Errors bars show

791 standard deviation.

792

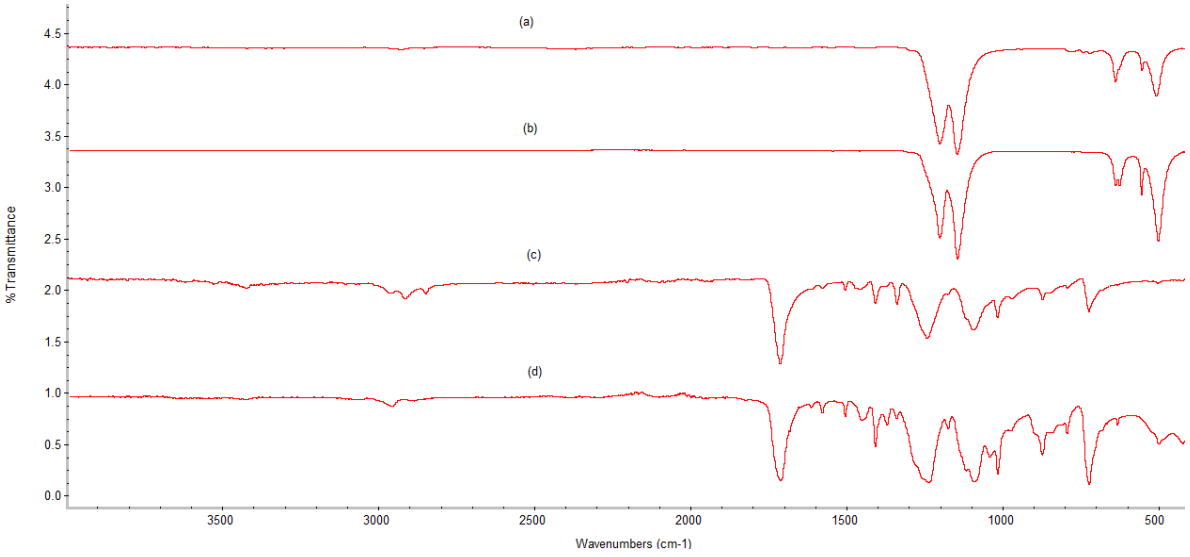


793

794 **Figure 5.** Box plot comparing the recovery of MP particles and fibres from the Glensaugh soil sample

795 by HGMS and DS. Error bars depict standard deviation.

796



797

798 **Figure 6.** FTIR spectra of (a) a PTFE particle, and (c) a PET-glycol fibre recovered from the Glensaugh

799 sample. Spectra (b) and (d) are their respective reference spectra.

800

801

Table 1. Soil Chemistry. Particle size ranges for clay, silt and sand, respectively, are indicated in the brackets.

Soil Type	Clay Content (%) (<2 µm)	Silt Content (%) (2-20 µm)	Sand Content (%) (20-2000 µm)	Carbon Content (%)	pH (in water)
Loam	10.07	43.17	46.76	3.00	5.17
High-Carbon Loamy Sand	1.05	13.94	85.01	14.40	5.36
Sandy Loam	4.98	21.55	73.47	2.33	5.08
High-Clay Sandy Loam	21.00	20.00	59.00	4.79	5.45
Glensaugh (sandy loam)	3.40	37.82	58.78	7.36	5.73

Highlights

- Rapid High-Gradient Magnetic Separation method for microplastic extraction from soil
- The HGMS method performed significantly better than the density separation method
- It was able to recover high- and low-density microplastics
- Could recover microplastic particles and fibres 63 µm – 15 mm in size (≥ 87%)
- Avoided the use and disposal of hazardous salts associated with density separation

Supplementary Material

Figure S1. Photograph of a red fibre (identified predominantly as polyester by FTIR) partially embedded in a soil aggregate under the stereomicroscope recovered from the Glensaugh sample using the developed HGMS method.

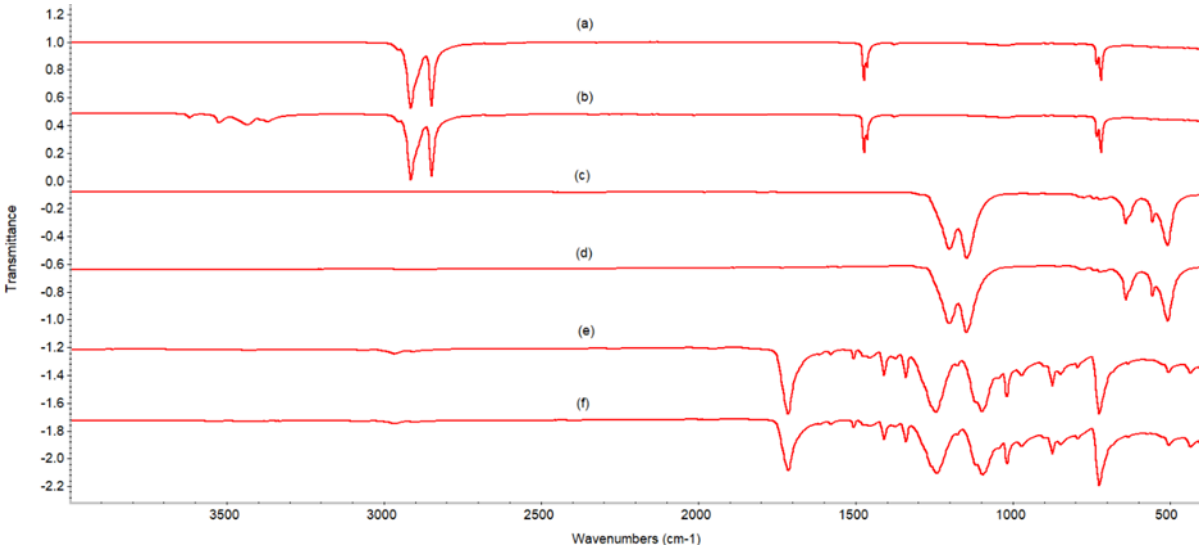


Figure S2. Comparison of FTIR spectra of pristine (a) PE, (c) PTFE, and (e) PET particles to modified iron-bound (b) PE, (d) PTFE, and (f) PET particles recovered from a test soil. The PE MPs used here contained aluminium trihydrate (gibbsite) (troughs around 3500 cm^{-1} region) – a common plastic flame retardant filler (Shah et al., 2014).

824 **REFERENCES**

825 Shah AUR, Lee D, Wang Y, Wasy A, Ham KC, Jayaraman K, Kim B, Song J. Effect of concentration
826 of ATH on mechanical properties of polypropylene/aluminium trihydrate (PP/ATH) composite.
827 *Trans. Nonferrous Met. Soc. China.* 2014; 24, s81-s89. DOI: https://doi.org/10.1016/S1003-
828 6326(14)63292-1

829