Final Abstract

Final Report Approved on September 25, 2025

M.L. 2020 Project Abstract

For the Period Ending June 30, 2025

Project Title: Microplastics: Transporters Of Contaminants In Minnesota Waters

Project Manager: Lee Penn

Affiliation: U of MN - College of Science and Engineering

Mailing Address: Department of Chemistry -- University of Minnesota - Twin Cities 207 Pleasant St SE

City/State/Zip: Minneapolis, MN 55455

Phone: (612) 626-4680

E-mail: rleepenn@umn.edu

Website: https://cse.umn.edu/

Funding Source:

Fiscal Year:

Legal Citation: M.L. 2021, First Special Session, Chp. 6, Art. 5, Sec. 2, Subd. 04c

Appropriation Amount: \$425,000

Amount Spent: \$279,917

Amount Remaining: \$145,083

Sound bite of Project Outcomes and Results

Sorption of polycyclic aromatic hydrocarbons did not alter plastic particle settling, while exposure to biosolids and minerals did. Among 14 sampled lakes, both high and low microplastic counts were observed in lakes located in urbanized areas, revealing inconsistent patterns. Contaminants on microplastics collected from the environment were below detection limits.

Overall Project Outcome and Results

We quantified the sorption of polycyclic aromatic hydrocarbons (PAHs), which are contaminants commonly observed in waste water treatment sludge, by polylactic acid (PLA) and polyethylene (PE) films. We observed decreased sorption by PE versus PLA and decreased sorption with increasing size of the PAH molecules tested. We observed no detectable difference in settling of plastics after sorption of the PAHs. However, exposure to sludge and aggregation with iron oxide particles, which was a new experimental direction for this project, both result in faster settling. We conclude that the PAH sorption does not change settling but other changes caused by exposure to sludge does change settling behavior.

We successfully sampled a total of 14 water bodies, including Square Lake, St. Croix River, Forest Lake, Keller Lake, Big Marine, Cedar Bog, Green Lake, Lake Johanna, Little Carnelian, Peltier, Lake Harriet, Cedar Lake (Minneapolis), Walsh Lake, and Lake Nokomis. While the lakes with the highest concentrations of microplastics were also the most urbanized (Forest, Keller), others that were also in highly urbanized areas and of high recreational use did not have such high microplastic content. We were unable to quantify contaminants on the microplastic particles collected from the environment because they were all below detection limits.

Project Results Use and Dissemination

One paper appeared in the peer reviewed literature.

Sewage sludge induces changes in the surface chemistry and crystallinity of polylactic acid and polyethylene films Ariana L Campanaro, Matt F Simcik, Melissa A Maurer-Jones, R Lee Penn Science of the Total Environment https://doi.org/10.1016/j.scitotenv.2023.164313

One paper is currently under review with Chemosphere.

Manuscript Number: CHEM135174

Manuscript Title: Sorption of polycyclic aromatic hydrocarbons by microplastic films: Characterizing kinetics, isotherms,

and impacts of sludge exposure

Journal: Chemosphere

In addition, data were presented in numerous presentations at conferences, seminars, and other regional and national meetings.



Environment and Natural Resources Trust Fund

M.L. 2020 Approved Final Report

General Information

Date: December 22, 2025

ID Number: 2020-040

Staff Lead: Michael Varien

Project Title: Microplastics: Transporters Of Contaminants In Minnesota Waters

Project Budget: \$425,000

Project Manager Information

Name: Lee Penn

Organization: U of MN - College of Science and Engineering

Office Telephone: (612) 626-4680

Email: rleepenn@umn.edu

Web Address: https://cse.umn.edu/

Project Reporting

Final Report Approved: September 25, 2025

Reporting Status: Project Completed

Date of Last Action: September 25, 2025

Project Completion: December 31, 2024

Legal Information

Legal Citation: M.L. 2021, First Special Session, Chp. 6, Art. 5, Sec. 2, Subd. 04c

Appropriation Language: \$425,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to study how several types of common microplastics transport contaminants of concern in Minnesota

waters.

Appropriation End Date: June 30, 2024

Narrative

Project Summary: Microplastics are ubiquitous and may contain chemicals of concern (COCs). We propose to determine the effect that microplastics have on the fate and transport of COCs in Minnesota waters.

Describe the opportunity or problem your proposal seeks to address. Include any relevant background information.

Plastic pollution is a growing environmental problem. Microplastics are tiny pieces of plastics that have broken off bigger plastic objects (e.g., clothing, bags, containers) or were added to products (e.g., microbeads). Microplastics pose a major threat to our environment. We propose to study how microplastics can serve as vehicles to transport contaminants of concern (COCs) within the environment.

Microplastics are problematic for three reasons. First, organisms, on land and in water, eat microplastics, and those microplastics can severely disrupt digestion, sometimes even resulting in death. Second, microplastics can absorb contaminants (i.e. plasticizers, pesticides, drug molecules). This makes microplastics potential vehicles for transporting contaminants within the environment and delivering contaminants to organisms that eat those microplastics. Third, microplastics may act as reservoirs for many contaminants of concern (COCs) in the environment, including pesticides and plasticizers. There are two important types of COCs to consider: molecules used in the fabrication of plastics (e.g., plasticizer) and molecules absorbed from the plastic product's surroundings (e.g., pesticides or herbicides). How much and which COCs are carried by microplastics in water has not been studied in the environment, and not at all in Minnesota.

What is your proposed solution to the problem or opportunity discussed above? Introduce us to the work you are seeking funding to do. You will be asked to expand on this proposed solution in Activities & Milestones.

Here, we propose to examine how microplastics change the fate and transport of COCs in Minnesota waters. We propose to do this by:

- Determining how much and which COCs are taken up by several types of common microplastics
- Determining how microplastics continue to break down and how they settle out from water
- Modeling the fate and transport of COCs, in order to learn how things change with microplastics present
- Collecting and characterizing microplastics collected from Minnesota waters to ground-truth what we learn from the above three activities.

Major Results Expected:

- 1. Determination of how much and which COCs are taken up by common microplastics.
- 2. Improved understanding of how microplastics change the fate and transport of COCs in Minnesota Waters, which will lead to better predictions about environmental impact.

What are the specific project outcomes as they relate to the public purpose of protection, conservation, preservation, and enhancement of the state's natural resources?

The results from this project will enable the State of Minnesota to better predict the impact of environmental contamination with chemicals and microplastics and develop better approaches to prevention and remediation. In addition, the team will give open scientific presentations and publish scientific papers addressing the above objectives.

Project Location

What is the best scale for describing where your work will take place?

Statewide

What is the best scale to describe the area impacted by your work?

Statewide

When will the work impact occur?

During the Project and In the Future

Activities and Milestones

Activity 1: Lab Studies to Determine Fate and Transport of COCs by Microplastics

Activity Budget: \$306,000

Activity Description:

We will combine select COCs and common types of microplastics in batch experiments. Target COCs include plasticizers (e.g., per- and polyfluoroalkyl substances (PFAS), polychlorinated biphenyls (PCBs)) and current-use organochlorine pesticides. Target microplastics include fibers of polyester, Rayon, Nylon, polyurethane, and polyethylene terephthalate (fleece). Fibers will be introduced to glass containers of aqueous solutions with known amounts of COCs, allowed to equilibrate for 24 hours on a wrist-action shaker, filtered, and analyzed for COCs in the water and microplastic. How much COC is taken up by each plastic will be calculated.

Many COCs are "removed" from water through settling and burial in sediments. Settling of naturally occurring particles is already well understood. However, microplastics have different shapes, densities, and surface chemistry, which affect how quickly particles settle and are burried. We will use glass columns to measure settling rates of microplastics in waters. Because particles scatter light, small lasers will enable detection of particles at specified heights along the column. We will perform these experiments with "virgin" microplastic particles and microplastic particles after exposure to COCs in purified water and lake water samples.

Results will be used in models designed to predict fate and transport of COCs associated with microplastics.

Activity Milestones:

Description	Approximate Completion Date
Determine Partitioning of COCs with Each Type of Microplastic	June 30, 2022
Measure Settling Velocities of Microplastics	June 30, 2022
Fate and Transport Model: Use Experimental Results to Develop a Predictive Model	June 30, 2023

Activity 2: Ground-truthing with Environmental Samples

Activity Budget: \$119,000

Activity Description:

Twenty Minnesota waters (rivers and lakes) will be sampled and filtered for both microplastics and natural particles. Both the filters and filtrates will be analyzed for COCs and microplastics. Initial determination of the amount of microplastics in a field sample will use light microscopy after dying with Nile Red or another dye that does not dye the naturally occurring particles (e.g., small sediment particles or organisms) but only dyes the plastics. Settling experiments, as described above, will be performed using the plastics collected from the environment. The microplastic particles will be further characterized in order to identify the polymer (e.g., polyurethane, polyethylene terephthalate, etc...) and identify whether biofilms are present. Results from the settling experiment will enable characterization of the potential impact of biofilms on settling velocities. Results from the field samples will be compared to the laboratory results and predictions produced from activity one.

Both activity one and two have been updated to reflect feedback received during the peer review of our submission, after it was recommended for funding.

Activity Milestones:

Description	Approximate Completion Date
Environmental Sampling from Twenty MN Locations (Rivers and Lakes)	November 30, 2022

Characterize Samples Collected from the Field	March 31, 2024
Measure Settling Velocities of Microplastics Collected from the Field	March 31, 2024
Validation of Models Using Experimental and Field Results	May 31, 2024
Prepare Final Report and Disseminate Data and Results	June 30, 2024

Project Partners and Collaborators

Name	Organization	Role	Receiving Funds
Matt Simcik	University of Minnesota - Twin Cities School of Public Health	Dr. Simcik is in the Division of Environmental Health Sciences in the School of Public Health. Dr. Simcik is an expert in the fate and transport of organic contaminants in the environment. Dr. Simcik will serve as primary supervisor to the lab manager and the graduate assistant.	Yes

Dissemination

Describe your plans for dissemination, presentation, documentation, or sharing of data, results, samples, physical collections, and other products and how they will follow ENRTF Acknowledgement Requirements and Guidelines.

The team will give open scientific presentations at both local and national meetings and publish scientific papers addressing the above objectives. We will also prepare a webpage to convey results to the public.

The Minnesota Environment and Natural Resources Trust Fund (ENRTF) will be acknowledged through use of the trust fund logo or attribution language on project print and electronic media, publications, signage, and other communications per the ENRTF Acknowledgement Guidelines.

Long-Term Implementation and Funding

Describe how the results will be implemented and how any ongoing effort will be funded. If not already addressed as part of the project, how will findings, results, and products developed be implemented after project completion? If additional work is needed, how will this work be funded?

Results from this project will enable the State of Minnesota to better predict the impact of environmental contamination with chemicals and microplastics and develop better approaches to prevention and remediation. The results of this project will enable managers of Minnesota's water resources and legislators to better address the issue of environmental contamination.

Other ENRTF Appropriations Awarded in the Last Six Years

Name	Appropriation	Amount Awarded
Solar Cell Materials from Sulfur and Common Metals	M.L. 2014, Chp. 226, Sec. 2, Subd. 08a	\$494,000

Budget Summary

Category / Name	Subcategory or Type	Description	Purpose	Gen. Ineli gible	% Bene fits	# FTE	Class ified Staff?	\$ Amount	\$ Amount Spent	\$ Amount Remaining
Personnel										
Lab Manager		Manage PI lab operations			25.4%	0.24		\$17,736	-	-
Principal		Supervise graduate student; perform			36.5%	0.27		\$62,228	-	-
Investigator		electron microscopy on samples; co- lead sample collection in the field; evaluate data and design experiments.								
Co-Principal Investigator		Supervise graduate student;lead sample collection in the field; evaluate data and design experiments.			36.5%	0.27		\$45,673	-	-
Graduate		Design and execute experiments and			44.54%	1.41		\$140,771	-	-
Research		sample collection; characterize								
Assistant		standard and field samples of								
(Beginner)		polymer fibers.								
Graduate		Co-advised and working in close			22.77%	1.5		\$108,261	-	-
Research		collaboration with members of each								
Assistant		PI's research group; Design and								
(Advanced)		execute experiments and sample								
		collection; quantify absorption of								
		contaminants in standard and field								
		samples of polymers.					Sub Total	\$374,669	\$260,572	\$114,097
Contracts and Services										
University of	Internal	Internal user fees for				0.03		\$9,000	\$9,000	-
Minnesota -	services or	instrumentation (microscopy and								
Twin Cities	fees	spectroscopy for polymer								
College of	(uncommon)	characterization) at the University of								
Science and		Minnestoa - College of Science and								
Engineering		Engineering's Characterization								
Characterization		Facility (\$3k/yr). Personnel								
Facility		supported by this award will perform the characterization.								
		personn the characterization.					Sub Total	\$9,000	\$9,000	-

Equipment, Tools, and Supplies								
	Tools and	Model contaminant compounds	Model contaminant			\$4,000	\$1,807	\$2,193
	Supplies		compounds					
	Tools and	long glass column, six small lasers	Supplies for settling			\$3,331	\$1,796	\$1,535
	Supplies	for light scattering measurements	experiments					
	Tools and	Supplies for Materials	microscopy and			\$2,000	\$1,197	\$803
	Supplies	Characterization	spectroscopy for polymer					
			characterization before and					
			after use in batch					
			experiments and for					
			characterization of samples					
			collected from the field;					
			microscopy slides and stubs,					
			conductive glue and paste,					
			standards					
	Tools and	Chemical Supplies	salts, water purification			\$9,000	\$2,610	\$6,390
	Supplies		cartridges, glass containers					
	Tools and	Filters	Filters for removal of			\$12,000	\$2,621	\$9,379
	Supplies		microplastics from					
			experimental and natural					
			waters					
					Sub Total	\$30,331	\$10,031	\$20,300
Capital Expenditures								
					Sub Total	-	-	-
Acquisitions								
and								
Stewardship								
•					Sub Total	-	-	1
Travel In Minnesota								
	Miles/ Meals/ Lodging	Travel to/from field site	Travel to/from field sites for sample collection; travel to/from University of Minnestoa - Duluth for collaborative meetings,			\$1,000	-	\$1,000

		sample collection, and					
		experiments					
		experiments		Sub	\$1,000	_	\$1,000
				Total	31,000	-	31,000
Travel Outside				Total			
Minnesota							
Willinesota				Sub			_
				Total	_	_	_
Printing and				Total			
Publication							
Publication				Sub			
					-	-	-
Oth				Total			
Other Expenses							
	REPAIR Research X-ray	The instrument in question			\$10,000	\$314	\$9,686
	Diffractometer requires repair to	is an X-ray diffractometer					
	return to functioning status	that was acquired years					
	(essential method for the project)	before the start of this					
		particular project, which is					
		true for several pieces of					
		equipment that we use in					
		connection to this project.					
		The instrument is used for					
		research on several					
		projects. We use the					
		instrument for					
		characterization of the					
		plastics involved in this					
		project's research.					
		Specifically, we can					
		characterize changes in					
		crystallinity before and after					
		exposure to various					
		conditions. This is					
		important because changes					
		in crystallinity are					
		associated with changes in					
		uptake of contaminants of					
		concern by the plastics.					
		Over the course of this					
		project, the instrument has					
		been used extensively for					
		characterization of plastics					
		characterization of plastics					

	and also, more recently, the mineral particles that stick to the plastics and result in changes in settling rates. We would like to cover a reasonable portion of the cost to repair the instrument using funds from this project. Without this instrument, we won't be able to perform the characterization necessary. The remainder of the cost will be shared across other chart strings / accounts.					
	charestings / decounts.		Sub Total	\$10,000	\$314	\$9,686
			Grand Total	\$425,000	\$279,917	\$145,083

Classified Staff or Generally Ineligible Expenses

Category/Name	Subcategory or	Description	Justification Ineligible Expense or Classified Staff Request
	Туре		

Non ENRTF Funds

Category	Specific Source	Use	Status	\$ Amount	\$ Amount Spent	\$ Amount Remaining
State						
			State Sub Total	-	-	-
Non- State						
In-Kind	University of Minnesota	The investigators will also devote 1% time per year in-kind (\$9,089 3 year total).	Potential	\$19,231	\$19,231	-
In-Kind	University of Minnesota	In-kind Overhead for administrative and operational expenses that will support the research described within this application.	Potential	\$202,106	\$153,955	\$48,151
			Non State Sub Total	\$221,337	\$173,186	\$48,151
			Funds Total	\$221,337	\$173,186	\$48,151

Attachments

Required Attachments

Visual Component

File: 3af18d68-174.pdf

Alternate Text for Visual Component

Microplastics are ubiquitous and may contain chemicals of concern (COCs). Microplastics pose a major threat to our environment. The schematic shown here highlights some of the places we find microplastics contamination (water, lake sediment, plant materials, fish, animals, and more). We propose to study how microplastics can serve as vehicles to transport contaminants of concern (COCs) within the environment....

Supplemental Attachments

Capital Project Questionnaire, Budget Supplements, Support Letter, Photos, Media, Other

Title	File
UMN Letter of Intent from Sponsored Projects	<u>407810a9-bc3.pdf</u>
Tab 7 background check form	f65adf65-0ef.pdf
Proof of UMN's tax exemption status	452eef4d-eb2.pdf
IRS Support Letter	73fbd18f-649.pdf
board-reviewed financial statement	63598a6b-ef4.pdf
UMN Audit Report	<u>7e16ac9a-3ed.pdf</u>
Sewage Sludge Induces Changes in the Surface Chemistry and	<u>e43b666d-dc8.pdf</u>
Cyrstallinity of Polylactic Acid and Polyethylene Films (STOTEN	
2023 publication)	

Media Links

Title	Link
Sewage sludge induces changes in the surface chemistry and	https://doi.org/10.1016/j.scitotenv.2023.164313
crystallinity of polylactic acid and polyethylene films	

Difference between Proposal and Work Plan

Describe changes from Proposal to Work Plan Stage

We added milestones as requested. We updated dates for milestone completion. We modified the budget so that it matches with the amount recommended.

We moved User fees for instrumentation (microscopy and spectroscopy for polymer characterization) at the University of Minnestoa - College of Science and Engineering's Characterization Facility (\$3k/yr) to professional, tech, service, contracts.

Additional Acknowledgements and Conditions:

The following are acknowledgements and conditions beyond those already included in the above workplan:

Do you understand and acknowledge the ENRTF repayment requirements if the use of capital equipment changes? $\ensuremath{\text{N/A}}$

Do you understand that travel expenses are only approved if they follow the "Commissioner's Plan" promulgated by the Commissioner of Management of Budget or, for University of Minnesota projects, the University of Minnesota plan?

Yes, I understand the UMN Policy on travel applies.

Does your project have potential for royalties, copyrights, patents, sale of products and assets, or revenue generation?

No

Do you understand and acknowledge IP and revenue-return and sharing requirements in 116P.10?

N/A

Do you wish to request reinvestment of any revenues into your project instead of returning revenue to the ENRTF? N/A

Does your project include original, hypothesis-driven research?

Yes

Does the organization have a fiscal agent for this project?

No

Work Plan Amendments

Amendment ID	Request Type	Changes made on the following pages	Explanation & justification for Amendment Request (word limit 75)	Date Submitted	Approved	Date of LCCMR Action
1	Amendment Request	 Other Budget - Personnel Budget - Other 	Requesting an amendment to the budget to cover the cost of repair of the Research X-ray Diffractometer that is used used extensively for characterization of plastics and also, more recently, the mineral particles that stick to the plastics and result in changes in settling rates. The amendment request would cover a reasonable portion of the cost of repair.	April 12, 2024	Yes	May 29, 2024
2	Completion Date	Previous Completion Date: 06/30/2024 New Completion Date: 12/31/2024	Winter 23-24 posed major challenges with regard to winter lake sampling due to thin ice. Winter is the best time to sample because lake water clarity is at its highest, making separation of microplastics from samples far easier. In addition, we faced staffing challenges, which delayed completion of sampling work.	April 12, 2024	Yes	May 29, 2024

Final Status Update February 14, 2025

Date Submitted: June 5, 2025

Date Approved: June 26, 2025

Overall Update

We quantified the sorption of polycyclic aromatic hydrocarbons (PAHs), which are contaminants commonly observed in waste water treatment sludge, by polylactic acid (PLA) and polyethylene (PE) films. We observed decreased sorption by PE versus PLA and decreased sorption with increasing size of the PAH molecules tested. We observed no detectable difference in settling of plastics after sorption of the PAHs. However, exposure to sludge and aggregation with iron oxide particles, which was a new experimental direction for this project, both result in faster settling. We conclude that the PAH sorption does not change settling but other changes caused by exposure to sludge does change settling behavior.

We successfully sampled a total of 14 water bodies, including Square Lake, St. Croix River, Forest Lake, Keller Lake, Big Marine, Cedar Bog, Green Lake, Lake Johanna, Little Carnelian, Peltier, Lake Harriet, Cedar Lake (Minneapolis), Walsh Lake, and Lake Nokomis. While the lakes with the highest concentrations of microplastics were also the most urbanized (Forest, Keller), others that were also in highly urbanized areas and of high recreational use did not have such high microplastic content. We were unable to quantify contaminants on the collected particles because they were all below detection limits.

Activity 1

We quantified sorption of polycyclic aromatic hydrocarbons (PAHs) by polylactic acid (PLA) and polyethylene (PE) films. We observed decreased sorption by PE versus PLA and decreased sorption with increasing PAH molecular weight. Results have been submitted to a peer-reviewed journal. In addition, we tested for the leaching from plastics after exposure to solutions of one of the PAH molecules, and no detectable leaching of the PAH molecule back into solution was observed. Three types of settling experiments were performed. The first series of experiments quantified settling rates of pieces of PLA films before and after sludge exposure, with increased settling with increasing sludge exposure time (up to 3 weeks). Sludge exposure results in surface roughening of the plastic particles. In the second type of experiment, settling velocities were quantified for PLA exposed to PAHs, with no significant changes in settling observed with PAH sorption. Finally, we quantified the rate of PLA and PE settling in the presence of iron oxide mineral particles, which are common in natural waters. The presence of iron oxide mineral particles substantially increases aggregation and the rate of settling of plastic particles. Due to personnel challenges, we were not able to complete work related to modeling.

(This activity marked as complete as of this status update)

Activity 2

An additional 9 lakes were sampled and analyzed for microplastics. Forest Lake, Keller, and Big Marine had the highest microplastic counts per liter of water: 61.25 particles and 70 fibers in Forest Lake, 188 particles and 38.5 fibers in Keller, and 53.3 particles and 17 fibers in Big Marine. The other six lakes had substantially fewer particles and fibers per liter of water: 19.5 particles and 5.5 fibers in Cedar Bog, 25.5 particles and 24.25 in Green Lake, 29.5 particles and 17 fibers in Lake Johanna, 34.75 particles and 14.75 fibers in Little Carnelian, 4.25 particles and 3.5 fibers in Peltier, and 23 particles and 8.25 fibers in Square Lake. In addition, we sampled the St. Croix River and found 11.5 particles and 1.25 fibers per liter). While the lakes with the highest concentrations of microplastics were also the most urbanized (Forest, Keller), others that were also in highly urbanized areas and of high recreational use did not have such high microplastic content. We were unable to quantify contaminants on the collected particles because they were all below detection limits. (*This activity marked as complete as of this status update*)

Dissemination

"Sorption of polycyclic aromatic hydrocarbons by microplastic films: Characterizing kinetics, isotherms, and impacts of sludge exposure" has been submitted to the peer reviewed journal "Chemosphere" and is currently under review after submission of requested revisions.

Status Update October 1, 2024

Date Submitted: June 5, 2025

Date Approved: June 26, 2025

Overall Update
Nothing to report

Activity 1

Nothing to report

Activity 2

Nothing to report

Dissemination

Nothing to report

Additional Status Update Reporting

Additional Status Update August 14, 2024

Date Submitted: June 5, 2025

Date Approved: June 26, 2025

Overall Update
Nothing to report

Activity 1

Nothing to report

Activity 2

Nothing to report

Dissemination

Nothing to report

Status Update April 1, 2024

Date Submitted: April 12, 2024

Date Approved: May 29, 2024

Overall Update

We have obtained significant results tracking sorption of polycyclic aromatic hydrocarbons (PAHs) by polylactic acid (PLA) and polyethylene (PE) films. We observed decreased sorption by PE versus PLA and decreased sorption with increasing PAH molecular weight. Results will be submitted to a peer-reviewed journal within the next four weeks. Two types of settling experiments were performed. The first series of experiments quantified settling rates of pieces of PLA films before and after sludge exposure, with increased settling with increasing sludge exposure time (up to 3 weeks). In addition, settling velocities were quantified for PLA exposed to PAHs, with no significant changes in settling observed with PAH sorption. Next, we quantified the rate of PLA and PE settling in the presence of iron oxide mineral particles, which are common in natural waters. The presence of iron oxide mineral particles substantially increases settling of plastic particles. Despite a challenging winter (limited access to lakes for sampling, winter is ideal as water clarity is at a maximum), we successfully sampled one lake in February, and the sample analysis is in progress. Results will help improve predictions of the fate and transport of environmental PAHs in the presence of microplastics.

Activity 1

Experiments examining settling were expanded to include the presence of mineral particles. We used UV-Visible spectroscopy to determine the effects of solution conditions (i.e., pH and ionic strength) and the presence of iron oxide and oxyhydroxide minerals (goethite and hematite) on the settling of PLA and PE microspheres (1-4 microns). In addition, we quantified surface charge of both the plastic particles and the hematite and goethite mineral particles. Generally speaking, less surface charge means faster settling and opposite surface charge on the plastic versus mineral particles would mean faster settling. The fraction that settled was determined by the difference in absorbance of the suspensions before and after 24 hours of settling. In general, settling was enhanced when solution conditions meant that particles had little to no surface charge (i.e., near the isoelectric point), and the presence of goethite and hematite increased settling. Dynamic light scattering, zeta potential measurements, and scanning electron microscopy were used to relate particle aggregation to the settling percent of microplastics. When solutions resulted in enhanced aggregation, overall settling increased.

Activity 2

Winter lake sampling was compromised by the very short time period during which ice was safe. We did successfully sample one lake this winter: A 4L water sample was collected from Walsh Lake in Lauderdale, MN on 25 February 2024. Plastic particles were stained using iDye fabric dye and isolated using vacuum filtration. Particles will be analyzed using light microscopy to determine particle size and morphology and FTIR microscopy to determine plastic composition.

Dissemination

Results highlighting the sorption of PAHs by PE and PLA will be submitted to a peer-reviewed journal within the next four weeks.

Presentation this month: Understanding Microplastic Interactions in Environmentally Relevant Conditions. Civil, Environmental, and Geo-engineering Departmental Seminar, Minneapolis MN April 2024. https://doi.org/10.1016/j.scitotenv.2023.164313 appeared in 2023.

Status Update October 1, 2023

Date Submitted: October 12, 2023

Date Approved: January 17, 2024

Overall Update

We achieved substantial progress tracking the uptake of polycyclic aromatic hydrocarbons (PAHs) by polylactive acid (PLA) and polyethylene (PE) films, with significant differences in uptake observed for aged versus unaged PE. Two types of settling experiments were performed. The first series of experiments quantified settling rates of pieces of PLA films before and after sludge exposure. The settling velocity of PLA was found to increase with increasing sludge exposure time up to 3 weeks. In addition, settling velocities were quantified for PLA exposed to PAHs before and after sludge exposure. It's unclear whether the PAH sorption results in a change in the settling velocity of PLA. The second series of experiments quantified the rate of PLA settling in the presence of iron oxide mineral particles. Those experiments are in progress, with preliminary results indicating that salt concentration and pH impacts settling rate. Finally, established settling velocity models have been applied to experimental data describing the settling velocity of PLA films. Generally speaking, the models fit the data collected using unaged PLA better, with high absolute error and root-mean-square error values for the sludge-aged PLA.

Activity 1

Settling Velocities: Settling velocities of PLA film particles pre- and post-sludge exposure were quantified. The settling velocity of PLA increased with increasing sludge exposure time, up to 3 weeks. Settling velocities of PLA film particles exposed to sludge and subsequently solutions of PAHs were also quantified. For unaged PLA films and those aged for 1 week in sludge, the settling velocity increased after PAH sorption. However, for PLA aged in sludge for 3 weeks, the settling velocity decreased after PAH sorption.

Settling velocities were quantified for suspensions containing the goethite mineral particles and PLA particles. Preliminary results suggest that the settling rates are dependent on the ionic strength and pH of the water.

Fate and Transport/Modeling: Established settling velocity models have been applied to experimental data describing the settling velocity of PLA films. The calculated settling velocities have been plotted against the experimental settling velocities and the slope and coefficient of determination used to compare the fits of different models. Overall, these models tend to fit the unaged PLA data much better, with high absolute error and root-mean-square error values for the sludge-aged PLA films.

Activity 2

Lake sampling during the last reporting period was complicated by lake clarity, which makes separating plastic particles from the lake water challenging. We are working to address this challenge and will also take advantage of the increasing lake clarity with cooling temperatures.

Dissemination

Three presentations in the last reporting period, with graduate student Ari Campanaro presenting. Impacts of Sludge Exposure on the Properties and Sorption Interactions of Plastic Films. Industrial Partnership for Research in Interfacial & Materials Engineering Annual Meeting, Nanostructural Materials and Processes Poster Session, Minneapolis, MN. May 2023.

Characterizing the Sorption Interactions Between Microplastic Films and Polycyclic Aromatic Hydrocarbons. Jeannette

Brown Lectureship Student Flash Talks, Minneapolis, MN. April 2023.

Impacts of Sludge Exposure on the Properties and Sorption Interactions of Plastic Films. Sustainability Symposium, St. Paul, MN. April 2023.

One paper appearing in the peer reviewed literature during the last reporting period.

Epub 2023 May 19.

Sewage sludge induces changes in the surface chemistry and crystallinity of polylactic acid and polyethylene films Ariana L Campanaro, Matt F Simcik, Melissa A Maurer-Jones, R Lee Penn

Science of the Total Environment

2023 Sep 10:890:164313.

DOI: 10.1016/j.scitotenv.2023.164313

Status Update April 1, 2023

Date Submitted: April 7, 2023

Date Approved: May 15, 2023

Overall Update

We have quantified how much of three different Polycyclic Aromatic Hydrocarbons (PAHs) are taken up by two types of common microplastics, polyethlene and polylactic acid. Subsequent settling measurements show that the sorption of the PAHs changes settling behavior substantially.

Activity 1

We characterized the uptake of naphthalene (Nap), phenanthrene (Phen), and pyrene (Pyr), three different polycyclic aromatic hydrocarbon (PAH) compounds commonly observed as pollutants, by the plastics polylactic acid (PLA) and polyethylene (PE). We used three models to compare sorption capacities. We performed these experiments using plastics before and after exposure to sewage sludge. Both molecular weight and hydrophobicity of the plastics play important roles in determining the relative sorption capacity for PAHs. All PE samples exhibited greater PAH sorption than PLA. Exposure to sludge significantly changes changes the PAH sorption capacity. For example, after 2 weeks of sludge exposure, PE sorbed significantly more Phen and Pyr than PE without the sludge exposure.

A glass column fitted with laser pointers and camera was assembled and used to quantify settling velocities of PLA before and after sorption of PAHs. Statistical analysis was performed on the data. After PAH (either naphthalene, phenanthrene, or pyrene) sorption, the settling velocity of PLA films increased from 8.22.1 to 10.31.3 mm/s. Preliminary experiments indicate that one week of exposure to sewage sludge does not significantly alter the settling velocity of PLA and no difference in settling velocities in purified versus lake water.

Activity 2

Water samples were collected from Cedar Lake and Lake Nokomis. Plastic particles were isolated using a combination of vacuum filtration and a staining method using iDye fabric dye, then analyzed using light microscopy and Fourier-transform infrared spectroscopy. Particles were characterized by size, morphology, and plastic type. For both Cedar Lake and Lake Nokomis water samples, the majority of recovered particles (75% for Cedar and 54% for Nokomis) were in the size range of <500 micron, followed by 500-1000 micron, then >1000 micron. Cedar Lake samples were composed of fragments (54%), fibers (27%), and spheres (20.%). The breakdown of particles in Lake Nokomis water samples were fragments (66%), fibers (20.%), and spheres (14%). The largest fraction of particles recovered were identified as nylon (78% for Cedar and 88% for Nokomis). The remaining particles recovered from Cedar Lake included polyurethane, polyethylene, polycarbonate, polystyrene:4-vinyl pyridine, and polyvinyl acetate:polyethylene. Interestingly, the remaining particles recovered from Lake Nokomis were composed of different plastics, including polyvinyl chloride, polyvinyl butyral, polyisobutylene:isoprene, and polystyrene 4-vinyl pyridine.

Dissemination

Results have been presented to other research groups engaged in research related to microplastics and also local meetings (e.g., the Jeanette Brown memorial lecture series at the U of MN).

Status Update October 1, 2022

Date Submitted: October 7, 2022

Date Approved: October 28, 2022

Overall Update

To date, we have characterized the samples collected in winter (when the water clarity was greater). Microscopy and spectroscopy were used to identify the plastics. The primary plastics detected from the ice swimming holes were nylon fibers and fragments. Standard plastic samples (polylactic acid, polyethylene, polyurethane, and polyethylene terephthalate) have been exposed to aqueous solutions containing polycyclic aromatic hydrocarbons (PAHs). Through this work, the degree of PAH uptake was found to be dependent on both the type of plastic and the PAH identity. Additionally, the time it takes for sorption equilibrium to be reached varies between different plastic types. From these early results, we can conclude that different plastics will behave differently from the perspective of fate and transport of contaminants of concern.

Activity 1

The rate and extent of PAH uptake by PLA were characterized. The experimental measurements of uptake of three polycyclic aromatic hydrocarbons (PAHs) – naphthalene (ten carbons), phenanthrene (fourteen carbons), and pyrene (sixteen carbons) – has been modeled for each microplastic type using a linear isotherm and the Freundlich isotherms. For both naphthalene and phenanthrene, it took much longer for the PAH to equilibrate with PLA microplastics as compared to the results using PE microplastics. In the case of pyrene, equilibration time with PLA was shorter than that of naphthalene and phenanthrene with PLA, but longer than that of pyrene with PE. These results suggest that experiments determining sorption capacities of PLA will require longer equilibration times to allow for accurate quantification.

Activity 2

Water samples collected from four locations during winter 2021-2022 were extensively characterized. Water samples were filtered through sieves and then stained using an aqueous solution containing iDye fabric dye. Vacuum filtration was then used to isolate the dyed particles. Isolated particles were analyzed using light microscopy and Fourier-transform infrared spectroscopy. Particles were characterized by size, morphology, and plastic type. The microplastics collected from Celdar Lake were, on average, quite a bit smaller than those collected from Lake Harriet. In both samples, the recovered morphologies were fragments, fibers, and spheres. The particles detected were mostly nylon and cellulose, with some polystyrene and polyethylene. The Lake Harriet sample contained ~23 particles/L water, while the Cedar Lake sample contained 132 particles/L water. With the decreasing temperatures and improving water clarity, additional samples will be collected before the lakes freeze.

Dissemination

Results were presented on 9 June 2022 at the Graduate Student Research Symposium in Minneapolis, MN: "Changes in Surface Chemistry and Crystallinity of Plastic Films with Exposure to Sludge from a Wastewater Treatment Plant" by Ariana Campanaro..

Results were presented on 24 August 2022 at the ACS National Meeting in Chicago, IL: "Changes in Surface Chemistry and Crystallinity of Poly(lactic acid) and Polyethylene Films with Exposure to Sludge from a Wastewater Treatment Plant" by Ariana Campanaro.

Status Update April 1, 2022

Date Submitted: April 27, 2022

Date Approved: May 24, 2022

Overall Update

To date, we have collected samples from four locations in winter (when the water clarity is greater). Samples were collected from locations with active ice swimming holes (Lake Harriet and Cedar Lake) and from locations with active ice fishing (Square Lake and the St. Croix River). The primary plastics detected from the ice swimming holes were nylon fibers and fragments. Standard plastic samples (polylactic acid, polyethylene, polyurethane, and polyethylene terephthalate) have been exposed to aqueous solutions containing polycyclic aromatic hydrocarbons (PAHs). Through this work, the degree of PAH uptake was found to be dependent on both the type of plastic and the PAH identity. From these early results, we can conclude that different plastics will behave differently from the perspective of fate and transport of contaminants of concern.

Activity 1

Partitioning of COCs with each type of microplastic -- in progress:

Sorption capacities have been determined for a range of microplastic samples in aqueous solution, including polylactic acid (PLA), polyethylene (PE), polyurethane (PU), and polyethylene terephthalate (PET). The experimental measurements of uptake of three polycyclic aromatic hydrocarbons (PAHs) – naphthalene (ten carbons), phenanthrene (fourteen carbons), and pyrene (sixteen carbons) – has been modeled for each microplastic type using a linear isotherm and the Freundlich isotherms. All sorption experiments were performed in triplicate. Kinetics studies were performed to determine how long it takes for the model PAH solutions to equilibrate with polyethylene, and results show that 48 hours equilibration is appropriate for making quantitative comparisons between microplastics and which PAH was used. Results show that substantially more phenanthrene (the fourteen carbon molecule) was taken up by the microplastic samples, and PE and PU sorbed approximately twice as much as did PLA and PET. Far less of the smaller napthalene and larger pyrene was sorbed by the microplastics.

Measure Settling Velocities of Microplastics -- currently setting up apparatus for performing these experiments.

Fate and transport model: as soon as we have more data -- nothing to report yet.

Activity 2

Four locations were sampled during winter 2021-2022. Winter sampling has the advantage of the greatest water clarity, which facilitates the identification of microplastics and particles that are of a natural origin (e.g., algae or plant matter). Samples were collected from the locations of active ice swimming holes (Lake Harriet and Cedar Lake in Minneapolis MN) and from locations with active ice fishing (Square Lake and the St. Croix River, Stillwater MN).

Water samples from Lake Harriet were filtered through sieves and then stained using an aqueous solution containing iDye fabric dye. Vacuum filtration was then used to isolate the dyed particles. Isolated particles were analyzed using light microscopy and Fourier-transform infrared spectroscopy. Particles were characterized by size, morphology, and plastic type. The size breakdown of the particles was <500 micron (40.3%), 500-1000 micron (34.7%), and >1000 micron (25%). The recovered morphologies were fragments, fibers, and spheres. The majority of the recovered particles were nylon (52.2%), then cellulose (26.1%), polystyrene (13%), and polyethylene (8.7%).

Dissemination

We have presented early results on 7 April 2020 at the Jeannette Brown Lectureship 2022 in Minneapolis, MN:

"Changes in Surface Chemistry and Crystallinity of Plastic Films with Exposure to Sludge from a Wastewater Treatment Plant," presented by Ariana Campanaro.				
28				