An Investigation of Physicochemical Processes that Influence Heavy Metals Fate within Plastic Materials

Md Hadiuzzaman

Follow this and additional works at: https://digitalcommons.memphis.edu/etd

Recommended Citation

This Dissertation is brought to you for free and open access by University of Memphis Digital Commons. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of University of Memphis Digital Commons. For more information, please contact khggerty@memphis.edu.
AN INVESTIGATION OF PHYSICOCHEMICAL PROCESSES THAT INFLUENCE HEAVY METALS FATE WITHIN PLASTIC MATERIALS

By

Md Hadiuzzaman

A Dissertation
Submitted in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy

Major: Civil Engineering

The University of Memphis

May 2023
To those whom I loved, love, or will love…
My foremost and warmest thanks go to my adviser, Dr. Maryam Salehi, and being her first Ph.D. student was an honor. I am grateful for her time, ideas, and funding in making my Ph.D. experience inspirational and productive. I am grateful to my mentors and committee members, Dr. Paul J Palazolo, Dr. Farhad Jazaei, Dr. Dave DeSimone, and Dr. Shawn Paul Brown, for their continuous help and support. I would like to thank my wife, Israt Jahan, for her support throughout the Ph.D. journey. I am also grateful to my daughter Illina for making my life more colorful during even the most challenging time. I would like to thank my parents, siblings, friends, lab mates, teachers, lab technicians, and all who made this journey easier with their continuous support, care, and help.

The following individuals deserve my gratitude for their technical support during this endeavor:

University of Memphis
Civil Engineering: Dr. Shahram Pezeshk, Angela Graves, Melanie Young, Erica MeShelle Boyce
Department of Biological Science: Dr. Omar Skalli
Materials Science Laboratory: Dr. Felio Perez
Department Of Chemistry: Dr. Tomoko Fujiwara

Clemson University
Department of Environmental Engineering and Earth Sciences: Dr. David A. Ladner

Research Funding
Funding for this work was provided by the National Science Foundation grant CBET-2309475 and CEBT-2305189, and the United States Department of Agriculture, National Institute of Food and Agriculture (USDA/NIFA) Award number 2020-67019-31166.
Preface

In this dissertation, three different manuscripts are presented as chapters, and the research spans four major fields of study, including environmental engineering, polymer and surface science, and water chemistry. Results from three separate multidisciplinary research are presented in the dissertation. Each chapter included a scientific literature review and a description of the present knowledge gap. Each chapter begins with a presentation of the paper's title, the authors who contributed, and an abstract, and is completed by an introduction, experimental, results and discussion, conclusion, and reference sections. The organization of the dissertation is described in the introduction chapter.
Abstract

Acute and chronic toxicity resulting from exposure to heavy metals in natural and built environments critically affects public health and aquatic safety. Heavy metals such as lead (Pb), zinc (Zn), and copper (Cu) are released into the urban runoff by vehicles emission. They also could be released from corroded metallic potable water plumbing fixtures to the tap water. In this dissertation, several knowledge gaps regarding the combined physical and chemical processes that control Pb accumulation onto plastic materials, including microplastics (MPs) as urban litter and plastic potable water pipes, were addressed. In the second chapter, the surface morphology and chemistry alterations of low-density polyethylene (LDPE) and polyethylene terephthalate (PET) MPs due to accelerated photodegradation were studied. Moreover, the impacts of MPs photodegradation on their Pb uptake from urban stormwater were examined. The surface morphology investigation revealed the formation of crazes and the crack networks, and the surface chemistry analysis revealed the generation of several oxidized carbon functional groups onto the photodegraded MPs. The degradation of the MPs increased Pb accumulation which followed the pseudo-second-order reaction model. The third chapter examined the role of plastic potable water pipes’ surface aging on their Pb deposition characteristics. The accelerated aging of crosslinked polyethylene-A (PEX-A) and high-density polyethylene (HDPE) pipes was conducted. Surface chemistry analysis of aged pipes revealed the formation of several oxidized carbon functional groups on the surface of the pipes. The kinetics experiments showed that the aged plastic pipes accumulated a significantly greater amount of Pb, which followed the first-order kinetics. The fourth chapter elucidates the mechanistic role of biofilm presence on Pb accumulation onto the PEX-A and HDPE potable water pipes compared to the copper pipes. The kinetics experiments under stagnant conditions showed the biofilm-
laden PEX-A and HDPE pipe accumulated more than three times Pb than their new pipes, but the biofilm presence did not influence Pb accumulation onto the copper pipes. However, under the flow condition, the Pb accumulation on biofilm-laden plastic pipes was lower than their new pipes.
Table of Contents

Chapter One: Introduction 1
   Background and Significance 1
   Problem Statement 3
   Research Goals and Objectives 4
   Dissertation Organization 5
   Products 7

Chapter Two: Plastic Litter Fate and Contaminant Transport within the Urban Environment, Photodegradation, Fragmentation, and Heavy Metal Uptake from Storm Runoff 8
   Abstract 8
   Introduction 10
   Experimental 13
      Materials 13
      Accelerated Degradation Experiments 13
      Quantification of Plastic Fragments 14
      Surface Chemistry Characterizations 14
      Surface Morphology Characterizations 15
      Lead Exposure Experiments and Kinetics Modeling 16
   Results and Discussions 17
      Surface Chemistry Alterations of MPs due to the Photodegradation 17
      Surface Morphology Alterations of MPs due to the Degradation Experiments 22
      MPs Fragmentation due to the Combined Photo and Mechanical Degradations 24
      The kinetics of lead (Pb) uptake by new and photodegraded MPs 27
   Conclusion 30
   Acknowledgment 31
   Reference 32

Chapter Three: Investigation of the Impacts of Potable Water Plastic Pipes’ Surface Aging on their Lead Deposition Characteristics 37
   Abstract 37
   Introduction 39
List of Figures

Figure 1. ATR-FTIR spectra of new, 21 d, and 48 d UVB exposed LDPE MPs

Figure 2. ATR-FTIR spectra of new, 21 d, and 48 d photodegraded PET MPs

Figure 3. Water contact angle analysis of new and UVB-exposed LDPE and PET MPs

Figure 4. FE-SEM images of new, 48 d UVB exposed, and 48 d UVB exposed + 28 d mechanically degraded MPs

Figure 5. The fluorescence microscopy image of the fragments generated by 28 d of mechanical degradation of 48 d photodegraded LDPE

Figure 6. The number of fragments generated by 28 d of mechanical degradation of new (0L), 21 d (21L) and 48 d (48L) photodegraded LDPE, and new (0P), 21 d (21P), and 48 d (48P) photodegraded PET MPs

Figure 7. The size distribution of plastic fragments generated by 28 d of mechanical degradation for (a) new (0L), 21 d (21L), and 48 d (48L) photodegraded LDPE, and (b) new (0P), 21 d (21P), and 48 d (48P) photodegraded PET MPs

Figure 8. (a) The pseudo 2nd order kinetics model and experimental Pb surface loadings for new and photodegraded LDPE MPs, and (b) Pb surface loading on New and photodegraded PET MPs

Figure 9. ATR-FTIR spectra of new, 7 d, and 14 d aged (a) PEX-A and (b) HDPE plastic pipes

Figure 10. High resolution deconvoluted C1s spectra of (a) new PEX-A, (b) 14 d aged PEX-A, (c) new HDPE, and (d) 14 d aged HDPE pipes

Figure 11. The zeta potential of new and aged HDPE pipes versus the pH

Figure 12. First order reaction kinetics model for lead (Pb) accumulations onto the (a) new PEX-A, (b) aged PEX-A, (c) new HDPE, and (d) aged HDPE

Figure 13. Equilibrium Pb surface loading for new and aged (a) PEX-A and (b) HDPE pipes with respect to the residual Pb in the bulk solution

Figure 14. The schematic demonstrating the mechanisms leading to the Pb deposition onto the new and aged plastic water pipes

Figure 15. (a) The rigs used to grow the biofilm onto the pipes' inner wall, and (b) custom apparatus used to measure the zeta potential of HDPE pipes’ inner walls

Figure 16. The zeta potential variations versus pH for new and biofilm-laden HDPE water pipe

Figure 17. The first order kinetics results for Pb accumulation onto new and biofilm-laden water pipes under stagnant conditions
Figure 18. The first order kinetics results for Pb accumulation onto new and biofilm-laden water pipes under flow conditions

Figure 19. Equilibrium Pb surface loading for (a) new and (b) biofilm-laden PEX-A, HDPE, and copper pipes versus residual Pb in the contact water under stagnant condition

Figure 20. Equilibrium Pb surface loading for (a) new and (b) biofilm-laden PEX-A, HDPE, and copper pipes versus residual Pb in the contact water under flow conditions

Figure 21. Schematic demonstrating the mechanisms of the heavy metal adsorption process onto the new and biofilm-laden pipe
List of Tables

**Table 1.** Elemental atomic concentration percentage for C 1s and O 1s in new and aged PEX-A and HDPE pipe samples with 0.1 % uncertainty 51

**Table 2.** The kinetics models’ parameters and non-linear chi-square ($\chi^2$) values for Pb accumulation onto the new and aged plastic pipes 57

**Table 3.** The kinetics models’ parameters and non-linear chi-square ($\chi^2$) values for Pb accumulation onto the new and biofilm-laden water pipes under stagnant and flow conditions 94
Chapter One: Introduction

Background and Significance

Heavy metals [e.g., Zn, Pb, Cu, As, Cr] release into the urban environment could originate from various sources, such as vehicle exhaust emissions and inappropriate industry discharge.\textsuperscript{1–4} They could also be released into potable water from corroded metallic water infrastructure and plumbing materials. Due to the non-destructive, widely dispersible (in water), and highly virulent nature, the bioaccumulation of the heavy metals is a serious threat to the ecosystem affecting the whole food chain, especially humans on top of the food chain.\textsuperscript{5–9} Particularly, lead exposure through tap water can result in severe acute and chronic health impacts such as irreversible developmental and behavioral delays in children, hearing problems, renal dysfunction, and delay in postnatal growth.\textsuperscript{10–13} On the other hand, the superior properties [e.g., durability, lightweight, waterproof, low cost] of plastics have led to a rapid increase in their manufacture for use in packaging, medical treatment, electronics, electrical equipment, building construction, and agriculture. For instance, plastic pipes are increasingly being used to rehabilitate aged water infrastructure and construct new potable water systems, which reduces cost and ameliorates drinking water quality concerns associated with metal pipe corrosion. Rather than durable plastic products, an increasing volume of plastic products are disposable, which could be released to the environment as litter.\textsuperscript{8,14,15} Unlike heavy metals, plastics are degraded during their life cycle, including use and disposal stages, as they expose to external environmental factors such as temperature, pressure, exposure to corrosive chemicals, solar radiation, and abrasive forces.\textsuperscript{1} For instance, plastic pipes conveying the disinfected tap water may get oxidized due to exposure to the free chlorine residuals [degradation during the use cycle]. On the other hand, plastic litter released to the urban environment could be fragmented into smaller plastic particles called
microplastics (d < 5 mm) as they are exposed to solar radiation and mechanical forces [degradation during disposal cycle]. Most of the plastic products contain certain additives [e.g., antioxidants, plasticizers, UV stabilizers, flame retardants, surfactants] added to the polymeric matrix during the molding process to enhance the plastic properties. These additives could be leached out to the environment during degradation and/or fragmentation process, enhancing the risk of the plastics to the environment.

Heavy metals present within the natural and built environment could interact with plastic materials during their use and disposal. Plastic pipes could be exposed to heavy metals in tap water. However, urban litter is exposed to heavy metals in stormwater runoff. The mechanism of heavy metals deposition onto plastic surfaces has been attributed primarily to surface complexation, intraparticle diffusion, and electrostatic attraction. Zou et al. (2020) found the affinity of the heavy metals (i.e., Pb$^{2+}$, Cd$^{2+}$, and Cu$^{2+}$) towards low- and high-crystallinity polyethylene (LPE and HPE), chlorinated polyethylene (CPE), and polyvinyl chloride (PVC) MPs. This study showed that the greater loading of the heavy metals depended on the MPs’ electronegativity and chemical structure rather than their crystallinity. They also showed Cu$^{2+}$ and Cd$^{2+}$ accumulated onto the MPs through surface complexation and electrostatic interaction, whereas the interaction of Pb$^{2+}$ and the MPs were the stronger electrostatic attraction. Another study also showed that the mechanism of Pb$^{2+}$ onto aged nylon MPs is governed by surface complexation. Aged LDPE pipes were found five-times greater heavy metals (i.e., copper, lead, zinc, and manganese) accumulation than new LDPE pipes through electrostatic attraction and surface complexation. Therefore, it is important to comprehend how heavy metals interact with plastic material to better control their persistence within the natural and built environment. The literature demonstrated that the accumulation of heavy metals onto microplastics makes them more toxic. For instance, a
study showed the combined toxicity of nickel (Ni) and carboxyl group present on polystyrene resulted in greater toxicity for water flea *Daphnia magna* than the toxicity of only Ni.\textsuperscript{24} Studying the combined effect of Cu\textsuperscript{2+} and polyacrylonitrile polymer on phytoplankton algae (*C. pyrenoidosa*) growth resulted in the reducing levels of chlorophyll.\textsuperscript{25} Due to the persistence of plastic materials within the environment and their capability to transport heavy metal species, its critical to study the physicochemical mechanisms that control the heavy metals and plastics associations through different stages of their life cycle.

**Problem Statement**

Although there is significant literature concerning heavy metals’ adsorption onto plastic debris in freshwater and marine environments, knowledge regarding the combined physicochemical mechanisms that control the heavy metals’ deposition on the plastic materials within the built environment is limited. However, the water chemistry, hydraulics, and environmental weathering conditions within the built environment could be significantly different from the natural environment. Moreover, lack of knowledge of plastics’ degradation during their use and disposal stages limits the ability of decision-makers and relevant stakeholders to conduct the appropriate management strategies to reduce their environmental and public health risks. This study considers the urban area and building plumbing system as the built environment where heavy metals interact with the plastic litter and plastic potable water pipes.

Stormwater could wash off heavy metals and plastic pollutants to the surrounding water resources.\textsuperscript{26} Despite significant literature on the marine environment, limited understanding is available on the interaction of new and weathered microplastics with heavy metals in stormwater. However, conceptualizing the mechanisms controlling microplastics’
persistence and contaminant transport within the urban environment is crucial to estimate their negative impacts on the ecosystem and develop effective stormwater management practices.

The installation of plastic drinking water materials presents a new and unexplored dilemma in terms of water safety. Moreover, there is a significant knowledge gap regarding the physicochemical and biological mechanisms that control the lead fate and transport within the plastic potable water plumbing materials, which inhibits taking proper control actions to prevent human exposure to lead in tap water. However, this critical knowledge would inform the water providers to select optimal water chemistry conditions to limit metal release from polymer surfaces. The fundamental processes that control heavy metals’ interactions with plastic water infrastructures remain poorly understood. Moreover, the existing literature does not address how heavy metals interact with polymer pipes when biofilms are present and also which water quality factors and water flow conditions facilitate lead accumulation onto and release from inner plastic pipe surfaces.

Research Goals and Objectives

This multidisciplinary research aimed to understand the combined physicochemical processes that control lead deposition onto the plastic surface. This study targets the heavy metal, Lead (Pb), and plastic association within the built environment that includes the urban area and building plumbing systems. Considering the heavy metal's association with microplastics present in urban stormwater, the specific objectives were to (1) investigate the role of microplastics’ photodegradation on their surface morphology and chemistry variations, (2) examine the kinetics of heavy metals uptake by new and photodegraded microplastics, and (3) explore the influence of photodegradation on the fragmentation of the microplastics. Considering the heavy metal's association with plastic potable water pipes, the
specific objectives were to (1) examine the impact of plastic pipe surface aging and biofilm presence on the kinetics of lead accumulation onto the plastic pipes and (2) elucidate the role of Pb initial concentration on the rate of its accumulation onto the new, aged, and biofilm-laden water pipes under water flow and stagnant conditions.

In this dissertation, the following research questions are addressed:

(1) How do the surface morphology and chemistry of microplastics alter due to photodegradation? (2) How does the MPs photodegradation influence their lead uptake in stormwater? (3) How does photodegradation influence the MPs’ fragmentation? (4) What fundamental mechanisms control the heavy metal accumulation onto the plastic pipe? (5) How does plastic pipes’ surface aging influence their heavy metal deposition behavior? (7) How does biofilm presence influence heavy metal deposition onto plastic pipes? (8) How does flow condition influence heavy metal deposition onto the plastic pipes?

Dissertation Organization

Chapter 1 of this dissertation primarily discusses the background, research questions, and objectives. The remaining chapters of this dissertation include three papers presented in chapters 2, 3, and 4. Chapter 5 summarizes the findings of this dissertation. The organization of this dissertation is described as follows:

Chapter 2. Plastic litter fate and contaminant transport within the urban environment, photodegradation, fragmentation, and heavy metal uptake from storm runoff, investigated the surface morphology and chemistry alterations of low-density polyethylene (LDPE) and polyethylene terephthalate (PET) microplastics due to the photodegradation
process. Furthermore, the influence of microplastics’ photodegradation on their heavy metal accumulation and fragmentation behavior was studied as well.

Chapter 3, Investigation of the Impacts of Potable Water Plastic Pipes Surface Aging on their Lead Deposition Characteristics, examined the surface chemistry variations of plastic pipes due to the accelerated aging process, studied its link to the lead deposition behavior and the influence of initial Pb concentration on the rate of its surface loading on the aged plastic pipes.

Chapter 4, Studying Lead (Pb) Deposition onto New and Biofilm-laden Potable Water Pipes, investigated the impacts of biofilm presence on the kinetics of lead accumulation onto the plastic pipes in comparison to copper pipes under stagnant and flow conditions. It also examined the influence of Pb initial concentrations on the rate of its accumulation onto the new and biofilm-laden plastic and metal pipes under water stagnant and flow conditions.

In Chapter 5, Conclusion and Directions for Future Study, the findings of this study are summarized, and the direction for future research is discussed.
Products

Publications


Poster Presentations

1. Association of Environmental Engineering & Science Professors (AEESP) Research and Education Conference – St. Louis, MO (Jun 28-30, 2022)  
   “Investigation of the Combined Physicochemical & Microbiological Processes that Influence Lead Accumulation Within Plastic Potable Water Pipes”

2. The 34th Annual Student Research Forum, The University of Memphis – Memphis, TN (Mar 28th, 2022)  
   “The Surface Oxidation of Plastic Potable Water Plumbing Materials and Its Impacts on Heavy Metal Accumulation”

   “Investigate the Role of Plastic Pipes Aging on Lead Accumulation onto The Plastic Surface”
Chapter Two: Plastic Litter Fate and Contaminant Transport within the Urban Environment, Photodegradation, Fragmentation, and Heavy Metal Uptake from Storm Runoff

Md Hadiuzzaman, Maryam Salehi, Tomoko Fujiwara

Published in *Journal of Environmental Research, Volume 212, Part A, September 2022, 113183*

**Abstract**

A significant portion of urban litter is plastic which contaminates the environment and threatens ecological safety. The conversion of plastic litter into small fragments called microplastics (MPs) intensifies their critical risks by facilitating their transport and altering their physicochemical features. This study focuses on low density polyethylene (LDPE) and polyethylene terephthalate (PET) as the main components of urban litter. The photodegradation of LDPE and PET MPs due to the accelerated weathering experiments is investigated through surface chemistry and morphology analysis. The influence of MPs’ photodegradation on their fragmentation behavior is evaluated through the innovative accelerated mechanical weathering experiments that simulated the abrasion of MPs with the road deposits. Furthermore, the role of MPs as the vehicles to transport heavy metals from the urban environment to the water resources is evaluated by studying the kinetics of lead (Pb) uptake by new and weathered MPs in synthetic stormwater. The surface morphology investigation revealed the formation of crazes and crack networks onto the MPs due to the weathering experiments. The surface chemistry analysis revealed the generation of several oxidized carbon surface functional groups onto the photodegraded MPs and their increased susceptibility to fragmentation due to the abrasion with the road deposits. The photodegradation increased the Pb accumulation onto the LDPE and PET MPs from 467 µg/m² and 21 µg/m² to 2,290 µg/m² and 725 µg/m², respectively, after five days of metal exposure. The fundamental knowledge developed in this research provides a better
conceptual understanding of the mechanisms controlling MPs persistence and contaminant transport within the urban environment, which is crucial to estimate their negative impacts on the ecosystem.
Introduction

Littering within the urban area is a global problem with aesthetic, economical, and environmental impacts.¹ It was estimated to have around 50 billion of litter pieces around the roadways and water ways in the U.S., which counts as 152 pieces of litter per each U.S. resident.² A significant portion of this litter is plastic, which unlike the food scrape and paper wraps, does not decompose readily and rapidly. This is alarming as plastic production has grown rapidly grown from 1.5 million tons annually in 1945 to 359 million tons in 2019.³ Moreover, the COVID-19 pandemic and the urgent need for disposable personal hygiene products and disposable supplies have intensified the plastic pollution problem.⁴ Due to COVID-19 pandemic, the personal protective equipment (PPE) demand increased worldwide.⁵,⁶ For instance, in the U.S., the estimated monthly demand for face masks has risen to 129 billion.⁷ Furthermore, in the U.S., plastic medical waste increased by six-folds to 8.85 million tons at the end of 2020.⁵

Plastic litter exposure to the external mechanical forces within the urban environment, such as vehicles passing the litter, entanglement to the trees/plants or urban structures, and stresses caused by the wind action may result in their conversion to small fragments called microplastics (MPs). The MPs smaller size compared to the original litter could facilitate their transport via wind or storm runoff. Thus, rather than a potential risk to the terrestrial ecosystem, they can impact the aquatic systems or expose humans through inhalation and ingestion.⁸ The literature suggests that stormwater from urban areas and highways is among the major routes conveying MPs from land sources to surface waters.⁹ Stormwater retention ponds have been reported as hotspots for MPs accumulation and their critical role in transporting MPs to the aquatic environment.¹⁰ The presence of MPs in urban storm runoff threatens the aquatic environment and endangers human health.¹¹ Rather than physical threats
caused by the MPs, they can release toxic chemicals and accumulate other contaminants.\textsuperscript{12} Having the water shortage crises growing worldwide, it’s critical to protect the safety of our freshwater resources.\textsuperscript{13}

The MPs’ exposure to solar radiation as they are left within the urban environment could alter their physicochemical characteristics and their subsequent fragmentation behavior. A growing number of studies have been conducted to quantify the MPs’ fragmentation under different environmental conditions.\textsuperscript{14–16} Song et al. (2017) studied the combined effect of UV and mechanical degradation of low-density polyethylene (LDPE), polypropylene (PP), and expanded polystyrene (EPS) within the simulated beach environment.\textsuperscript{17} Julienne et al. 2019 studied fragmentation of LDPE film due to photodegradation in air and water.\textsuperscript{18} Chubarenko et al. (2020) examined the fragmentation behavior of sinking polystyrene (PS), flexible LDPE, foamed PS, and buoyant PP simulating sea swash region with natural beach sediments.\textsuperscript{14} Mechanical degradation is critical as it influences the fragmentations of MPs to smaller fractions and impacts their sinking and buoyancy behavior.\textsuperscript{19} Several studies have reported accumulation of MPs within the road deposits,\textsuperscript{20,21} however, the extent of MPs fragmentation due to the abrasion by the silt and sand particles present within the road deposit is still unknown. The MPs present within the road deposits around the roadways and water ways could be transported via stormwater runoff to the water resources.\textsuperscript{22} MPs’ environmental degradation may impact the propensity of MPs to accumulate contaminants and transport them over long distances.\textsuperscript{23} Our recent study revealed an increased Pb accumulation onto the low density polyethylene (LDPE) pellets that were aged by ozonation compared to the new LDPE pellets.\textsuperscript{24,25} The literature has reported elevated concentrations of heavy metals such as Ni, Cu, Pb, and Zn on parking lots and paved roads due to vehicle emissions.\textsuperscript{26} On the other hand, lots of plastic fragments may also be found within this area due to the common plastic littering. Stormwater could wash off both these contaminant and
transport them to the surrounding water resources.\textsuperscript{27} Despite significant literature on the marine environment, a very limited understanding is available on the interaction of new and weathered MPs with heavy metals in stormwater. In this study lead (Pb) was selected as a model heavy metal due to its significant health impacts and toxicity toward the aquatic organisms.\textsuperscript{28}

This study aims to better understand the fate and contaminant transport behavior of plastic litter within the urban environment. The specific objectives are to (1) investigate the degree of surface chemistry and morphology changes of LDPE and PET MPs due to the photodegradation, (2) examine the influence of MPs’ photodegradation on their fragmentation behavior due to their simulated abrasion with the road deposits, and (3) investigate the critical role of MPs weathering on their Pb uptake in stormwater. LDPE and PET were selected as they are two of the most common manufactured non-biodegradable thermoplastics in the world, widely used as disposable plastic bags and beverage bottles.\textsuperscript{29, 30} This research particularly targets the plastic pollutants within the urban environment and customizes the fragmentation investigations to simulate the conditions where microplastics are abraded with the sediments present within the road deposits. Linking the microplastics’ photodegradation to their heavy metals transport within the storm runoff is another innovative aspect of this research that underscores the potential environmental risks associated with plastic pollution within the urban environment.
Experimental

Materials

The LDPE and PET films (thickness 0.01 cm) were purchased from McMaster-Carr, USA. The Lead (Pb) ICP-MS standard (1000 mg/L in 3% nitric acid) was purchased from RICCA Chemical Company (Arlington, TX, USA). Sodium Chloride (NaCl), Zinc Chloride (ZnCl₂), and Nile Red were purchased from Fisher Scientific (Waltham, MA, USA). Whatman No. 1 filter paper of pore size 1.2 µm and 11 µm were purchased online from Cole-Parmer, USA. Ultrapure Milli-Q™ (18MΩ*cm) treated water was used for conducting all the experiments. The particle size for the sand used for mechanical fragmentation varied between 425 µm and 1000 µm. The sand was pretreated before the experiments, as described elsewhere.³⁰

Accelerated Degradation Experiments

The QUV accelerated weathering tester (Model: QUV, Serial No.: 84-2132-27, Volts: 120, Hz: 60, Watts: 1200, The Q-Panel Company, Ohio, USA) was utilized for the accelerated photodegradation experiments. Ultraviolet B (UVB) radiation extends from around 280 nm to 315 nm wavelength within the UV spectrum. The UVB bulbs with wavelength 313 nm were used to accelerate the degradation of the plastic films as this radiation wavelength simulates the UVB radiation of the sunlight. More information is provided in A-1 (Appendix A). For accelerated mechanical degradation experiments, 10 g of sand was added to 250 mL of an amber glass bottle containing a single 0.5 cm × 0.5 cm square-sized LDPE or PET MPs sample. An amber glass bottle was used to prevent further photo exposure to the MPs. Three replicates were used for each condition. The bottles were
shaken by a Lab-Line Orbital Shaker (Lab-line Instruments Inc.) for 28 days at 200 rpm at room temperature.

Quantification of Plastic Fragments

The plastic fragments generated by accelerated mechanical degradation of LDPE and PET samples were separated from the sand by floating in a NaCl solution (density of 1.2 g/cm$^3$) and ZnCl$_2$ solution (density of 1.5-1.7 g/cm$^3$), respectively. Fragmented MPs were filtered using filter paper (pore size of 1.2 µm) and stained with Nile Red solution (5 mg/L Nile Red in hexane) on the filter paper. The fluorescence microscope was a Nikon A1R laser confocal scanning fluorescence microscope with 488 nm excitation and 568 nm solid-state lasers for emission and photomultiplier tubes (PMT) to collect emitted light. The images were analyzed with the ImageJ (version, 1.53a) software to count the number of fragmented MPs. The MPs quantification method utilized in this research was able to quantify the MPs with the size range of 10 µm to 120 µm. More information regarding the quantification and control samples is provided in A-2 (Appendix A).

Surface Chemistry Characterizations

The surface chemistry characterization was conducted for photodegraded MPs. The ATR-FTIR transmission spectra were recorded using a Perkin-Elmer Universal ATR-FTIR spectrophotometer from 4000 to 650 cm$^{-1}$ with a 4 cm$^{-1}$ resolution. The degree of photodegradation of LDPE films was evaluated by determining the presence of carbonyl (C=O) and vinyl (CH$_2$=CH$_2$) groups at the wavenumbers of 1715 cm$^{-1}$ and 909 cm$^{-1}$, respectively. On the other hand, the photodegradation of PET was determined from the comparative spectra and carboxyl index (CXI). The carbonyl index (CI), vinyl index (VI),
and CXI were calculated as described in A-3 (Appendix A). The X-ray photoelectron spectroscopy (XPS) measurements of photodegraded LDPE and PET were performed using a Thermo Scientific Spectrometer XPS equipped with a monochromatic Al Kα radiation (hν = 1486.6 eV) with an X-ray source operating power of 75 W at 12 kV. More information is provided in A-3 (Appendix A). The surface wettability alterations of the MPs due to the photodegradation were characterized by the water contact angle measurements. The Biolin Scientific Attention Tetha attached with Vivitar lenses was used to measure the water contact angles. LDPE and PET MP samples were mounted on a glass slide with double-sided clear tape. The water was used as a sessile drop, and it was Millipore grade with pH 7. For all the measurements, three replicates were used.

Surface Morphology Characterizations

The FE-SEM imaging was employed to evaluate the surface morphology of MPs due to the photo and mechanical degradation. An FEI Nova NanoSEM 650 attached to Oxford X-MaxN Silicon Drift detector was used at 10 kV with uniform 2500× magnification. More information is provided in A-4 (Appendix A). The alterations of MPs’ surface roughness due to the photodegradation were examined using Atomic Force Microscopy (AFM Workshop, TT-AFM). The scanning rate was 0.5 Hz with tapping mode, and a silicon probe was used with a constant force of 58 N/m on a scan area of 25 µm² for a sample at room temperature. The average roughness (nm), \( R_{av} \) was calculated using Equation (1) \(^{30} \)

\[
R_{av} = \frac{\sum_{i=1}^{N} |Z_i - \bar{Z}|}{N}
\]

(1)
The new and 48 d photodegraded LDPE and PET MPs were exposed to Pb solution at pH=7.0, using synthetic stormwater in the 50 mL polytetrafluoroethylene (PTFE) bottles. The chemical composition of the synthetic stormwater is listed in Table A-1 (Appendix A). Kinetic experiments were conducted by exposing MPs to 300 µg/L Pb solution for six (2, 6, 12, 24, 48, and 120 h) time intervals at 21.6 ± 1 °C. Eight MPs were added to a 12 mL of Pb solution (S/V ratio of 1:3 cm²/mL) in a 50 mL PTFE bottle, and three replicates were used for each sample (each time interval). The MPs were removed from the exposed solutions with tweezers at different time intervals and digested in 10 mL of 2% nitric acid for at least 24 h. Only for a few of the bottles, the 48-d photodegraded LDPE MPs were broken into smaller pieces and separated using the 11 µm pore size filter paper. However, for reporting the metal accumulation data, it was assumed that surface area was constant throughout the experiments. The kinetics of Pb adsorption onto the new and photodegraded LDPE and PET MPs were examined through pseudo 1st and 2nd order kinetics models. The pseudo 1st order kinetics model best describes the physical adsorption; however, the pseudo 2nd order kinetics model best describes the adsorption process where chemical association occurs between adsorbents and adsorbate species. Information regarding the Pb quantification and statistical analysis is provided in A-6 and A-7 in Appendix A, respectively.
Results and Discussions

Surface Chemistry Alterations of MPs due to the Photodegradation

(A) *ATR-FTIR spectroscopy*: The ATR-FTIR spectra of new LDPE MPs demonstrated the asymmetric and symmetric bands of C-H stretching at 2915 and 2845 cm\(^{-1}\), respectively. The asymmetric and symmetric bending vibrations of CH\(_2\) appeared at 1467 and 1462 cm\(^{-1}\). The peaks due to the bending vibrations of CH\(_3\) and rocking vibrations of CH\(_2\) appeared at 1377 cm\(^{-1}\) and 730 cm\(^{-1}\), respectively (Figure 1).\(^{33}\) The new peaks appeared at 1715 cm\(^{-1}\) and 909 cm\(^{-1}\), representing the carbonyl (C=O) and vinyl (CH\(_2\)=CH\(_2\)) groups for LDPE MPs after UVB irradiation for 21 d and 48 d.\(^{34}\) The carbonyl and vinyl indices for new LDPE MPs were increased from 0.0 to 1.9 and from 0.1 to 1.1, respectively, after 21 d of UVB radiation. The 48 d of UVB exposure has increased the carbonyl index to 2.91 and the vinyl index to 1.92. Our results were confirmed by prior studies that reported increased carbonyl and vinyl indices with exposure time for LDPE films exposed to sunlight for up to 21 months.\(^{33,35}\)

The photodegradation of LDPE initiates by absorbing UV radiation due to the chromophoric defects present in the polymer structure. The UVB radiation (wavelength 360-280 nm with a peak at 313 nm) has sufficient energy (79.42 to 102.11 kcal/mol) to break down the chemical bonds in LDPE (e.g., C-C \(\rightarrow\) 77-83 kcal/mol; C-H \(\rightarrow\) 94-99 kcal/mol).\(^{36,37}\) Thus, the hydrogen abstraction may occur following the UV absorbance, which leads to the formation of radicals, intermediate hydroperoxide products, and finally, the carbonyl groups.\(^{38}\) Additional UV exposure causes the carbonyl functional groups to follow the Norrish type I and/or Norrish type II reactions, leading to the chain scission. In the Norrish type I reaction, the chain scission is caused by the cleavage of a C-C bond which results in the formation of two free radicals to be reacted and creates the fragments of the
polymer chain. The Norrish type II reaction also causes the chain scission by forming vinyl groups and diradical moiety within the chain.\textsuperscript{39}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{ATR-FTIR spectra of new, 21 d, and 48 d UVB exposed LDPE MPs}
\end{figure}

The ATR-FTIR spectra of new and photodegraded PET MPs are shown in Figure 2. The main peaks of the new PET MPs appeared at 1713 cm\textsuperscript{-1} and 1370 cm\textsuperscript{-1}, representing the carbonyl (C=O) and gauche wagging CH\textsubscript{2}, respectively. The trans wagging CH\textsubscript{2} and aromatic ether (C-O) were found at 1340 cm\textsuperscript{-1} and 1241 cm\textsuperscript{-1}. The bands that appeared at 1094 cm\textsuperscript{-1}, 870 cm\textsuperscript{-1} and 720 cm\textsuperscript{-1} demonstrated the aliphatic ether (C-O), aromatic out of plane wagging C-H, and aromatic in-phase wagging C-H, respectively\textsuperscript{40}. Decreasing the intensity of all characteristic peaks of PET MPs (except gauche wagging CH\textsubscript{2}) due to the UVB radiation indicates the possible photodegradation of this polymer.\textsuperscript{41} This result is confirmed by other studies which reported decreasing the peak intensity for carbonyl or ketone, aromatic ether, aliphatic ether, aromatic out of the plane, and in-phase wagging C-H, due to the photodegradation of PET bottles in the marine environment.\textsuperscript{40} As reported in the literature, the carboxyl end groups are forming due to the photodegradation of PET, thus, further information regarding the extent of PET photodegradation can be inferred from the magnitude of the carboxyl index (CXI). The carboxyl end groups are expediting further
The 21 d UVB radiation of PET MPs increased the carboxyl index for the new PET MPs from 0.67 to 0.71. Additional exposure to UVB radiation (up to 48 d) increased CXI to 0.78. The CXI value increased from 56.1% to 73.2% after 21 and 48 days, respectively, of UVB exposed compared to the new PET. The broad peak appeared approximately from 3650 to 2150 cm\(^{-1}\) on ATR-FTIR spectra of 48 d UVB irradiated PET MPs can be assigned to the -OH vibration of the –COOH functions in carboxylic acid end groups that were generated by further degradation and chain scission of PET.\(^{44,45}\) Literature suggested the Norrish Type II pathway for the photodegradation of PET in the air.\(^{42,44}\) In this process, hydrogen abstraction occurs through the chain propagations and results in the generation of initial radicals. Then hydroxyl and alkoxy radicals are generated through photolysis of hydroperoxides. These hydroxyl radicals will substitute in the phenylene ring to generate the monohydroxy terephthalate groups in the polymeric chain.\(^{46}\) The schematics of photodegradation processes for LDPE and PET are shown in Schematic-1 and Schematic-2 in Figure A-1 (Appendix A).

![Figure 2. ATR-FTIR spectra of new, 21 d, and 48 d photodegraded PET MPs](image-url)
(B) XPS analysis: The XPS survey spectra and high-resolution C 1s spectra for new and UVB-exposed LDPE and PET MPs are shown in Figure A-2 and Figure A-3, respectively, in Appendix A. For both polymers, the C 1s peak at 284.6-284.7 eV was the dominant feature associated with the LDPE and PET chemical structures. The O 1s peak for both new LDPE and PET samples was found at 532.1-534.1 eV binding energy. The O 1s peaks for the new LDPE and PET MPs could be due to their intrinsic surface oxidation. As expected, the percentage of oxygen for photodegraded LDPE and PET samples was greater compared to the new samples, confirming their photooxidations due to UVB exposure. The ratios of oxygen to carbon (O/C) and oxidized carbon to unoxidized carbon (C$_{\text{ox}}$/C$_{\text{unox}}$) demonstrate an ascending trend of oxygen content with increasing the duration of UVB exposure for both LDPE and PET MPs (Table A-2, Appendix A). Analyzing the C 1s spectra revealed four types of oxidation states for carbon, including C-C, C-O, C=O, and O-C=O for both 21 d and 48 d UVB-exposed LDPE MPs. On the other hand, for the new, 21 d, and 48 d UVB exposed PET MPs, three types of oxidation states were found for carbon as C-C, C-O, and O-C=O. Carboxylic (O-C=O) end groups could be generated on the PET surface through the Norrish Type II reactions where an intramolecular γ-hydrogen abstraction occurred, creating a cyclic intermediate resulting from the polymer chain scission. The oxygen content on the surface of the PET MPs has been increased with the increased duration of UVB exposure as the generated radicals reacted further with the surrounding atmospheric oxygen.

(C) Water contact angle analysis: Significant reductions in water contact angles were found for both LDPE and PET MPs due to the photodegradation (Figure 3). The water contact angle for new LDPE MPs was reduced by 31 % (from 92 ° to 63 °) due to 48 d of UVB exposure. The water contact angle for new PET MPs was reduced by 44 % (from 85 ° to 48 °) due to 48 d of UVB exposure. The reduction in the water contact angles for LDPE MPs,
compared to their new MPs, after 7 d, 14 d, and 21 d of UVB exposure were 4 %, 16 %, and 29 %, respectively. Similarly, the water contact angles were reduced by 11 %, 36 %, and 37 % for the PET MPs after the same UVB exposure durations. Thus, the increased duration of photodegradation promoted hydrophilicity for two studied MPs. Generally, the surface wettability increases with increasing the surface roughness and developing of the polar surface functional groups. The AFM analysis conducted in this study revealed the greater surface roughness of MPs with an increased duration of UVB exposure. The increased polarity of LDPE and PET MPs could be due to the formation of oxidized carbon and hydroxyl surface functional groups due to the UVB exposure, as confirmed by ATR-FTIR spectroscopy.51

Figure 3. Water contact angle analysis of new and UVB-exposed LDPE and PET MPs
(A) **FE-SEM Imaging:** The visual observations revealed an opaque appearance for LDPE MPs and discoloration of clear PET MPs to yellowish as early as seven days of the UVB exposure. The FE-SEM images demonstrated the alteration of the smooth, homogenous, and compact surfaces of new LDPE and PET MPs to the nonhomogeneous and rough surfaces after 48 d of UVB exposure (**Figure 4**). Wrinkles and flakes were identified on the surface of LDPE and PET MPs after 48 d of UVB exposure. This result of LDPE MPs is confirmed by Ranjan and Goel. (2019) that reported an increased surface roughness and flakes formation on the LDPE surface after 30 d of UVB exposure.\(^{52}\) Other studies showed that the photodegradation of PET occurs by developing hydroperoxides, which produce free radicals to initiate degradation and contributes to surface roughness.\(^{53,54}\) Subsequent exposure of our 48 d photodegraded LDPE and PET MPs to the mechanical forces applied for 28 d through abrasion with sand particles resulted in creating a network of cracks and granular texture on the surface of both MPs; however, the cracks on LDPE surfaces were wider and deeper than those on the PET MPs. The granular texture was generated mainly through sand/silt accumulated onto the plastic surfaces after the subsequent mechanical abrasion. As discussed in our recent study, during the accelerated mechanical degradation experiments, the sharp edge of sand/silt particles could abrade the plastic surface and create the resting space for penetration and further accumulation of smaller silt particles onto the MPs surface.\(^{30}\) However, the lower hardness and greater plasticity of LDPE MPs (41-46 D) compared to the PET MPs (84 D) promoted its deformation by the sand/silt particles and enhanced the silt accumulation onto its surface.\(^{30}\) The study conducted by Gewert et al. (2015) confirmed similar surface morphology alterations for LDPE and PET plastics that were degraded in natural solar radiation and under natural mechanical forces, where the LDPE plastics were
found more brittle, degraded, and fragmented than PET samples. Therefore, though both the polymer MPs were exposed to a similar duration of UVB exposure before subsequent mechanical abrasion, the LDPE MPs became more brittle than PET MPs, as reported by the previous studies, thus, LDPE MPs showed greater morphological changes than PET MPs after a similar duration of subsequent mechanical degradation.

![Image of FE-SEM images](image)

**Figure 4.** FE-SEM images of new, 48 d UVB exposed, and 48 d UVB exposed + 28 d mechanically degraded MPs

(B) **Atomic Force Microscopy (AFM) analysis:** The AFM analysis also confirmed the increases in surface roughness of LDPE and PET MPs with an increased duration of UVB exposure. **Figure A-4 in Appendix A** shows the slight increases in surface roughness of photodegraded LDPE and PET MPs compared to their new MPs. After 21 d of UVB exposure, the surface roughness of new LDPE and PET MPs was increased from 30.3 to 35.6 nm and from 1.9 to 2.1 nm, respectively. However, after 48 d of UVB exposure, the surface roughness of LDPE and PET MPs increased to 52.20 nm and 7.00 nm, respectively (**Figure A-4, Appendix A**). The FE-SEM images confirmed this finding by demonstrating the generation of nonhomogeneous and rough MPs’ surfaces after UVB exposure. This increased
roughness could be due to photoinduced reactions that occurred during the UVB exposure.\textsuperscript{58} The FE-SEM images of UVB exposed and mechanically weathered MPs also clearly demonstrated significant changes in surface morphology, which could be mainly due to the silt/sand accumulation onto the MPs due to the mechanical weathering process. Our recent study also demonstrated an increased surface roughness for MPs that were mechanically weathered using a similar procedure.\textsuperscript{30}

\textit{MPs Fragmentation due to the Combined Photo and Mechanical Degradations}

The mechanical disintegration of plastics into smaller segments is defined as fragmentation. In this study, the degree of fragmentation of new and 48 d photodegraded LDPE and PET MPs were examined by applying the abrasive wear forces as they were shaken with the sand particles to simulate their abrasion with the sediments present in the road deposits. Surface abrasion is reported by literature as one of the primary mechanisms contributing to the generation of many daughter fragments following plastic weathering.\textsuperscript{17, 59} As we described in our recent study, the abrasion of plastics with the sharp edge of sand particles could generate grooves, scratches, and a network of microcracks onto the surface of the plastic.\textsuperscript{30} The repetitive process of plastics abrasion with sand particles resulted in the penetration of these microcracks into the plastic structure and, subsequently chipping of the small plastic fragments, as shown in Figure 5. The results demonstrated that after 28 d of mechanical degradation experiments, a greater number of fragments were generated from a single 21 d UVB exposed LDPE MPs (3,986 ± 706) and PET (3,179 ± 751) MPs compared to a single new LDPE MPs (2,250 ± 233) and PET MPs (1,549 ± 171) (\textit{p}-value < 0.05) (Figure 6). Although a significant increase in the number of fragments generated by 48 d UVB exposed LDPE MPs (8,397 ± 2259) compared to the 21 d UVB exposed MPs (\textit{p}-value < 0.05), the number of fragments released from 48 d UVB exposed PET MPs (4,238 ± 1002)
was not significantly increased compared to the 21 d UVB exposed PET MPs ($p$-value > 0.05) (Figure 6). The order of LDPE_{uv48d} > PET_{uv48d} > LDPE_{uv21d} > PET_{uv21d} > LDPE_{new} > PET_{new} in terms of fragments generated after 28 d of mechanical degradation. Loss of plastics’ mechanical properties due to the photodegradation in combination with applied shear forces and tensile stresses has been suggested in the literature to result in plastic fragmentation.\textsuperscript{60} The weakening, breakage, and shortening of the polymeric chain backbone and leaching of plasticizers due to the UVB irradiation make the plastics more brittle, and subsequent exposure to mechanical forces accelerate the formation of cracks and surface defects in the plastics.\textsuperscript{14,17} Formation of a greater degree of surface cracks stimulates the generation of plastic fragments as these cracks to connect and chip off the debris.\textsuperscript{61} Our visual observations showed that the erosion of MPs mainly occurred around their edges. The greater number of fragments generated by LDPE MPs compared to PET MPs can be explained by the physical and mechanical properties of these polymers. The LDPE film (0.913 g/cm$^3$) was less dense than the PET film (1.384 g/cm$^3$). Therefore, LDPE was more susceptible to being torn apart when exposed to mechanical force as loosely packed material is more likely to fragmentation compared to densely packed material.\textsuperscript{17} In addition, LDPE’s lower hardness and tensile strength (41-46 D and 9.65-21.99 MPa) compared to the PET (84 D and 193.05 MPa) could be responsible for its more significant fragmentation. Despite the similar duration of UVB exposure, the LDPE MPs became more brittle than PET, as reported by the previous studies.\textsuperscript{56,57} Therefore, LDPE MPs generated a greater number of fragments due to the combined photo and mechanical degradations than PET MPs.
The diameter of 84.8% of the fragments generated by mechanical degradation of new LDPE MPs varied between 10 µm to 30 µm (Figure 7a). However, the diameter of 15.2% of these generated fragments was between 30 µm to 120 µm. This size distribution was slightly changed for the fragments generated from 21 d and 48 d UVB-exposed LDPE MPs. The diameter of 79.6% and 75.8% of generated LDPE fragments was between 10 µm to 30 µm, respectively, for 21 d and 48 d UVB-exposed LDPE MPs (Figure 7a). On the other hand, the diameter of 80.5% of the fragments generated from new PET MPs varied from 10 µm to 30 µm, and only the diameter of 19.5% of the generated fragments varied from 30 µm to 120 µm (Figure 7b). This size distribution was slightly changed for the fragments generated from 21 d and 48 d UVB-exposed PET MPs. The diameter of 90.0% and 85.7% of generated PET fragments were between 10 µm to 30 µm, respectively, 21 d and 48 d UVB exposed PET MPs (Figure 7b). As reported by the literature, the photodegradation made the LDPE MPs more brittle than PET MPs\textsuperscript{56,57}; therefore, the implemented accelerated mechanical degradation resulted in the generation of greater number of larger diameter fragmented...
particles from LDPE MPs than PET MPs. Future quantification of polymeric chain scissions, plasticizers leaching, and tensile strength variations due to the UVB radiation could promote understanding of photodegraded LDPE and PET MPs fragmentation behavior. The size of generated MPs is very critical as it determines their transport mechanism within the environment, potential ecological hazards, and contaminant transport behavior. The larger surface of smaller MPs provides a greater number of adsorption sites for the contaminant accumulation. Furthermore, the greater degree of LDPE MPs fragmentation could be due to their lower density, hardness, and tensile strength compared to the PET MPs.  

**Figure 7.** The size distribution of plastic fragments generated by 28 d of mechanical degradation for (a) new (0L), 21 d (21L), and 48 d (48L) photodegraded LDPE, and (b) new (0P), 21 d (21P), and 48 d (48P) photodegraded PET MPs

*The kinetics of lead (Pb) uptake by new and photodegraded MPs*

In this study, the kinetics of Pb adsorption onto the new and 48 d UVB-exposed LDPE and PET MPs were investigated through the five-day metal exposure experiments. The results revealed a significantly greater (p-value < 0.05) level of Pb surface accumulation onto the photodegraded LDPE MPs compared to the new samples (Figure 8a). During the first
two hours of Pb exposure, the photodegraded LDPE MPs accumulated 47.3 % of their equilibrium Pb surface loadings, while the new LDPE MPs obtained 53.6 %. However, the equilibrium Pb surface loading on photodegraded LDPE MPs (2,264 µg/m²) was almost five folds greater than the new samples (464 µg/m²). The Pb accumulation onto the new LDPE MPs followed the pseudo 1\textsuperscript{st} order kinetic model ($r^2 = 0.98$) as the adsorption of Pb occurred mostly through the mass transfer process with presumably no chemical association occurring.\textsuperscript{47} However, the oxidized carbon functional groups (C-O, C=O, O=C=O) present on the 48 d photodegraded LDPE surface promoted the accumulation of the positively charged Pb species present in the synthetic stormwater through surface complexation\textsuperscript{62}, and/or electrostatic attractions.\textsuperscript{63} Therefore, the pseudo 2\textsuperscript{nd} order kinetic model ($r^2 = 0.92$) best described the Pb uptake by the photodegraded LDPE MPs. Increased accumulation of Pb species onto degraded polymeric surfaces has been reported previously, attributing to the increased specific surface area\textsuperscript{64}, presence of polar functional groups, and increased hydrophilicity.\textsuperscript{65} The half-life ($t_{1/2}$), from the pseudo 1\textsuperscript{st} order kinetic model, for Pb species was longer for the photodegraded LDPE MPs (8.9 h) than the new LDPE MPs (7.1 h) (Table A-3, Appendix A). The maximum Pb accumulation onto the photodegraded LDPE MPs was found as 25.5 %, and for new LDPE MPs were found as 5.2 % of the total Pb present in the synthetic stormwater. The Pb surface loading onto the new PET MPs after 2 h of metal exposure was found as 136 µg/m² (1.51 % of Pb\textsubscript{t}) and increased to the maximum of 265 µg/m² (2.94 % of Pb\textsubscript{t}) after 6 h of the exposure. This Pb surface loading was gradually decreased to 21 µg/m² after five-day of exposure (Figure 8b). The maximum Pb adsorption onto the photodegraded PET MPs was found as 1,314 µg/m² (14.60 % of Pb\textsubscript{t}) after 24 h exposure. This Pb surface loading gradually decreased to 725 µg/m² (8.05 % of Pb\textsubscript{t}) after five-day exposure period (Figure 8b). The greater level of Pb accumulation onto the photodegraded PET MPs, compared to the new PET MPs, could be due to the presence of
carboxyl (O-C=O) group on their surface, which promoted electrostatic interaction, surface complexation and/or surface coordination with the Pb species present in the aqueous solution. However, we were not able to fit neither the pseudo 1\textsuperscript{st} order nor the pseudo 2\textsuperscript{nd} order kinetic model to the Pb adsorption data for both new and photodegraded PET MPs, similar to the study conducted by Coskun and Soykan (2006).\textsuperscript{66} Godoy et al. (2019) also showed a lower adsorption capacity of heavy metals onto PET compared to polyethylene.\textsuperscript{67} Our further investigation demonstrated significantly greater Pb surface loadings ($p$-value < 0.05) onto the 48 d UVB exposed LDPE (2,237 ± 225 µg/m\textsuperscript{2}) and PET MPs (1,084 ± 108 µg/m\textsuperscript{2}) compared to the 21 d UVB exposed LDPE (783 ± 140 µg/m\textsuperscript{2}) and PET MPs (834 ± 88 µg/m\textsuperscript{2}), respectively (Figure A-5, Appendix A). These greater Pb surface loadings could be explained by the presence of greater percentages of oxidized carbon functional groups onto the 48 d UVB exposed LDPE MPs (14.3 \%) compared to the 21 d UVB exposed LDPE MPs (19.2 \%) as discussed in XPS analysis. Furthermore, the greater carboxyl index of 48 d UVB-exposed PET (0.78) compared to the 21 d UVB exposed PET MPs (0.71), also indicates the greater polarity of the plastic surface due to the longer UVB exposure, which promoted the electrostatic interaction and coordination with the Pb species.

Figure 8. (a) The pseudo 2\textsuperscript{nd} order kinetics model and experimental Pb surface loadings for new and photodegraded LDPE MPs, and (b) Pb surface loading on New and photodegraded PET MPs
Conclusion

In this study, the fate and contaminant transport behavior of LDPE and PET MPs as the model urban litter were investigated. Calculation of carbonyl and carboxyl indices for the UVB-exposed LDPE and PET MPs demonstrated an increased degree of photodegradation over longer UVB exposure periods. The photodegradation of both LDPE and PET MPs increased the degree of their fragmentation by making them more brittle. A greater number of fragments were released from new and photodegraded LDPE MPs compared to new and photodegraded PET MPs. The kinetics study demonstrated a greater level of Pb accumulation onto the photodegraded LDPE and PET MPs compared to the new MPs. With the rapidly growing consumption of plastic products and an increasing number of intensive storm events, it is critical to develop effective municipal policies and initiatives to limit and control the extent of this plastic pollutant released to the urban environment, particularly in areas of low socioeconomic status and urban communities where there is little awareness of environmental pollution. This study will inform necessary changes in regulatory systems to address MPs’ release to storm runoff. Implementing plastic pollution control policies could be promoted through effective social engagements and motivations.
Acknowledgment

The authors would like to thank Dr. Felio Perez, Dr. Omar Skalli, Tanvir Ahmed, and Khashayar Aghilinasrollahabadi for their assistance during experiments or sample analysis.

Funding for this work was provided by the National Science Foundation grant CBET-2044836 and the United States Department of Agriculture, National Institute of Food and Agriculture (USDA/NIFA) Award number 2020-67019-31166.


15. Lambert S, Wagner M. Formation of microscopic particles during the degradation of


28. DeSimone D, Sharafoddinzadeh D, Salehi M. Prediction of children’s blood lead levels from exposure to lead in schools’ drinking water—A case study in Tennessee,


56. Íñiguez ME, Conesa JA, Fullana A. Recyclability of four types of plastics exposed to


Chapter Three: Investigation of the Impacts of Potable Water Plastic Pipes’ Surface Aging on their Lead Deposition Characteristics

Md Hadiuzzaman, David Ladner, Maryam Salehi

Abstract

The application of plastic potable water pipes to replace corroded metallic plumbing and construct new potable water plumbing systems is rapidly increasing due to their low cost, noncorrosive characteristics, and easy installation. However, unlike metallic pipes, knowledge of heavy metals’ fate within plastic potable water is limited. Thus, this study was conducted to elucidate the role of plastic pipe surface aging on their lead (Pb) deposition characteristics under stagnant conditions. For this purpose, the accelerated aging of crosslinked polyethylene-A (PEX-A) and high-density polyethylene (HDPE) pipes was conducted by exposure to the concentrated solution of chlorine residuals at an elevated temperature. The surface chemistry variations of plastic pipes due to the aging process were examined via attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS) analysis. The kinetics of Pb deposition onto the new and aged pipes were studied through 5 d Pb exposure experiments. Moreover, the influence of initial Pb concentration [50-1000 µg/L] on the rate of Pb deposition onto the plastic pipes was investigated. The ATR-FTIR and XPS analysis revealed the formation of several oxidized carbon functional groups [>C-O, >C=O, >O-C=O] on PEX-A pipe and HDPE pipe surfaces after 14 d of accelerated aging. The zeta potential measurement of HDPE pipes showed a slightly more negative surface charge for the aged pipe than the new pipe. The kinetics experiments showed that at equilibrium, the aged PEX-A (380 µg/m²) and HDPE (420 µg/m²) pipes deposited greater levels of Pb compared to the new PEX-A (265 µg/m²) and HDPE (329 µg/m²) pipes, respectively. However, the difference was not
statistically significant \((p\text{-value} > 0.05)\) for neither PEX-A nor HDPE pipes. The Pb deposition onto the new and aged PEX-A and HDPE pipes followed first order kinetics model implying diffusion of Pb species into the pipe micropores. A significantly \((p\text{-value} < 0.05)\) greater rate of Pb deposition was found for aged PEX-A compared to the new PEX-A with increasing the Pb initial concentration; however, this rate was not significantly \((p\text{-value} > 0.05)\) different for aged and new HDPE pipes. This study provides the groundwork for future investigations into the fate of heavy metals in potable water infrastructure.
Introduction

In the U.S., plastic pipes and fittings have been used in water distribution networks for more than 60 years. Metallic pipes are replaced with plastic pipes that are lightweight, inexpensive, easy to install, and do not face corrosion problems.\(^1\) Polyethylene (PE) and polyvinyl chloride (PVC) comprise more than 90% of the plastic materials used for water distribution systems.\(^2\) Crosslinked polyethylene (PEX) and high density polyethylene (HDPE) pipes are being installed primarily for service line connections and building potable water plumbing systems.\(^3\) Among the three types of commercially available PEX pipes [PEX-A, PEX-B, PEX-C], types A and B are more commonly used for drinking water plumbing systems. The PEX pipe installation rate has increased from 7% in 2001\(^4\) to 54% for the renovations and 75% for the new building construction in 2013.\(^5\) On the other hand, utilization of HDPE pipes for new buildings construction has been estimated as 13%, which was doubled during the last decade.\(^2\)

Although the plastic potable water pipes are not subjected to corrosion, they may get chemically aged as they are used to convey the disinfected drinking water. Free chlorine (Cl\(_2\)) and chlorine dioxide (ClO\(_2\)) are two strong oxidants that are used for the disinfection of drinking water. Previous studies demonstrated that disinfectant residuals present within the tap water could attack and oxidize the PEX pipes.\(^6\)–\(^8\) Antioxidants such as 2,4, di-tert-butylphenol, and 2,6-di-tert-p-benzoquinone are added to PEX pipes during the manufacturing process to prevent their oxidation due to the chlorinated drinking water.\(^9\) However, leaching the antioxidants out of the plastic pipes during the first couple of years of their service makes them susceptible to oxidation by chlorine residuals.\(^6\),\(^7\) The field investigations have demonstrated the formation of carbonyl (>C=O) and ether (>C-O-C<)
functional groups onto the PEX pipe's surface as a result of exposure to chlorinated water.\textsuperscript{8,10,11}

The polyethylene degradation mechanism was described to initiate with a hydrogen abstraction process, free radicals formation, and generation of peroxyl radicals, resulting in the creation of alcohols, acids, aldehydes, ketones, and unsaturated groups.\textsuperscript{12,13} Carbonyl groups on the plastic pipe surfaces are formed due to the chlorine free radicals attacking the pipe material, where hydrogen abstraction is followed by oxygen insertion.\textsuperscript{14–16} Plastic pipes exposed to the aqueous free chlorine solution undergo surface oxidation, polymer chain scission, and finally, mechanical failure by developing cracks along the pipe wall.\textsuperscript{16} Carbonyl groups are the foremost indicators of polyethylene degradation and the formation of the group on the pipe surfaces exposed to chloramine and chlorine dioxide. HDPE and PEX pipes were found aged with the free chlorine at 2 mg/L concentration, which is typically present within the drinking water.\textsuperscript{17} Rather than durability issues raised by the oxidation of plastic pipes, the polar surface functional groups created on the plastic surface as the result of this oxidation may alter the physicochemical interactions of the pipe surface with the chemical and microbiological contaminants that are generally present within the tap water, enhancing the risk of their accumulation onto the pipe surface.\textsuperscript{3}

Heavy metals could be released into the plastic potable water plumbing system from raw water sources [e.g., Fe, As], treatment practices [e.g., Mg, Mn], water distribution systems [e.g., Fe], and building plumbing systems [e.g., Cu, Pb].\textsuperscript{18–20} Previous studies have shown leaching of metals from metallic pipes and brass fittings.\textsuperscript{21} Metal-plastic hybrid potable water plumbing is commonly found within residential buildings, as existing metallic pipes are partially replaced with new plastic pipes. In the case of the complete replacement of metallic pipes with plastic pipes, metallic fittings such as brass connections, valves, and
copper elbows are still used. Moreover, many plastic potable water plumbings are connected to metallic service lines [e.g., lead, copper]. A recent study reported the metal deposition on downstream PEX pipe due to corrosion of upstream copper pipe and brass fittings. The accumulation of Ca, Mn, and Zn onto the downstream HDPE water mains was reported.

There is extensive literature investigating the effect of microplastics’ aging on their heavy metal adsorption behavior in the marine environment. However, only a few studies have examined this process under potable water chemistry conditions. The degraded microplastics provided a greater heavy metal adsorption capacity than the virgin microplastics as the degradation alters their physicochemical properties, such as surface functional groups, specific surface area, and zeta potential. Heavy metal adsorption varies depending on the plastic type and aging condition. Salehi et al. (2017) and Holmes et al. (2012 & 2014) have reported increased adsorption of Cd, Co, Cr, Cu, Ni, and Pb onto the aged polyethylene compared to the new plastic. The oxidized surface functional groups present in the plastic structure were found responsible for the greater metal uptake.

Holmes et al. (2012) reported that the adsorption process achieved equilibrium or new and aged pellets within 25 h to 100 h of exposure duration. Li et al. (2020) demonstrated that UV and chromic acid degraded microplastics adsorbed a greater level of heavy metals than the new microplastics.

The physical confinement of heavy metals onto the plastic surface, electrostatic interaction, and chemical association of heavy metal species with plastic surface functional groups could be impacted by surface morphological and chemical changes caused by plastic degradation and environmental weathering. The previous studies demonstrated that oxidized LDPE pellets and films had a higher surface area and hydrophilicity than new LDPE, resulting in a greater Pb^{2+}, Cu^{2+}, Mn^{2+}, and Zn^{2+} uptake from water. Mao et al.
(2020) studied the adsorption of Pb$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, Ni$^{2+}$, and Zn$^{2+}$ onto the new and aged polystyrene (PS) and found increased adsorption capacity as a function of aging intensity. They attributed this greater amount of heavy metal accumulation possibly due to the PS's physicochemical features, such as surface roughening and the emergence of oxygen-containing groups on the PS's surface. Evidence from the plastic pollution literature also showed other plastics such as HDPE and PVC sorb heavy metals. However, information regarding the influence of plastic pipe surface aging on the heavy metal accumulation on their surface is lacking. Thus, this study aimed to investigate the influence of plastic pipe surface oxidation on Pb deposition behavior for PEX-A and HDPE pipes. The specific research objectives were to (1) examine the surface chemistry changes of plastic pipes due to the accelerated aging process, (2) investigate the kinetics of Pb accumulation onto the new and aged plastic pipes, and (3) identify the influence of Pb initial concentration on the rate of its accumulation onto the plastic pipes.
Experimental

Materials

Cross-linked polyethylene-A (PEX-A) and high-density polyethylene (HDPE) pipes were purchased from McMaster-Carr, USA. Lead (Pb) ICP-MS standard (1000 mg/L in 3% nitric acid) was purchased from RICCA Chemical Company (Arlington, TX, USA). The 7.5% sodium hypochlorite (NaOCl) solution was obtained from a local store (Memphis, TN, USA). Nitric acids (68 % purity) were purchased from fisher scientific (Hanover Park, IL, USA). All the experiments were conducted using Ultrapure Milli-Q™ (18MΩ*cm) treated water unless described otherwise.

Pipe Disinfection and Accelerated Aging Experiments

The PEX-A and HDPE pipes were rinsed with tap water and disinfected with chlorinated water to clean the manufacturing residues prior to the experiments. For this purpose, the pipes were filled with approximately 100 mg/L as total Cl₂ solution prepared using tap water and kept for 24 h at room temperature. Then, the chlorinated water was dumped from the pipes, and rinsed with tap water and ultrapure water. The accelerated aging process of the plastic pipes was conducted by filling the plastic pipe segments with 5000 mg/L as total Cl₂ solution at 70 °C, at pH 6.5 for up to 14 d. The chlorinated water was stagnant in the filled pipes during this aging process, and the contact water was replaced every 3 d with newly prepared fresh chlorinated water. Filling all the pipes with chlorinated water, both ends of the pipes were sealed with PTFE-wrapped rubber stoppers and placed in an electric oven to maintain the temperature of 70 °C. After 7 d, some of the pipe sections were collected for ATR-FTIR analysis, and the rest of the pipes were removed from the oven.
after 14 d. Then the chlorinated water was dumped from the pipes and rinsed with tap water and ultrapure water prior to further experiments and analysis.

Surface Chemistry Characterizations

(a) Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) Spectroscopy: The ATR-FTIR absorption spectra were acquired by a Perkin-Elmer Universal ATR-FTIR spectrophotometer from 4000 to 400 cm\(^{-1}\) with 8 cm\(^{-1}\) spectral resolution. Polymer oxidation has been frequently estimated using the intensity of carbonyl and vinyl bonds in previous studies.\(^{42-45}\) In this study, the extent of the pipes' surface aging was examined by determining the development of carbonyl and vinyl groups at wavenumber 1715 cm\(^{-1}\) and 909 cm\(^{-1}\), respectively.\(^{46,44}\) Using Equations (2) and (3), carbonyl index (CI) and vinyl index (VI) values were determined, whereas \(A_{1715}, A_{1715}, \) and \(A_{909}\) represent the absorbance of methylene (>CH\(_2\)), carbonyl (>C=O), and vinyl (>CH\(_2\)=CH\(_2\)<) functional groups, respectively.\(^{43,44}\)

\[
\text{Carbonyl index (CI)} = \frac{A_{1715}}{A_{2870}} \tag{2}
\]

\[
\text{Vinyl index (VI)} = \frac{A_{909}}{A_{2870}} \tag{3}
\]

(b) X-ray Photoelectron Spectroscopy (XPS): The X-ray photoelectron spectroscopy (XPS) quantifications were accomplished by a Thermo Scientific K-Alpha XPS equipped with a monochromatic Al K\(\alpha\) radiation (\(h\nu = 1486.6\) eV). The X-ray source operating power was 75 W at 12 kV, and the analysis area was 400 \(\mu m^2\) for each sample. During the experiment, the analysis chamber base pressure was maintained 8.0 \(x\) 10\(^{-10}\) mBa. Photoelectrons were accumulated from a 90\(^\circ\) takeoff angle relative to the sample surface. The survey spectra were taken with a pass energy of 200 eV, and the high-resolution spectra were taken at 40 eV, with 0.1 eV energy step size, using an average of 40 scans. The XPS data analysis was
accomplished using Thermo Avantage Software v5.995. Gaussian Lorentzian peaks were used for fitting all the core level experimental data, and Shirley backgrounds were used as background corrections. Curve-fittings were performed until good fittings were obtained.

Zeta Potential Measurement

The zeta potential measurements were carried out utilizing an electrokinetic analyzer (SurPASS, 2010 model, Anton Paar USA, Ashland, VA) on new and aged HDPE pipes to determine how the surface charge of the plastic pipe fluctuates because of the degradation of the surface of the pipes. According to the pipe size and the dimensions of the cell holder, the customized adapters were designed to measure the zeta potential. Figure B-1 in Appendix B illustrates how the pipe was pinched to squeeze it into a narrow channel. The flow rate was maintained at 50 to 100 mL/min at a pressure drop of 300 mbar. This analysis was carried out using tap water. The titration curve was produced using zeta potential against pH (3.0-9.5). More information regarding this experiment is described in the Experimental section of chapter 4.

Metal Exposure Experiments

The new and aged PEX-A and HDPE pipes were cut into 30 cm segments for Pb exposure experiments. Synthetic tap water was used; the constituents of synthetic tap water are mentioned in Table B-1 in Appendix B. For the kinetics experiments, 18 pipe segments were utilized to have three replicates for 6-time intervals (2, 6, 12, 24, 48, and 120 h). They were filled with 300 µg/L Pb solution at pH=7.8. To study the influence of initial Pb concentration on its rate of deposition onto the pipes, pipe segments with three replicates filled with the Pb aqueous solution at five concentrations (50, 150, 500, 750, and 1000 µg/L)
at pH=7.8. The solution pH was adjusted using sodium hydroxide (NaOH) and hydrochloric acid (HCl). An Oakton® pH 450 portable pH Meter was used to measure the pH of the solutions. Pipe ends were sealed with PTFE-wrapped rubber stoppers and were placed horizontally on a benchtop at room temperature during the metal exposure experiments. For kinetics experiments, 3 replicates were removed after each time interval, and the solution was collected for Pb quantifications. However, for the experiments conducted to study the impact of initial Pb concentration, the samples were removed after 48 h, and the solution was analyzed for the Pb quantifications. Concentrated nitric acid was added to make all the solutions a 2 % nitric acid solution for quantifying the remaining Pb in the solutions. The solutions were analyzed using a Perkin Elmer Analyst 400 Atomic Absorption Spectrometer attached to an HGA 900 graphite furnace to quantify the Pb concentrations. Pb calibration curve was prepared using 0, 5, 10, 25, 50, 75, and 100 μg/L of Pb solutions with the coefficient of determination ($r^2$) value 0.993 and detection limit of 10 μg/L. Statistical analysis is described in the supplemental section (B-1, Appendix B).

**Kinetics Modeling**

The kinetics of Pb accumulation onto the new and aged plastic pipes were investigated through first order (Equations 4-6) and second order kinetics models (Equations 7, 8). The parameters in these equations demonstrate that $t$ is time, $q_t$ is the Pb surface loading at time $t$, $q_e$ is Pb surface loading at equilibrium, $k_1$ and $k_2$ are first order rate constant and second order rate constant, respectively. The half-life, $t_{1/2}$, is the amount of time needed for the pipe to deposit half of the equilibrium Pb surface loading. The first order kinetics model best describes physical adsorption. It assumes that the rate of the accumulation of solute onto the adsorbent is proportional to the difference between saturation surface loading and the amount of adsorbed solute over time as shown in Equation 4. But the second
order kinetics model best describes chemical associations between adsorbents and adsorbate species during the adsorption process. The second model assumes that the rate controlling step is the chemical association between the solute and adsorbate surface functional groups. In this model, the rate of adsorption relies on the adsorption capacity of the adsorbent and not the solute concentration. Chi-square ($\chi^2$) was employed as a goodness of fitting test by comparing the equilibrium adsorption data of experimental and calculated from the models (Equation 9). The parameters $q_{e,exp}$ and $q_{e,m}$ are experimental and calculated model equilibrium adsorption data, respectively.

\[
\frac{dq_t}{dt} = k_1(q_e - q_t) 
\]

(4)

\[
q_t = q_e(1 - e^{-k_1t}) 
\]

(5)

\[
t_{1/2} = \frac{\ln 2}{k_1} 
\]

(6)

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2 
\]

(7)

\[
q_t = \frac{q_e k_2 t}{1 + q_e k_2 t} 
\]

(8)

\[
\chi^2 = \sum_{i=1}^{n} \frac{(q_{e,exp} - q_{e,m})^2}{q_{e,m}} 
\]

(9)
Results and Discussion

Plastic Pipes Surface Chemistry Variations due to the Aging

(A) ATR-FTIR Spectroscopy: The ATR-FTIR spectroscopy analysis of new and aged plastic pipes revealed significant variations in PEX-A and HDPE pipes due to the accelerated aging process. As shown in Figure 9a, the ATR-FTIR characteristic bands of new PEX-A pipes are the asymmetric band of >C-H stretching at 2915 cm\(^{-1}\), a symmetric band of >C-H stretching at 2846 cm\(^{-1}\), >CH\(_2\) symmetric bending vibrations at 1470 cm\(^{-1}\) and >CH\(_2\) asymmetric bending vibrations 1465 cm\(^{-1}\). Moreover, the bending vibrations of >CH\(_3\) appeared at 1370 cm\(^{-1}\), and the rocking vibration of >CH\(_2\) was found at 730 cm\(^{-1}\).\(^{51,52}\) The surface chemistry of PEX-A after undergoing 7 d and 14 d of accelerated aging experiments was altered significantly. For the PEX-A pipe that underwent 7 d of accelerated aging, the new peaks appeared at 1715 cm\(^{-1}\), 1260 cm\(^{-1}\), and 909 cm\(^{-1}\), which indicate the formation of carbonyl (>C=O), ether (>C-O-C), and vinyl (>C=C) groups, respectively, on the inner surface of the PEX-A pipes.\(^{53,54}\) The presence of >C=O functional group is an important indicator of PEX-A pipe aging and the subsequent formation of aldehydes, ketones, or carboxylic acids on its surface.\(^{53}\) The presence of vinyl groups at the end of the polymeric chain leads to the chain session.\(^{55}\) The carbonyl and vinyl indices of the new PEX-A pipe were increased from 0.25 to 0.69 and from 0.27 to 0.82, respectively, after 7 d aging. However, the extent of PEX-A pipes aging remained almost unchanged even if they undergone an additional 7 d aging under similar conditions. It could be due to the limited strength of the chlorinated aqueous solution in further degradation of the PEX pipe, as suggested by the literature.\(^{56}\) Whelton et al. (2011) also reported that accelerated aging using 45 mg/L as free chlorine at pH 6.5 for 141 d at 37 °C left no impact on the bulk or surface characteristics of PEX-A pipe.\(^7\) The aging of PEX-A was confirmed by the studies that showed the degradation and even chain sessions occur due
to the presence of the oxidized functional groups and unsaturated carbon-carbon double bonds.\textsuperscript{11,44,57} Our previous study on exhumed one-year-old PEX-A pipes used for hot and even cold water supply in a residential plumbing system in Indiana revealed that the white PEX-A pipe became yellowish and the oxidized groups such as \( >\text{C}-\text{O}-\text{C} \) and \( >\text{C}-\text{O} \) were found on the inner surface of the pipes which confirmed degradation.\textsuperscript{32,53}

\textbf{Figure 9.} ATR-FTIR spectra of new, 7 d, and 14 d aged (a) PEX-A and (b) HDPE plastic pipes
The ATR-FTIR characteristic spectra of the new and aged HDPE pipes are shown in Figure 9b. The main three methylene (>CH\textsubscript{2}) group absorption peaks appeared as doublets at 2917 and 2849 cm\textsuperscript{-1} (asymmetric and symmetric stretching), 1472 and 1460 cm\textsuperscript{-1} (bending angular strain), and 730 and 718 cm\textsuperscript{-1} (rocking), respectively.\textsuperscript{58,59} The new peaks appeared as a broad hydroxyl (>\text{O-H}) at around 3370 cm\textsuperscript{-1}, carbonyl (>\text{C=O}) at 1650 cm\textsuperscript{-1}, and vinyl (>\text{C=C}) at 909 cm\textsuperscript{-1} due to the HDPE pipe aging.\textsuperscript{60,61} The carbonyl and vinyl indices were 0.54 and 0.64 for the new HDPE pipe and were increased to 0.84 and 1.11, respectively, due to 7 d of aging. By extending the degradation process up to a total of 14 d, unlike PEX-A pipes, the HDPE pipes showed enhanced degradation, demonstrating the carbonyl and vinyl indices increased to 0.95 and 1.12, respectively. Different aging behavior for PEX-A and HDPE pipes due to the increased duration of aging, in addition to their microstructural differences, might be related to the type and percentage of the antioxidants present within their structure. Our results are in agreement with the recently published studies that reported the appearance of carbonyl (>\text{C=O}) functional group onto the HDPE pipe surface due to accelerated degradation (45 mg/L as Cl\textsubscript{2}, 50 mg/L alkalinity, pH 6.5, temperature 37 °C, and exposure 141 d).\textsuperscript{7}

(B) X-Ray Photoelectron Spectroscopy (XPS) Analysis: The XPS analysis was conducted to better understand the extent of oxidized surface functional groups formed on the pipe surface due to the accelerated aging experiments. Analyzing the XPS survey spectra for new and aged PEX-A and HDPE pipes revealed a strong peak at 284.9 – 285.0 eV for the convoluted C1s and a comparatively weaker peak at 534.1 eV for O1s (Figure B-2, Appendix B).\textsuperscript{18,62} In addition to carbon and oxygen, chlorine was also detected on the pipe surface due to its usage for conducting accelerated aging experiments, although we have rinsed the pipes after aging experiments with tap water and then with ultrapure water. The elemental atomic percentage
(%) of C and O were resolved with 0.1\% uncertainty by analyzing the XPS high resolution spectra (Table 1). Figure 10 shows the deconvolution of C 1s high-resolution spectra into three or four subpeaks (e.g., >C-C/<C-H, >C-O, >O-C-O/<C=O, and >O-C=O). The deconvoluted subpeaks are assigned as >C-C/<C-H, >C-O, >O-C-O/<C=O, and >O-C=O for corresponding binding energies at 284.95 – 285.02, 286.38 – 286.64, 287.91 – 288.25, 288.94 – 289.50 eV, respectively. It's possible that the O 1s peaks for the new PEX-A and HDPE are the results of their inherent surface oxidation. Due to the interaction of >C-C< with the chlorine, the extent of >C-C< bonds in new PEX-A and HDPE pipes reduced from 80.4\% and 90.7\% to 71.1\% and 67.7\%, respectively, after 14 d of aging. On the other hand, the percentage of >C-O< group increased from 17.6\% to 27\% by 14 d aging the PEX-A pipes, and the percentage of >C-O< and >C=O increased from 7.8\% and 1.4\% in new HDPE pipes to 24\% and 5.5\% in 14 d aged HDPE pipes. The degree of surface oxidation was calculated using carbon oxidized to unoxidized carbon (C_{ox}/C_{unox}) and is shown in Table 1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Parameters</th>
<th>C 1s</th>
<th>O 1s</th>
<th>Cl 2p</th>
<th>C_{ox}/C_{unox}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C-C</td>
<td>C-O</td>
<td>C=O</td>
<td>O-C=O</td>
</tr>
<tr>
<td>PEX-A</td>
<td>New</td>
<td>80.4</td>
<td>15.0</td>
<td>4.6</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>14 d Aged</td>
<td>77.2</td>
<td>17.6</td>
<td>-</td>
<td>5.2</td>
</tr>
<tr>
<td>HDPE</td>
<td>New</td>
<td>90.7</td>
<td>8.1</td>
<td>1.2</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>14 d Aged</td>
<td>73.6</td>
<td>9.3</td>
<td>17.1</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>67.7</td>
<td>23.7</td>
<td>5.5</td>
<td>3.0</td>
</tr>
</tbody>
</table>
Figure 10. High resolution deconvoluted C1s spectra of (a) new PEX-A, (b) 14 d aged PEX-A, (c) new HDPE, and (d) 14 d aged HDPE pipes

Variations in Surface Charge due to Aging

Zeta potential measurements were conducted for the new and aged HDPE pipes to better understand how surface oxidation of this plastic pipe influences its electrostatic interactions with the Pb species that are present in water. As shown in Figure 11, the zeta potential for new HDPE pipe varied between 0 to -137 mV, however, it varied from -27 to -121 mV for aged HDPE pipe. There was a more negative surface charge with increasing pH,
as is typical for virtually all surfaces, due to lower H\textsuperscript{+} and higher OH\textsuperscript{-} concentrations. The presence of oxidized carbon functional groups such as carbonyl (>C=O), ether (>C-O-C<), and carboxyl (>O-C=O<) in aged HDPE surface increase the negative charge. This finding agrees with the results reported by Liu (2021) who also found a more negative surface charge for UV/O\textsubscript{3} treated poly (methyl methacrylate) PMMA. The oxygen containing surface functional groups, specifically carboxyl (>COOH) was, presented as the major contributor to the more negative surface charge.\textsuperscript{65} Moreover, the study conducted by Asadinezhad et al. (2012) also demonstrated a more negative surface charge for the plasma-treated PVC compared to the new PVC samples due to the presence of a greater level of oxidized carbon surface functional groups [e.g., >C=O, >COOH, >C-O-C<].\textsuperscript{66} More negative surface charge may have promoted the electrostatic attraction of neutral and positively charged Pb species to the plastic pipe surface and consequently increased their surface deposition.

![Figure 11](image.png)

**Figure 11.** The zeta potential of new and aged HDPE pipes versus the pH
The Pb deposition experiments were conducted using synthetic tap water at pH=7.8 and [Pb]₀=300 µg/L initial concentration. Solving the relevant complexation and solubility reactions revealed that at this condition, 93.55% of total Pb existed as insoluble species of the Pb(OH)_2 and the rest were dissolved species. This indicates that for the kinetic experiments, in addition to the adsorption of dissolved Pb species into the plastic pipe surface, precipitation also occurred. Thus, we refer to the Pb uptake by plastic pipe surface as Pb deposition that involves adsorption and precipitation. The kinetics of Pb deposition onto the plastic pipes surface was examined to better explain how aging and surface oxidation of plastic pipe surface alters their physicochemical interactions with the Pb in water. The Pb equilibrium surface loading showed that the aged PEX-A pipes (380 µg/m²) deposited greater level of Pb compared to the new PEX-A pipes (265 µg/m²), and the aged HDPE pipes (420 µg/m²) also deposited greater level of Pb than the new HDPE pipes (329 µg/m²). However, the difference was not statistically significant (p-value > 0.05) for neither PEX-A nor HDPE pipes. During the first two hours of exposure, the aged PEX-A pipe deposited 94.8% of its equilibrium Pb surface loading, whereas the new PEX-A pipes nearly completely obtained their equilibrium Pb surface loading. On the other hand, during the first two-hour of Pb exposure, the aged HDPE pipes showed a similar trend as new and aged PEX-A pipes, whereas the aged HDPE pipes accumulated 92.8% Pb surface loading of their equilibrium, and the new HDPE pipe accumulated almost all the equilibrium amount. The equilibrium Pb surface loading onto the aged PEX-A pipe was found to be 31.7%, whereas the equilibrium Pb surface loading onto the new PEX-A pipe was only 22.1% of the total Pb [Pb]₀ in the synthetic tap water. The aged HDPE pipes accumulated 31.7% of the total Pb [Pb], like the aged PEX-A, in the synthetic tap water as their equilibrium surface loading, but the new
HDPE pipes obtained only 24.0 %. In addition, the comparison with Pb accumulation showed the surface loading of Pb onto the new HDPE (329 µg/m²) pipe was not significantly (p-value > 0.05) greater than the new PEX-A (265 µg/m²). Similarly, the aged HDPE pipes (420 µg/m²) deposited greater amount of Pb than aged PEX-A (380 µg/m²) however, the difference was not statistically significant.

First order and second order reaction models were used to describe the Pb deposition mechanisms onto the plastic pipes. First order model demonstrates a more physical process involving diffusion of adsorbate from the aqueous solution to the micropores present on the adsorbent surface.\(^{67}\) However, the second order model considers the chemical association as the rate-controlling step.\(^{50,68}\) The non-linear first and second order models were compared using a nonlinear chi-square (\(\chi^2\)) test to ascertain which model better suited the kinetics of Pb onto the plastic pipes (Table 2). The experimental data of Pb accumulation onto the new and aged PEX-A and HDPE pipes were fitted to the non-linear first and second order models (Figure 12). The \(\chi^2\) values of the first order models were found to be slightly smaller than second order models for all the studied pipes indicating the diffusion of Pb species onto the surface micropores as the dominant mechanism resulting in Pb accumulation onto the pipe surface. This agrees with our recent study demonstrating the pseudo first order kinetics model for the new LDPE pellets,\(^{45}\) however is different from our past finding of pseudo second order kinetics model for the ozone-aged LDPE and UVB degraded LDPE and PET plastic films.\(^{48}\) It should be noted that the Pb kinetics experiment on the ozone-aged LDPE pellets was conducted in ultrapure water. However, the kinetics on the UVB-degraded plastic films were conducted in synthetic stormwater. Moreover, the differences in the applied methods of surface aging and the intrinsic differences [e.g., surface morphology, porosity] of pellets and films with the plastic pipes (used for the current work) could have contributed to this finding.\(^{45,48}\) In this study, surface diffusion plays a greater role in Pb deposition onto the pipes
rather than rate-controlled chemical association processes as the calculated $\chi^2$ values (of the first and second order models) were so close to each other for the aged pipes. The half-life ($t_{1/2}$) calculation revealed that the half-life duration for degraded (0.4 h) and new (0.4 h) PEX-A were similar; however, the half-life for aged HDPE (0.8 h) pipes was slightly greater than new HDPE (0.6 h) pipes.

![Diagram](image)

**Figure 12.** First order reaction kinetics model for lead (Pb) accumulations onto the (a) new PEX-A, (b) aged PEX-A, (c) new HDPE, and (d) aged HDPE pipes.
Table 2. The kinetics models’ parameters and non-linear chi-square ($\chi^2$) values for Pb accumulation onto the new and aged plastic pipes

<table>
<thead>
<tr>
<th>Samples</th>
<th>Parameters</th>
<th>First order reaction model</th>
<th>Second order reaction model</th>
<th>$q_e, \text{exp}$ (µg/m$^2$)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEX-A</td>
<td>New</td>
<td>$q_e, \text{model}$ (µg/m$^2$)</td>
<td>$K_1$ (h$^{-1}$)</td>
<td>$t_{1/2}$ (h)</td>
<td>$q_e, \text{model}$ (µg/m$^2$)</td>
</tr>
<tr>
<td></td>
<td>14 d Aged</td>
<td>288.0</td>
<td>1.89</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>HDPE</td>
<td>New</td>
<td>387.1</td>
<td>1.91</td>
<td>0.4</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>14 d Aged</td>
<td>335.3</td>
<td>1.20</td>
<td>0.6</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Influence of Lead (Pb) Initial Concentration on its Deposition Rate onto the New and Aged Plastic Pipes

The influence of Pb initial concentration on the rate of its deposition onto the new and aged plastic water pipes was investigated. At equilibrium, Pb surface loading with respect to the residual Pb concentration remaining in the solution was graphed, and slopes were determined as the rate of the Pb deposition. The linear regression revealed, with increasing the Pb initial concentration from 50 µg/L to 1000 µg/L, Pb surface loadings on the aged and new PEX-A increased linearly with a very good coefficient of determination ($r^2$) (Figure 13a). The values of the $r^2$ for aged PEX-A and new PEX-A pipes were 0.96 and 0.97, respectively. The maximum Pb surface loading onto the aged PEX-A pipe was found as 2,304 µg/m$^2$ greater than the Pb surface loadings onto the new PEX-A (1,859 µg/m$^2$), but the difference was not significant ($p$-value > 0.05). However, the rate of Pb deposition (slope) onto the aged PEX-A pipes was found to be greater than the new PEX-A pipes, and the difference was statistically significant ($p$-value < 0.05). This maximum Pb surface loading obtained by our bench-scale experiments is within the range of Pb loadings reported by the field experiments. For instance, the study conducted by Huang et al. (2019) showed that six-month old exhumed PEX-A pipe from a U.S. residential house contained 100 – 135,200 µg/m$^2$ Pb surface loading. The metal deposition on the PEX-A pipes can be attributed to the
possible formation of metal oxides and oxyhydrides at elevated temperatures and a slightly basic system within the potable water plumbing. 

**Figure 13.** Equilibrium Pb surface loading for new and aged (a) PEX-A and (b) HDPE pipes with respect to the residual Pb in the bulk solution
The Pb surface loading onto the aged and new HDPE pipes increased linearly with raising the Pb initial concentration from 50 µg/L to 1000 µg/L (Figure 13b). The $r^2$ values for aged and new HDPE pipes were $r^2 = 0.99$ and $r^2 = 0.95$, respectively. Unlike PEX-A pipes, the maximum Pb surface loading onto the aged HDPE pipes was found as 1,868 µg/m² less than the maximum Pb surface loading onto the new HDPE (1,909 µg/m²); however, the difference was not statistically significant ($p$-value > 0.05). Similarly, the rate of Pb deposition onto the aged HDPE was lower than new HDPE pipes, and the difference was insignificant ($p$-value > 0.05). At the lower initial concentrations of Pb$^{2+}$ solutions majority of Pb species are present as dissolved species (Pb$^{2+}$, PbOH$^+$), thus surface adsorption is the process that controls the deposition of Pb species onto the plastic pipe surface. However, with increasing the Pb$^{2+}$ initial concentration and exceeding the solubility constants for Pb(OH)$_2$ (s) [$K_s=10^{8.15}$] and PbCO$_3$ (s) [$K_s=10^{-13.13}$], the precipitate is formed in the solution and on the inner surface of the plastic pipes. As our previous research reported, the metal species initially adsorbed onto the plastic could act as nucleation sites for the metal crystals to grow and precipitate to accumulate on the plastic surface (Figure 14).$^{72}$ Thus, under a lower range of Pb concentrations, the pipe aging and thus surface oxidation influenced the adsorption of Pb species; however, by increasing the Pb initial concentrations, we had increased layers of insoluble Pb species that are precipitating onto the pipe surface; therefore we did not find a significant difference in the maximum Pb surface loadings for new and aged PEX-A and HDPE pipes.
Figure 14. The schematic demonstrating the mechanisms leading to the Pb deposition onto the new and aged plastic water pipes

Limitations and Practical Implications

This study was associated with some limitations in terms of conducting accelerated aging process and running the metal exposure experiments only under stagnant condition. Due to the logistic considerations to complete the aging process within a short duration, the elevated dosage of free chlorine residuals at high temperatures was utilized for the creation of oxidized surface functional groups onto the pipe surfaces. However, under real operational conditions, the plastic potable water pipes were exposed to a lower concentration of free chlorine (< 2.0 mg/L) at a lower temperature for years. Moreover, although in this study, the Pb exposure experiments were conducted only under stagnant conditions, the plastic pipes used for building plumbing are experiencing both stagnant and flow conditions that vary by the buildings’ residents’ water use behavior. Shorter contact between the plastic pipes’
surface sites and metal species present in the water under water flow conditions and greater mass transfer gradient adjacent to the pipe surface may alter the rate of Pb accumulation onto the new and aged plastic pipes. Despite the limitations, this study provided valuable insights regarding the critical roles of plastic pipes’ surface aging/oxidation on their association with Pb and consequently its transport behavior. Antioxidants are added to the plastic pipes during the manufacturing process to prevent their oxidations due to exposure to the disinfectant residuals in tap water. However, the gradual leaching of antioxidants out of the pipe structure over time makes plastic pipes more susceptible to aging, specifically those pipes carrying hot water. The creation of oxidized surface functional groups onto the plastic surface and slight changes in the surface charge impacts the physicochemical interactions of the pipe's inner walls with the organic, inorganic, and microbiological contaminant that are present within the tap water. Although this study only focused on Pb due to its significant acute and chronic toxic effects, future research is needed to examine how plastic pipe surface aging impacts biofilm accumulation or organic contaminant diffusion onto the pipe surface. Moreover, this study only focused on the deposition of Pb species onto the pipes; future research is needed to identify the physicochemical drivers of Pb mobilization within the plastic potable water system.
Conclusion

In this study, the mechanistic role of plastic potable water pipes’ surface aging on Pb deposition onto their inner surface was examined under stagnant conditions. The accelerated aging of these plastic pipes using the chlorine residuals at an elevated temperature significantly altered their surface chemistry by creating the oxidized carbon functional groups [e.g., >C=O, >C-O-C<]. The surface aging and formation of oxidized carbon functional groups made the plastic surface more negative compared to the new pipes. The kinetics experiments revealed a significantly greater level of Pb deposition onto the aged PEX-A and HDPE pipes compared to the new pipes at the equilibrium. The greater electrostatic interactions and potential surface complexations could have promoted Pb accumulation onto the aged pipes compared to the new pipes. Increasing the Pb initial concentration resulted in a greater Pb surface deposition onto the new and aged PEX-A and HDPE pipes. A greater rate of Pb deposition was found for aged PEX-A pipes compared to the new PEX-A pipes. The Pb adsorption onto the new and aged PEX-A and HDPE pipes followed first order kinetics model implying the diffusion of Pb species onto the pipe micropores as the major mechanism leading to the Pb deposition onto the new and aged plastic pipes. The results of this study could serve as a foundation for future studies on the fate of heavy metals in water infrastructure.
Acknowledgement

Funding for this work was provided by National Science Foundation grant CEBT-2309475. The authors thank Colton Kirby and Marvin Dassael Lopez for their assistance with the pipe loop experiments. The authors also thank Dr. Felio Perez for their assistance with conducting the XPS analysis.
Reference


6. Whelton A, Dietrich AM, Duncan SE. Edamame Variety Development-Sensory and Chemical Quality View project Cyberbiosecurity for Agriculture and Food System View project. 2007. doi:10.2166/wst.2007.190


67. Rodrigues AE, Silva CM. What’s wrong with Lagergreen pseudo first order model for


Chapter Four: Studying Lead (Pb) Deposition onto New and Biofilm-Laden Potable Water Pipes

Md Hadiuzzaman, Nahreen Mirza, Shawn P Brown, David A Ladner, Maryam Salehi

Abstract

With badly corroded metal pipes and an increased rate of plastic water pipes installation for municipal potable water, understanding the drivers of heavy metals' fate within these plumbing materials is crucial but lacking. Heavy metal interactions with plumbing material are further complicated due to the differential formation of biofilms within pipes that can modulate, transform, or sequester heavy metals. This research elucidates the mechanistic role of biofilm presence on Lead (Pb) accumulation onto crosslinked polyethylene (PEX-A) and high-density polyethylene (HDPE) potable water pipes as compared to copper pipes. For this purpose, biofilms were grown on these pipes for three months. Five-day Pb exposure experiments were conducted to examine the kinetics of Pb accumulation onto the new and biofilm-laden pipes. Biofilm biomass was quantified, and zeta potential measurements were conducted to quantify the extent of biofilm growth and its effects on the pipe’s inner walls’ surface charge variation. Moreover, the influence of the initial concentration of Pb [50-1000 µg/L] on the rate of Pb accumulation onto pipes was examined. All metal exposure experiments were conducted at stagnant and water flow conditions to simulate various water use behavior often found within residential buildings. The results revealed greater biofilm biomass on PEX-A pipes (2.97×10^9 copies/cm^2) than both copper (1.07×10^8 copies/cm^2) and HDPE pipes (1.19×10^8 copies/cm^2). The zeta potential of biofilm-laden HDPE pipes was found to be slightly more negative compared to the new HDPE pipes. After five days of Pb exposure under stagnant conditions, the biofilm-laden PEX-A (980 µg/m^2) and HDPE (1.170 µg/m^2) pipe accumulated more than three times
the Pb loading rates compared to the new PEX-A (265 µg/m²) and HDPE pipes (329 µg/m²), respectively. Biofilm presence did not alter the extent of Pb accumulation onto the copper pipes under stagnant conditions. Under flow conditions, Pb accumulation on biofilm-laden plastic pipes was lower than on new pipes, which might be due to the shorter interactions of Pb species with the biofilm surface. The first order kinetics model best described the Pb accumulation onto both new and biofilm-laden water pipes under both stagnant and flow conditions, indicating diffusion as the significant mechanism transporting Pb species from the aqueous solution to the pipe surface. This study will provide a foundation for continued exploration of heavy metal fate in water infrastructure and provide an understanding of metal adsorption and biofilm interactions.
Introduction

Drinking water quality can deteriorate substantially within building plumbing systems. The surface area to volume ratio of buildings’ water pipes is significantly greater than water distribution systems, allowing potential for greater physicochemical and microbiological interactions between the pipe wall and bulk water.\(^1\) With the rapid movement toward sustainability, plastic pipes are increasingly being used to rehabilitate aged water infrastructure and construct new potable water systems, which reduces cost and ameliorates drinking water quality concerns associated with metal pipe corrosion. The global demand for plastic pipes has been estimated to grow by more than 4 % per annum.\(^2\) Cross-linked polyethylene (PEX) plumbing has emerged as a common material with prevalent applications starting in the mid to late 1990s.\(^3,4\) High density polyethylene (HDPE) pipes initially replaced stormwater culverts in the 1980s and were continuously utilized for the water supply pipes.\(^5\) Despite increased demand and installation of plastic piping materials for potable water systems, how these pipes interact with microbial and heavy metal contaminants in water remains largely unexplored. Research is essential to understand the drivers of contaminant fate and transfer within these materials to ensure safe drinking water for the consumer.

Lead (Pb) in tap water remains an ongoing serious threat to public health.\(^6,7\) Lead exposure can result in severe acute and chronic health impacts such as irreversible developmental and behavioral delays in children, hearing problems, renal dysfunction, and delay in postnatal growth.\(^8\)\(^-\)\(^12\) Lead in tap water predominantly originates from the corrosion of lead-bearing plumbing materials, including lead service lines, brass valves and fittings, galvanized iron, lead-tin solder, and faucets.\(^13\)\(^-\)\(^15\) Lead service lines, which are frequently found in older buildings, are often connected to the recently renovated building plastic plumbing systems. Thus, service line corrosion products can be released into the building
plumbing and subsequently accumulate on the inner surface of plastic pipes. In our recently published field study, we quantified lead concentrations at cold and hot water fixtures during the first three months after installation of the new PEX plumbing. Even though new plastic plumbing was used, we found a greater level of lead inside the building than in the water service line. Lead concentrations varied across plumbing fixtures and were influenced by ball valves, brass barb tees, and brass elbows. Despite the assumption by water utilities and regulatory agencies about the inert nature of plastic plumbing materials, our recent bench-scale experiments and field study demonstrated that plastic surfaces act as resting sites for lead species. We demonstrated that aged LDPE pellets adsorbed five times greater lead than new LDPE pellets. The research conducted by Huang et al. (2019) revealed the deposition of lead was released by upstream brass and metal pipes onto the downstream PEX plumbing. Our recent discovery, as well as the findings of others, showed that plastic pipes could accumulate metal coatings in addition to biofilms on their drinking water contact surface after years of use. Biofilm is a layer of microorganisms adhering to a surface on the pipe that is in contact with water and grows up there. Although drinking water is disinfected prior to distribution, the disinfectant decay allows the survival of some microorganisms and their subsequent regrowth on the pipe's inner walls as a biofilm. Still, no studies have been carried out to examine the interactive mechanisms of biofilm formation and persistence and heavy metals in plastic piping used for drinking water.

While the metal adsorption onto plastic potable plumbing materials received less attention, there is vast literature concerning heavy metal adsorption onto plastic debris in freshwater and marine environments. Microplastic pollution in aquatic and marine environments has been shown to be an important vehicle for heavy metals’ transport. Holmes et al. (2014) found that aged plastic pellets removed from the beach accumulated
greater levels of heavy metals (Cr, Co, Ni, Cu, Cd, Pb) compared to new plastic pellets, and it could be due to polymer aging, biofilm accumulation and/or chemical precipitates. Evidence from the plastic pollution literature shows other plastics common to water piping networks (e.g., HDPE, PVC) sorb lead. Plastic pipe surfaces are generally exposed to lead concentrations above the USEPA action level (> 15 µg/L). This exposure could be under stagnant water conditions, elevated temperatures, or pressurized conditions that might impact adsorption. Increased temperature is reported to reduce metals’ adsorption. Systematic research is needed to identify how heavy metal uptake by plastic pipes differs from pellets, which have been studied extensively, to better understand mechanistic findings in the built environment.

One major factor influencing heavy metal deposition and scale formation onto plumbing surfaces is biofilms, which are complex matrices consisting of microorganisms and associated extracellular substances and can interact with and influence metal ion sequestration and movement. The interactions between biofilms and scale may facilitate the continued development of each on pipe surfaces. Reports suggest that water chemistry influences biofilm growth on plastic plumbing materials. However, there is a knowledge gap on how biofilms affect contaminant fate in this system. Most water-biofilm research has focused on wastewater heavy metal remediation in bioreactors, where biofilms have been applied successfully in fixed-bed reactors to remove low concentrations of heavy metals from industrial wastewater. While research has been conducted on the interactive effects of biofilms on pipe corrosion, the mechanistic role of how plastic pipes are impacted by biofilms has been overlooked. Plastic pipes may be more susceptible to biofilm development than metal pipes due to their organic leaching. Biosorption involves the transport of metals across cell walls, complexation, ion exchange, precipitation, and physical adsorption. It was
also reported that biofilm accumulation might enhance heavy metal adsorption from the aquatic environment onto microplastics. Given that microplastics play critical roles in heavy metal uptake, it is expected that similar processes occur within plastic plumbing, but given the dearth of investigations into plastic plumbing, this has not yet been quantified.

Plastic usage in plumbing systems will continue to grow; thus, it is imperative that research is conducted to elucidate the fundamental interactions that are taking place at this new interface. The installation of plastic drinking water materials presents a new and unexplored dilemma to safe drinking water provision in the US. As our recent studies have revealed, the fundamental processes that control metal interactions with water infrastructure plastics remain poorly understood. Moreover, the existing polymer literature does not address how metals interact with polymer pipes when biofilms are present and which water quality factors and water flow conditions facilitate sorption. This research aims to elucidate the influence of biofilm presence on Pb deposition onto the PEX-A and HDPE potable water pipes compared to the copper pipes under water flow and stagnant conditions. The specific objectives are to (1) study the impact of biofilm presence on the kinetics of Pb accumulation onto plastic pipes in comparison to copper pipes, (2) examine the influence of Pb initial concentrations on the rate of its accumulation onto the new and biofilm-laden water pipes under water flow and stagnant conditions, and (3) compare the impacts of water flow conditions on Pb accumulation onto new and biofilm-laden water pipes.
Experimental

Materials

Cross-linked polyethylene (PEX-A), high-density polyethylene (HDPE), and copper pipes were used in this study. The inner diameters of the PEX-A, HDPE, and copper pipes were 1.7 cm, 2.1 cm, and 1.91 cm, respectively. The PEX-A and HDPE pipes were obtained from McMaster-Carr, USA. Copper pipes were purchased from a local hardware store (Memphis, TN, USA). Inductively coupled plasma mass spectrometry (ICP-MS) lead (Pb) (1000 mg/L in 3% nitric acid) standard solution was purchased from RICCA chemical company (Arlington, TX, USA). Clorox disinfectant comprised of 7.5% sodium hypochlorite (NaOCl) was purchased from a local store (Memphis, TN, USA). Nitric acid (70% purity) was purchased from Fisher Scientific (Hanover Park, IL, USA). All the experiments were performed using ultrapure Milli-Q™ (18MΩ*cm) treated water unless it is described otherwise.

Pipe Disinfection and Biofilm Growth

The individual pipe loop for PEX-A and HDPE were built by connecting 2.7 m (9 ft.) of ten pipes, whereas a copper pipe loop was developed by connecting 3.0 m (10 ft.) of ten pipes. After constructing separate pipe loops for the new PEX-A, HDPE, and copper pipes, the pipes were disinfected through shock chlorination, in which the pipe loops were filled with the chlorinated municipal tap water (20 ± 1 mg/L as Cl₂) for 40 min. After that, each of the pipe loops was flushed with tap water for 30 min. Then, the pipe rigs were connected, as shown in Figure 15a, to the municipal tap water supply to develop biofilm within the pipes. The municipal tap water was treated groundwater that was chlorinated for primary and
secondary disinfection processes, aerated, and filtered. The corrosion inhibitor was orthophosphate. Tap water ran through the pipe loop at 2.0 ± 0.2 L/min for a daily cycle of 16 h of flow and 8 h of stagnation at room temperature. Tap water quality parameters, including temperature, pH, and total chlorine, were measured weekly. After biofilm generation, pipes were removed from the stand and sectioned into 30 cm segments to undergo metal adsorption experiments. In addition, representative pipe sections were used for microbial biomass measurements and zeta potential measurements.

Figure 15. (a) The rigs used to grow the biofilm onto the pipes’ inner wall, and (b) custom apparatus used to measure the zeta potential of HDPE pipes’ inner walls

Biofilm Characterization

Representative samples of each pipe type (9 cm in length) were sectioned and placed into 50mL centrifuge tubes and immediately frozen at -20 ºC until processed. Total genomic DNA (gDNA) was extracted from biofilms using PureLink® Genomic DNA Mini Kit (Invitrogen, Carlsbad, CA) following standard protocols. Prior to extraction, pipes were placed into sterile 50 mL centrifuge tubes and filled with sterile molecular grade water, and
biofilms were liberated from the pipe surface using two strategies, first by sonication by placing tubes into a sonicating water bath (Branson 2800, Branson Ultrasonics, Brookfield CT, USA) at maximum oscillation for 10 minutes to aid separation and second, by physically scraping with a sterile syringe use a single stiff bristle brush for 5 minutes into molecular grade water, following Chatterjee et al., 2012 with modifications. The liberated biofilms were centrifuged at 10,000 x g for 10 minutes at 4 ºC, and the supernatant was removed, pellets were resuspended in 500 µL of molecular grade water and transferred to extraction tubes, and DNA was extracted. Extracted DNA was quantified using a Nanophotometer (N60; Implen, Munich, Germany). The internal surface area of each pipe was calculated with the aid of digital calipers to a resolution of 0.1 mm (Fisher Brand Traceable, Waltham, MA). Biomass was determined by absolute quantification of the number of copies of the V4 region of the 16S ribosomal DNA and normalized to a per surface area unit (cm²) using a droplet digital PCR system (QX200; Bio-Rad, Hercules, CA, USA). Briefly, 20 µL ddPCR reactions were conducted using 12.5 µL Evagreen Supermix (Bio-Rad, Hercules, CA), 6.25 µL gDNA (diluted in molecular grade H₂O to 1:10-1:1000, optimized per sample), 125 nM each gene primer (515F.Prada and 806R.Apprill), and molecular grade water. Reactions were run on a QX200™ Droplet Digital PCR System (Bio-Rad, Hercules, CA) using the following parameters: denaturation at 95 ºC for 30 sec., combined annealing and extension 60 ºC for 1 min, signal stabilization at 4 ºC for 5 minutes, and 90 ºC for 5 minutes respectively for a total of 40 cycles. Positive droplets were quantified using the QX200 Droplet Reader (Bio-Rad, Hercules, CA) using QuantaSoft software (v.1.4, Bio-Rad, Hercules, CA), and the number of copies per reaction was determined using Poisson statistics. To determine the number of copies/cm², we calculated the total number of 16S copies in the DNA extraction (considering DNA dilution factor, the total volume of extraction, and the volume of DNA used in ddPCR reactions) and divided by the internal surface area of each pipe.
Zeta Potential Measurement

Zeta potential measurements were conducted using an electrokinetic analyzer (SurPASS, 2010 model, Anton Paar USA, Ashland, VA) for new and biofilm-laden HDPE pipes to identify how the plastic pipe surface charge varies due to the biofilm accumulation. To mount the samples for analysis, customized adapters were made to accommodate the inside diameter of the pipes and connect them with the outside diameter of the fluid nozzles on the analyzer. A roughly six-inch (15 cm) section of pipe was then clamped between two custom-built metal bars to squeeze it into a thin channel \textbf{(Figure 15b)}. A 500 mL solution of 1 mM KCl was added to a beaker feeding the instrument, and between 50 and 200 mL of the solution was passed through the channel with the flow ramped gradually until reaching a pressure of 300 mbar. Because of the electrical double layer created by the inner pipe/biofilm surface interacting with the electrolyte solution, an electrical current was induced.\textsuperscript{49} The current was measured during the flow rate ramp and used by the instrument software to calculate the zeta potential. We were not able to measure the zeta potential for the copper pipes using this approach due to the conductive nature of those pipes, which interfered with the electrical current measurement.

An automated titration was performed. After measuring the zeta potential at the original solution pH (usually between 5.5 and 6), small (~0.1 mL) doses of 0.1 N HCl were added to the solution until the pH dropped by at least 0.3 pH units. The zeta potential was measured four times (two in one flow direction and two in the reverse flow direction) at each pH point. This continued until the solution pH was near 3. The solution was then replaced by a fresh 500 mL of 0.1 mM KCl, and a similar titration was performed but with 0.1 N NaOH until the pH was near 9. Total titration and measurement time were between three and four
hours. Data from the two runs were combined, and a titration curve of zeta potential versus pH between 3 and 9 was generated.

Lead (Pb) Exposure Experiments

Synthetic tap water was used to conduct the metal exposure experiments. The chemical constituents of this synthetic tap water are listed in Table B-1 (Appendix B). Pb speciation in synthetic tap water was determined by chemical equilibrium and constants which are shown elsewhere. The 5-day kinetics experiments were conducted in triplicate through six-time intervals (2, 6, 12, 24, 48, and 120 h) under stagnant and flow conditions. To conduct kinetic experiments under stagnant conditions, pipe segments were filled with Pb solution (300 µg/L at pH=7.8) and sealed with polytetrafluoroethylene (PTFE) wrapped rubber stoppers. To study the influence of initial Pb concentration on its accumulation on the new and biofilm-laden water pipes, five different Pb aqueous concentrations (50, 150, 500, 750, and 1000 µg/L) at pH=7.8 were used. For this purpose, triplicate pipe samples were filled with the aqueous Pb solutions and sealed with the PTFE-wrapped stoppers. Then, the sealed pipe segments were placed horizontally on the bench top at room temperature (22 ± 1°C) for 48 h for all five concentrations. The aqueous solutions were removed from the pipe segments after elapsed time intervals and acidified to obtain 2% nitric acid solution to quantify the residual Pb in the solution. To conduct the Pb exposure experiments under flow conditions, a small pipe loop was built by connecting a 30 cm pipe segment to polyvinyl chloride (PVC) tubing, and a submersible pump was placed in a water tank that contained 1.0 L of the Pb aqueous solution (Figure C-1, Appendix C). The water flow in this small pipe loop was adjusted at 2 L/min. For the kinetic experiments, 5.0 mL samples were collected from the water tank at different time intervals (2, 6, 12, 24, 48, and 120 h). However, for studying the influence of Pb initial concentration, 5.0 mL samples were collected after 48 h.
The connecting tubing, pump, and water tank were acidified at the end of the experiments to quantify the extent of Pb accumulated on their surface. The statistical analysis conducted to compare the Pb accumulation results is described in C-1 in Appendix C.

**Water Quality Analysis and Lead Quantification**

The acidified solutions were analyzed with a Perkin Elmer Analyst 400 atomic absorption spectrometer attached to an HGA 900 graphite furnace. This instrument was calibrated using 0, 5, 10, 25, 50, 75, and 100 µg/L Pb standard solutions. The coefficients of determination range for the standard calibration curves were found to be 0.992-0.998. Using a similar method for Pb quantification, the instrument's detection limit varied between 4-12 µg/L. Water pH was measured using an Oakton® pH 450 portable pH meter. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to adjust the pH for the experiments. Total chlorine residuals were measured using a Hach Pocket Colorimeter™ II using diethyl-p-phenylene diamine (DPD) reagent. The dissolved oxygen (DO) and temperature of the tap water were measured using the Oakton® DO 450 portable DO instrument.
**Kinetics Modeling**

The kinetics of Pb adsorption onto the new and biofilm-laden PEX-A, HDPE and copper pipes were investigated through first order and second order kinetics models according to Equations (10, 11) and (12, 13), respectively.\(^{52,53}\) In these equations \(q_t (\mu g/m^2)\) is the surface loading of Pb on the pipe surface at time \(t\) (h), \(q_e (\mu g/m^2)\) is the surface loading at equilibrium, \(k_1 (h^{-1})\) is the first order rate constant, and \(k_2 (m^2 \mu g^{-1} h^{-1})\) is the second order rate constant. In Equation (14), \(t_{1/2}\) is the half-life which represents the required time for the adsorbent pipe to uptake half of the equilibrium Pb surface loading.\(^ {54}\) The equilibrium Pb surface loading was calculated by averaging the Pb surface loadings during the last two exposure periods (48 h and 120 h).

\[
\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (10)
\]

\[
q_t = q_e (1 - e^{-k_1 t}) \quad (11)
\]

\[
\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (12)
\]

\[
q_t = \frac{q_e k_2 t}{1 + q_e k_2 t} \quad (13)
\]

\[
t_{1/2} = \frac{\ln 2}{k_1} \quad (14)
\]
Results And Discussions

Biomass Accumulation onto the Pipe Surfaces

The biomass accumulation onto the inner pipe surfaces after three months of running the municipal tap water through the pipe loops was studied through the quantification of 16S ribosomal RNA genes (rDNA) using triplicate technical replicates. The results revealed the most extensive initial biofilm formations were on PEX-A pipes \( (2.97 \times 10^9 \pm 3.24 \times 10^8 \text{ copies/cm}^2, \text{mean} \pm \text{standard deviation}) \) compared to HDPE \( (1.19 \times 10^8 \pm 2.03 \times 10^8 \text{ copies/cm}^2) \) and copper pipes \( (1.07 \times 10^8 \pm 9.29 \times 10^7 \text{ copies/cm}^2) \). The biofilm biomass was similar for Copper and HDPE pipes. It is uncertain at this time if the communities that make up these biofilms are similar across this pipe material or if they are distinct, which may indicate differential microbial-mediated adsorption potential. Organics leached by plastic pipes [e.g., antioxidants, stabilizers, monomers] can further support the growth of microorganisms on the pipe surface.\(^{17,55}\) The finding of a smaller extent of biofilm formation in the copper pipes versus the PEX-A pipes is in agreement with the other published studies that reported this result due to the antibacterial properties of the copper pipes.\(^{56}\) On the other hand, the organics leached by plastic pipes are reported to promote microbial regrowth.\(^{56}\) PEX-A pipes are known to significantly contribute to the assimilable organic carbon (AOC) release that could promote microbial regrowth within the pipes.\(^{57}\) The study conducted by Connell et al. (2016) revealed a greater rate of AOC release from PEX pipes compared to the HDPE pipes after 7 d exposure to the water.\(^{57}\) The lower organics released by HDPE pipes compared to the PEX-A pipes could be the reason for a lower microbial growth on these pipes. Although it should be noted that biofilm growth onto the PEX-A pipe was conducted from April to July, biofilm growth onto the HDPE pipes was conducted from May to August. However, water flow and room temperature were constant during the biofilm growth process for all three types of
pipes, but the weekly average for temperature, total chlorine residuals, and DO concentration during the biofilm growth on PEX-A pipes were recorded as 21.2 °C, 0.9 mg/L, and 9.3 mg/L and for HDPE pipes were recorded as 22.7 °C, 1.0 mg/L, and 9.1 mg/L. Moreover, the microbial content and the physicochemical characteristics [e.g., temperature] of the water that entered the pipe loops might be slightly different and, consequently, may have influenced the extent of biomass accumulated onto each type of pipe.

**Surface Charge Variations due to the Biofilm Accumulation**

Zeta potential, also known as electrokinetic potential, demonstrates the potential difference between the electric double layer (EDL) of electrophoretically mobile particles and the dispersant layer around them at the slipping plane. Electrophoretic mobility of charged particles under an applied electric field is used to deduce the zeta potential as it cannot be measured directly. It presents the charge at the surface-water interface that critically influences the interaction and association of the surface function with the charged species present in the water. Studying the zeta potential is the key parameter to understand how electrostatic attractions of lead species toward the pipe surface vary by biofilm presence. The literature indicated that the negative charge associated with the bacterial cells could promote electrostatic attractions of heavy metal ions present within the contact water aquatic and thus enhance their uptake. In this study, zeta potential measurements were conducted for new and biofilm-laden HDPE pipes to obtain a better insight into the pipes’ surface chemistry, which influences their interactions with the charged Pb species present in the aqueous solution. As inferred from Figure 16, all new and biofilm-laden pipes demonstrated a negative surface charge. The extracellular polymer substances (EPS), lipoteichoic and lipopolysaccharide components present in biofilm tend to make more negative surface charge. The magnitude of zeta potential is reduced with increasing the pH. This finding
corroborates those found by Chu et al. (2019), which reported a negative zeta potential for microplastics. The zeta potential of both new and biofilm-laden pipes showed a similar descending trend with increasing the pH, with biofilm-laden HDPE pipes being slightly more negative than the new HDPE pipes. At low pH values, the hydrophilic sites on the pipe surface have a great tendency to adsorb protons due to the elevated proton concentration, which results in less negative zeta potential; however, with increasing the pH, the pipe surface became more negatively charged, this process called deprotonation. The zeta potential of new and biofilm-laden HDPE varies between 0 to -125 mV and -26 to -124 by increasing the pH from 3.1 to 8.6. The increased negativity of zeta potential for the biofilm-laden HDPE pipes suggests that biofilms may facilitate general increases in the magnitude of negative zeta potentials, which overall increases the negative charge, which may result in increased Pb cation attachment to the pipe surface; similar results have been found to indicate that an increase in the magnitude of negatively charged biofilms increases the likelihood of heavy metal sorption.

**Figure 16.** The zeta potential variations versus pH for new and biofilm-laden HDPE water pipe
In this study, the kinetics of Pb accumulation onto the new and biofilm-laden PEX-A, HDPE, and copper pipes under stagnant were compared. As shown in Figure 17, during the entire exposure period, Pb accumulation onto the new copper pipes was significantly greater than both new PEX-A (p-value < 0.05) and new HDPE pipes (p-value < 0.05), and even biofilm-laden PEX-A (p-value < 0.05), and biofilm-laden HDPE pipes (p-value < 0.05). The equilibrium Pb surface loading on new copper pipes (1,391 µg/m²) was more than 5 times greater than new PEX-A (265 µg/m²) and 4 times greater than new HDPE pipes (329 µg/m²). However, the biofilm presence significantly increased the Pb accumulation onto the PEX-A (p-value < 0.05) and HDPE (p-value < 0.05) pipes compared to their new pipes during the 5 d metal exposure experiments under stagnant conditions (Figure 17). At equilibrium, the biofilm-laden PEX-A pipes have more than three times greater Pb loading (980 µg/m²) compared to the new PEX-A pipes (265 µg/m²). For the first two hours of Pb exposure, the biofilm-laden PEX-A pipe accumulated 88% of its equilibrium Pb surface loadings, while the new PEX-A pipes almost obtained all their equilibrium Pb surface loading. The equilibrium Pb loading onto the biofilm-laden PEX-A pipe was found as 82%, while for the new PEX-A pipe, the accumulation was only 22% of the total Pb (Pbₜ) present in the synthetic tap water.

The biofilm-laden HDPE pipe accumulated approximately three times more Pb at equilibrium (1,170 µg/m²) than the new HDPE pipe (329 µg/m²). The biofilm-laden HDPE pipe accumulated 90% of its equilibrium Pb surface loadings, while the new HDPE pipes obtained almost all their equilibrium Pb surface loadings during the first two hours of Pb exposure.

The biofilm-laden HDPE pipes acquired 85% of [Pb]ₜ in the synthetic tap water as their equilibrium surface loading after 5 d of metal exposure experiments; however, the new HDPE pipes only accumulated 24% of [Pb]ₜ at their equilibrium. Despite the findings for
PEX-A and HDPE pipes, the biofilm accumulation onto the copper pipes did not significantly increase the Pb accumulation under stagnant conditions. The biofilm-laden copper pipe (1,527 µg/m²) accumulated more than the new copper pipe (1,352 µg/m²), whereas the difference was not statistically significant (p-value > 0.05). During the kinetic experiment, for the first two hours of Pb exposure, the biofilm-laden copper pipe accumulated 79% of its equilibrium Pb surface loadings, while the new copper pipes obtained 82%. The equilibrium Pb accumulation was found to be 93.36 % for the biofilm-laden copper pipe and 84.62 % for the new copper pipe from the total Pb (Pbₜ) in the synthetic tap water.
Figure 17. The first order kinetics results for Pb accumulation onto new and biofilm-laden water pipes under stagnant conditions.
The kinetics of Pb accumulation onto the plastic and copper water pipes under flow conditions were compared with the stagnant condition to better understand how variations of water use behave within the residential and commercial buildings influence the extent of Pb accumulation onto the potable water pipes. Unlike our findings of increased Pb accumulation onto the plastic pipes due to the biofilm presence under stagnant conditions, we have found reductions in Pb surface loadings on both biofilm-laden PEX-A and HDPE pipes compared with their new pipes, under water flow conditions (Figure 18). For HDPE pipes the difference was statistically significant (p-value < 0.05). The reduction in Pb surface loading might be due to the shorter duration of Pb species interactions with the biofilm surface under flow conditions, which may not be sufficient to allow their removal from the aqueous system. The metal exposure experiments were conducted under consistent flow conditions to prevent the creation of the shear forces and subsequent biofilm detachment. Although, it might be possible that some of the metal accumulated biofilm were released into the water due to their reduced internal cohesive strength caused by the aging of biofilm or its nutrient starvation as exposed to the synthetic water and not the tap water.\textsuperscript{54,55} Pb accumulations onto the new copper (15,918 µg/m\(^2\)) was reduced in biofilm-laden copper (15,898 µg/m\(^2\)) pipes, but the reduction was not significantly different (\(p\)-value > 0.05). Similarly, biofilm-laden PEX-A (18,300 µg/m\(^2\)) pipes accumulated less than the new PEX-A (18,219 µg/m\(^2\)) pipes and the difference was not statistically significant (\(p\)-value > 0.05). However, only for the biofilm-laden HDPE (12,938 µg/m\(^2\)) pipes the reduced amount of Pb accumulation was found significantly different (\(p\)-value < 0.05) compared to the new HDPE (14,739 µg/m\(^2\)) pipes. It should be mentioned that during our water flow experiments, a total of 1 L Pb aqueous solution of \([\text{Pb}]_t=300\) µg/L at pH=7.8 was circulated through the 30 cm pipe sections,
however, in our stagnant experiments, the PEX-A, HDPE, and copper pipe sections were filled with 65 mL, 92 mL, and 100 mL of the Pb aqueous solution, respectively. Thus, the total mass of Pb present within the flow system was 300 µg, significantly greater than the Pb mass that was available for PEX-A, HDPE, and copper pipes, respectively. Therefore, it was expected that our results would demonstrate a greater level of Pb accumulation onto all examined pipes under water flow conditions compared to the stagnant condition.
Figure 18. The first order kinetics results for Pb accumulation onto new and biofilm-laden water pipes under flow conditions.
In this paper, a kinetics modeling was conducted to provide a better mechanistic understanding of the combined physicochemical mechanisms that control the rate of Pb accumulation onto the new and biofilm-laden potable plastic and copper water pipes. First order and second order kinetic models were applied to explain the mechanism of metal accumulation on the pipes. The first order model assumes that the rate of changes in the solute uptake over time is proportional to the difference in the saturation concentration and the amount of adsorbed solute over time, as shown in Equations 10 and 11. First order model mostly fits the experimental metal adsorption data when the solute adsorption proceeds through the diffusion to the solid micropores. However, the second order model (Equation 13) assumes that rate-limiting step is the chemisorption process. Its differential equation is shown in Equation 12. In this model, the rate of adsorption depends on the adsorption capacity of the adsorbent and not the adsorbate concentration. A non-linear chi-square ($\chi^2$) test comparisons were conducted between the models (first and second order) to determine the best-fitted kinetic model for the studied pipes (Table 3). The lower $\chi^2$ values found here suggest that the first order reaction model better describes the Pb accumulation onto almost all water pipes tested. Thus, the diffusion of Pb species from the bulk aqueous phase to the pipe surface was the leading mechanism that resulted in Pb accumulation onto the pipe surface. This agrees with the Azizian (2004) theoretical study, which demonstrated that at the high initial adsorbate concentration, the adsorption process of the kinetics studies could be described by first order model; however, at low initial adsorbate concentration, it obeys the second order model.70 The half-life ($t_{1/2}$) calculation revealed a longer duration half-life for biofilm-laden PEX-A (6.7 h) and HDPE (9.9 h) pipes compared to the new PEX-A (0.4 h) and HDPE (0.6 h) pipes. This finding suggests that Pb accumulation onto the new plastic
pipes occur more rapidly, as the most readily available surface deposition sites were rapidly occupied by the Pb species. However, despite the greater adsorption capacity of the biofilm-laden plastic pipes, they were not readily accessible for the Pb species, and consequently, a longer duration took to reach the half-life. It was completely different for the copper pipe as the half-life for new copper pipes (6.9 h) was greater than half-life for the biofilm-laden copper pipe (1.8 h). The kinetics data collected under water flow conditions also revealed that first order best describes the Pb accumulation onto the new and biofilm-laden water pipes. This is clearly a mass transfer process due to the abundance of available Pb species in the system as water circulates through the pipes. The increased half-lives for the plastic pipes and decreased half-lives for the metal pipes due to the presence of biofilm were similar under both stagnant and flow conditions; however, the difference in half-lives between the new and biofilm-laden pipes under flow conditions was smaller than the ones under stagnant conditions. It could be due to the abundance of Pb species in the system as water circulated in the pipes. Moreover, this finding explains our results regarding the lower Pb accumulation onto the biofilm-laden plastic pipes compared to the new plastic pipes under flow conditions due to the short durations of Pb species contact with the biofilm that was not sufficient to allow a significant uptake of Pb species.
Table 3. The kinetics models’ parameters and non-linear chi-square ($\chi^2$) values for Pb accumulation onto the new and biofilm-laden water pipes under stagnant and flow conditions

<table>
<thead>
<tr>
<th>Pipe</th>
<th>Model</th>
<th>First order reaction model</th>
<th>Second order reaction model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$q_{e, exp}$ ($\mu g/m^2$)</td>
<td>$q_{e, mod}$ ($\mu g/m^2$)</td>
</tr>
<tr>
<td><strong>Stagnant</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>New</td>
<td>Copper</td>
<td>1.391</td>
<td>1.416</td>
</tr>
<tr>
<td>PEX-A</td>
<td>265</td>
<td>288</td>
<td>1.890</td>
</tr>
<tr>
<td>HDPE</td>
<td>329</td>
<td>335</td>
<td>1.200</td>
</tr>
<tr>
<td>Biofilm-laden</td>
<td>Copper</td>
<td>1.535</td>
<td>1.553</td>
</tr>
<tr>
<td>PEX-A</td>
<td>981</td>
<td>1.011</td>
<td>0.104</td>
</tr>
<tr>
<td>HDPE</td>
<td>1.170</td>
<td>1.275</td>
<td>0.070</td>
</tr>
<tr>
<td><strong>Flow</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>New</td>
<td>Copper</td>
<td>15.917</td>
<td>16.380</td>
</tr>
<tr>
<td>PEX-A</td>
<td>18,300</td>
<td>18,410</td>
<td>0.148</td>
</tr>
<tr>
<td>HDPE</td>
<td>14,739</td>
<td>14,835</td>
<td>0.147</td>
</tr>
<tr>
<td>Biofilm-laden</td>
<td>Copper</td>
<td>15,898</td>
<td>16,284</td>
</tr>
<tr>
<td>PEX-A</td>
<td>18,219</td>
<td>18,412</td>
<td>0.122</td>
</tr>
<tr>
<td>HDPE</td>
<td>12,938</td>
<td>13,734</td>
<td>0.073</td>
</tr>
</tbody>
</table>

Influence of Lead (Pb) Initial Concentration on the Rate of its Accumulation onto the Water Pipes

The influence of Pb concentration on the rate of its accumulation onto the new and biofilm-laden water pipes was investigated under stagnant and water flow conditions. The Pb surface loading versus the residual Pb concentration remaining in solution at the equilibrium was graphed for stagnant (Figure 19) and flow (Figure 20) conditions. Increasing the Pb concentration from 50 µg/L to 1000 µg/L resulted in an increasing rate of Pb surface accumulation onto the new and biofilm-laden PEX-A, HDPE, and copper pipes under both stagnant and water flow conditions. Under stagnant conditions, both new and biofilm-laden water pipes revealed a similar order of copper > PEX-A > HDPE for the increased rate of Pb surface accumulation by increasing the Pb initial concentration. Under stagnant conditions, biofilm presence drastically increased the rate of Pb accumulation onto all water pipes with increasing the Pb concentration. A linearly increased Pb surface loading was found for new and biofilm-laden PEX-A and HDPE pipes ($R^2 \geq 0.90$) and copper pipes ($R^2 \geq 0.84$) with increasing the Pb concentration under stagnant conditions as shown in Figure 19 (a & b). By applying a linear model, the slopes are defined as the Pb accumulation rate at each condition.
The Pb accumulation rate for new PEX-A, HDPE, and copper pipes under stagnant conditions varied from 0.004, 0.003, and 0.002 m to 0.099, 0.014, and 0.011 m due to the presence of biofilm. The maximum Pb surface loading onto the new PEX-A, HDPE, and copper pipes were found as 1,859, 1,472, and 2,536 µg/m² and were significantly smaller than the Pb surface loadings onto the biofilm-laden PEX-A (3,162 µg/m²), HDPE (3,094 µg/m²), and copper pipes (5,240 µg/m²), respectively, under stagnant conditions. Under flow conditions, the Pb surface loading onto the new PEX-A, HDPE, and copper pipes increased linearly with raising the Pb concentration ($R^2 \geq 0.84$) (Figure 20a). Despite a similar trend, the coefficient of determination for this linear regression reduced when biofilm was present on the pipe surfaces ($R^2 \leq 0.74$) (Figure 20b). The maximum Pb surface loadings onto the new PEX-A, HDPE, and copper pipes under flow conditions varied from 58,427, 46,947, and 48,579 µg/m² to 51,468, 29,185, and 41,288 µg/m² due to biofilm presence. At almost all concentrations, less Pb surface loadings were found on the biofilm-laden water pipes compared to the new pipes under flow conditions. The Pb accumulation rates onto the new PEX-A (120.49 m), HDPE (248.5 m), and copper pipes (0.688 m) reduced to the biofilm-laden PEX-A (0.397 m), HDPE (0.082 m), and copper pipes (0.234 m). As it was mentioned earlier, the short contact of the Pb species and biofilm surface during the water flow experiments may have resulted in insufficient interaction between those and, consequently a lower accumulation rate compared to the new plastic pipes.
Figure 19. Equilibrium Pb surface loading for (a) new and (b) biofilm-laden PEX-A, HDPE, and copper pipes versus residual Pb in the contact water under stagnant condition.
Figure 20. Equilibrium Pb surface loading for (a) new and (b) biofilm-laden PEX-A, HDPE, and copper pipes versus residual Pb in the contact water under flow conditions.
Solving the solubility and complexation equations revealed that the ligands present within our synthetic tap water \([OH^-, SO_4^{2-}, NO_3^-, Cl^-, HPO_4^{2-}, HCO_3^-, SiO_3^{2-}]\) could form both dissolved [e.g., Pb\(^{2+}\), Pb(OH)\(^+\)] and insoluble Pb [e.g., Pb(OH)\(_2\)] complexes with Pb\(^{2+}\).

The Pb exposure experiments were conducted at the initial concentration of [Pb]\(_t\)=300 µg/L and pH=7.8, where a total of 93.55 % of [Pb]\(_t\) was precipitated as Pb(OH)\(_2\) and the rest were dissolved species. Thus, both adsorption and precipitation processes [accumulation] have occurred simultaneously in the studied aqueous system. The Pb species adsorption onto the new plastic pipe surface may occur in three phases, external diffusion, intraparticle diffusion, and adsorption equilibrium.\(^{71,72}\) During the early phase of external diffusion, rapid Pb adsorption occurs during the first 1 h to 5 h exposure period. In this phase, the dissolved Pb species diffuse throughout the water film of the hydrated pipe walls from the aqueous solution onto the external surface of the pipe. Intraparticle diffusion is an intermediate stage where the Pb species diffuse into the adsorbed species and diffuse into the pipe surface pores after overcoming the resistance of the water film. After the intraparticle diffusion, the process of adsorption proceeds onto the surface-active sites and becomes relatively slower but continues until reaching the equilibrium phase. At the final step, the equilibrium is achieved, and the rate of adsorption declines to zero as most of the available surface sites have been occupied by the Pb species.\(^{50,72,73}\) As we reported earlier, the metal species adsorbed onto the plastic surface could act as nucleation sites to grow the precipitates. The low energy polymeric sites, such as surface impurities, polymer terminal groups, or an arrangement of polymeric chains, could act as the nucleation sites for the precipitate formation.\(^8\)

Although the biofilm \((2.97\times10^9\ \text{copies/cm}^2)\) present onto the PEX-A pipes at the beginning of the Pb exposure period was an order of magnitude higher than HDPE pipes
(1.19×10^8 copies/cm²), biofilm accumulation onto both plastic pipes resulted in a significant increase in Pb surface loading. Biofilm accumulation onto the pipe surface could alter the metal accumulation behavior by facilitating the biosorption and transport of metals across cell walls, complexation, precipitation, and physical adsorption.\textsuperscript{43} Moreover, as our zeta potential measurements revealed, biofilm formation on the pipe surface could make the surface charge more negative and promote the electrostatic attraction of the positively charged metal ions to the pipe surface. Biofilm and heavy-metal interactions may occur through several potential mechanisms, including microbial-mediated biosorption, metal-mediated alterations in microbial communities, metal-mediated changes in biofilm gene expression, and microbial-mediated metal transformations; additional work is needed to identify the primary mechanism by which biofilms increase metal adsorption. Adsorption and sequestration of heavy metals into biofilms is facilitated by two major steps: 1) Metal ions undergo bulk diffusion into biofilm extracellular matrices, which is a complex amalgam of exopolysaccharides, proteins, fats, and free DNA that is heterogeneously and locally charged, and 2) Metal ions interact with solid surface and biofilm cellular walls. This interaction is complex and includes biosorption, bioaccumulation, resistance, and detoxification processes. Bioaccumulation occurs through metabolic activity between metals and living cells and may facilitate community turnover via local toxicity, favoring community members who can utilize or be minimally affected by these heavy metal species, which can lead to rapid turnover in biofilm communities when exposed to heavy metals.\textsuperscript{74,75} \textbf{Figure 21} demonstrates the potential mechanisms of the heavy metal adsorption process onto the new and biofilm-laden plastic pipes. However, for copper pipes, biofilm surface accumulation is known to promote pipe corrosion and consequently release copper ions. Some of these released copper ions could be stored within the biofilm structure, forming the complexation with the ligands that are already present within the extracellular polymeric substance (EPS) of biofilm.\textsuperscript{76} The occupation of
these available surface sites by Cu$^{2+}$ ions likely reduces the available sites to accumulate Pb$^{2+}$ species during the metal exposure experiments.

Figure 21. Schematic demonstrating the mechanisms of the heavy metal adsorption process onto the new and biofilm-laden pipe
Conclusion

In this study, the mechanistic role of biofilm presence on Pb accumulation onto the PEX-A, HDPE, and copper potable water pipes was investigated under stagnant and flow conditions. The biofilm presence on the plastic pipes' inner walls promoted the negative surface charge and provided more available surface sites for Pb accumulation onto water pipes under stagnant conditions. However, the biofilm presence on copper pipes did not enhance the Pb uptake, which might be due to its saturation with the Cu$^{2+}$ ions. The water flow conditions significantly influenced the extent of Pb accumulation onto the new and biofilm-laden water pipes. Although biofilm accumulation significantly increased the Pb accumulation onto the PEX-A and HDPE pipes, it did not alter the Pb accumulation onto the copper pipes under stagnant conditions. However, under flow conditions, Pb accumulations onto both biofilm-laden PEX-A and HDPE pipes were reduced compared to the new pipes, which might be due to the shorter interactions of Pb species with the biofilm surface. The results demonstrated the Pb accumulation onto the pipe surfaces to be primarily a mass-transfer process described by the first order model. The Pb accumulation rates were greater for biofilm-laden water pipes compared to the new pipes under stagnant conditions. Biofilm presence on the pipe surface enhanced the Pb accumulation by possibly facilitating the biosorption and transport of metals across cell walls, complexation, precipitation, and physical adsorption. This study will provide a foundation for continued exploration of heavy metal fate in water infrastructure and provide an understanding of metal adsorption and biofilm interactions.
Acknowledgments

Funding for this work was provided by National Science Foundation (NSF) grant CBET-2309475. The authors thank Barry Wymore, the research technician in the College of Engineering at the University of Memphis, for building the pipe rig. The authors also thank Shima Ghoochani, the graduate research assistant, and Colton Kirby, Carla Meier, Lauren Nichole Mitchell, and Rhianna Cameron Munns undergraduate research assistants in the Civil Engineering Department at the University of Memphis, for their assistance with conducting the metal exposure experiments. The authors would also like to thank Amy Abell and Nathan Mullins in the Department of Biological Sciences at the University of Memphis for their assistance in conducting ddPCR-based biomass quantification.
Reference


5. Gabriel, L. H. History and Physical Chemistry of HDPE WE TAKE CARE ABOUT THE FUTURE.


The toxicity of heavy metals due to acute and chronic exposure has a significant adverse effect on both human health and aquatic safety in natural and built environments. The release of heavy metals such as Pb, Zn, and Cu into the urban runoff from vehicles emission. They also could be released into the potable water from corroded potable water plumbing fixtures. It’s important to identify the physicochemical mechanisms that influence the transport of heavy metals within the natural and built environments to develop effective management and control strategies. Plastic residuals released into the urban environment could accumulate the heavy metals that are present in storm runoff and transport them to the surface waterbodies. Moreover, plastic potable water pipes could provide the resting sites for the accumulation of heavy metals present in tap water. This research was conducted to identify the physicochemical mechanisms that control the association of lead (Pb) with the plastic materials found as microplastics within the urban environment and plastics used as potable water pipes.

The first chapter of this dissertation focused on studying the influence of photodegradation of low-density polyethylene (LDPE) and polyethylene terephthalate (PET) microplastics (MPs) on their lead (Pb) accumulation in urban stormwater. The photodegradation of LDPE and PET MPs due to the accelerated UVB irradiation experiments was investigated through surface chemistry and morphology analysis. The influence of MPs’ photodegradation on their fragmentation behavior was examined through innovative accelerated mechanical weathering experiments that simulated the abrasion of MPs with road deposits. Furthermore, the role of MPs as the vehicles to transport heavy metals from the urban environment to the water resources was evaluated by studying the kinetics of lead (Pb) uptake by new and weathered MPs in synthetic stormwater. The surface morphology and
chemistry analysis demonstrated an increased degree of photodegradation over longer UVB exposure durations. The kinetics study demonstrated a greater level of Pb accumulation onto the photodegraded LDPE and PET MPs compared to the new MPs. A greater number of fragmentations was found from the LDPE (new and photodegraded) MPs compared to PET (new and photodegraded) MPs. The fundamental knowledge developed in this study provides a better conceptual understanding of the mechanisms controlling MPs persistence and contaminant transport within the urban environment, which is crucial to estimate their adverse impacts on the ecosystem.

The second chapter of this dissertation focused on studying the role of plastic potable water pipe surface aging on lead deposition onto the crosslinked polyethylene-A (PEX-A) and high-density polyethylene (HDPE) pipes. The accelerated aging of the plastic pipes was completed using an elevated dosage of chlorinated water under an elevated temperature at a slightly acidic condition for up to two weeks. The surface chemistry variations of plastic pipes due to the aging process were examined, and the results showed that several oxidized carbon functional groups were formed on the inner surface of the pipes due to the aging process. In addition, the zeta potential measurement of HDPE pipes revealed a slightly more negative surface charge for the aged pipes than the new pipe. The kinetics of Pb deposition onto the new and aged pipes were studied through 5 d Pb exposure experiments under stagnant conditions. The experiments revealed that the aging of PEX-A and HDPE pipes significantly increased the Pb accumulation onto these pipes under stagnant conditions. The Pb adsorption onto the new and aged PEX-A and HDPE pipes followed a first order kinetics model, suggesting the diffusion of Pb species into the micropores present on the pipe surface. This study will lay the groundwork for future investigations into the fate of heavy metals in potable water infrastructure.
The third chapter of this dissertation examined the mechanistic role of biofilm presence on Pb accumulation onto the PEX-A, HDPE, and copper potable water pipes under stagnant and water flow conditions. The pipe loops were constructed, and biofilm was grown onto the pipes for three months. Then, biomass and zeta potential were analyzed, and pipe segments were subjected to the Pb exposure experiments. The results showed that the biofilm presence on the plastic pipes' inner walls promoted the negative surface charge and provided more available surface sites for Pb accumulation onto water pipes under stagnant conditions. However, the biofilm presence on copper pipes did not enhance the Pb uptake, which might be due to its saturation with the Cu^{2+} ions. The water flow conditions significantly influenced the extent of Pb accumulation onto the new and biofilm-laden water pipes. Although biofilm accumulation significantly increased the Pb accumulation onto the PEX-A and HDPE pipes, it did not alter the Pb accumulation onto the copper pipes under stagnant conditions.

However, Pb accumulations onto both biofilm-laden PEX-A and HDPE pipes were slightly reduced compared to the new pipes under flow conditions, which might be due to the shorter interactions of Pb species with the biofilm surface. The results demonstrated the Pb accumulation onto the pipe surfaces obeyed first order kinetics model due to the diffusion of Pb species into the surface micropores. The Pb accumulation rates were greater for biofilm-laden water pipes compared to the new pipes under stagnant conditions. Biofilm presence on the pipe surface enhanced the Pb accumulation by possibly facilitating the biosorption and transport of metals across cell walls, complexation, precipitation, and physical adsorption. This study will provide a foundation for continued exploration of heavy metal fate in water infrastructure and provide an understanding of metal adsorption and biofilm interactions.

Future research could be conducted to determine the other possible ways of natural degradation, such as the biological degradation of the most found plastic litter and their
interaction with different heavy metals. To better understand the individual and combined toxicity of microplastics and heavy metals, additional factors, such as how biofilm growing on the surface of MPs’ influence the attachment of the contaminants. Additionally, how microplastics and heavy metals can permeate through the soil can be another important investigation. On the other hand, in the built environment, future research is needed to examine how plastic pipe surface aging impacts biofilm accumulation or organic contaminant diffusion onto the pipe surface. Future study is needed to identify which factors influence the accumulated heavy metals’ release back into the bulk water. Most importantly, the influence of temperature on heavy metal accumulation and release needs to be better explained. Moreover, the heavy metals’ fate in plastic plumbing in a real setting, especially in low socioeconomic areas, should be conducted to predict the lifetime of plastic plumbing materials.
Appendix A

A-1 Accelerated Degradation Experiments

The plastic samples were cut into 10 cm × 15 cm rectangles and mounted on both side racks of the tester at 5 cm from the bulbs and irradiated with 18.74 W/m² with UVB-313EL 40 W fluorescent bulbs (The Q-Panel Company, Ohio, USA). This accelerated weathering tester was operated at 52 ± 2°C in the presence of air. The intensity of UVB was measured by UV-AB meter (Anaheim Scientific M150 Mini UV-AB Meter, Wilmington, NC, USA).

A-2 Quantification of Plastic Fragments

Approximately 200 μL Nile Red solution was used to stain the fragmented MP particles, and then each filter paper was rinsed with 200 μL of hexane to remove the extra Nile Red stains remaining on the filter paper. Then, from each filter paper, 100 stitched images were captured with 10× magnification using a fluorescence microscope. Each image covered approximately 9.3% (1.2 cm²) of filter paper. Control samples were analyzed from Millipore treated water and did not identify any MPs in the studied size range. The samples were kept in closed containers to prevent the deposition of indoor MPs onto the samples.

A-3 Surface Chemistry Characterizations

The ATR-FTIR data were used in Equations (1) and (2), where $A_{1715}$, $A_{2870}$, and $A_{909}$ denote the absorbance of carbonyl (C=O), methylene (CH₂), and vinyl (CH₂=CH₂) functional groups, respectively, to calculate the carbonyl index (CI) and vinyl index (VI).\(^1\) On the other hand, photodegradation of PET was determined from the comparative spectra and carboxyl
index (CXI). The CXI was calculated from the ATR-FTIR data using **Equation (3)**, where $A_{3290}$ and $A_{2970}$ denote the absorbance of carboxyl (COOH) and asymmetric C-H groups, respectively. As the spectral data is presented in percentage transmittance (%T) format, **Equation (4)** was used to calculate the absorbance (A) values for CI, VI, and CXI index calculations:

- Carbonyl index (CI) = $A_{1715} / A_{2870}$
- Vinyl index (VI) = $A_{909} / A_{2870}$
- Carboxyl index (CXI) = $A_{3290} / A_{2970}$
- Absorbance (A) = $2 - \log_{10} (%T)$

Throughout the X-ray photoelectron spectroscopy (XPS) experiment, the base pressure for the analysis chamber was at 8.0 x 10-10 mBa. The instrument was calibrated to provide a binding energy 284.6 for the C 1s adventitious (aliphatic) carbon line present on the nonsputtered samples. Photoelectrons were collected from a 90° takeoff angle relative to the surface of the samples. Gaussian Lorentzian peaks were used for fitting all the core level experimental data, and Shirley backgrounds were used as background corrections. The survey spectra and the high-resolution spectra were taken with a pass energy of 200 eV with 1.0 eV energy step size and 40 eV with 0.1 eV energy step size, respectively, using an average of 40 scans. The analysis area was 400 μm$^2$ for each sample. Data analysis was performed using Thermo Avantage Software v5.995.

### A-4 Surface Morphology Characterizations

The detector was 5.0 mm above the mounted plastic sample surface. Samples were coated with a 5 nm thick conductive Gold/Palladium (60:40) layer prior to analysis to prevent surface charging. The coating was done using an EMS 550X sputter coater under a high vacuum.
A-5 Lead Exposure Experiments and Kinetics Modeling

For few of the bottles, the 48-d photodegraded LDPE MPs were broken into smaller pieces and those were separated using the 11 μm pore size filter paper but in all other cases the MPs were separated with tweezers. However, for reporting the metal accumulation data it was assumed that surface area was constant through the experiments. Finally, the adsorbed Pb on the MPs surfaces were quantified from the acidified solution.

A-6 Water Quality Measurement and Heavy Metal Quantification

The pH value for the aqueous solutions was measured using an Oakton® pH 450 portable pH Meter. The Pb concentrations were quantified by a Perkin Elmer AAnalyst 400 Atomic Absorption Spectrometer equipped with an HGA 900 graphite furnace. Pb calibration curve was prepared using 0, 5, 10, 25, 50, 75 and 100 μg/L Pb solutions with coefficient of determination ($r^2$) value 0.993 and detection limit 10.4 μg/L.

A-7 Statistical Analysis

The statistical analyses were performed using the IBM SPSS 26 software. To determine the significant difference between the Pb accumulation onto the different samples and the number of generated fragments, the student one-way ANOVA and Post Hoc tests were performed. Statistical significances were determined with a 95 % corresponding confidence interval.
Figure A-1. (Schematic 1) Photodegradation mechanisms of polyethylene redrawn from Krehula et al. (2014), and (Schematic 2) demonstrating the possible mechanism for photodegradation of PET redrawn from Day and Wiles (1972) and Ferreira et al. (2020)

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Concentration (g/L)</th>
<th>Chemicals</th>
<th>Concentration, (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO$_4$.7H$_2$O</td>
<td>0.201</td>
<td>CaSO$_4$.2H$_2$O</td>
<td>0.051</td>
</tr>
<tr>
<td>Al$_2$(SO$_4$)$_3$.18H$_2$O</td>
<td>0.004</td>
<td>CaCl$_2$.2H$_2$O</td>
<td>0.120</td>
</tr>
<tr>
<td>KNO$_3$</td>
<td>0.013</td>
<td>Na$_2$HPO$_4$.7H$_2$O</td>
<td>0.003</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>0.039</td>
<td>NaNO$_3$</td>
<td>0.012</td>
</tr>
<tr>
<td>Na$_2$SiO$_3$.9H$_2$O</td>
<td>0.049</td>
<td>C$_2$H$_5$NO$_2$</td>
<td>0.021</td>
</tr>
</tbody>
</table>

Table A-1: The chemical constituents of synthetic stormwater

App.-A
Figure A-2. XPS survey spectra of (a) new LDPE, (b) 21 d photodegraded LDPE, (c) 48 d photodegraded LDPE, (d) new PET, (e) 21 d photodegraded PET, and (f) 48 d photodegraded PET MPs.
Figure A-3. High resolution deconvoluted C 1s spectra of (a) new LDPE, (b) 21 d photodegraded LDPE, (c) 48 d photodegraded LDPE, (d) new PET, (e) 21 d photodegraded PET, and (f) 48 d photodegraded PET MPs.
**Table A-2:** Elemental atomic concentration percentages of new and UVB exposed LDPE and PET MPs

<table>
<thead>
<tr>
<th>LDPE MPs</th>
<th>C 1s</th>
<th>O 1s</th>
<th>O/C</th>
<th>C_{ox}/C_{unox}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C-C</td>
<td>C-O</td>
<td>C=O</td>
<td>O-C=O</td>
</tr>
<tr>
<td>New</td>
<td>90.0</td>
<td>10.0</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>21 d UVB exposed</td>
<td>85.7</td>
<td>14.3</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>48 d UVB exposed</td>
<td>80.8</td>
<td>7.7</td>
<td>5.1</td>
<td>2.8</td>
</tr>
<tr>
<td>PET MPs</td>
<td>C 1s</td>
<td>O 1s</td>
<td>O/C</td>
<td>C_{ox}/C_{unox}</td>
</tr>
<tr>
<td></td>
<td>C-C</td>
<td>C-O</td>
<td>O-C=O</td>
<td></td>
</tr>
<tr>
<td>New</td>
<td>75.8</td>
<td>24.2</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>21 d UVB exposed</td>
<td>68.4</td>
<td>31.6</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>48 d UVB exposed</td>
<td>73.0</td>
<td>27.0</td>
<td>0.4</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Table A-3:** The Pb accumulation behavior onto the new and UVB exposed LDPE MPs

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pseudo 1st order</th>
<th>Pseudo 2nd order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R^2</td>
<td>t_{1/2} (hr)</td>
</tr>
<tr>
<td>Samples</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDPE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>New</td>
<td>0.975</td>
<td>7.07</td>
</tr>
<tr>
<td>48 d UVB exposed</td>
<td>0.919</td>
<td>8.94</td>
</tr>
</tbody>
</table>

App.-A
Figure A-4. AFM images of (a) new, (b) 21 d, (c) 48 d UVB exposed LDPE and (d) new, (e) 21 d, (f) 48 d UVB exposed PET MPs

(a) New LDPE; RMS: 30.4 nm
(b) 21 d photodegraded LDPE; RMS: 35.6 nm
(c) 48 d photodegraded LDPE; RMS: 52.2 nm
(d) New PET; RMS: 1.9 nm
(e) 21 d photodegraded PET; RMS: 2.1 nm
(f) 48 d photodegraded PET; RMS: 7.0 nm
Figure A-5. The Pb surface loadings onto the new and UVB exposed (a) LDPE and (b) PET MPs as a function of UVB exposure duration

Reference


IBM SPSS version: 29.0.0.0 (241) and Microsoft Excel were used to conduct the statistical analysis. ANCOVA and student's t-test were used to examine whether the Pb accumulation on the various samples differed significantly from one another. A 95% corresponding confidence range was used to calculate statistical significance.

**Figure B-1:** Custom apparatus used to measure the zeta potential of HDPE pipes’ inner walls

**Table B-1:** The chemical constituents of synthetic tap water

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Concentration (g/L)</th>
<th>Chemicals</th>
<th>Concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO₄·7H₂O</td>
<td>0.201</td>
<td>Na₂SiO₃·9H₂O</td>
<td>0.049</td>
</tr>
<tr>
<td>Al₂(SO₄)₃·18H₂O</td>
<td>0.004</td>
<td>CaSO₄·2H₂O</td>
<td>0.051</td>
</tr>
<tr>
<td>KNO₃</td>
<td>0.013</td>
<td>CaCl₂·2H₂O</td>
<td>0.120</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.039</td>
<td>Na₃HPO₄·7H₂O</td>
<td>0.003</td>
</tr>
</tbody>
</table>
Figure B-2: XPS long scans of (a) new PEX-A, (b) 14 d aged PEX-A, (c) new HDPE, and (d) 14 d aged HDPE
Appendix C

C-1 Statistical Analysis

The statistical analyses were performed using the IBM SPSS version: 29.0.0.0 (241) and Microsoft Excel. The Pb accumulation on the different samples was compared using student’s t-test and ANCOVA to see whether there were any significant differences. The confidence interval of 95% was used to calculate statistical significance.

Figure C-1: The small pipe loop used to conduct the metal exposure experiments under flow condition