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Sep 19th, 10:20 AM

## Session 1B: Contaminant Exposure and Treatment

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Research Institute, Kentucky Water, "Session 1B: Contaminant Exposure and Treatment" (2022). *Kentucky Water Resources Annual Symposium*. 5.

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**Session 1B: Contaminant Exposure and Treatment**

## **Cyanobacteria, Cyanotoxin Synthetase Genes, and Cyanotoxin Occurrence Among Selected Large River Sites in the Lower Ohio River Basin, 2020–21**

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Cyanobacteria cause a multitude of water-quality concerns, including the potential to produce toxins that can affect water bodies used for recreation and drinking-water supplies. More than five million people utilize the Ohio River as their source of drinking-water. In 2015 and 2019, toxic cyanobacteria harmful algal bloom (cyanoHAB) events were recorded, and health-advisories issued in the same 300 mile stretch of the Ohio River from Ashland, Kentucky to Louisville, Kentucky. Currently, there is not a system in place for source-water facility operators or state agencies to quickly respond to changing water-quality conditions due to cyanoHABs. Thus, developing tools for predicting when and where a cyanobloom may occur is important to aiding management decisions in protecting the public.

To increase our understanding on the occurrence and severity of toxic cyanoHABs and on measures that may be useful for predicting their future occurrence and/or severity in rivers, the U.S. Geological Survey and its cooperators in this study initiated a cyanoHAB monitoring strategy using discrete samples and continuous measurements at select sites on the Ohio River (7 sites including two source-water facilities) and a Wabash River site during the summer and fall of 2020 and 2021. Sampling frequency differed among the sites based on current in-place discrete sampling programs with higher frequency sampling occurring during August–September (3 of 4 weeks each month) and October (bi-weekly) when cyanoHABs are most common. Discrete samples were analyzed for total and dissolved nutrients, four cyanotoxins, seven cyanotoxin synthetase genes, and phytoplankton assemblages. Existing continuous water-quality monitors with total algae sensors were operated at five Ohio River sites (excluding the two source-water facilities) and the Wabash River site. This presentation will describe the occurrence of the toxin-producing cyanobacteria, cyanotoxin concentrations, and possibly any identified water-quality and environmental factors that are statistically related to cyanotoxin concentrations as part of a cyanoHAB early warning system. Although the data collected for this study occurred in the Ohio and Wabash Rivers, the methods used should be applicable for future studies designed to address cyanoHAB community dynamics in large rivers, lakes, and reservoirs.

## **Emerging Contaminant Exposure Following WWTP Processes to Surface Waters\***

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Per- and polyfluoroalkyl substances (PFAS) and neonicotinoid insecticides are persistent environmental contaminants that have been recently detected in many environmental compartments including soil, surface water, groundwater, and finished drinking water in Kentucky. Exposure to these emerging contaminants has been associated with human health impacts including high cholesterol and cancers, as well as stressors to ecological food webs and agroecosystems. Therefore, the objective of this project was to investigate the occurrence and implications of PFAS and neonicotinoid insecticides in relation to wastewater treatment plant (WWTP) end products (biosolids and effluent) in central Kentucky. PFAS and neonicotinoid insecticides were monitored at two distinct WWTPs in central Kentucky during Spring and Summer 2022. Sampling locations were upstream to the WWTPs, downstream to the WWTPs, influent, effluent, and finished biosolids. Data was collected using a polar organic chemical integrative samplers and analyzed using a Waters Xevo TQS UPLS tandem mass spectrometer to determine concentration and mass loadings of the two emerging contaminants classes. Findings from this work will provide guidance regarding implications of WWTP processes to transformation of PFAS and neonicotinoid insecticides in two watersheds.

*\*This presentation is based upon work supported by the U.S. Geological Survey under Grant/Cooperative Agreement No. G21AP10631-00, WRR1 104B Annual Grant Program.*

## **Reactive Membrane Synthesis for Capture and Degradation of Toxic Water Contaminants**

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The need for clean water has become prominent in recent years due to the widespread presence of toxic chemicals, such as perfluorooctanoic acid (PFOA) and polychlorinated biphenyls (PCBs), in water sources. Exposure to such compounds can result in a weakened immune system, neurological problems, and birth defects in humans, thus source filtration and contaminant removal is becoming increasingly vital for health longevity. To combat this problem, novel responsive materials were synthesized to capture and degrade these pollutants from water sources. Commercial microfiltration membranes were functionalized with poly(N-isopropylacrylamide) (PNIPAm), a thermo-responsive polymer that can exhibit both hydrophilic and hydrophobic behavior, depending on the temperature of the system. The resulting membranes utilized a temperature-swing adsorption/desorption process to effectively remove PFOA from water samples above the lower critical solution temperature (LCST) of PNIPAm. Then, below the LCST, the system can release the adsorbed contaminant to obtain a concentrated sample for further treatment. For PCB treatment in industrial water sources, similar reactive membranes were synthesized using zero-valent iron-palladium nanoparticles. With these particles, the membranes can dechlorinate PCBs and other harmful chlorinated compounds via electron-transfer reactions, thus significantly lowering the toxicity of such pollutants. The synthesis of these membranes shows exciting advances in creating the next-generation of filtration systems for water remediation. This research is supported by the NSF-RAPID program and by NIEHS.

## **Implications to Tap and Stream Water Chemistry Due to Variations in Sampling Location and Watershed Land Use**

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Heavy metals and sulfate are persistent environmental contaminants in Appalachian communities. Exposure to heavy metals and sulfate has been associated with human health impacts including gastrointestinal and kidney dysfunction, nervous system disorders, birth defects, and various forms of cancer. To date, there is limited information regarding the potential exposure and introduction of heavy metals and sulfate entering rural water treatment plants, resulting in a notable and concerning knowledge gap in these regions. Therefore, the following research objectives included: 1. Conducting a citizen science tap water campaign, including 70 residential homes, with a variety of water outlets (indoor faucet vs. outdoor spigot), source water (well, spring, water treatment plant), and counties and 2. Complete a six month in-stream monitoring campaign at nine field sites. Heavy metals, specifically copper, cobalt, cadmium, lead, and aluminum, were found to be statistically higher in outdoor spigot samples compared to water samples collected at indoor faucets, with many outdoor spigot samples exceeding human health limits. However, after allowing water to flush from outdoor spigots for five minutes, no differences were observed between indoor faucets and outdoor spigot heavy metal concentrations. Additionally, residential tap water samples with groundwater wells as the source water had significantly higher iron and aluminum concentrations compared to water from the municipal water treatment plants. In contrast, sulfate concentrations were significantly higher in tap water from municipal water treatment plants. Surface water monitoring sites had significantly different heavy metal and sulfate concentrations depending on monthly precipitation and watershed land use. Findings from this work provide guidance on metal accumulation in tap water pipes along with guidance on heavy metal and sulfate concentration environmental exceedances depending on watershed land use.

## Examining Toxicity of 2D Nanomaterial Phosphorene, Free-Standing and Embedded onto Membranes, and Its Application for Removal of Per- and Polyfluoroalkyl Substances (PFAS)

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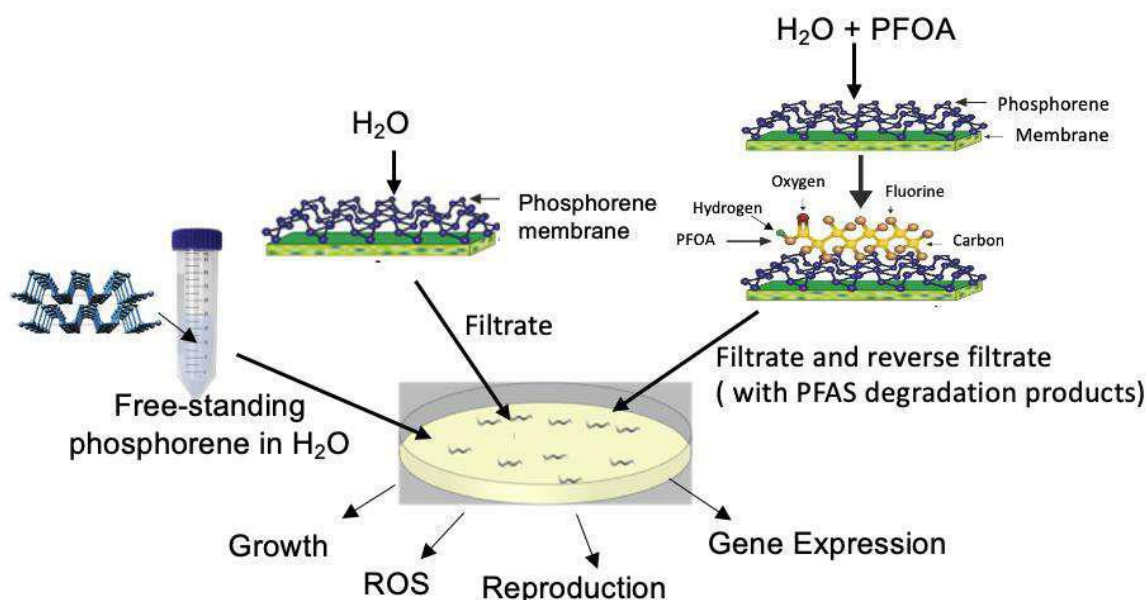
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An inorganic 2D nanomaterial, phosphorene, due to its unique electronic and photocatalytic properties has a potential for environmental applications such as the development of the safe catalytic nanocomposite membranes with the purpose of removal and degradation of the persistent organic pollutants, such as per- and polyfluoroalkyl substances (PFAS), in drinking water. PFAS are surfactant chemicals with broad uses that are now recognized as contaminants of global concerns with a significant risk to human health. They are commonly used in household and industrial products. They are extremely persistent in the environment because they possess both hydrophobic fluorine-saturated carbon chains and hydrophilic functional groups, along with being oleophobic. In order to design safe nanocomposite phosphorene membranes, we followed the below diagram (Fig. 1) and started with the toxicity assessment of the free-standing phosphorene to a model organism, *Caenorhabditis elegans*. The results showed that phosphorene concentration of 2 mg/L can cause toxicity (reproduction), and if there is any potential release of phosphorene from the nanocomposite membranes, it should be at non-toxic concentrations. Nanocomposite membranes were composed of sulfonated poly ether ether ketone



**Fig. 1.** Workflow diagram to assess phosphorene toxicity in free-standing and bound to membrane forms as well as toxicity of the PFOA breakdown products after filtration through phosphorene membranes to a model organism, *Caenorhabditis elegans*.

(SPEEK) and two-dimensional phosphorene. After confirmation that there was a minimal release of the phosphorene under different tested conditions and during multiple filtration experiments, we tested potential of these nanofiltration membranes to remove and degrade one of the long carbon chains PFAS representatives, Perfluorooctanoic acid (PFOA) under ultraviolet (UV) photolysis and liquid aerobic oxidation treatments. On average we observed 99% rejection of PFOA alongside with a 99% removal from the PFOA that accumulated on surface of the membrane after the treatments.

The images and data from Scanning Electron Microscopy (SEM), the atomic profile scans of the membrane surface and its pores via X-ray photoelectron spectroscopy (XPS) and contact angle data provide some evidence for potential degradation of PFOA into smaller fluorine compounds on the phosphorene membranes after oxygenation. In addition, comparisons of the toxicities of the PFOA solution prior and after filtration through nanocomposite membranes suggest that PFOA breakdown products after filtration are less toxic than the initial PFOA solutions. Thus, our results indicate that even though the mineralization of the PFOA after filtration through phosphorene membranes was not achieved, our data provide some evidence for breakdown of PFOA to the products with lessened toxicity.