Analysis of Road Dust Sediment from Valparaiso, Indiana

Nolan Brezina, Emily Broniewicz, Cady Caldwell, Ali Egertson, Yanni Flaherty, Cas Grant, Desirae Kahn, Abraham Orozco, Yaasantewa Mustapha, Emma Pasco, Margot Santana, Allison Schoenbeck, Zach Stewart, Alyssa Suprenant, Gabrielle Unzicker, Dr. Julie Peller,
Valparaiso University Department of Chemistry

Abstract

One effective way to assess contaminant exposure is by studying road dust sediment (RDS), which contains particles created by vehicles, deposited from air and water and more. We collected and examined the roadside sediment at seven sites in Valparaiso, Indiana. Those were chosen based on traffic and potential variety of vehicles. Each sample was analyzed for microplastics, metal content, and carbon content. Traces of several plastics were found, including polyurethane, nylon, and polyamide. The carbon analysis indicated high percentages of carbonate at a few locations. The metal analysis showed mostly low concentration of heavy metals from these locations in Valparaiso, especially when compared to neighboring industrial sites in Gary, IN.

Sampling Locations

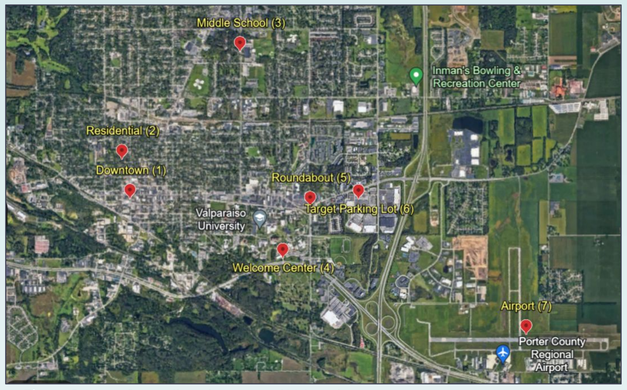

Figure 1. Map of sampling sites around Valparaiso

Table 1. Sampling site locations and notes taken while collecting samples

Sampling Sites	Description/Notes
1. Downtown	Samples were wet; samples hard to place into the container; many cars on the street led to difficulty collecting samples; samples collected next to ice rink and a bus stop
2. Residential	Lafayette St; samples were wet and hard to place into the container
3. Public School	Thomas Jefferson Middle School; samples collected in front of school; samples were hard to collect; wet
4. VU Welcome Center	Samples collected were wet; easy to collect; low traffic
5. Lincolnway Ave/Sturdy Rd Roundabout	Samples were wet; samples taken from three different areas of the roundabout; cars passing through the roundabout led to difficulty collecting samples
6. Target Entrance	Samples were taken from the front entrance and parking lot; samples were wet
7. Airport Runway	Porter County Regional Airport; samples were retrieved from three separate areas of the runway; samples retrieved from the tarmac itself were very fine; samples retrieved right next to the runway were fine but also contained grainy dirt; samples retrieved from the grassy area were harder to retrieve due to muddy conditions

Carbon & Carbonate

Soil is composed of many inorganic and organic components. Carbonate is a common mineral in healthy soil and is the major inorganic form of carbon. Organic carbon is found in carbon-rich soils, but numerous pollutant organic compounds are created from engine combustion tire wear, and asphalt.

Analysis of organic carbon and carbonate matter was conducted by first drying samples in an oven at 100℃. Masses were recorded for each sample. Organic Carbon was burned off at 500℃, at which point the samples were again massed. Carbonate masses were determined by heating samples at 1000℃.
Percentages of organic matter (OM) and carbonate matter (CM) are represented in Figure 3. Samples that contained low OM% & CM% are likely to be composed mostly of silicas and silicates.

Figure 2 demonstrates the reproducibility of multiple samples taken at the same location.

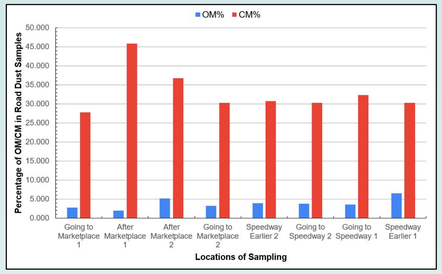

Figure 2. Percentage of OM and CM from duplicate samples at the roundabout of sturdy Rd and Lincolnway.

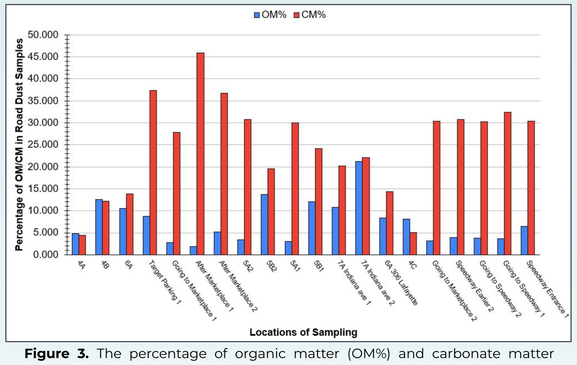

Figure 3. The percentage of organic matter (OM%) and carbonate matter (CM%) for Valparaiso, IN samples.

Elemental Analysis

XRF (X-Ray Fluorescence) analysis was used to determine the concentrations of metals in each sample. The samples were also analyzed at the University of Notre Dame using PIXE (Proton-induced X-ray Emission) for analytical comparisons.

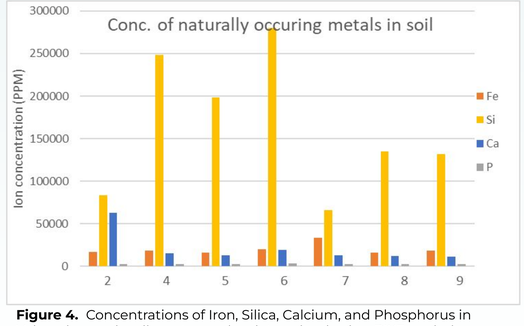

Figure 4. Concentrations of Iron, Silica, Calcium, and Phosphorus in Valparaiso road sediment samples determined using PIXE analysis.

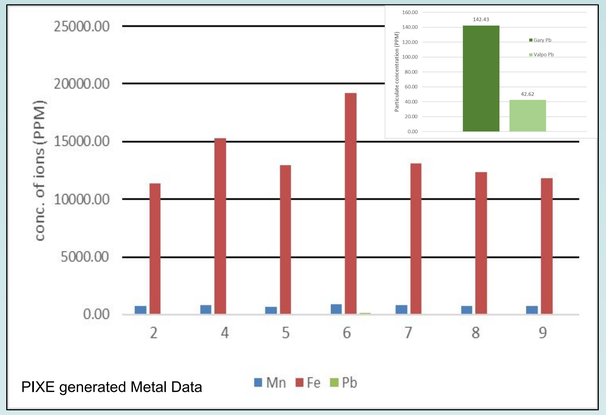

Figure 5. Concentrations of Lead, Manganese, and Iron in road sediment samples using PIXIE. The insert shows the average lead values in Valparaiso (n=7) compared to Gary RDS (n = 100).

Microplastic analysis

To isolate microplastics, sediment samples were processed using density separations ($ZnCl_2$ solution; ~ 1.4 g/mL) and then vacuum filtered. To reduce remaining organic content, the contents of the filter papers were subject to oxidation using UV light and H_2O_2(aq). These samples were then filtered again (Fig 8).

RAMAN microscopy and spectroscopy was used to image the particles and determine the presence of plastic in the sample sediments. We were able to confirm the presence of polyamide, a type of nylon polymer, in sample 7a (Figures 6 and 7).

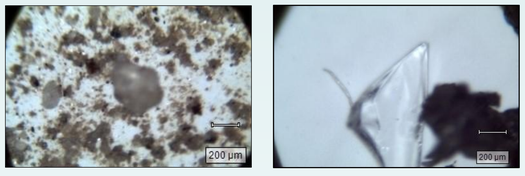

Figure 6. RAMAN microscope 5x views of assumed polyurethane from sample 6A1 (left) and polyamide from sample 7A (right).

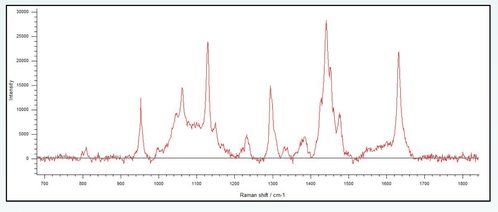

Figure 7. Sample 7A spectrum matches polyamide (nylon-type polymer) as shown in raman analysis

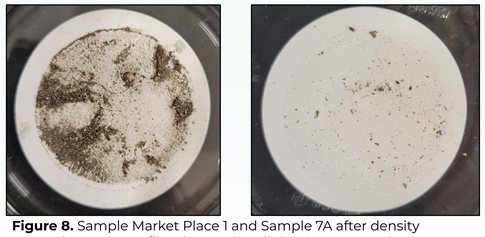

Figure 8. Sample Market Place 1 and Sample 7A after density separation, vacuum filtration, and UV light exposure to clean up samples.

Conclusions

Due to its potential as both a sink and a source of natural and man-made particles, road dust sediment (RDS) is a useful, yet understudied, material for understanding pollution within our environment (Dietrich, et.al.). RDS plays a major role in the resuspension of particles within our atmosphere, and understanding what it contains is vital.

Organic and inorganic carbon make up part of all the samples. Those with high percentages of organic carbon could likely be due to a small percentage being microplastics. For the samples with low overall percentage of carbon, it is likely that much of the contents are minerals other than carbonates, such as silicates.

It was determined that the road dust samples had low levels of heavy metals, such as lead, from all locations. The parking lot RDS had the highest lead concentration at close to 120 ppm. Overall, the lead concentrations in Valparaiso samples were lower than those recently measured from the nearby industrial city, Gary.

Microplastics, plastic particles less than 5mm, are a growing concern as a global pollutant. Plastics also contain many additives and/or unreacted monomers; together, they can result in human and environmental concerns when released into the environment. We expected to find microplastics in our RDS samples, in particular, from tire wear. While we were able to confirm microplastic presence, we did not have the time to quantitatively analyze them.

Our findings support the presence of polyurethane, along with many other polymers. However, we need to improve our experimental procedure for isolating microplastics to facilitate analysis and better confirm the structure of particulates with the RAMAN library.

Good or bad?

References

Dietrich[1], M.; O'Shea, M. J.; Gieré, R.; Krekeler, M. P. S. Road Sediment, an Underutilized Material in Environmental Science Research: A Review of Perspectives on United States Studies with International Context. *Journal of Hazardous Materials* **2022**, *432*, 128604. https://doi.org/10.1016/j.jhazmat.2022.128604.
Järlskog[2], I.; Jaramillo-Vogel, D.; Rausch, J.; Gustafsson, M.; Strömvall, A.-M.; Andersson-Sköld, Y. Concentrations of Tire Wear Microplastics and Other Traffic-Derived Non-Exhaust Particles in the Road Environment. *Environment International* **2022**, *170*, 107618. https://doi.org/10.1016/j.envint.2022.107618.
Knight[3], L. J.; Parker-Jurd, F. N. F.; Al-Sid-Cheikh, M.; Thompson, R. C. Tyre Wear Particles: An Abundant yet Widely Unreported Microplastic? *Environ Sci Pollut Res* **2020**, *27* (15), 18345–18354. https://doi.org/10.1007/s11356-020-08187-4.
Hann[4], S.; Sherrington, C.; Jamieson, O.; Hickman, M.; Kershaw, P.; Bapasola, A.; Cole, G.; Plymouth University; Mepex; MRAG; Finnish Environment Institute (SYKE); Aalto University; Eunomia Research & Consulting; ICF; Amec Foster Wheeler; Jarvis, A. *Investigating Options for Reducing Releases in the Aquatic Environment of Microplastics Emitted by (but Not Intentionally Added in)* Products; report; **2018**.
Wiesinger[5], H.; Wang, Z.; Hellweg, S. Deep Dive into Plastic Monomers, Additives, and Processing Aids. *Environmental Science & Technology* **2021**, *55* (13), 9339–9351. https://doi.org/10.1021/acs.est.1c00976.

Acknowledgements

We would like to extend our gratitude to Notre Dame student, Dan Baudendistel, and his advisor, Dr. Graham Peaslee, Dr. Peller, Dr. McCool, and the VU Chemistry department.