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Analysis of PFAS release following the April 2018 refinery fire in Superior, Wisconsin

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SUMMARY

This report summarizes monitoring data collected by the Lake Superior National Estuarine Research Reserve during and after an explosion and series of fires at a refinery facility in Superior, Wisconsin in 2018. Many other organizations were engaged in collecting a wide breadth of information related to the impacts of the fire and the subsequent mitigation of hazards. For more information about the event and ongoing environmental monitoring, visit the Wisconsin Department of Natural Resources Remediation and Redevelopment Program database at https://dnr.wi.gov/botw

What are PFAS?

Produced since the 1950s, per- and polyfluoroalkyl substances (PFAS) are synthetic chemicals that repel both water and oil. They are used in many industrial and consumer products, such as cookware and water-resistant fabrics.[1]

PFAS enhance the performance of fire-fighting products and are active ingredients in aqueous film-forming foams (AFFFs). These foams are used to put out petroleum-based fires and may be used at military sites, airports, and flammable liquid storage and processing facilities.[2,3] Some PFAS chemicals are extremely stable in the environment and do not have any known natural degradation processes.[4] In addition to being persistent, PFAS may build up, or bioaccumulate, in humans and animals. Certain PFAS chemicals are associated with negative effects on human health, such as higher risk of kidney and testicular cancers, affected immune system, interference with the hormone system, and increased cholesterol.[5]

What happened?

A punctured tank and subsequent fires at an oil refinery in Superior, Wisconsin on April 26, 2018 resulted in a local evacuation and a spill of around 17,000 barrels of asphalt.[6] Fires took several hours to put out, and water and firefighting foams were deployed in the process. Newton Creek, a small outflow from the refinery, drains into the St. Louis River Estuary at Hog Island Inlet, approximately 1.7 river miles from Lake Superior (Figure 1). The U.S. Environmental Protection Agency (EPA) assisted with air quality monitoring during and immediately after the fire. Wisconsin DNR and EPA provided regulatory oversight of environmental response actions while the refinery collected environmental data over subsequent days and into 2020. Before fires were fully extinguished, the Lake Superior National Estuarine Research Reserve deployed an

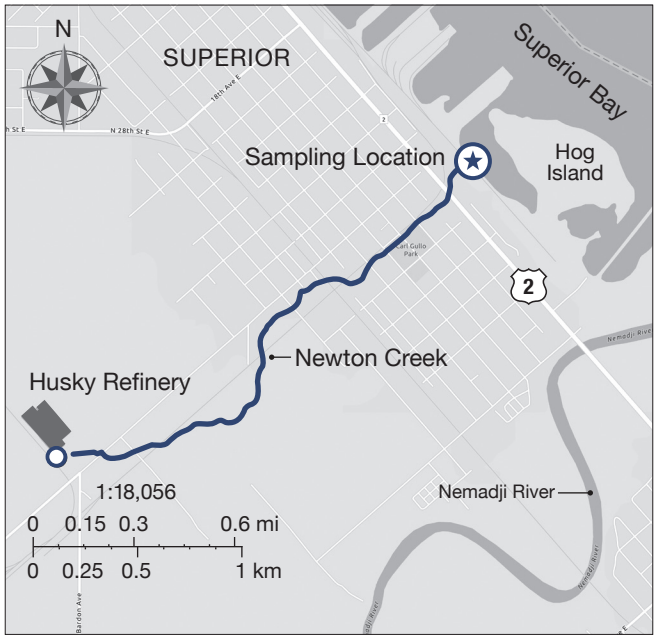

Figure 1. Location of Newton Creek relative to the refinery and St. Louis River Estuary, Superior WI (Credit: Esri)

automatic water sampler at the mouth of Newton Creek. The sampler remained at the site and collected a water sample every hour from April 26 at 6:30 p.m. until April 27 at 12:30 a.m. Samples were then collected once every three hours until April 28 at 6:30 p.m. and once every six hours until the final sample was collected on April 30 at 12:30 p.m. Samples were analyzed for PFAS at the Northern Lake Service Environmental Analytical Laboratory in Crandon, Wisconsin. Further information regarding the sampling procedure and analysis is available by contacting the Lake Superior Reserve at deanna.erickson@wisc.edu.

Lake Superior National Estuarine Research Reserve monitoring

Concentrations of four PFAS chemicals commonly found in firefighting foams were analyzed: perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), 6:2 fluorotelomer sulfonate (6:2 FTS), and 8:2 fluorotelomer sulfonate (8:2 FTS). PFOS and PFOA are commonly detected and, due to their health effects, are listed in the Stockholm Convention on Persistent Organic Pollutants, a treaty designed to protect human health and the environment from chemicals.[7] PFOS and PFOA have been phased out by manufacturers in the United States. 6:2 fluorotelomer sulfonate and 8:2 fluorotelomer sulfonate, on the other hand, are understudied and their health effects less well known, but they can be found at high concentrations in certain AFFF formulas.

During the first 24 hours after the explosion, elevated levels of all four chemicals are observed (Figure 2). After 24 hours, PFOS and PFOA return to much lower concentrations, while concentrations of 8:2 FTS and 6:2 FTS fluctuate.

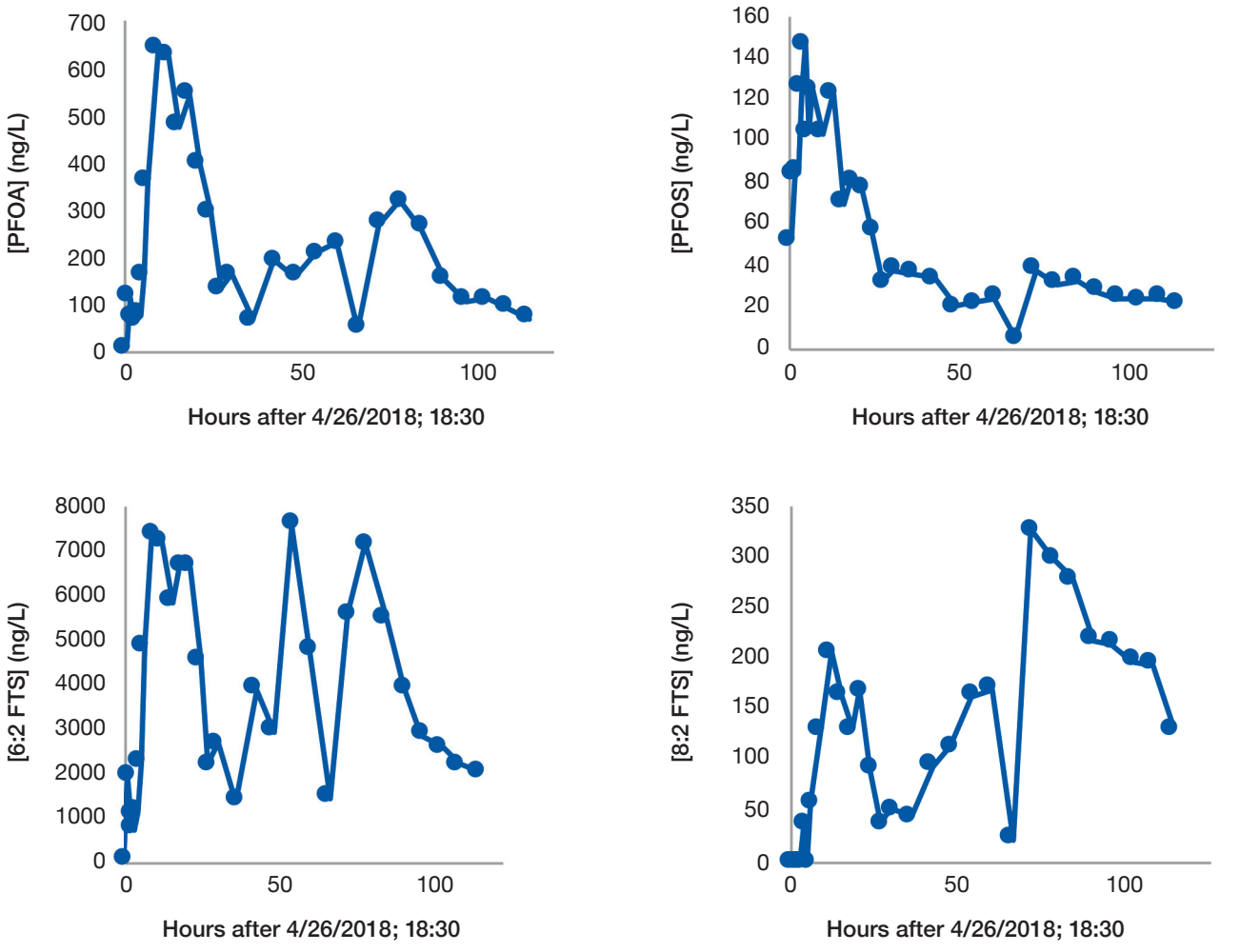

Figure 2. PFAS concentrations at the mouth of Newton Creek after the refinery fire.

AFFF compositions depend on when and where the AFFF was made. Certain types of legacy AFFF contain little to no PFOS or PFOA and instead contain large amounts of fluorotelomers, such as 6:2 FTS and 8:2 FTS.[8] These chemicals are known as precursor chemicals because they transform into other PFAS chemicals once released into the environment. For example, 8:2 FTS is transformed into both PFOS and PFOA, among other chemicals.[9] This may explain why there are relatively low concentrations of PFOA and PFOS at this site near the deployment of AFFF but high concentrations of fluorotelomer chemicals. After the release of a fluorotelomer mixture, PFOS, PFOA, and other PFAS chemicals would be found further downstream from the event. It should also be noted that a 0.5 inch rain event occurred between 80 and 100 hours after the initial sample was collected (Richard I. Bong Airport).

How do these results compare to other PFAS sites or events across Wisconsin?

Although limited data exist on PFAS concentrations across Wisconsin, efforts by the WDNR show that concentrations of PFOS and PFOA vary widely across the state as of 2019. In Starkweather Creek, a stream near the Dane County Regional Airport in Madison, PFOA is found at up to 43 ng/L, while PFOS is found at up to 360 ng/L. In the Wisconsin River, maximum concentrations of PFOA are 36 ng/L and maximum concentrations of PFOS are 5.6 ng/L. One sample was collected in the St. Louis River Estuary from Arrowhead Pier, upstream of where Newton Creek drains into the river. This sample, which was taken on July 1, 2019, had PFOA and PFOS concentrations of 0.6 ng/L each, while 8:2 FTS and 6:2 FTS were not detected.[10] Concentrations of PFOS and PFOA in Lake Superior are typically <1 ng/L.[11]

The state of Wisconsin has not yet adopted a surface water standard for PFAS. However, in the time immediately after the explosion, PFOS concentrations in Newton Creek exceeded the surface water standard set by the Michigan Department of Environmental Quality of 12 ng/L, but PFOA concentrations did not exceed the surface water standard of 12,000 ng/L.[12] Following the addition of onsite water treatment, Superior Refining Company is continuing to monitor Newton Creek with regulatory oversight provided by the Wisconsin DNR. Since the event, samples have averaged around <10ng/L PFOA and 40ng/L PFOS in early 2020.[13]

Responsive partnerships

A rapid response time allowed the Reserve to capture data in the first few critical hours following the fires. Partner support was essential to analyze data and continue monitoring efforts.

Colleagues at Wisconsin Sea Grant secured funds to analyze samples through National Oceanic and Atmospheric Administration's (NOAA) National Centers for Coastal Ocean Science Rapid Response program. As a result, Wisconsin Sea Grant recognized a need to augment PFAS analysis capacity in the state. They responded by securing funds for the Wisconsin State Laboratory of Hygiene, and investing in research with UW–Madison, to develop analysis capacity for PFAS. Sea Grant's support boosted subsequent monitoring efforts in Wisconsin and paved the way for the consideration of a potential PFAS standard in the future.

Staff at the WDNR worked with Reserve researchers to identify the most significant probable chemicals for sample analysis. They also provided initial analysis of the resulting data. In 2020, the DNR adopted 2019 Wisconsin Act 101 (WI Statutes 299.48) which prohibits the use of PFAS-containing firefighting foams except in emergency situations or controlled testing environments. A DNR-led PFAS Technical Advisory Group was formed in 2019 to discuss issues related to PFAS in Wisconsin. The group meets on a quarterly basis and meetings are open to the public.

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