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## **Interfacial Interactions of Uranium and HDPE in agricultural soil and their bioaccumulation in *Mentha arvensis***

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**Interfacial Interactions of Uranium and HDPE in agricultural soil and  
their bioaccumulation in *Mentha arvensis***

**by**

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**B.S., Biological Engineering, University of Georgia, 2020**

**M.S., Civil Engineering, University of New Mexico, 2022**

**ABSTRACT**

We investigated the adsorption, precipitation, and phytoavailability of uranium after reactions with soil, high-density polyethylene particles, and *Mentha arvensis* through the integration of batch experiments, plant exposure, microscopy, and spectroscopy. Soluble U (initially 100  $\mu\text{M}$ ) decreased by 98.6% (1.09  $\mu\text{M}$ ) at pH 5 and 86.2% (13.81  $\mu\text{M}$ ) at pH 7.5 after 0.1 h of reaction with 10 g of soil in solution. Heterogenous U precipitates were observed in weathered HDPE surfaces for experiments without soil at both pH conditions. This suggests the weathering of the microplastic surfaces enhanced the nucleation of the U precipitates. Plants exposed to both U and HDPE exhibited photosynthetic rates 76.3% lower and transpiration rates 86.6% lower than plants not exposed, possibly due to negative synergetic interactions of U and HDPE. These results give insight into the surface-controlled reactions of soluble U with microplastics, soils and plants which is relevant to environments in which those co-occur.

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## **Chapter 1: Research Overview**

### **1.1 Introduction**

In the Southwestern United states, the legacy of mining activities as well as the practice of open dumping have the potential to negatively impact Native American lands. Abandoned mines act as a source of metals, including uranium (U), and mining activities have caused U and other metals to contaminate soil, water, and plants <sup>1,2</sup>. The practice of open dumping causes pieces of plastic to degrade and results in the creation of microplastics <sup>3</sup>. Both of these processes have raised concern about the use of contaminated agricultural soils.

The global production of plastic currently exceeds 359 million tons per year, and as a result of poor disposal and management, plastic pollution has become a major environmental issue <sup>4,5</sup>. Currently, microplastics are defined as plastic particles between 0.1  $\mu\text{m}$  and 1 mm, and nanoplastics are defined as  $< 0.1 \mu\text{m}$  <sup>6</sup>. Microplastics are composed of synthetic polymers with an arrange of heterogeneous properties <sup>3</sup>. There are two types of microplastics: primary and secondary <sup>7</sup>. Primary microplastics are ones purposely designed that size for commercial use <sup>3,7,8</sup>. However, secondary microplastics are of particular interest for this research because of how they are generated. Secondary microplastics are ones developed by the fragmentation of bigger plastic pieces caused by environmental weathering and degradation such as UV exposure <sup>3,7,8</sup>. The practice of open dumping generates secondary microplastics and can be common in Native lands due to a lack of access to waste facilities. Additionally, one key characteristic of microplastics is their ability to adsorb and then act as a carrier for toxic metals and organic contaminants <sup>9</sup>. Their ability to do so is based on a variety of factors, so understanding these factors and microplastics' interactions is crucial to human health and to the environment.

As mentioned, one heavy metal to consider is uranium. Uranium is a naturally occurring, radioactive, silvery-white metal <sup>10</sup>. Uranium is naturally present in almost all soil; however, through weapon manufacturing, nuclear energy generation, and mining, uranium can contaminate the environment posing potential health risks to both human and environmental health <sup>11</sup>. Once in the soil, U can accumulate in plant roots and shoots where it then can enter the food chain <sup>11, 12</sup>. In addition, U can be transported into water systems where it then is able to increase the radioactivity of the water <sup>10</sup>. Abandoned mine sites from U mining operations in the Western United States during the mid to late 1900s have extensively negatively impacted nearby Native American Communities <sup>1, 2</sup>. A previous study in Navajo Nation has connected exposure to mine wastes to an increased chance of acquiring chronic diseases including diabetes and hypertension <sup>2</sup>. In general, U is a known kidney toxicant and has been linked to developmental issues in animals <sup>2</sup>. Now that research studies have shown how microplastics can act as a vector for toxic metals and contaminants, the ecological concern of co-occurring U and microplastics needs to be better understood.

## **1.2 Research Gaps**

A majority of microplastic research has focused on microplastics in aquatic environments, leaving limited information on microplastics in terrestrial environments. More documentation is needed to better understand how microplastics behave in soils and how this behavior affects plant species. Additionally, more information is needed on the mechanisms of microplastic accumulation and phytotoxicity in plant species. Furthermore, a thorough understanding of the interfacial interactions governing the fate of microplastics and metals in terrestrial environments is lacking. Previous studies have investigated the interaction between microplastics and cadmium (Cd), cobalt (Co), copper (Cu), nickel (Ni), lead (Pb), and zinc

(Zn)<sup>5, 13-15</sup>. Yet, recent research suggests the co-occurrence of microplastics and U near abandoned mine sites<sup>16</sup>. However, the association and interactions between microplastics and U are rather unexplored. A better understanding of these interactions is needed to evaluate the environmental health concern of sites where these constituents co-occur.

### **1.3 Research Objective**

The objective of this study was to investigate the adsorption, precipitation, and phytoavailability of uranium after reactions with soil, high-density polyethylene (HDPE) particles, and *Mentha arvensis* (wild mint). Solid characterization as well as two different laboratory experiments were conducted to evaluate the interfacial interactions between these contaminants. Multiple spectroscopy and microscopy techniques were first used to characterize the plastic particles according to their size, shape, surface characteristics, and functional chemistry. Batch experiments were then conducted to determine and compare uranium adsorption and interactions in the presence of plastic particles, soil particles, and a plants nutrient solution. A comparison of these results allows for a better understanding of surface-controlled processes on the reaction of soluble uranium with microplastics and soil. Wild mint plants, *Mentha arvensis*, were then exposed to uranium and microplastics to evaluate the phytoavailability, toxicity, and in planta distribution of these contaminants. These results can be used to evaluate the risk of exposure for communities where uranium and microplastics co-occur.

### **1.4 Research Overview**

This thesis document is divided into three chapters, an appendix, and a reference section. Chapter 2 consists of a literature review of research on the source of microplastics in the environment, physiochemical properties of microplastics affecting their behavior in the

environment, and the interfacial interactions and effects of microplastics in the terrestrial environment. The interfacial interactions between particulate plastics and metals and their effects on plants and soil are also discussed. Additionally, the source, abundance, and threat of U are discussed as well as the reactions of U in the environment. Chapter 3 investigates the interfacial interactions between microplastics and U in agricultural soil and their bioaccumulation in wild mint. The appendix contains the supplementary information and data collected from the study in Chapter 3.

## **Chapter 2: Literature Review**

### **2.1 Source of particulate plastics in the environment**

The global plastic pollution crisis has been raising concern in recent years, specifically in terms of microplastic pollution. The global production of plastic is currently exceeding 359 million tons per year <sup>4</sup>, with polyethylene (PE) being the most generated plastic type, at 31% [18% low-density polyethylene (LDPE) and 15% high-density polyethylene (HDPE)] of the total production <sup>17</sup>. Most plastic and microplastic research have focused on their occurrence and effects in marine ecosystems, which has led to a need for more research over plastics and microplastics in terrestrial ecosystems. So, how exactly do these plastics enter the terrestrial environment? One source is landfills and open dumps, accounting for ~42% of 358 Mt plastic waste generated in 2018 <sup>18</sup>. This is due to landfills and open dumps receiving large amounts of plastic waste from both household and industrial divisions. In addition, wastewater treatment plants contribute to plastic waste in the environment <sup>3</sup>. In 2018, 25.8 Mt of plastics entered the municipal waste stream in Europe, which resulted in plastics accounting for 12.4% of the total municipal solid waste (MSW) <sup>19</sup>. Plastic mulches, irrigation practices, sewage sludge implemented as fertilizer, fallout from the air, and precipitation are sources of microplastics found in soil <sup>20</sup>. Previous studies have investigated the specific type of plastics that are most prevalent in the terrestrial environment and the type of plastics that account for the largest portions of MSW. In 2019, 270 million tons of MSW was collected in the European Union, with 19 million tons being plastic <sup>4</sup>. Of that 19 million tons, an average of 36% of the weight was PE (8% linear low-density polyethylene (LLDPE), 13% LDPE, 15% HDPE) <sup>4</sup>. Polyethylene and polypropylene (PP) are the polymers most commonly found in global sediments <sup>21</sup>. PE actually contributed up to 89% of the microplastic composition in agricultural soil samples from a previous study <sup>3</sup>.

But what exactly are microplastics (MPs)? The definition of MPs continues to evolve, and the term “particulate plastics” now embodies the former definition of microplastics: synthetic polymers < 5 mm in diameter<sup>22</sup>. Currently, MPs are defined as plastic particles between 0.1 µm and 1 mm, and nanoplastics are defined as < 0.1 µm<sup>6</sup>. Microplastics are divided into two classes, primary and secondary, based on their source. Primary microplastics are plastics manufactured to be in the micrometer size range, including microbeads and microfibers used in personal care products<sup>6, 7, 22</sup>. Secondary microplastics originate from the fragmentation of bigger plastic particles in the environment<sup>6, 7, 22</sup>. The breakdown of these particles arises from environmental processes such as hydrolysis, photodegradation, and oxidation<sup>22</sup>. Furthermore, the improper disposal of plastics, such as the practice of open dumping, encourages the generation of secondary microplastics.

## **2.2 Physiochemical properties of particulate plastics**

The fate of particulate plastics in the environment is highly dependent on the properties of the plastic particles<sup>13, 23</sup>. These properties include particle size, polymer type and chemistry, density, polarity, surface charge, morphology, and the presence of manufacturing additives<sup>6, 14, 23</sup>. Furthermore, the physiochemical properties of particulate plastics are altered through weathering and aging events<sup>23</sup>. The details of these properties and effects are discussed in the following sections.

### **2.2.1 Polymer type**

Different types of plastic polymers have differences in chemical makeup, surface functional groups, polarity, and hydrophobicity<sup>5, 13</sup>. These properties affect the interfacial interactions of particulate plastics with soil, plants, and environmental pollutants. de Souza Machado et al. (2019) conducted a study to see how six different microplastic polymers affect soil properties and plant performance. Polyamide (PA) beads significantly increased

the leaf nitrogen content, increased total biomass, and decreased the root-leaf ratio <sup>24</sup>. These observed effects could be attributed to an enhancement of soil nitrogen <sup>24</sup>. The production of PA requires the polymerization of amines and carboxylic acids, so the remaining monomers could leach into the soil having similar effects to fertilization <sup>24</sup>. A previous study investigated the adsorption mechanisms of cadmium ( $\text{Cd}^{2+}$ ) on various MPs [PA, polystyrene (PS), polyvinyl chloride (PVC), and polyethylene terephthalate (PET)], and found that PA had the highest adsorption capacity <sup>25</sup>. This was attributed to the presence of C-O and N-H functional groups in PA <sup>13,25</sup>. Another study observed higher adsorption of  $\text{Cu}^{2+}$  onto PA and polymethyl methacrylate (PMMA) possibly due to the presence of polar functional groups (e.g. -NHCO- and -COO-) <sup>13,26</sup>. These functional groups increased the hydrophilicity of the MPs leading to more attraction to cationic species <sup>13,26</sup>. Other studies have observed metal interactions with PVC due to the presence of chlorinated functional groups <sup>5,13,27,28</sup>. One study observed significantly higher adsorption of Cu to PVC than to PS due to the polar (chlorine) groups <sup>27</sup>. Another study observed  $\text{Cd}^{2+}$  interacting with the functional groups of PVC involving the C-H, C-O, C=C, and C=O bonds as well <sup>28</sup>.

### **2.2.2 Hydrophobicity**

Microplastics are hydrophobic by nature, which affects their behavior in the environment <sup>29,30</sup>. A previous study observed the inhibition of root activity due to the adsorption of PS and polytetrafluoroethylene (PTFE) to the surface of rice roots <sup>31</sup>, and studies suggest this sorption is due to the hydrophobic properties of the MPs <sup>24,31,32</sup>. Hydrophobic interactions are a predominate mechanism for the adsorption of many chemical contaminants <sup>29,33</sup>. The high hydrophobicity of MPs surface aids in adsorption of various chemical contaminants in the environment <sup>5,31</sup>. A previous study found that trace metal sorption to MPs could involve

non-specific interactions between the metal-organic complexes adsorbed in the neutral region and the hydrophobic surface of the MPs <sup>5, 30</sup>.

### **2.2.3 Shape**

The morphology of the particulate plastics can affect their transport through the environment, their impact on soil-plant systems, and their impact on living organisms. A previous study found that irregular shaped PE decreased the swimming behavior (i.e., total distance travelled and maximum velocity) of sheepshead minnow compared to spherical PE <sup>34</sup>. Another study investigated the migration of four different MPs shapes (i.e., particles, fiber, foam, and fiber) in agricultural soil <sup>35</sup>. Their results indicate that film and fiber MPs have higher mobility due to a larger exterior surface to volume ratio <sup>35, 36</sup>. It was also found that microfibers were most commonly found in deep-sea sediments due to their shape allowing for gravity current transport <sup>36</sup>. In the study from de Souza Machado et al. (2019), MPs that were similar in size and shape to the soil particles (HDPE, PET, PP, and PS) had less pronounced effects on the soil structure and plant traits compared to MPs that are very different in size and shape (PES fibers) <sup>24</sup>. Another study also investigated the effect of four different microplastic shapes (fibers, films, foams, and fragments) on soil properties and plant biomass <sup>37</sup>. The root mass was found to be higher for LDPE films compared to LDPE foams <sup>37</sup>. Soil aggregation was also higher PET fragments compared to PET films <sup>37</sup>.

### **2.2.4 Size and Surface Area**

Particulate plastic size, especially related to specific surface area, can have a great impact on their interfacial interactions with other constituents and organisms. Generally, smaller sized MPs have a larger specific surface area than bigger MPs <sup>13, 38</sup>. A larger specific surface area can enable a higher adsorption capacity for the smaller MP particles <sup>13</sup>. A previous study found that the adsorption of metals (Pb, Cu, and Cd) onto PP decreased significantly with an

increase of particle size <sup>5, 39</sup>. Another study similarly saw the smallest HDPE particles investigated (100-154  $\mu\text{m}$ ) had the highest adsorption capacity for Cd compared to the larger particles (1-2 mm; 0.6-1 mm) <sup>40</sup>. Interesting results were observed in a previous study on the size effect of PS on the sorption of phenanthrene and nitrobenzene <sup>41</sup>. After reactions, their results indicate an increase in both specific surface area and adsorption with a decrease in particle size from the micron- (170, 102, 50, and 30  $\mu\text{M}$ ) to the submicron-sized (800 and 235 nm) PS particles after reactions <sup>41</sup>. However, a reduced adsorption coefficient and effective specific surface area were measured for the nano-sized PS (50 nm) compared to the submicron-sized PS particles (235 nm) <sup>41</sup>. The authors hypothesized aggregation of the nanoplastics and size-exclusion effects caused these results <sup>41</sup>. J. Wang et al. (2020) investigated PE as a vector for HOC (hydrophobic organic contaminants) bioaccumulation in *Eisenia fetida* (earthworm) in soil. They noted that smaller particle sizes can expedite the HOC transfer process to the ambient environment <sup>9</sup>. The results of the experiment also showed an overall decrease in bioaccumulation with an increase in particle size, meaning an increase in mass transfer for smaller particles <sup>9</sup>. Previous studies have also observed higher mobility and transport of smaller-sized MPs (<500  $\mu\text{m}$ ) <sup>35, 36</sup>.

In terms of accumulation and effects on plants, smaller particles (i.e., nanoplastics) generally are taken up easier by plants <sup>32, 42</sup>. Effects of this uptake are thought to bring about stress responses to the plants <sup>32, 43-46</sup>. A previous study observed more significant effects on the root morphology, photosynthesis fluorescence parameters, and antioxidant system of lettuce exposed to 100 nm to 18  $\mu\text{m}$  PVC particles compared to PVC particles ranging from 18  $\mu\text{m}$  to 150  $\mu\text{m}$  <sup>32, 45</sup>. It is hypothesized that while the larger particles have poor mobility in the plant, the smaller particles can enter the root epidermis causing physical and/or chemical

toxic effects <sup>32, 43, 47</sup>. Jiang et al. (2019) observed higher genotoxic and oxidative damage in *Vicia faba* exposed to 100 nm PS nanoplastics compared to 5 mm PS microplastics <sup>32, 43</sup>.

### **2.2.5 Surface Charge and Zeta potential**

The interactions of particulate plastics with environmental pollutants, plants, and soil are dependent on the surface charge of the plastic particles <sup>13, 29, 32, 48</sup>. A previous study reported the pH point of zero charge (pH<sub>pzc</sub>) of PE, PP, and PS MPs to be 4.30, 4.26, and 3.96, respectively <sup>49</sup>. Thus, when the solution pH is higher than the pH<sub>pzc</sub> of the particles, the plastic particles carry a negative charge, increasing electrostatic interactions with cationic species <sup>30, 33, 48, 49</sup>. Holmes et al. (2014) investigated the adsorption of trace metals (Cd, Co, Cr, Cu, Ni, and Pb) to various plastic pellets in estuarine conditions. The results show increased adsorption of Cd, Co, Ni, and Pb and a decreased adsorption of Cr with an increase in pH <sup>50</sup>. These results are contributed to the negative surface charge of the plastic pellets electrostatically attracting the divalent cations (Cd<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, and Pb<sup>2+</sup>) and electrostatically repulsing oxyanions (HCrO<sub>4</sub><sup>-</sup> and CrO<sub>4</sub><sup>2-</sup>) as the pH increased <sup>5, 50</sup>. Another study investigated the transport of PS nanoplastics in natural soils, and the results show that soil pH and minerals significantly affect the mobility of the nanoplastics <sup>51</sup>. An increase in soil pH (4.97 – 9.75) increased negative surface potentials for both the soil and the nanoplastics, enhancing the mobility of the PS nanoplastics through electrostatic repulsion <sup>51</sup>. Furthermore, an increased presence of positively charged soil minerals (i.e., Fe/Al oxides) increases the retention of the PS nanoplastics in the soil due to greater electrostatic interactions <sup>50</sup>.

### **2.2.6 Structures and Properties of Polyethylene**

As this study focuses on the PE polymer, what exactly are the structures and properties of PE? Polyethylene is produced from the polymerization of ethylene and is one of the two most

important members of the polyolefin resins <sup>52</sup>. Polyethylene has the structure of  $(C_2H_4)_n$  <sup>52</sup>, and PE does not degrade easily, primarily due to its composition consisting mainly of C-C and C-H bonds <sup>53</sup>. The main applications of PE are for manufacturing plastic bottles, bags, and containers for packaging <sup>54</sup>. There are three main forms of PE- linear low density (LLDPE), low density (LLDPE), and high density (HDPE) <sup>52</sup>. A summary of the structures, properties, and applications of PE are shown in Table 2.1.

LDPE or LLDPE is preferred for film-based packaging due to its flexibility <sup>52</sup>. In terms of the structure of LDPE, there are typically 20 branches per 100 carbon atoms, and these branches impact the physical properties of the polymer <sup>55</sup>. Because of this branching, the molecules are unable to fit closely together, so LDPE has a low density <sup>55</sup>. LDPE is usually transparent with approximately 50% crystallinity <sup>55</sup>. Additional applications of LDPE include trash bags, squeeze bottles, and toys <sup>52</sup>.

HDPE is highly crystalline, has high tensile strength, and strong chemical resistance <sup>54</sup>. The physical properties of HDPE can be explained by its structure. HDPE is made up of linear polymer chains with little branches <sup>55</sup>. Because of this, the molecules can fit closely together, which results in strong intermolecular bonds making the polymer denser, more rigid, and stronger than LDPE <sup>55</sup>. The surface of HDPE is large, possibly reactive, and can have strong interactions with hydrophobic species <sup>53</sup>. The applications of HDPE include shopping bags, food packaging, and containers for household chemicals <sup>55</sup>.

### **2.2.7 Additives**

Most commercial plastic products are produced with manufacturing additives integrated into the polymer <sup>17</sup>. These additives are chemical compounds incorporated into the plastic polymer in order to improve the functionality, performance, and ageing properties <sup>17</sup>. For plastic packaging materials, the most commonly used additives are plasticizers, antioxidants,

lubricants, thermal stabilizers, acid scavengers, lubricants, and pigments <sup>17</sup>. Because these additives typically are physically mixed with the plastic polymers, they can leach into the environment in the usage and weathering processes of the plastics <sup>56</sup>. The release of these additives into the environment has raised concern due to the potential of the chemicals having toxic or hazardous effects on biota <sup>57</sup>.

So, what additives can be incorporated onto the surface of polyethylene-based plastics? Lahimer et al. (2017) characterized the additives involved in plastic packaging and identified their subsequent toxicity. The main additive in LDPE identified was the lubricant Methylpalmitate (Methyl hexadecanoate) or its derivative (Benzaldehyde 3,4-dimethyl-Methylpalmitate). This additive is considered toxic due to its potential of tumorigenic effects <sup>58, 59</sup>. LDPE packaging was found to be absent of any antioxidants <sup>58</sup>. Multiple additives were identified for HDPE- plasticizers, antioxidants, and stabilizers <sup>58</sup>. The plasticizer identified was DIOP (Diisooctyl phthalate), which is not toxic unless in contact with fatty foods <sup>58</sup>. Both a phenolic antioxidant, Irganox 1076 [octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate] (or its derivatives), and a phosphite antioxidant, Irgafos 168 [tris(2,4-ditert-butylphenyl) phosphite] (or its oxidized forms), were identified <sup>58</sup>. Irganox 1076 is on the negative toxicity list due to it containing a higher concentration of Pb compared to other additives <sup>58</sup>. However, Irganox 168 is not toxic <sup>58</sup>. Lastly, the stabilizer Benzoic acid, 4-ethoxy-ethyl ester, was identified in HDPE and was placed on the negative toxicity list <sup>58</sup>. Other studies have reported the associated additive and hazardous substances of the most commonly produced polymers <sup>60, 61</sup>. They reported hazardous antioxidants (Bisphenol A, Octylphenol, Nonylphenol) present in both HDPE and LDPE <sup>60, 61</sup>. A summary of the

additives commonly found in PE polymers and their corresponding toxicity are shown in Table 2.2.

#### **2.2.8 Effects of weathering**

Particulate plastics are subject to weathering and aging processes in the environment including physical abrasion, UV radiation, and chemical oxidation<sup>48, 62, 63</sup>. These processes can alter the surface properties of MPs, can encourage the release of additives, and thus, affects their fate in the environment<sup>3, 6, 14, 56</sup>. Previous studies observed the generation of cracks on the plastic surface due to and subsequent fragmentation due to weathering<sup>64-67</sup>. These cracks increase the specific surface area of the particles<sup>48, 68</sup>. Another study investigated how accelerated oxidation processes alter the properties of HDPE and PE<sup>68</sup>. Various oxygen-containing functional groups formed on the aged PS and PE, such as hydroxyl, carbonyl, and carbon-oxygen groups<sup>48, 68</sup>. The carboxyl group was the dominant functional group for PE, while ketone (carbonyl group) was for PS<sup>48, 68</sup>. Weathering also increases the specific surface area of the particles<sup>13, 27, 68</sup>, and both of these changes can enhance the adsorption properties for metals<sup>13, 27, 30, 48</sup>. Previous studies have observed higher adsorption of metals (Cd, Co, Cr, Cu, Ni, and Pb) onto beached (aged) plastic pellets compared to pristine plastic pellets<sup>30, 50</sup>. This is attributed to the increased polarity, charge, and surface reactivity<sup>30, 50, 69, 70</sup>.

Weathering can easily release additives into the environment because most additives are physically mixed with the polymer components<sup>17, 60</sup>. The release of additives is controlled by the properties of the plastics and additives as well as weathering conditions, including UV light, oxygen, pH and temperature<sup>71-74</sup>. Studies have reported the release of additives including nonylphenols<sup>75, 76</sup>, bisphenol A<sup>77, 78</sup>, brominated flame retardants<sup>71, 72, 79</sup>, and phthalates from plastic polymers<sup>73, 77</sup>.

## **2.3 Interfacial interactions and effects of particulate plastics in the environment**

### **2.3.1 Soil**

Particulate plastic accumulation in soil can result in a series of effects in soil ecosystems<sup>3</sup>. de Souza Machado et al. (2018 and 2019) observed that particulate plastics can affect the soil bulk density, water holding capacity, and the functional relationship between the microbial activity and water stable aggregates<sup>24, 80</sup>. In these studies, HDPE decreased the soil bulk density, decreased soil pH, and altered water stable aggregates<sup>24, 80</sup>. Of all polymers investigated, HDPE was the only one to significantly decrease the soil pH<sup>24, 80</sup>. This might have been due to the presence of phosphite additives on the surface of the HDPE particles<sup>24, 80</sup>. Another study similarly observed a significant decrease in pH in HDPE contaminated soil<sup>20</sup>. The authors suggested that HDPE particles enable free proton exchange in the soil water and alter the cation exchange capacity in the soil, given the large and potentially reactive surface area of HDPE<sup>20</sup>. Other reported microplastic effects include changes in soil microbial activity and negative effects on soil organic carbon and nitrogen cycles<sup>14, 20, 81-83</sup>.

As mentioned previously, the soil pH, soil minerals, and solution pH affect the interactions of particulate plastics in the environment<sup>51, 84</sup>. Previous research shows an increase in pH increases the mobility of nanoplastics in soil<sup>51, 84</sup>. An increase in pH causes both the zeta potentials of the nanoplastics and soil particles to become more negative, enhancing electrostatic repulsion, and therefore, increasing the mobility of nanoplastics<sup>51, 84</sup>. The charge and concentration of soil minerals (i.e., Fe/Al oxides) also affects nanoplastic transport<sup>51, 84</sup>. When these oxides are present at a high concentration and positively charged (acidic soil pH), greater electrostatic attraction occurs between the oxides and nanoplastics, leading to higher retention in the soil<sup>51</sup>.

### 2.3.2 Plants

As shown in the above sections, particulate plastics can have a series of effects on plants. Particulate plastics can affect plant mechanisms by three possible mechanisms: (1) Plastic particles altering soil structure, function, and properties, invoking plant responses<sup>20, 24, 32</sup>, (2) Plastic particles adsorbing to the root surface, affecting root activity and uptake of nutrients and water<sup>31, 32, 85</sup>, (3) Plastic particles are taken up by plants via transpiration pull, causing high stress on the plants<sup>32, 44, 46, 47, 86</sup>.

Previous studies have observed a decrease in soil bulk density, changes in the functionality and structure of the soil, a decrease in water stable aggregates, and an increase in the root biomass and root to shoot ratio of spring onion in the presence of HDPE (2%)<sup>24, 80</sup>. Similar results were observed by Boots et al. (2019) where altered soil water stable aggregates, an increased root to shoot ratio, and an increased chlorophyll-a/chlorophyll-b (chl-a/chl-b) ratio occurred in pot experiments of perennial ryegrass (*L. perenne*) exposed to HDPE and polylactic acid (PLA)<sup>20</sup>. The chl-a/chl-b ratio is a principal parameter of photosynthetic activity, and diversions in this ratio are an indicator of stress in plants<sup>20, 87</sup>. So, the elevated ratio in *L. perenne* suggests a stronger inhibition of the production of chlorophyll-b as a response to microplastic exposure<sup>20</sup>. In plants, chlorophyll-b is an essential pigment with the purpose of improving photosynthesis efficiency<sup>20, 88</sup>. The mechanism of how MPs caused this change in chl-a/chl-b was not investigated in this study. However, one possibility is that biophysical changes in the soil altered the availability of macro- and micronutrients (e.g., magnesium and potassium) to the plant, resulting in cascading effects on the photosynthetic capacity measured by chlorophyll content<sup>20</sup>. Alterations in the water dynamics can result in responses from physiological proxies of photosynthetic efficiencies<sup>24</sup>. Changes in water dynamics, such as water cycling, has the

potential to change chemical speciation processes within soils or to impact the activity of soil microbes, affecting the availability of nutrients in the soil <sup>24</sup>. In the previous study, cascading effects on the soil-spring onion system were observed, such as decreases in soil microbial activity in the presence of HDPE <sup>24</sup>. This could also explain the increased root/shoot ratio observed in both studies mentioned <sup>20, 24</sup>. When plants are under stress (i.e., reduction in water and nutrient availability), plants will expand their root system to increase the uptake of water and nutrients <sup>20, 89, 90</sup>. However, another study observed similar physiochemical alterations in soil by PE (1%), leading to reductions in root and shoot biomass of lettuce <sup>91</sup>. Therefore, further research is required to investigate how physiochemical alterations of soil by MPs affects the photosynthetic mechanisms of various plants.

Other studies have suggested that MPs attachment to the root surface leads to decreases in the plant photosynthetic mechanisms <sup>31, 32, 85, 92</sup>. One study observed a decrease in photosynthetic rate, stomatal conductance, transpiration rate, chlorophyll leaf content, and Rubisco activity in lettuce plants exposed to PE and di-*n*-butyl (DBP) <sup>85</sup>. These effects were attributed to PE attachment to the roots, inhibiting photoelectron flow and enhancing the effects of DBP on the lettuce <sup>85</sup>. Another study observed inhibition of photosynthetic rate, stomatal conductance, photochemical efficiency, and electron transfer rate in rice in exposed to PS and PTFE <sup>31</sup>. The authors speculated that these effects were caused by the MPs adsorbing onto the rice root due to their hydrophobic nature <sup>31</sup>. The attachment of MPs on the root surface can block the ion channel causing a decrease in the uptake of nutrients, and essential elements and enzymes, increasing their phytotoxicity in plants <sup>31, 32, 85, 92</sup>. A summary of studies on PE polymers and their effects on soil and plants are shown in Table 2.3.

From the studies mentioned above, it is known that MPs affect both soil and plants, but can MPs accumulate in plants? A previous study investigated the presence of both microplastics and nanoplastics in edible fruit and vegetables purchased from the market through extraction methods <sup>93</sup>. Their results indicate that fruits had higher contamination of MPs (<10 µm) compared to vegetables; however, both fruits and vegetables exhibited low variability in terms of size of the extracted MPs <sup>93</sup>. The smallest microplastic size, 1.51 µm, was found in carrot samples, and the largest size, 2.52 µm, was found in lettuce samples <sup>93</sup>. From this study, it is confirmed that MPs can accumulate in plants, so what are the mechanisms of uptake? The uptake mechanism of particulate plastics by plants needs further research. However, one study investigated the accumulation of PS microbeads (0.2 and 1.0 µm) in lettuce using fluorescent markers <sup>44</sup>. The authors first found that the 0.2 µm beads were trapped extracellularly in the root cap mucilage, and through imaging, PS luminescence signals were observed on the cell walls of the cortex tissue of the roots and in the vascular system <sup>44</sup>. These observations suggest that the plastics followed the apoplastic transport system to pass through the intercellular space of the plant <sup>44</sup>. After the 0.2 µm beads were transported inside the central cylinder, they were then transported from the roots to the stems and leaves following the transpiration stream via the vascular system <sup>44</sup>. In the intercellular space of the root and stem vascular tissue, the beads attached to each other systematically into a “grape like” and “(chain) string-like” clusters <sup>44, 47</sup>. Lastly, the 0.2 µm beads were distributed within the leaf tissue <sup>44</sup>. These observations fit a hypothesis from Zhu et al., 2019, which suggested that smaller plastics can bypass the plant cell wall and membrane barriers. Other studies have also observed the micro- and nanoplastics adsorbed to the root surface, which can be taken up into the plant stems and leaves via transpiration pull <sup>32, 44, 46, 47, 86</sup>. This

uptake of particulate plastics can cause a level of stress that the plants are not able to overcome, resulting in cellular damage of the plants <sup>32, 44, 46, 85, 92</sup>.

## **2.4 Interfacial reactions of particulate plastics and metals**

### **2.4.1 Adsorption of metals to particulate plastics**

Particulate plastics adsorb heavy metals and act as carrier in the environment <sup>5, 13, 29</sup>.

Previous studies reported the adsorption of heavy metals (Cu, Zn, Co, Cr, Ni, Cd, and Pb) on various microplastics suspended in marine ecosystems of England <sup>14, 30, 50</sup>. Another study reported that MPs extracted from freshwater wetland systems carried large amounts of heavy metals (Pb, Cd, Cu, Cr, Ni, As, and Zn) <sup>5, 94</sup>.

Many factors affect the adsorption of heavy metals onto particulate plastics in the environment including environmental factors (i.e., weathering and pH), plastic properties (i.e., functional groups and polarity), and metal properties (i.e., charge and speciation) <sup>13, 14, 29</sup>. For example, metals producing cationic species (i.e.,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ) have higher sorption capacities with increasing pH, whereas anionic species (i.e.,  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$ ) have lower sorption capacities with increasing pH <sup>14, 29, 40, 50, 95</sup>. This is because the predominate mechanism of adsorption for heavy metals are electrostatic interactions <sup>29, 33, 96</sup>. At  $\text{pH} > 4.5$  many microplastic surfaces (i.e., PE, PS, and PVC) have a net negative charge due to the pH of point of zero charge ( $\text{pH}_{\text{pzc}}$ ) being lower than the solution pH leading <sup>6, 13, 29, 97</sup>, and thus, enhancing attraction of cationic species. The pH can also affect the speciation of the metals in solution (i.e., uranium and arsenic), thereby affecting the electrostatic interactions between the constituents <sup>5, 8, 13, 14</sup>.

Studies have shown that weathering enhances the adsorption of heavy metals, as mentioned previously <sup>48, 50</sup>. Weathering can decrease the hydrophobicity of MPs by increasing the roughness of the surface and generating oxygen functional groups <sup>48, 68, 98</sup>. This

can increase the polarity of the polymer and enhance the accumulation of biofilms and hydrogenous precipitates <sup>69, 70</sup>. These changes can lead to enhanced adsorption of heavy metals to the microplastic surface <sup>48</sup>.

#### **2.4.2 Effects on plants and soil**

What happens when microplastics and metals are both present in our ecosystems?

Research has shown that particulate plastics can affect the bioavailability of metals. PET particles facilitated the contact between heavy metals (Zn, Cd, and Pb) and wheat roots, increasing the metal uptake in wheat <sup>99</sup>. PE also increased both the bioavailability and accumulation of Cd in wheat by altering soil physiochemical and microbial properties <sup>91</sup>. However, PS and PTFE decreased the accumulation of arsenic (As) in plants by (1) directly adsorbing As, (2) competing with As for adsorption sites on the root surface, and (3) inhibiting root activity <sup>31</sup>. Another study observed contradicting results where HDPE and PS increased the bioavailability of Cd in soil, but the accumulation of Cd in maize was not identified <sup>100</sup>.

Previous studies found the synergetic effect between environmental pollutants and microplastics can enhance their toxicity in plants. PE and Cd exhibited a coupled toxicity on lettuce and maize plants <sup>91, 100</sup>. The co-exposure of PE and Cd increased the uptake, accumulation, and bioavailability of Cd in lettuce plants, while more toxic effects were observed on the root biomass of the maize plants <sup>91, 100</sup>. A previous study observed decreases in the photosynthetic rate, transpiration rate, stomatal conductance, and Rubisco activity of rice when exposed to MPs and As <sup>31</sup>. Similar results were observed in lettuce plants exposed to both PE and DBP <sup>85</sup>. In all PE and DBP treatment groups, lettuce growth, photosynthetic parameters (i.e., photosynthetic rate, stomatal conductance, transpiration rate), and chlorophyll content were all significantly decreased <sup>85</sup>. The root tissue of the lettuce were

always found to have a higher degree of damage compared to that of the leaves<sup>85</sup>. Both of these studies hypothesize the accumulation of the constituents in the epidermis or phloem of the roots, leading to the inhibition of root activity, thereby reducing photosynthesis<sup>31,85</sup>. The inhibition in photosynthesis in lettuce was credited to PE exacerbating DBP's effects on photosynthesis and the inhibition of photoelectron flow<sup>85</sup>. In all combination treatment groups, there was an increase in superoxide radicals and hydrogen peroxide in lettuce leaves and roots<sup>85</sup>. Similarly in the rice study, an oxidative burst was identified in the roots and leaves<sup>31</sup>. Oxidative bursts are an indication that the plant was under stress<sup>31</sup>. In the combined treatments, the excessive amount of oxygen species led to the observed inhibition of photosynthetic mechanisms on the plants<sup>31,85</sup>.

## **2.5 Source, abundance, and threat of uranium in the environment**

Uranium is a naturally occurring, radioactive, and silvery-white metal<sup>10</sup>. Uranium is naturally present in most soil; however, through anthropogenic activities such as mining, weapon manufacturing and nuclear energy generation, U can contaminate soil, water, and plants, posing potential health risks to both humans and the environment<sup>2,11</sup>. Once in the soil, U can accumulate in plant roots and shoots through the apoplastic pathway, as predicted with particulate plastics<sup>32</sup>, where it then can enter the food chain<sup>11</sup>. Additionally, U can be transported into water systems where it then is able to increase the radioactivity of the water<sup>10</sup>. Many abandoned U mine sites are in close proximity to Native communities<sup>2</sup>. According to the EPA, over 500 abandoned U mines are located in Navajo Nation alone<sup>101</sup>. These abandoned mine sites have led to elevated concentrations of U in water sources and in mine waste solids. A previous study found elevated U concentrations in spring water near Navajo Nation in NE Arizona measuring at a range of 67-170 µg/L<sup>1</sup>. Another study on the Jackpile

Mine in NM near the Laguna pueblo found U concentrations in surface water ranging from 35.3-711  $\mu\text{g/L}$ <sup>2</sup>. These U concentrations are a concern for nearby communities as the EPA established a maximum contaminant level for uranium in water to be 30  $\mu\text{g/L}$ <sup>101</sup>.

Consequently, what are the threat factors that exist because of this U contamination? In terms of environmental factors, the behavior of U in the environment can affect sediment and surface water chemistry, which in turn can impact the natural ecosystems of the surrounding areas<sup>2</sup>. Environmental conditions also impact other threat factors such as disparities in infrastructure and the consequential health effects<sup>102</sup>. For example, a study conducted on the Rio Pagate river in New Mexico showed that U concentrations vary seasonally, with higher concentrations reported during monsoon season (June 15 to September 30)<sup>2</sup>. Additionally, the semi-arid climate conditions and water scarcity in these regions only exacerbate the concern for the quality of the limited water sources<sup>2</sup>. For reference, around 14% of Native households lack access to a public water system, and some tribes lack access for more than 30% of their population<sup>102</sup>. Furthermore, the drinking water systems in Native lands that are regulated experience “significant violations” or health-based violations of the Safe Drinking Water Act twice as frequently as those not located on Native lands<sup>102</sup>. So, how does all of this lead to negative health effects in humans? Once U has contaminated the soil, water, and plants, there are two main exposure pathways for humans, inhalation and ingestion<sup>1, 103</sup>. Ingestion also affects the livestock in the area as they often drink the contaminated water<sup>1, 103</sup>. Exposure to U mine wastes is linked to an increase chance of acquiring chronic diseases including hypertension and kidney disease<sup>103</sup>. Long-term exposure to lower concentrations of U and other heavy metals has harmful effects, including an increased risk of various cancers<sup>102</sup>.

## 2.6 Reactions of uranium in the environment as a function of uranium speciation

### 2.6.1 Water and Soils

In the environment, uranium commonly exists as either U(IV) or U(VI), and these oxidation states control its fate and transport <sup>104, 105</sup>. Typically, U is present as U(VI) in the form of the free uranyl ion ( $\text{UO}_2^{2+}$ ) in near-surface and oxic groundwater, and its solubility and mobility is greatly affected by the pH <sup>105, 106</sup>.

At  $\text{pH} < 6.5$ , U(VI) mainly exists as  $\text{UO}_2^{2+}$  and positively charged U-hydroxides in natural waters <sup>107, 108</sup>. These forms of U are relatively soluble and mobile; however, these species can readily complex and precipitate with soil components, making U relatively immobile <sup>105, 106</sup>. A mineral very present in many sandy soils is silica. Previous studies have observed that  $\text{UO}_2^{2+}$  and positively charged U-hydroxides will readily adsorb onto silica particles at acidic pH conditions <sup>109-112</sup>. Some studies have identified electrostatic adsorption and inner sphere complexation as the dominant mechanisms leading to U-Si surface complexation <sup>110, 112</sup>. Many soil particles, such as silicate clay minerals, have a net negative charge <sup>112-114</sup>. Thus, these positive U species can adsorb to soil silica particles via electrostatic attraction <sup>112-114</sup>. The complexes can precipitate if the solution is supersaturated. A previous study identified U-K, U-Na, and U-Na-K bearing precipitates of varying speciation on natural organic matter (NOM) at pH 4 <sup>115</sup>. The authors determined that multiple solid phases could be present, all of which are forms of uranyl oxide hydrates <sup>115-117</sup>. These precipitates could be a result of ion substitution, as U-oxides can substitute any of the cations present in these minerals (i.e., Ca, Na, K) with each other <sup>114</sup>. As the solids can substitute different ions with the main structure, these various elements are all then present in the precipitate coating <sup>114, 117</sup>.

At pH > 6.5, U(VI) mainly exists as neutral and negatively charged aqueous complexes with calcium and carbonate<sup>12, 118, 119</sup>. The complexes increase the mobility and solubility of U(VI) in natural systems, decreasing sorption of U(VI) to soil and other constituents<sup>105, 113, 120</sup>. Previous studies have identified the precipitation of U with Ca without bicarbonate present in solution at pH 7<sup>115, 121</sup>. In the presence of bicarbonate however, U-Ca precipitates were found to partially or completely solubilize by the end of the experiment at pH 7<sup>118</sup>. Despite this, previous studies have observed the sorption of U(VI) onto silica particles, quartz, and ferrihydrite at neutral pH in the presence of calcium carbonates<sup>113, 122</sup>. One study observed rapid initial adsorption of U onto the silica particles<sup>113</sup>. A fast initial step attributed to reaction-controlled sorption is a common behavior in metal-mineral sorption systems<sup>113, 123</sup>.

### **2.6.2 Plants**

As mentioned above, the mobility and ultimately the fate of U in the soil environment is greatly impacted by the forms at which the U exists<sup>105</sup>. Because of this, the water chemistry strongly influences uranium's bioavailability<sup>12, 113, 122</sup>. When calcium and carbonate are present in waters at circumneutral pH, binary and ternary uranyl-carbonate complexes are common, with ternary complexes reducing the rate of U uptake in invertebrates<sup>12</sup>. For plants, the free uranyl ion can readily adsorb and/or accumulate in the roots at low pH (pH 4) and low concentrations of phosphate and sulfate<sup>12, 121</sup>. This study found the uranyl ion complexes with citrate and carbonate can increase the root-to-shoot translocation, but an overall decrease in U accumulation in plants was observed<sup>12, 121</sup>. In literature, this increase in U translocation in plants is likely due to electrostatic interactions between the complexes and the cell wall, particularly phosphate<sup>11</sup>. To start, the phosphate component of the cell wall and the negatively charged uranyl carbonate/citrate electrostatically repulse each other, which

averts U precipitation and enhances U root-to-shoot translocation. Then, the negatively charged cell wall components of the roots and the uranyl cations ( $\text{UO}_2^{2+}$ ) attract each other electrostatically, resulting in the enhancement of U precipitation in the roots and the decrease of U translocation <sup>11</sup>. Once inside the plant roots  $\text{UO}_2^{2+}$  can actually precipitate with the endogenous phosphorus in the form of U(VI)-phosphate, while U-citrate can be accumulated as U- carboxylate <sup>12</sup>. In oxidizing environment, this U(VI)-phosphate is the main form in which U is accumulated on the root surface, yet U accumulation in plant tissues is decreases when U(VI) complexes with phosphate <sup>11</sup>. When calcium is present in high concentrations in carbonate water (circumneutral pH), the accumulation of U in plants is inhibited, possibly due to the uranyl carbonate complexes ( $\text{Ca-U-CO}_3$ ) <sup>11</sup>. Yet, calcium was also found to facilitate the symplastic transport and translocation of U toward the shoots despite inhibiting U transport and precipitation in the root cortical apoplast <sup>11</sup>.

Polymer	Structure	Properties	Applications	References
LDPE or LLDPE	20 branchers per 100 carbon atoms	Transparent 50% crystallinity Amorphous Low density High flexibility	Film-based packaging Trash bags Squeeze bottles toys	52, 55
HDPE	Linear polymer chains with little branching Surface- strong interactions with hydrophobic species	Highly crystalline High tensile strength Moderate stiffness Great chemical resistance High Density	Shopping bags Food packaging Containers for household chemicals	52-55

**Table 2.1:** Summary of the types of polyethylene (PE) and their corresponding structures, properties, and applications.

<b>Polymer</b>	<b>Type of Additive</b>	<b>Additive</b>	<b>Toxicity/Hazardous</b>
LDPE	Lubricant	Methylpalmitate (Or its derivative)	Toxic
	Phenolic Antioxidant	Bisphenol A Octylphenol Nonylphenol	Hazardous Hazardous Hazardous
HDPE	Plasticizer	DIOP (Diisooctyl phthalate)	Not Toxic unless in contact with fatty foods
	Phenolic Antioxidant	Irganox 1076 (octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate) Bisphenol A Octylphenol Nonylphenol	Toxic  Hazardous Hazardous Hazardous
	Phosphite Antioxidant	Irgafos 168 (tris(2,4-ditert-butylphenyl) phosphite)	Not Toxic
	Stabilizer	Benzoic acid	Toxic

**Table 2.2:** Summary of additives commonly found in PE polymers and their corresponding toxicity <sup>58, 60, 61</sup>:

Polymer	Study	Effects	Reference
HDPE	Biophysical soil response to microplastics in soil containing the earthworm ( <i>Aporrectodea rosea</i> ) and planted with perennial ryegrass ( <i>Lolium perenne</i> )	Germination of <i>L. perenne</i>	Boots et al., 2019
HDPE	Impacts of microplastics on the soil biophysical environment and on performance of spring onion ( <i>Allium fistulosum</i> )	Increased biomass of the roots in <i>Allium fistulosum</i> Decrease in soil bulk density Decrease in soil pH Functionality changes to soil structure and function	Machado et al., 2018 Machado et al., 2019
LDPE	Effects of plastic mulch residues on wheat ( <i>Triticum aestivum</i> ) growth	Negative effects on wheat both above- and below-ground Negative effects on vegetative and reproductive growth of the wheat plant	Qi et al., 2018

**Table 2.3:** Summary of studies on the effects of PE polymers on soil and plants.

### Chapter 3

#### Interfacial Interactions of Uranium and HDPE in agricultural soil and their bioaccumulation in *Mentha arvensis*

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**ABSTRACT:** The interaction of particulate plastics with co-occurring toxic metals can affect the accumulation of both constituents and contributes to their environmental health risks. Here, we investigated the adsorption, precipitation, and phytoavailability of U after reactions with soil, high-density polyethylene (HDPE) particles, and *Mentha arvensis* (wild mint) through the integration of batch experiments, plant exposure, microscopy, and

spectroscopy. Aqueous chemistry analyses indicate that soluble U (initially 100  $\mu\text{M}$ ) decreased by 98.6% (1.09  $\mu\text{M}$ ) at pH 5 and decreased by 86.2% (13.81  $\mu\text{M}$ ) at pH 7.5 after 0.1 h of reaction with 10 g of soil. Heterogenous U precipitates were observed in weathered HDPE surfaces for experiments without soil (pH 5 and pH 7.5) using electron microscopy analyses. Our findings suggest that the weathering of the microplastic surfaces enhanced the nucleation of the U precipitates. HDPE aggregated with soil particles after reactions at pH 5 and pH 7.5, possibly altering soil structure and functionality. Plants exposed to both U and HDPE exhibited photosynthetic rates 76.3% lower and transpiration rates 86.6% lower than plants not exposed, possibly due to negative synergetic interactions of U and HDPE. These results give insight into the surface-controlled reactions of soluble U with microplastics, soils and plants which is relevant to environments in which those co-occur.

**Keywords:** heavy metals, microplastics, soil, adsorption, precipitation, uranium, polyethylene, microscopy, spectroscopy

**Synopsis:**

Uranium can adsorb and precipitate on the surface of HDPE at weakly acidic and circumneutral pH conditions relevant to natural and anthropogenic environments.

### **3.1 Introduction**

Plastic pollution is a global concern due to its excessive production and poor waste management. The global plastic production is currently exceeding 359 million tons per year <sup>4</sup>. <sup>5</sup>. Plastics can enter the terrestrial ecosystem through landfills, open dumps, and municipal solid waste where they then can fragment into particulate plastics or microplastics (MPs) <sup>9, 19</sup>. As the definition of “microplastics” continues to evolve, the term “particulate plastics” is

often used to describe plastic particles of various sizes in the environment <sup>22</sup>. The current definition describes microplastics as 0.1  $\mu\text{m}$  – 1 mm and nanoplastics as  $<0.1 \mu\text{m}$  <sup>6</sup>.

Microplastics and nanoplastics have also gained attention due to their ability to transport heavy metals in the environment <sup>124 6, 13, 84</sup>. The co-occurrence of MPs and metals, like uranium (U), can be a concern in waters with intrinsically high concentrations of metals or to sites affected by anthropogenic activities, such as mining, nuclear weaponry, and nuclear energy. However, the interactions between microplastics and U are poorly understood.

The behavior of particulate plastics is largely dependent on the polymer type and properties including particle size, polymer chemistry, manufacturing additives, density, polarity, surface charge, and morphology <sup>6, 14, 23, 125</sup>. Previous studies have observed higher mobility and transport of smaller-sized MPs ( $<500 \mu\text{m}$ ) <sup>35, 36</sup>. Brittle polymers [i.e., polyvinyl chloride (PVC), polystyrene (PS), and polyethylene terephthalate (PET)] are more susceptible to fragmentation, so more smaller particles are generated <sup>36</sup>. Furthermore, film and fiber MPs have higher mobility than other particles due to a larger exterior surface to volume ratio <sup>35, 36</sup>. Polyethylene (PE) has the highest production rate (31%: 18% low-density PE, 15% high-density PE) of all polymers and is one of the most commonly found polymers in global sediments and waste streams <sup>17, 21, 126, 127</sup>. Therefore, we chose to focus on high-density polyethylene (HDPE) for this study. HDPE is constituted by regular C-C and C-H bonds with a nonpolar nature and is characterized by high flexibility, resistance, hydrophobicity, and crystallinity <sup>53, 128, 129</sup>. Additives associated with HDPE from manufacturing include antioxidants, plasticizers, and stabilizers <sup>17, 130</sup>. Weathering of HDPE particles, or any plastic polymer, can cause the release of these additives from the main

polymer structure<sup>17, 48</sup>. Yet, little is known about the potential impacts of these additives on the behavior of particulate plastics in the environment.

Particulate plastics have a notable adsorption capacity for a variety of organic and inorganic constituents, including heavy metals<sup>14, 15, 125</sup>. This is due to the large specific surface area and high hydrophobicity of MPs providing ionic active sites for various reactions with metals<sup>5, 85, 131, 132</sup>. However, the capacity for adsorption is based on environmental factors and the physiochemical properties of the MPs and metals<sup>13, 14, 29</sup>. For example, weathering and aging events significantly enhance cationic metal adsorption to MPs due to the formation of more heterogeneous and reactive surfaces (i.e., an increase in specific surface area and presence of oxygen functional groups)<sup>6, 8, 14, 15</sup>. These functional groups can make the microplastic surface more reactive by increasing the polarity<sup>30, 50, 95</sup>. A previous study reported greater adsorption of cadmium, cobalt, nickel, and lead on the surface of aged pellets versus pristine polyethylene<sup>50</sup>. Furthermore, metals are affected differently by environmental conditions and have differing affinities for various polymers<sup>27, 29, 95, 97</sup>. For example, metals producing cationic species (i.e.,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ) have higher sorption capacities with increasing pH, whereas anionic species (i.e.,  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$ ) have lower sorption capacities with increasing pH<sup>14, 29, 40, 50, 95</sup>. The predominate mechanism of adsorption for heavy metals are electrostatic interactions<sup>29, 33, 96</sup>. Electrostatic interactions are induced by the attraction of oppositely charged molecules and the repulsion of similarly charged molecules<sup>13, 15, 29</sup>. At  $\text{pH} > 4.5$ , many microplastic surfaces (i.e., PE, PS, and PVC) have a net negative charge due to the pH of point of zero charge ( $\text{pH}_{\text{pzc}}$ ) being lower than the solution pH leading to electrostatic attraction of cationic species<sup>6, 13, 29, 49, 97</sup>. PE is also an aliphatic polymer, so it can interact directly with contaminants via van der Waals forces<sup>6, 29</sup>.

However, the microplastic form of PE can increase its polarity thereby enhancing adsorption via polar or electrostatic interactions <sup>6</sup>. Further research is needed to understand the adsorption mechanisms of MPs given the variety of factors influencing metal and plastic interactions.

Particulate plastics in the terrestrial environment can affect soil properties and function, metal bioavailability, plant growth and health, and can accumulate in plant roots and shoots <sup>24, 31, 46</sup>. However, different polymers and metals have differing impacts on soil and plants. HDPE was found to decrease the bulk density and pH of soil, alter the soil water dynamics, and increase the root biomass of spring onion in previous studies <sup>24, 80</sup>. Whereas, another study observed that PS and polytetrafluoroethylene (PTFE) can damage roots, reduce root vigor and transpiration, and inhibit the photosynthetic capacity in rice <sup>31</sup>. Sub-micro and nanoplastics can also accumulate in the cells of various fruits and vegetables, possibly inducing direct toxicity within the plants <sup>44, 93</sup>. Previous research has observed that particulate plastics have various impacts on the bioavailability of metals. PET particles facilitated the contact between heavy metals (Zn, Cd, and Pb) and wheat roots, increasing the metal uptake in wheat <sup>99</sup>. PE also increased both the bioavailability and accumulation of Cd in wheat by altering soil physiochemical and microbial properties <sup>91</sup>. However, PS and PTFE decreased the accumulation of arsenic (As) in plants by (1) directly adsorbing As, (2) competing with As for adsorption sites on the root surface, and (3) inhibiting root activity <sup>31, 32</sup>. Another study observed contradicting results where HDPE and PS increased the bioavailability of Cd in soil, but the accumulation of Cd in maize was not identified <sup>100</sup>. Furthermore, the impacts of co-exposure to MPs and metals in the terrestrial environment is dependent on the polymer

type and dose, metal properties and concentration, soil properties, and plant behavior. Thus, further research is needed to understand effects of metals and MPs in the soil rhizosphere.

A thorough understanding of the interfacial interactions governing the fate of microplastics and metals in terrestrial environments is notably lacking. Previous studies have investigated the interaction between MPs and Cd, Co, Cu, Ni, Pb, and Zn <sup>5, 13-15</sup>. However, recent research suggests the co-occurrence of MPs and U near abandoned mine sites <sup>16</sup>. The mobilization, bioavailability, and accumulation of U in natural systems are highly influenced by its aqueous chemical speciation <sup>11, 12, 106, 114</sup>. Therefore, the behavior of U is affected by aqueous complexation with components such as calcium, carbonate, and oxides <sup>11, 12, 118, 119, 121</sup>. For example, the neutrally charged Ca-U-CO<sub>3</sub> complexes can increase U intracellular accumulation, enhancing U root-to-shoot translocation <sup>11, 12</sup>. However, the association and interactions between MPs and U are rather unexplored. This gap motivates the following question: how do microplastics impact the bioavailability of U in plants?

The objective of this paper is to investigate the adsorption, precipitation, and phytoavailability of uranium after reactions with soil, HDPE particles, and *Mentha arvensis* (wild mint) through the integration of batch experiments, plant exposure, microscopy, and spectroscopy. The identification of the combined effect of U and HDPE on interfacial reactions with water and soils that influence their bioavailability in plants is novel to this study. Additionally, we assessed the combined effects of U and HDPE on photosynthetic parameters of wild mint. The concentration of U used in this study is based on U concentrations found in sediments near abandoned mine sites <sup>1</sup>, and the concentration of HDPE is based on concentrations found in sediments globally <sup>3</sup>. This study has relevant implications for communities in which U and microplastics co-occur.

## **3.2 Materials and Methods**

### **3.2.1 Materials and Preparation:**

High-density polyethylene was chosen for experiments due to its high-production volume<sup>17</sup>. Thus, HDPE bottles were purchased from the United States Plastic Corporation. The HDPE bottles cut into small square pieces and ground in a KRUPS Silent Vortex Electric Grinder, generating micro- and submicro-sized particles. A sandy-loam soil was purchased from Agvise Laboratories and is representative of agricultural soil found near Navajo Nation in the Four-corners region<sup>133</sup>. The soil was collected a depth of 0-6 in, representing topsoil. The soil characterization is found in the Supplementary Information (Figure S1).

### **3.2.2 Solid Characterization:**

Microscopy and spectroscopy analyses on the HDPE particles were performed to characterize the particles according to their size, shape, surface, and functional chemistry before reactions. X-ray Photoelectron Spectroscopy (XPS), and Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR, Nicolet i10MX) were used to determine the surface chemistry composition and elemental identification of the HDPE particles. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were used to examine the microplastics size, morphology, and elemental composition. ImageJ software was used to estimate the HDPE particle size range from the SEM images.

Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR, Nicolet i10MX) was used to determine the chemical structure and composition of the HDPE polymer. Three particles were randomly selected and measured in triplicate. Measurements were taken following a previously documented procedure<sup>16</sup>. Measurements were taken using a 51 s detection time with 256 scans, and the aperture size was adjusted to fit each particle. The subsequent spectra were compared against the HR Polymer Additives and Plasticizers,

Polymer Laminate Films, and Hummel Polymer Sample libraries. The data is shown in the Supplementary Information (Figure S2).

A Kratos Ultra DLD X-ray Photoelectron Spectrometer 80 (XPS) survey scans were used to determine the elemental composition near the surface of the particles (<10 nm). A monochromatic Al source was used at 150 W power to acquire the high-resolution spectra of C from top ~4-10 nm of the surface. Charge neutralization was used during acquisition, and 99.9% pure Au reference powder was used to calibrate the spectra. Shirley background was used to process the spectra. Four peaks were used to curve high-resolution C 1s spectra – aliphatic C-C (C-H%) at 285 eV, secondary carbon (C=O) at 285.8 eV, carbonyl carbon at 288.0 eV, and carboxylic C at 289.2 eV. These values are based on the reference database<sup>134</sup>. The results of the survey scans are found in the Supplementary Information (Figure S3).

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) were conducted on a Tescan Vega3 to characterize the HDPE particles physically and chemically. The particles were prepared on silica mounts and were then coated with silver. Accelerating currents ranged from 10 to 15 kV, and beam currents ranged from 10 to 30 pA. The SEM and corresponding EDS spectra are shown in Figure 3.1. SEM Images were put into the ImageJ software to estimate the size of HDPE particles. 150 particles were counted and measured to generate a size distribution graph (Figure 3.2 and Figure S4).

Soil composition and characteristics were provided by Agvise Laboratories. Soil was then analyzed by X-ray Fluorescence (XRF) along with acid digestion and inductively coupled plasma-optical emission spectrometry (ICP-OES) to determine the elemental concentration and background U concentration. XRF was conducted using a Rigaku ZSX Primus II with Rhodium X-ray tube that quantitatively determine the major and minor elements. The ZSX

Primus II software performs both qualitative and quantitative analyses. The soil was dried at 60° C overnight before being analyzed. Results without normalization of the XRF data are presented in the Supplementary Information (Table S2). Standard soil acid digestion protocol was used to prepare the soil for ICP-OES analysis. The samples were dried overnight at 60° C, and triplicate 1 g samples were weighed into 50 mL centrifuge tubes. The soil was digested using 2 mL of HNO<sub>3</sub>, 4 mL of HCl, and 2 mL of HF and then heated at 95° C for 4 h. The acid digested solutions were then filtered using 0.45 µm syringe filters and diluted with 18 MΩ water to 25 mL. A PerkinElmer Optima 5300DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used to determine the elemental composition of the soil. The results of the ICP-OES are found in the Supplementary Information (Table S3).

### **3.2.3 Batch Experiment and Analyses:**

Batch experiments were conducted to measure the U adsorption over time on HDPE particles and soil particles at pH 5 and pH 7.5. Experimental units were run in quadruplicates. All glassware was rinsed with 10% (v/v) HNO<sub>3</sub> and DI water and then was sonicated for 30 minutes with ultra-pure water (18 MΩ) in a Cole-Parmer CPHX Series sonicator. The U concentration chosen for this study is based on the elevated concentrations of U identified in sediment samples from the Jackpile Mine, New Mexico, USA <sup>1</sup>.

A 50 mL stock solution of 4 mM of uranyl acetate [UO<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O] was prepared for use in both the batch and plant exposure experiments. The batch experiment consisted of four groups of reactors- the controls and three treatments. All reactors were conducted at both pH 5 and pH 7.5. pH 5 is representative of the weakly acidic pH in the microenvironments of plant roots, and pH 7.5 is representative of agricultural soils and natural waters. A volume of 50 mL of a plant nutrients solution (MgSO<sub>4</sub>, 0.5 mM; NH<sub>4</sub>NO<sub>3</sub>,

2 mM; KCl, 1 mM; 1 mM NaHCO<sub>3</sub>, 1 mM; CaCl<sub>2</sub>·2H<sub>2</sub>O, 3 mM) that was adjusted to the desired pH was added into every 125 mL Erlenmeyer flask to mimic the nutrients need for normal growth. Phosphate was not included to avoid the rapid precipitation of U with phosphate. For each group of reactors, there was a condition with soil (10 g) and without soil in solution to compare the adsorption characteristics. The three treatment groups consisted of 100 µM of U and/or 0.05 g of HDPE particles in each reactor. The plastic to soil ratio used was 0.5% w/w and is representative of plastic concentrations found in global sediments <sup>3</sup>. Controls represent flasks without U or HDPE. A table (Table S1) outlines the experimental matrix of the batch reactors. pH adjustments were made using 0.5 M HCl or 0.1 M NaOH. The flasks were covered with parafilm and placed on an orbital shaker (VWR Model DS2-500-1 Orbital Shaker), agitated at 150 rpm for 336 h (14 days) at room temperature. 1 mL samples were taken using a syringe tip at times 0, 0.5, 1, 2, 4, 8, 24, 72, 120, 168, and 336 h. The 1 mL samples were filtered with a Pall Laboratory Acrodisc 0.45 µm syringe filter and diluted with 2% nitric acid, HNO<sub>3</sub>, for metal analyses using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). After 336 h, the solutions in each batch reactor were filtered using a 0.5 µm glass microfiber filter and glass frit filter units. The collected solids from each pH condition (i.e., reacted HDPE, reacted HDPE + soil, and reacted soil) was analyzed using the SEM-EDS for the identification of U in the solids and to determine any physiochemical changes to the soil and plastic particles. The collected solids were added to the SEM mounts using carbon tape and were coated with gold to avoid spectral overlap with U. Further detail is provided in the Supplementary Information (SI).

### 3.2.4 Plant Experiment Preparation:

*Mentha arvensis* plants were chosen for this study due to their presence and use in Navajo Nation. Adult *Mentha arvensis* plants were acclimated in the UNM Biology greenhouse for 1 week under BML Spydr 600 LED grow lights. The plants were acclimated under 15 – 30 °C day and night temperature in 12 h/12 h light cycle. The plants were then washed with DI water and transported into pots containing the experimental soil to acclimate in the laboratory for 5 days in the same light cycle. During this time, the plants were watered once or twice a day using DI water. While the plants were acclimating, mason jars containing soil-HDPE mixtures were placed horizontally on the same rotator at 120 rpm for 4 days to ensure proper mixing. A hole was drilled into the experimental glass jars to allow for water drainage. All glassware was rinsed with 10% (v/v) HNO<sub>3</sub> and DI water and then was sonicated for 30 minutes with ultra-pure water (18 MΩ) in a Cole-Parmer CPHX Series sonicator. On the first day of the experiment, the plants were washed with DI water and transferred into their respective glass jars with the mixed soils.

### 3.2.5 Plant Experiment and Analyses:

*Mentha arvensis* plants (quadruplicates) were exposed to HDPE, U, and a combination of U and HDPE in 500 g of soil for 14 days. Plants were exposed to 100 µM of U and 2.5 g of HDPE (0.5% w/w to soil). Control plants (pots only containing soil) were not exposed to either U or HDPE. Plants were watered with 200 mL of U solution (100 µM) for experiments with U and experiments with U and HDPE using a pipette. *Mentha arvensis* were watered on Days 4, 8, and 11 of exposure with 100 mL of the plant nutrients solution used in the batch experiment (pH 7.5). Pore water was collected each watering day to measure the pH and U concentration. The photosynthetic parameters (photosynthetic and transpiration rates) of *Mentha arvensis* were measured on Days 2, 9, and 12 of exposure using a LI-6800 Portable

Photosynthesis System to analyze how the exposure affected the photosynthetic mechanisms. Images were taken of the leaves measured with the LI-6800 instrument next to a ruler to determine the leaf area using ImageJ software. The data from the LI-6800 was put into excel where we entered measured leaf area to determine the photosynthetic and transpiration rates of each plant.

The plants arrived in late October, so the plants were in a dormancy period during the time of the experiment. Because of this, only one to two replicates were able to be measured with the LI-6800 each measurement day. A few replicates died during the experiment as well. Thus, the obtained photosynthetic data represents preliminary results for future research.

### **3.3 Results and Discussion**

#### **3.3.1 Soil and Plastics Characterization**

Soil characterization confirmed the classification of the soil as sandy loam soil (Figure S1). XRF identified the presence of silica (36%), aluminum (3%), iron (2.5%), potassium (2%), calcium (1.8%), and other cations in the sediment (Table S2). The presence of these elements are also supported by the ICP-OES analysis on the soil (Table S3). This signifies the presence of quartz, aluminum silicates, and/or feldspar minerals in the soil, representing Si-O and Al-O functional groups. A previous study found that these functional groups can provide an electronegative surface charge to encourage the adsorption of metal ions <sup>135</sup>. Other studies found that heavy metal ions can also readily adsorb to these sandy-clay minerals via ion exchange <sup>136, 137</sup>. These studies used an experimental soil similar that of this study (i.e., mineral composition, textural class, and bulk density), giving insight into the possible mechanisms of U adsorption onto soil particles. Many studies have also observed the adsorption of U or other metals onto natural organic matter (NOM) <sup>115, 136, 138</sup>. Our

experimental soil has a low organic matter content (4%) (Figure S1) but could still contribute to metal adsorption in the soil.

Microplastic characterization indicated a polymer match (89%) to polyethylene (Figure S2). SEM-EDS and XPS of the unreacted plastics identify calcium, silicon, oxygen, titanium, sulfur, sodium, and magnesium on the surface of microplastic particles along with carbon (Figure 3.1 and Figure S3). These elements represent additives or impurities incorporated into the plastic polymer during the manufacturing process of the plastic bottles<sup>17, 58, 139</sup>.

Additives, such as plasticizers and antioxidants, can become more present and even leach off the plastics through weathering and aging processes<sup>17, 48, 57, 140</sup>. Thus, these elements can affect the adsorption of U to HDPE in the present experiments. The size distribution of 150 microplastics indicated that 97 (67%) were < 10  $\mu\text{m}$ , 51 (34%) were between 10 - 1000  $\mu\text{m}$ , and 2 (1.3%) were between 1-5 mm (Figure 3.2). Based on the SEM images and size distribution (Figure 3.1, Figure 3.2, Figure S4), the microplastic particles generated are heterogenous in size and have irregular morphology, and some particles are more irregular than others. This is consistent with the plastic particles that have been identified in global sediments and agricultural soils<sup>3, 21</sup>. It is likely that nanoplastics are also present and were not detected by the SEM images. Future imaging analyses on the nanoscale will be conducted to determine if nanoplastics are present in our system.

### **3.3.2 Uptake of Soluble U in reactions with soil and HDPE.**

Rapid U removal occurred in reactions with 10 g of soil at both pH 5 and pH 7.5 (Figures 3.3b-c and 3.3f-g). At pH 5, soluble U (initially 100  $\mu\text{M}$ ) decreased by 99.2% (0.84  $\mu\text{M}$ ) after 1h of reaction with soil (Figure 3.3d). Rapid U removal was similarly observed for experiments with the soil-HDPE mixture resulting in a 98.6% decrease of the total U concentration after only 0.1 h of reaction. However, between 0.5 h and 4 h of reaction, the

decrease of soluble U was 0.6% higher in experiments with the soil-HDPE mixture than in experiments with only soil. These results suggest the interfacial interactions between U and HDPE, such as the surface precipitation of U on HDPE. At pH 7.5, soluble U decreased by 98.0% (from 100 to 1.95  $\mu\text{M}$ ) after 1 h of reaction with soil (Figure 3.3h). Lower U removal was observed initially at pH 7.5 compared to pH 5 with an 86.2% decrease of soluble U in experiments with soil and 76.1% decrease in experiments with the soil-HDPE mixture within 0.1 h of reaction. Unlike at pH 5, the decrease of soluble U at pH 7.5 was detected 1.2% higher within the first 4 h of reaction in experiments with only soil than in experiments with the soil-HDPE mixture. The pH is likely affecting surface reactions by controlling the U speciation. Future statistical analysis will be conducted between the pH conditions and between the soil conditions within each pH to determine the significance of these differences.

Detectable U removal for both pH conditions was only observed in reactions with 10 g of soil. The 14 days of reactions showed that U removal from solution occurred mainly in the first 24 h, but specifically the first 0.5 h (Figures 3.3c-d and 3.3g-h). Final U removal was >99.9% with no detectable change in the soluble U concentration for experiments with just soil and soil-HDPE mixture at pH 5 and pH 7.5. In reactions without soil, the U concentration remained constant at  $98.5 \pm 2.2 \mu\text{M}$  for the extent of the experiment (Figure 3.3a and 3.3e). No detectable decrease in U concentration was measured in solutions with and without plastics. However, it is possible that 1  $\mu\text{M}$  of U was removed by interactions with the plastics, meaning possible interactions of 238 mg of U per kg of HDPE. Yet, from this analysis alone, it cannot be determined whether this small decrease in U could be due to U adsorbing and precipitating on HDPE, instrument error/variability, or personal error.

Our results show a higher initial uptake of U in soil reactions at pH 5 than in soil reactions at pH 7.5. Highest initial uptake (0.5 h) of U occurred in the soil-HDPE mixture in reactions at pH 5. Different processes can affect U adsorption to soil and HDPE particles such as U speciation and the charge of soil and HDPE particles.

$\text{UO}_2^{2+}$  and positively charged U-hydroxides are the predominate U species in natural waters at pH 5<sup>107, 108</sup> and can enhance the electrostatic attraction of U with the negatively charged soil or HDPE particles. Previous studies have found that  $\text{UO}_2^{2+}$  and U-hydroxides will readily adsorb onto silica particles at acidic pH conditions<sup>109-112</sup>. Soil particles, such as silicate clay minerals, have a net negative charge, so the rapid adsorption of the uranyl ion to silica soil particles could be a result of electrostatic attraction<sup>112-114</sup>. Therefore, the rapid U removal observed at pH 5 could be attributed to the sorption of uranyl hydroxides onto the soil silica particles. However, silica is not the only contributor to U removal. Previous studies have identified various U minerals and crystalline structures that can form under natural conditions<sup>116, 117, 141, 142</sup>. The formation of these U complexes can result from cationic exchange as seen with heavy metals in sandy loam soils<sup>137, 143-145</sup>. Uranium oxides can also substitute any of the cations present in these minerals (e.g., Ca, Na, K) with each other<sup>114</sup>. Thus, further analysis is needed to investigate the U complex and precipitate speciation in reactions with soil. Future ICP-OES analyses will also be conducted on solutions collected from both pH conditions to investigate the release of elements from the soil into solution.

Uranium speciation is dominated by aqueous  $\text{UO}_2\text{CO}_3$ ,  $\text{UO}_2(\text{CO}_3)^{2-}$ , and  $\text{CaUO}_2(\text{CO}_3)^{2-}$  at circumneutral pH<sup>12, 113, 118, 119</sup>. Calcium and carbonate are components found in the soil, plant nutrients solution, and HDPE in the batch reactors (Table S1-S3, Figure S1, and Figure 3.1). Uranium is less likely to be adsorbed by the soil particles or HDPE as U remains in these

aqueous complexes at pH 7.5. Less U is then available at pH 7.5 due to the presence of aqueous  $\text{U-CO}_3$  and  $\text{Ca-U-CO}_3$  complexes. These neutral and negatively charged aqueous complexes would be less reactive with the HDPE surface and soil particles, possibly explaining the lower initial removal of soluble U in experiments at pH 7.5 compared to experiments at pH 5. Previous studies have found that the sorption of  $\text{U(VI)}$  generally decreases in the presence of the calcium ion due to the increased mobility of these aqueous complexes<sup>113, 120, 122</sup>. However, previous studies have found that  $\text{U(VI)}$  adsorption onto silica particles, quartz, and ferrihydrite at neutral pH can still occur in the presence of calcium carbonates<sup>113, 122</sup>. Rapid initial U removal was observed in our pH 7.5 reactions regardless of the presence of Ca and  $\text{CO}_3^{2-}$  in solution. Another study by Saleh et al. (2018) also observed rapid initial  $\text{U(VI)}$  adsorption ( $> 96\%$  removal in less than 12 h) onto the silica particles at pH 7.3<sup>113</sup>. Other sandy-clay functional groups are present in the soil such as Al-O, Fe-O, and various cations, which can enhance the adsorption of U (Table S2 and S3).

HDPE can affect the physiochemical properties of soil and subsequently affect U mobility and accumulation in the soil. Micro- and nanoplastic particles typically have a negative surface charge at  $\text{pH} > 4.5$ <sup>6, 13, 29, 49, 84, 97</sup>. Al-oxides and Fe-oxides in soil have a positive charge except under basic pH conditions<sup>51, 84</sup>. Thus, at weakly acidic and circumneutral pH, micro- and nanoplastics can attach and aggregate to the soil mineral surfaces via electrostatic attraction or vice versa<sup>51, 84</sup>. These soil interactions with microplastics affect soil properties, structure, and function, all of which are related to the adsorption of heavy metals<sup>3, 20, 24, 80, 146</sup>. These effects, such as decreases in soil bulk density and changes in the water holding capacity, have been found in previous studies to decrease the metal adsorption capacity of soils<sup>147, 148</sup>. However, a decrease in metal sorption was not

observed at the end of our experiments with the soil-HDPE mixture at both pH conditions. Previous studies have identified the generation of oxygen functional groups in microplastics through weathering or aging processes, such as physical abrasion, that increase the charge and polarity of the microplastics, thereby enhancing the sorption characteristics of the microplastics<sup>56, 149</sup>. Thus, these changes can increase surface interactions between HDPE and cations like  $\text{UO}_2^{2+}$ . Further zeta-potential analyses will be conducted to determine the charge of the HDPE surface and of the soil particles after reactions.

### **3.3.3 Uranium accumulation on HDPE**

Uranium precipitates were identified on the weathered surface of the HDPE particles at both pH 5 and pH 7.5 (Figure 3.4a-c). The surface of the microplastics after reactions (Figures 3.4a-4c) appear fractured or cracked compared to the unreacted plastics (Figure 3.1 and Figure S4). The U precipitates were identified at weathered sites on the microplastic surfaces. (Figures 3.4a-c). Thus, weathering of the plastic surface allowed for the nucleation of the U precipitates.

The co-occurrence of U and Ca was observed in the precipitate on the weathered HDPE surfaces at pH 7.5 (Figure 3.4c). Uranium speciation at pH 7.5 is dominated by aqueous Ca-U- $\text{CO}_3$  complexes in natural waters<sup>12, 113, 118, 119</sup>. U could precipitate with these elements at circumneutral pH<sup>116, 117, 142</sup>. Calcium, titanium, and chlorine are the elements mainly present on the surface of the microplastics (Figure 3.4c) and are also seen on the unreacted microplastics (Figure 3.1). Weathering, such as physical abrasion, enables additives to become more interactive as the microplastic surface properties are altered<sup>48, 50</sup>. Thus, further analysis is needed to identify the phases of these solids. Additionally, future identification, extraction, and mineralization of additives present on the HDPE is needed.

Heterogenous U precipitates were observed on the HDPE particles collected at the end of the pH 5 batch experiments (Figure 3.4a-b). SEM-EDS results indicate the association of U with C, O and/or K for the identified precipitate (Figure 3.4a-b). Additional analyses are needed to confirm the phase of the identified precipitates.

Heterogenous U precipitation was observed on the surface of the microplastics at both pH conditions without soil. The weathered sites on the HDPE particles acted as a substrate for adsorption through electrostatic interaction or inner sphere complexation as shown in other studies <sup>5, 13</sup>. A similar study identified heterogeneous precipitation of U on the surface of pristine microplastics at pH 7 but not at pH 3 <sup>16</sup>. Weathering of microplastics can cause the generation of oxygen functional groups in the HDPE surface <sup>5, 13, 150</sup>. These oxygen functional groups can serve as reactive surface sites for U adsorption. Depending on the mechanism of adsorption, these active sites enable stronger bonds between the adsorbate and substrate, which can allow for the nucleation and precipitation of U minerals <sup>5, 13</sup>. Further XPS and FTIR analyses will be conducted to determine the chemical bonds and functional groups of the reacted microplastics to give insight into the adsorption mechanism of U on HDPE. Zeta potential analyses will also be conducted to see the effects of weathering on the HDPE surface charge. Additionally, SEM-EDS, XPS, FTIR, and zeta potential analyses should be conducted on the plastic pieces prior to grinding to investigate how the grinding process contributed to the weathering of the plastic particles.

Uranium precipitated with calcium on the HDPE surface at pH 7.5 despite the presence of bicarbonate in solution (Figure 3.4c). Previous studies identified the precipitation of U with Ca without bicarbonate present in solution at pH 7 <sup>118, 121</sup>. In one study, bicarbonate solubilized U solids partially or completely by the end of the experiment (50 h) at pH 7 <sup>118</sup>.

This coincides with the present study as U mostly remained in solution in experiments without soil at pH 7.5 (Figure 3.3e). However, U precipitates were still observed after 336 h of reaction, suggesting stronger bonds at the active weathered sites of HDPE with the U precipitates. Future analyses are needed to determine the chemical bonds associated with these adsorbed precipitates. Further TEM analyses will be conducted on these same HDPE particles to investigate the mineralogy of the precipitate.

Heterogeneous U precipitates were identified on the HDPE particles at pH 5 (Figures 3.4a-b). A previous study found both amorphous and crystalline U-K, U-Na, and U-Na-K bearing precipitates of varying speciation on natural organic matter (NOM) at pH 4<sup>115</sup>. The authors determined that multiple solid phases could be present, all of which are forms of uranyl oxide hydrates<sup>115-117</sup>. Similarly in the present study, U-oxides are the primary component of the solid structure at pH 5. The uranyl ion is the dominate aqueous species at pH 5, so inner sphere complexation could be the controlling mechanism of adsorption leading to surface precipitation<sup>114</sup>. By this, the solids can substitute different ions (e.g., Ca, K, Na) with the main structure<sup>114, 117</sup>. This ion substitution can lead to all of the elements present in the precipitate coating<sup>114</sup>. The spectra for the U precipitates at pH 5 suggest the presence of Na, K, Cl, and Ca in the area analyzed. Ion substitution is a possible mechanism of U precipitation on HDPE in weakly acidic environments. Additional analyses are needed to confirm the concentration of all major elements in solution and to confirm the phase of the U precipitates. Further TEM analyses will be conducted on these same HDPE particles to investigate the mineralogy of the precipitate.

#### **3.3.4 Plastic aggregation and Uranium accumulation in soil**

HDPE aggregates with the soil were identified at pH 5 and pH 7.5 (Figure 3.4d-e). The SEM images show that the mixtures of HDPE with soil creates solid components of plastics

and soil together. The impacts of the solid components on the removal of U in soil is still unknown. However, ICP-MS analysis confirmed acid extractable U concentrations of ~ 55-76 mg/kg in the soil at both pH conditions (Table S4). Previous studies have identified the rapid adsorption of U to silica particles at both weakly acidic and circumneutral pH environments as discussed previously<sup>109-113, 122</sup>. Thus, future analyses will try to identify the association of U with these soil minerals.

Previous studies have seen the effects of plastics on soil structure and function, where PE decreased the soil bulk density and altered water stable aggregates<sup>24, 80</sup>. Others observed effects include a decrease in soil pH, changes in soil microbial activity, and negative effects on soil organic carbon and nitrogen cycles<sup>14, 20, 80-83</sup>. However, a clear trend of the microplastic effects on soil has not been confirmed, and it is not clear if these effects consistently generate positive or negative effects in soil and plants. Additionally, soil minerals, soil pH, and solution pH greatly affect the interactions of nanoplastics with soils<sup>84</sup>. Previous studies have found that the mobility of nanoplastics increases with an increase in pH<sup>51, 84</sup>. This is because both the zeta potentials of nanoplastics and soil particles become more negative with an increase in pH, enhancing electrostatic repulsion and therefore, mobility of the nanoplastics<sup>51, 84</sup>. Furthermore, the presence and charge of Fe- and Al-oxides in soil can greatly affect nanoplastic transport<sup>51, 84</sup>. When these oxides are positively charged (acidic pH) and present at a high concentration, the electrostatic attraction between the oxides and nanoplastics is greater, leading to a higher retention in the soil<sup>51</sup>. The soil pH of the present study was neutral, so further analysis is needed to determine the mobility of HDPE particles in the soil. Further measurements are also needed to confirm the effects of HDPE on

the soil properties and structures in our study, which is relevant to the current and future plant exposure experiments.

### **3.3.5 Plant exposure to HDPE and U negatively affects plant photosynthetic parameters**

Preliminary results suggest the co-exposure of U and HDPE to *Mentha arvensis* has the greatest impact on the photosynthetic parameters of the plant. The photosynthetic and transpiration rates of *Mentha arvensis* exposed to both HDPE and U were 76% and 87% lower compared to the control plants following 10 days of exposure (days 2-12) (Figure 3.5). Uranium and HDPE could interact synergistically causing negative effects to these photosynthetic parameters. Plastic contamination in the soil-HDPE mixture can impact the mechanisms of the photosynthesis in *Mentha arvensis* following these proposed mechanisms: (1) Plastic aggregation in the soil can affect soil density and water flow, leading to a reduction of photosynthesis, (2) Plastic particles can adsorb on the root surfaces, affecting the water and nutrient uptake, and (3) Uptake of the HDPE particles via transpiration pull, affecting the water and nutrient flow in the xylem. Our SEM-EDS analyses determined that U can precipitate on HDPE particles, suggesting that HDPE could act synergistically with U to affect the plants.

Previous studies observed a decrease in soil bulk density, changes in the functionality and structure of the soil, a decrease in water stable aggregates, a decrease the soil pH, and an increase the root biomass and root to shoot ratio of spring onion in the presence of HDPE (2%) <sup>24, 80</sup>. A reduction in water and nutrient availability causes stress to the plants <sup>20</sup>. Plants will expand their root system, increasing their root/shoot ratio, to increase the uptake of water and nutrients when under stress <sup>20, 89, 90</sup>. However, another study observed similar physiochemical alterations in soil by PE (1%), leading to reductions in root and shoot

biomass of lettuce <sup>91</sup>. Therefore, further research is required to investigate how physiochemical alterations of soil by microplastics affects the photosynthetic mechanisms of different plants. Other studies have also found decrease in photosynthesis (i.e., photosynthetic rate, Rubisco activity, transpiration rate, and stomatal conductance) due to microplastics attaching to the root surface <sup>32, 85, 92</sup>. This attachment can block the ion channel causing a decrease in the uptake of nutrients, essential elements, and essential enzymes, increasing phytotoxicity in the plant <sup>32, 85, 92</sup>. Additionally, research has observed micro- and nanoplastic adsorbed to the root surface can be taken up into the plant stems and leaves via transpiration pull <sup>32, 44, 47, 86</sup>. This uptake of particulate plastics can cause a level of stress that the plants are not able to overcome, resulting in cellular damage of the plants <sup>32, 45, 46, 85, 92, 151</sup>.

Previous studies found the synergetic effect between environmental pollutants and microplastics can enhance their toxicity in plants. A previous study observed decreases in the photosynthetic rate, transpiration rate, stomatal conductance, and Rubisco activity of rice when exposed to microplastics and arsenic <sup>31</sup>. Similar results were observed in lettuce plants exposed to both PE and di-*n*-butyl phthalate <sup>85</sup>. Both of these studies hypothesize the accumulation of the constituents in the epidermis or phloem of the roots, leading to the inhibition of root activity reducing photosynthesis <sup>31, 85</sup>. Additionally, polyethylene (PE) and cadmium (Cd) exhibited a coupled toxicity on lettuce and maize plants <sup>91, 100</sup>. The co-exposure of PE and Cd increased the uptake, accumulation, and bioavailability of Cd in lettuce plants, while more toxic effects were observed on the root biomass of the maize plants <sup>91, 100</sup>. Furthermore, a previous study found higher accumulation and toxicity of U particulates than that of soluble U in mammalian cells <sup>152</sup>. Their findings suggest the organic particulate form of U influences the initiation of cellular toxicity. The precipitation of U with HDPE

generates an organic bearing particulate of U, possibly increasing U accumulation in the plant cells. Further analyses will be conducted to determine the accumulation of U and/or HDPE in the *Mentha arvensis* plants.

### **3.4 Environmental Implications**

This study provides insight about the surface-controlled reactions of U with microplastics, soils, and plants, which is relevant to environments in which these co-occur. The findings of this study show that U, microplastics, and soil can have physiochemical interactions that should be considered for the mobilization of these constituents for risk assessment and remediation. Specifically, our findings indicate that U can adsorb and precipitate on the surface of HDPE at pH 5 and pH 7.5. These findings have implications in natural and engineered systems as well as agricultural sites affected by anthropogenic activities, in which U and microplastics co-occur. The interactions of U and HDPE occurred at the typical pH of natural water, agricultural soils, and the soil rhizosphere. However, environmental conditions such as organic matter content can affect the interfacial interactions observed. Interactions of U and HDPE could have negative synergetic effects on the photosynthetic mechanisms of *Mentha arvensis*. Negative effects on the photosynthetic mechanisms of wild mint can raise ecological concern for communities that use this plant for agricultural, cultural, and medicinal purposes. Future research should investigate the minerology of the U precipitates and the interactions of U and HDPE at the root surface. Further plant exposure experiments are needed to better assess the effects on photosynthesis and accumulation of U and HDPE in the plant roots and shoots.

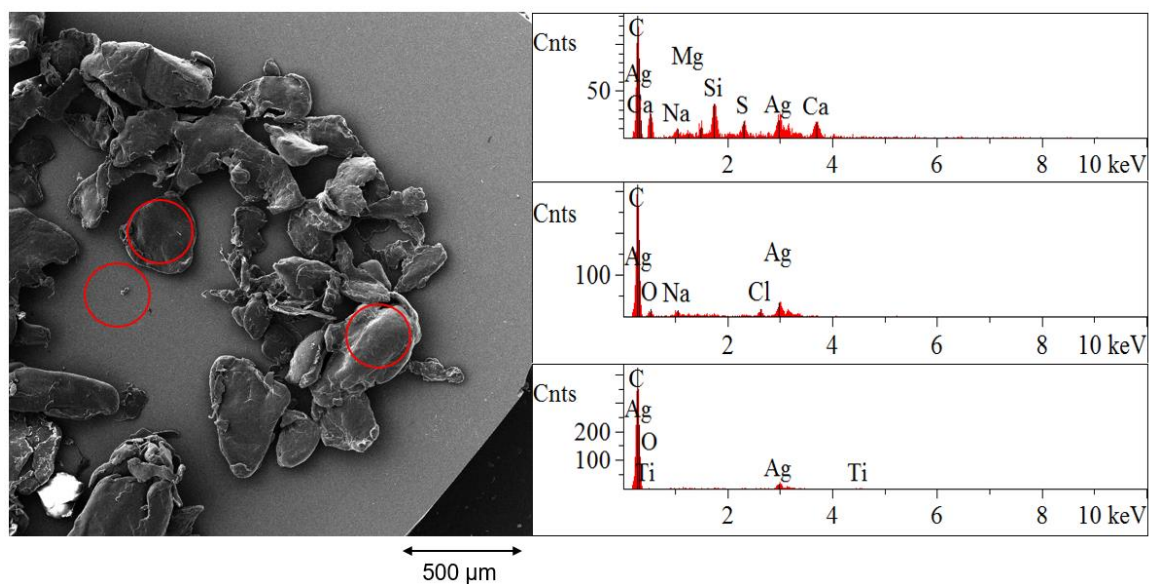
### **3.5 Conclusions**

Rapid U removal was observed with soil reactions at pH 5 and pH 7.5, possibly due to adsorption or precipitation of U with the silica and clay particles. Over 99% of soluble U was

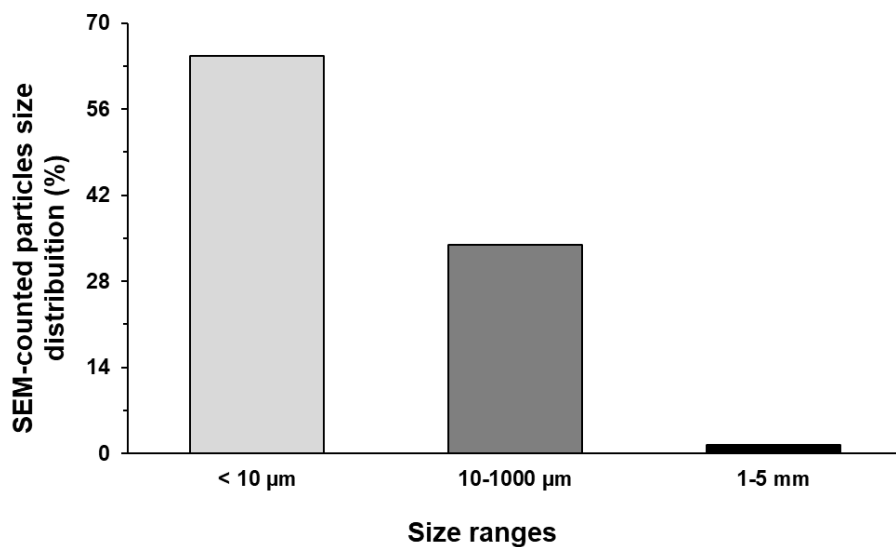
removed from solution at both pH conditions for soil experiments. While a majority of U remained in solution for reactions without soil, small amounts of U precipitates were identified on the weathered surface of HDPE particles, suggesting that the weathering enabled the adsorption and nucleation of U. HDPE aggregates were identified in the soil, indicating possible structural and functional changes to the soil. Preliminary results show the possibility of U and HDPE synergistically affecting the photosynthetic mechanisms of *Mentha arvensis*. This study provides insight about the surface-controlled reactions of U with microplastics, soils and plants, which is relevant to environments in which these co-occur.

### **3.6 Acknowledgements**

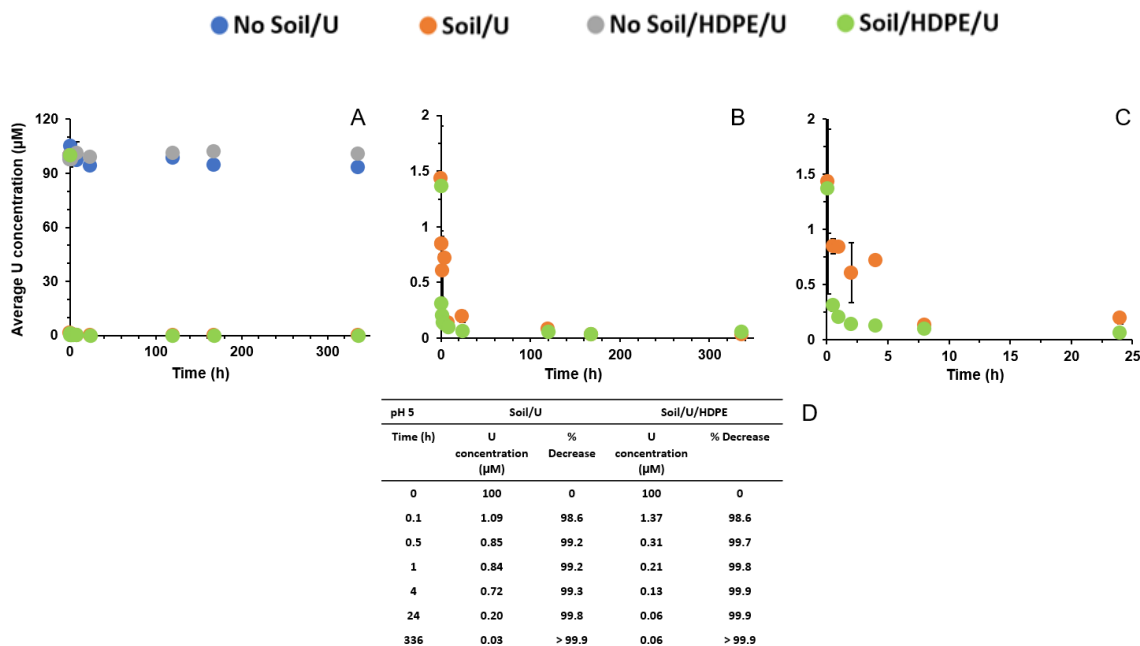
Funding for this research was provided by the National Institute on Minority Health and Health Disparities (NIMHD) Center for Native Environmental Health Equity Research at UNM under Award Number P50MD1570606 and the National Institute of Environmental Health Sciences (NIEHS) Superfund Research Program (P42 ES025589). The content, opinions, findings, conclusions, and recommendations are those of the authors and do not necessarily represent the official views of NIMHD, National Institutes of Health, or NIEHS Superfund Research Program.



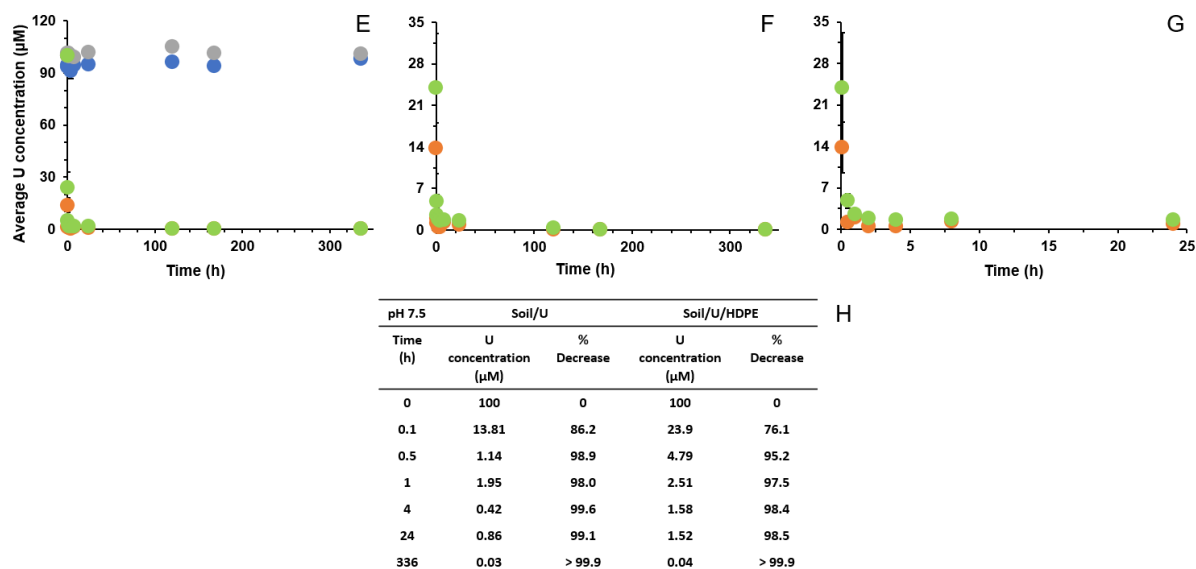
**Figure 3.1:** Scanning-electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) spectra of lab prepared plastic particles suspended in water prior to experiments. Sulfur, sodium, magnesium, calcium, and titanium were identified on the plastic particles and are representative of additives used to produce plastic bottles 17, 58, 60.



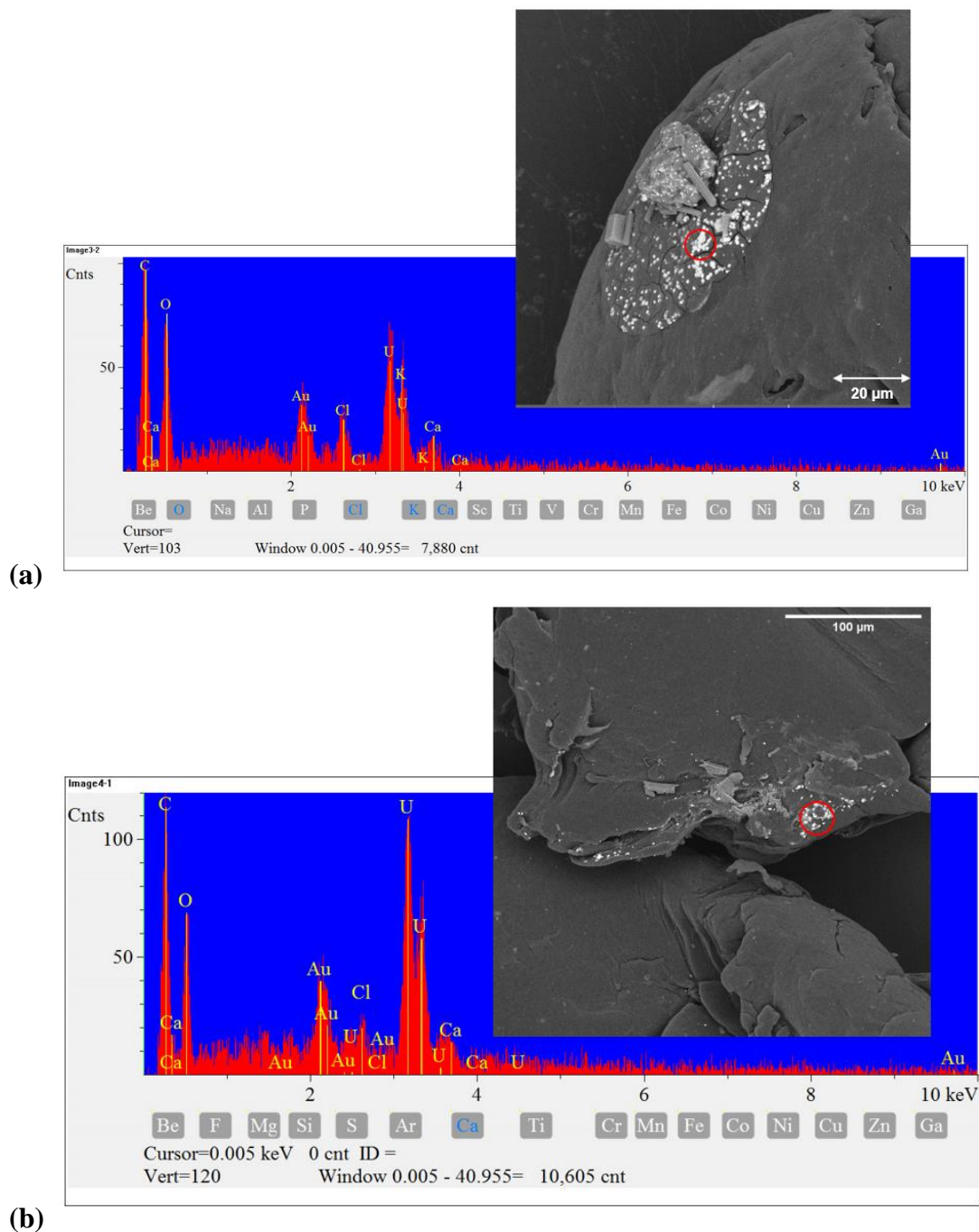
**Figure 3.2:** Size distribution (%) graph of plastic particles counted from SEM images for characterization. A total of 150 particles were measured and counted using the ImageJ software.



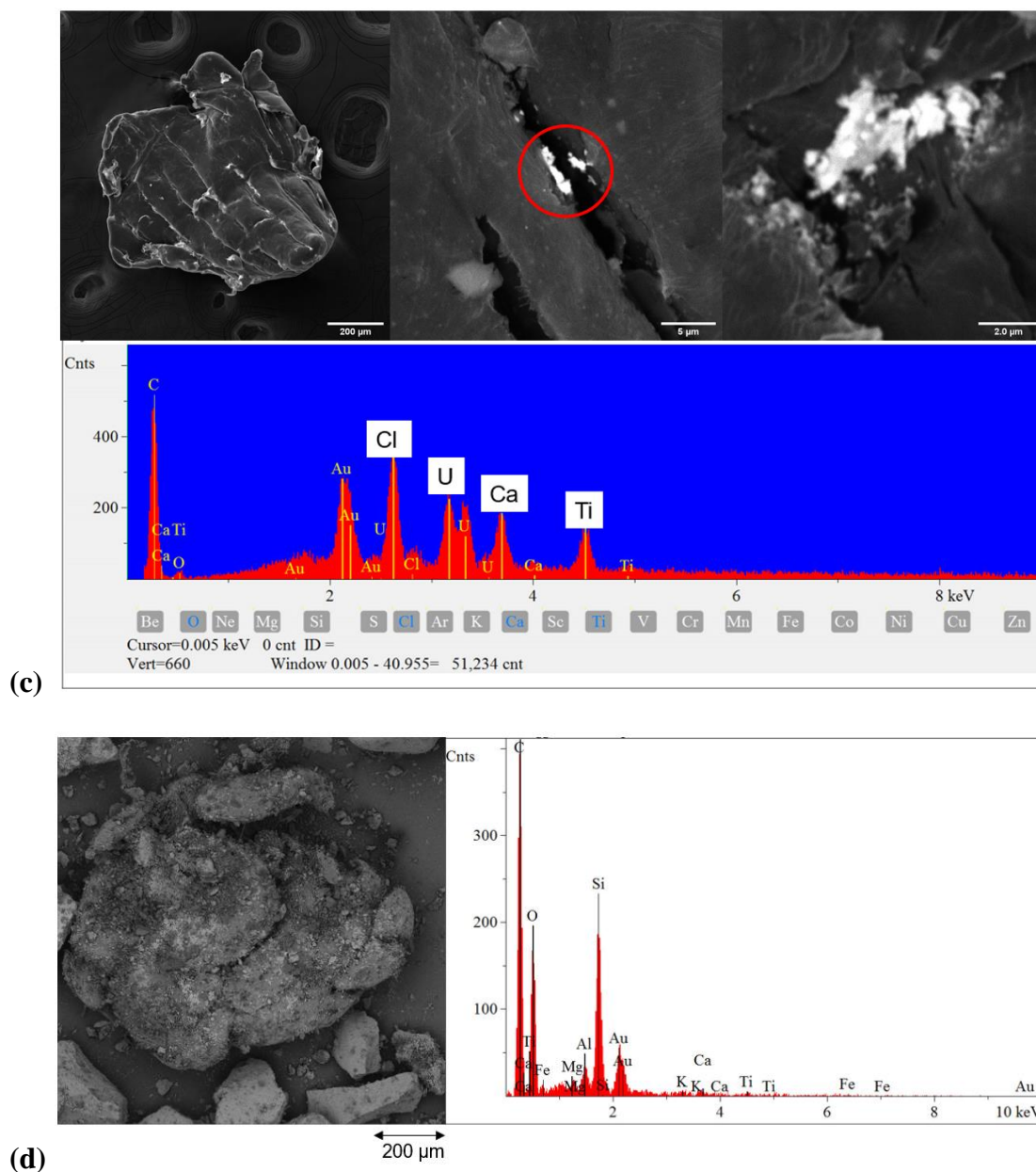
**Figure 3.3:** (a) Soluble U concentration over time in pH 5 batch experiments containing U with nutrients solution alone (blue), with plastics (grey), with soil (orange), and with soil and plastics (green). (b) Soluble U concentration over time in pH 5 batch experiments containing U with the soil conditions. (c) Soluble U concentration in the first 24 h in pH 5 batch experiments containing U with the soil conditions. (d) Summary of soluble U concentrations from soil reactions at pH 5. (e) Soluble U concentration over time in pH 7.5 batch experiments containing U with nutrients solution alone (blue), with plastics (grey), with soil (orange), and with soil and plastics (green). (f) Soluble U concentration over time in pH 7.5 batch experiments containing U with the soil conditions. (g) Soluble U concentration in the first 24 h in pH 7.5 batch experiments containing U with the soil conditions. (h) Summary of soluble U concentrations from soil reactions at pH 7.5 Initial concentrations used are 100 μM U and 0.5% w/w plastic (0.05 g plastic for 10 g of soil). Plant Nutrients Solution: 0.5mM MgSO<sub>4</sub> + 1mM NaHCO<sub>3</sub> + 2mM NH<sub>4</sub>NO<sub>3</sub> + 1mM KCl + 3mM CaCl<sub>2</sub>·2H<sub>2</sub>O



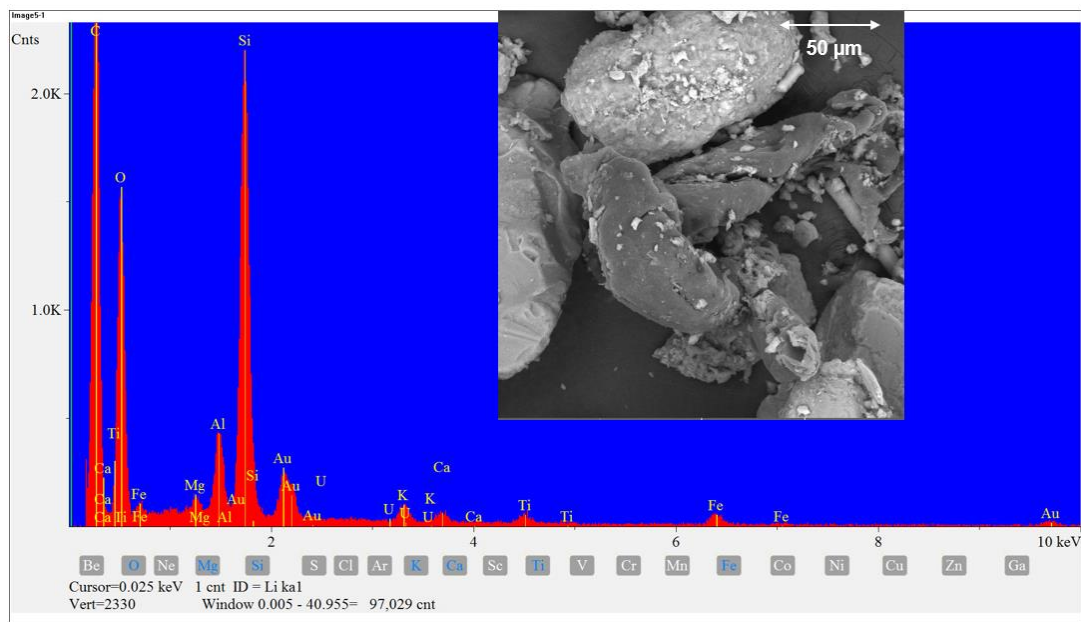
**Figure 3.3 (cont.):** (a) Soluble U concentration over time in pH 5 batch experiments containing U with nutrients solution alone (blue), with plastics (grey), with soil (orange), and with soil and plastics (green). (b) Soluble U concentration over time in pH 5 batch experiments containing U with the soil conditions. (c) Soluble U concentration in the first 24 h in pH 5 batch experiments containing U with the soil conditions. (d) Summary of soluble U concentrations from soil reactions at pH 5. (e) Soluble U concentration over time in pH 7.5 batch experiments containing U with nutrients solution alone (blue), with plastics (grey), with soil (orange), and with soil and plastics (green). (f) Soluble U concentration over time in pH 7.5 batch experiments containing U with the soil conditions. (g) Soluble U concentration in the first 24 h in pH 7.5 batch experiments containing U with the soil conditions. (h) Summary of soluble U concentrations from soil reactions at pH 7.5 Initial concentrations used are 100 μM U and 0.5% w/w plastic (0.05 g plastic for 10 g of soil). Plant Nutrients Solution: 0.5mM MgSO<sub>4</sub> + 1mM NaHCO<sub>3</sub> + 2mM NH<sub>4</sub>NO<sub>3</sub> + 1mM KCl + 3mM CaCl<sub>2</sub>·2H<sub>2</sub>O



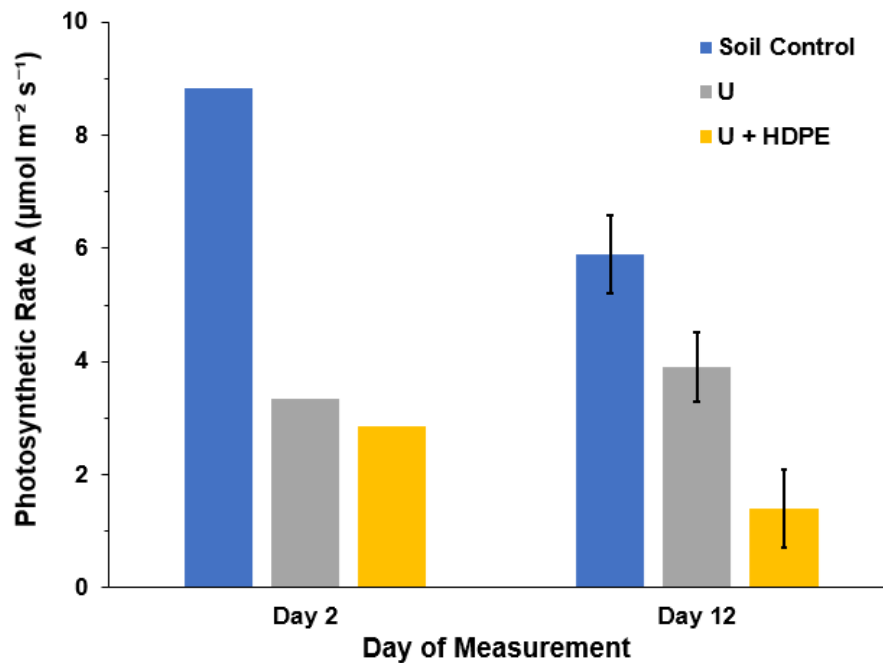
**Figure 3.4:** Scanning-electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) spectra on the solids collected from Batch experiments from (a) No Soil/HDPE/U pH 5, (b) No Soil/HDPE/U pH 5, (c) No Soil/HDPE/U pH 7.5, (d) Soil/HDPE/U pH 5, and (e) Soil/HDPE/U pH 7.5. Figures 4a-4c show HDPE particles and indicate U precipitates on the weathered surface of the HDPE particles. 4d and 4e show HDPE particles covered in soil, indicating the attachment and aggregation of soil with HDPE particles.



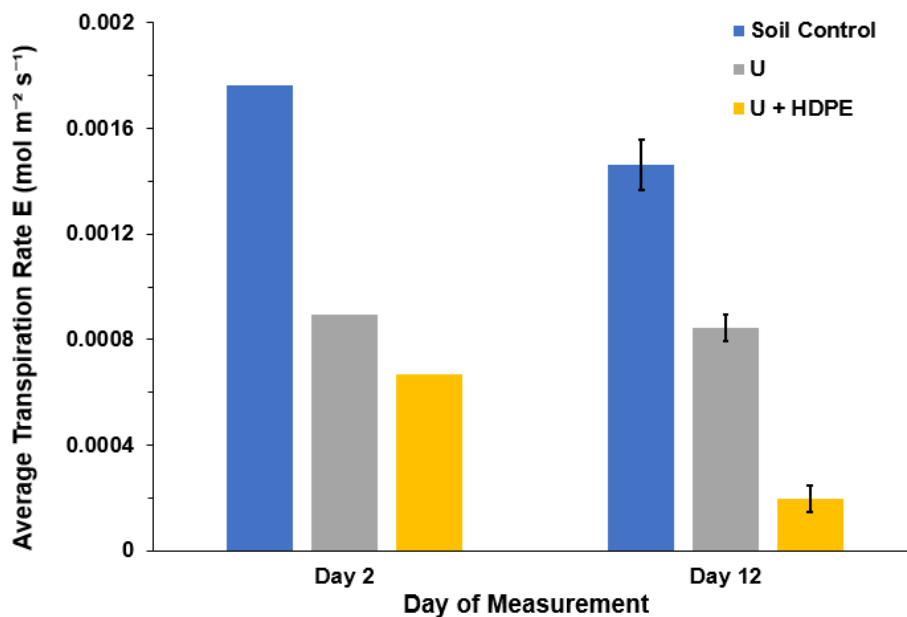
**Figure 3.4 (cont.):** Scanning-electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) spectra on the solids collected from Batch experiments from (a) No Soil/HDPE/U pH 5, (b) No Soil/HDPE/U pH 5, (c) No Soil/HDPE/U pH 7.5, (d) Soil/HDPE/U pH 5, and (e) Soil/HDPE/U pH 7.5. Figures 4a-4c show HDPE particles and indicate U precipitates on the weathered surface of HDPE particles. 4d and 4e show HDPE particles covered in soil, indicating the attachment and aggregation of soil with HDPE particles.



(e) **Figure 3.4 (cont.):** Scanning-electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) spectra on the solids collected from Batch experiments from (a) No Soil/HDPE/U pH 5, (b) No Soil/HDPE/U pH 5, (c) No Soil/HDPE/U pH 7.5, (d) Soil/HDPE/U pH 5, and (e) Soil/HDPE/U pH 7.5. Figures 4a-4c show HDPE particles and indicate U precipitates on the weathered surface of HDPE particles. 4d and 4e show HDPE particles covered in soil, indicating the attachment and aggregation of soil with HDPE particles.



(a)



(b)

**Figure 3.5:** Preliminary photosynthetic parameter results from Day 2 and Day 12 of plant exposure experiment for (a) Average photosynthetic rate A and (b) Average transpiration rate E. Measurements were taken from the control soil (blue), U exposure (grey), U and HDPE exposure (yellow). Standard error presented for the Day 12 data. Exposure to just HDPE was not included in this graph as the accuracy of the data could not be determined.

## Appendix: Supplementary Information

### Interfacial Interactions of Uranium and HDPE in agricultural soil and their bioaccumulation in *Mentha arvensis*

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## **Summary of Supporting Information**

Journal: Environmental Science and Technology

### **Supplementary Notes: Additional Materials and Methods**

**Aqueous and Solid Analyses of Batch Experiment:** Uranium concentration in solution was determined using a PerkinElmer nexION 300D (Dynamic Reaction Cell) Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). The collected 1 mL subsample was diluted (ranging from 20-200x) with nitric acid before analyzing the samples. The ICP-OES was used to determine the U concentration in the soil. Acid digestion was performed, and the samples were diluted 50x before analysis.

**Table S1 Batch Experimental Matrix:** Components incorporated into each batch reactor for every experimental condition (No soil control, soil control, No soil/HDPE, Soil/HDPE, No soil/Uranium, Soil/Uranium, No Soil/HDPE/Uranium, and Soil/HDPE/Uranium).

Reactor Component	Amount in Reactor	No Soil Control	Soil Control	No Soil / HDPE	Soil / HDPE	No Soil/ Uranium	Soil/ Uranium	No Soil/ HDPE/ Uranium	Soil/ HDPE/ Uranium
Uranium	100 $\mu$ M					X	X	X	X
HDPE	0.05 g			X	X			X	X
particles									
Soil	10 g		X		X		X		X
Plant	50 mL	X	X	X	X	X	X	X	X
Nutrients Solution									

**Table S2 Elemental composition of the unreacted soil determined by X-ray Fluorescence (XRF):** Components of the soil as determined by X-ray Fluorescence (XRF). Al, Si, Fe, K, Ca, and Ti are the components most present in the soil.

<b>Component</b>	<b>Result</b>	<b>Unit</b>	<b>Det. Limit</b>	<b>El. Line</b>	<b>w/o normal</b>
<b>Na</b>	1.48	Mass%	0.01137	Na-KA	0.7003
<b>Mg</b>	0.582	Mass%	0.00782	Mg-KA	0.2759
<b>Al</b>	6.94	Mass%	0.00567	Al-KA	3.2901
<b>Si</b>	75.5	Mass%	0.01648	Si-KA	35.8104
<b>P</b>	0.217	Mass%	0.00336	P-KA	0.1032
<b>S</b>	0.126	Mass%	0.00310	S-KA	0.0598
<b>Cl</b>	0.0201	Mass%	0.00805	Cl-KA	0.0095
<b>K</b>	4.49	Mass%	0.01407	K-KA	2.1316
<b>Ca</b>	3.77	Mass%	0.00857	Ca-KA	1.7861
<b>Ti</b>	0.495	Mass%	0.01352	Ti-KA	0.2349
<b>Cr</b>	0.0276	Mass%	0.00927	Cr-KA	0.0131
<b>Mn</b>	0.311	Mass%	0.00840	Mn-KA	0.1477
<b>Fe</b>	5.53	Mass%	0.00851	Fe-KA	2.6235
<b>Ni</b>	0.0123	Mass%	0.00498	Ni-KA	0.0059
<b>Zn</b>	0.0210	Mass%	0.00385	Zn-KA	0.0100
				(OV)	
<b>Rb</b>	0.0224	Mass%	0.00292	Rb-KA	0.0106
<b>Sr</b>	0.0849	Mass%	0.00278	Sr-KA	0.0403
<b>Y</b>	0.0044	Mass%	0.00266	Y-KA	0.0021
<b>Zr</b>	0.0608	Mass%	0.00250	Zr-KA	0.0288
<b>Ba</b>	0.241	Mass%	0.03268	Ba-LA	0.1142
<b>W</b>	0.0772	Mass%	0.01221	W-LA	0.0366
<b>Re</b>	0.0000	Mass%	0.01165	Re-LA	0.0000

**Table S3 Elemental composition of the unreacted soil determined by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES): ICP-OES elemental**

composition of the unreacted soil. The results of the four replicates were averaged, and the standard deviation is presented in the table.

<b>Analyte</b>	<b>Average Conc. (mg/kg)</b>	<b>Standard Deviation</b>
<b>Al 396.153</b>	29512.98076	3315.702511
<b>Ba 455.398</b>	334.4484749	31.9954091
<b>Ca 317.933</b>	8409.622502	1491.978081
<b>Fe 259.938</b>	16006.30473	602.8514821
<b>K 766.490</b>	9250.809695	124.129613
<b>Mg 285.213</b>	1502.098914	426.9106332
<b>Mn 257.610</b>	451.4445974	25.11893181
<b>Na 589.592</b>	9447.333517	402.1597573
<b>Si 251.611</b>	241733.1006	19666.9073
<b>Sr 407.771</b>	113.4958102	11.36171886
<b>Ti 334.940</b>	556.6409489	27.61898269
<b>U 367.007</b>	30.72179587	2.4608060583

**Table S4 Acid-Extractable U concentration in soil from batch experiments:** ICP-MS and acid digestions were performed on each of the four replicates from the batch experiment. The average U concentration (mg/kg) and standard deviation are presented in the table.

<b>Sample</b>	<b>Average Acid-Extractable U concentration in soil (mg/kg)</b>	<b>Standard Deviation</b>
<b>Soil Control pH 5</b>	1.31	0.36
<b>Soil/Uranium pH 5</b>	55.72	2.72
<b>Soil/HDPE/U pH 5</b>	63.91	17.93
<b>Soil Control pH 7.5</b>	1.37	0.08
<b>Soil/Uranium pH 7.5</b>	73.82	3.14
<b>Soil/HDPE/Uranium pH 7.5</b>	76.69	43.38

(a)

<b>Percent sand</b>	<b>80</b>
<b>Percent silt</b>	<b>8</b>
<b>Percent clay</b>	<b>12</b>

USDA Textural Class  
(hydrometer method) =  
Sandy loam

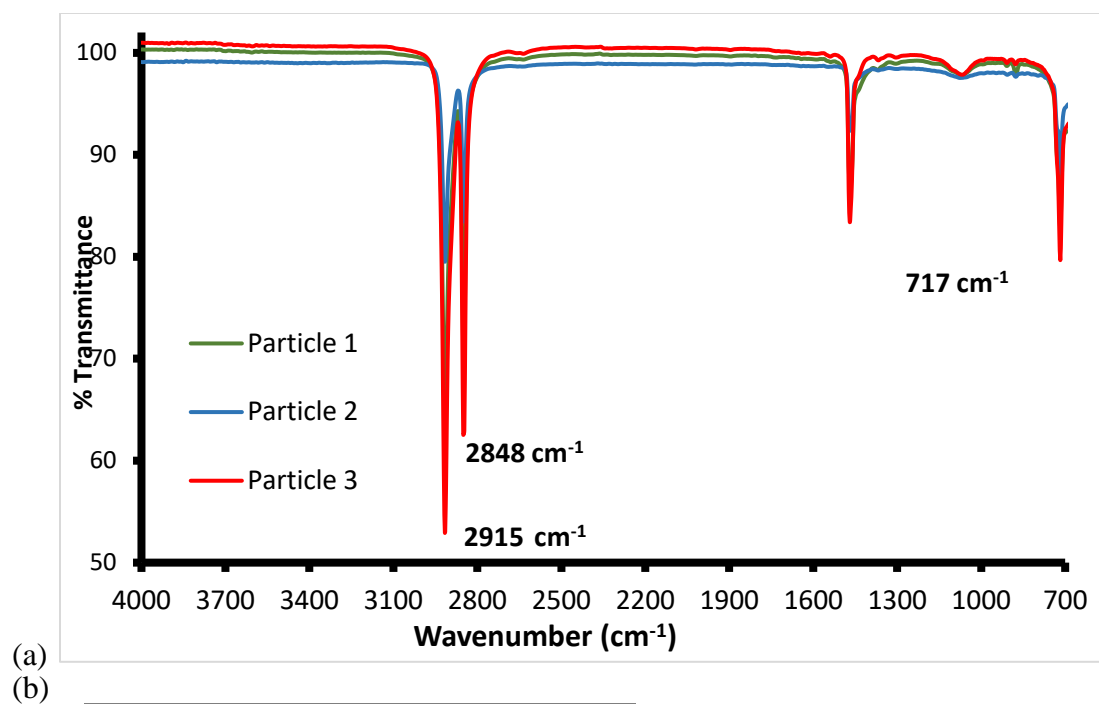
<b>Cation</b>	<b>Percent</b>	<b>ppm</b>
Potassium	5.1	337
Calcium	71.0	2409
Magnesium	14.2	290
Sodium	0.2	9
Hydrogen	9.4	16

(b)

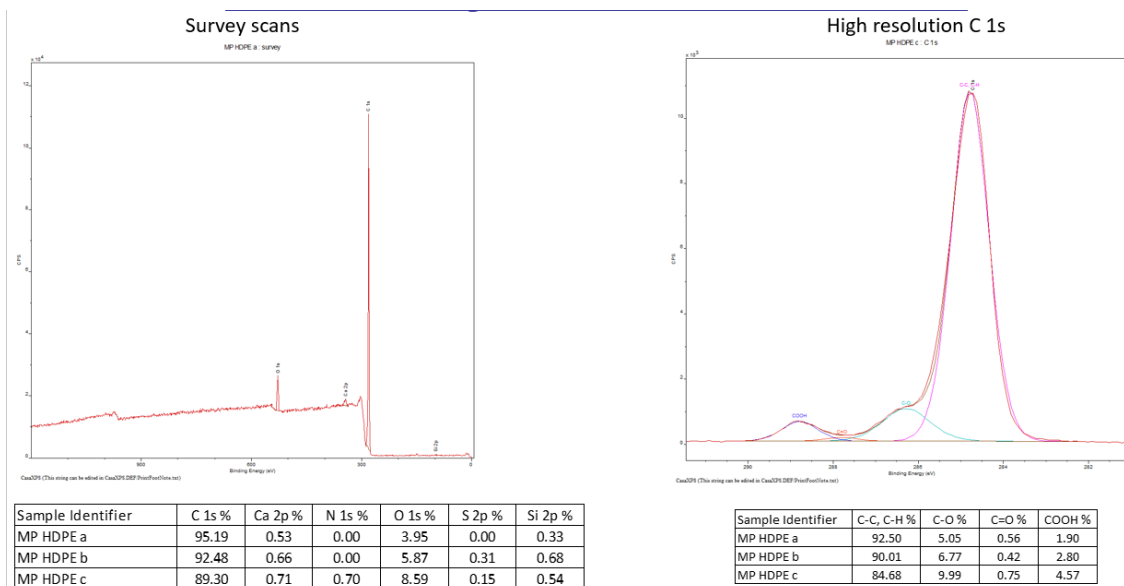
<b>Bulk Density (disturbed)gm/cc</b>	<b>1.16</b>
<b>Cation Exchange Capacity (meq/100 g)</b>	<b>17.0</b>
<b>% Moisture at 1/3 Bar</b>	<b>16.2</b>
<b>% Moisture at 15 Bar</b>	<b>12.1</b>
<b>% organic Matter (Walkley-Black)</b>	<b>4.0</b>
<b>% Carbonates (Pressure Method)</b>	<b>0.4</b>
<b>% Total Carbon (Carbon Analyzer)</b>	<b>2.0</b>
<b>% Inorganic Carbon</b>	<b>0.0</b>
<b>% Organic Carbon Analyzer</b>	<b>2.0</b>
<b>% Organic Matter Analyzer</b>	<b>3.4</b>

(c)

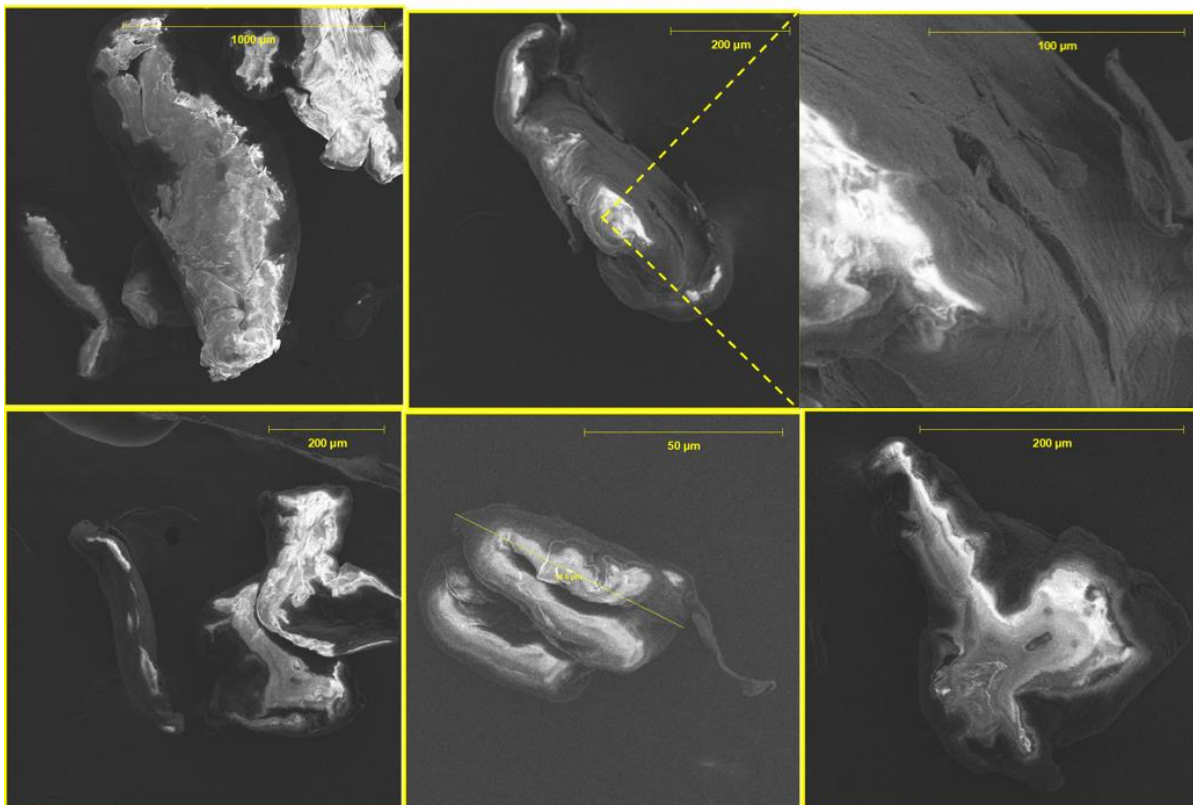
**Figure S1 Soil Characterization from Agvise Laboratories:** Soil characterization performed by Agvise Laboratories determining (a) Textural class of the soil, (b) Base Saturation Data of the soil, and (c) Properties of the soil.



**Figure S2 FTIR spectra and functional group peaks of unreacted plastic particles:** Micro-FTIR and ATR (a) Spectra of the plastic particles and (b) corresponding table of peaks.



**Figure S3 XPS survey scans of the unreacted plastic particles:** XPS survey scans and high resolution peaks near the surface of the unreacted plastic particles.



**Figure S4 SEM images of unreacted plastic particles:** SEM images of the unreacted microplastics performed at Oklahoma State University.

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