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The development of natural gas extraction from shale plays in the United States poses threats to our water resources. Relative to conventional oil and gas well drilling, the drilling and stimulation of unconventional oil & gas wells (hydraulic fracturing) requires larger volumes of water. The larger volumes of water used to stimulate hydrocarbon production via hydraulic fracturing lead to larger volumes of water returning to the surface (a.k.a. flowback and produced water) that need to be properly managed. Produced water can be disposed of into underground injection control wells, minimally treated for in-field reuse, or treated at centralized waste treatment plants and eventual discharged to surface water. Treated produced water is also used to irrigate crops in some areas. Flowback and produced waters associated with hydraulic fracturing typically contain high concentrations of salt as well as a variety of organic, inorganic, and radioactive contaminants. Discharge of this wastewater into surface waters is of significant concern because of the high concentrations of contaminants and the fact that wastewater treatment facilities are not adequately equipped to remove contaminants such as radioactive elements, surfactants, and petroleum distillates. Contamination to watersheds as a result of inadequate treatment poses a potential pollution problem for the general public and also ecosystems surrounding these areas.

Organic contaminants in shale gas derived waters and wastewaters are of growing concern. Depending on the drilling company and the local formation characteristics, between 10 and 20 chemical additives are utilized during fracturing. Hydraulic fracturing fluids include unique organic compounds designed to function as biocides, breakers, corrosion inhibitors, cross linkers, friction reducers, scale inhibitors, and surfactants. Organic contaminants of particular concern, and a main focus of this research, are biocides and surfactants. Biocides are of concern because these chemicals are used to suppress microbial populations at the well and are inherently toxic. Surfactants are of concern because these chemicals can be persistent and widespread in the environment. Additionally, surfactants produce a co-solvent effect that can dissolve previously immobile chemicals, thereby increasing the extent of contamination. In addition to the organic chemicals contained in hydraulic fracturing fluid, there are also organic contaminants that are native to shale formations that come to the surface as a component of the produced water. A main class of these is petroleum-derived hydrocarbons which include diesel range organics (DRO), gasoline range organics (GRO) and polyaromatic hydrocarbons (PAHs), some of which are toxic and/or carcinogenic.

This study analyzed the impacts of unconventional oil and gas operations on the Conemaugh River Lake in western Pennsylvania, an area that has experienced a substantial increase in oil and gas activity in the past decade. The Conemaugh River Lake was formed by a flood control dam built by the US Army Corps of Engineers in 1952. Five centralized waste treatment plants that are treating shale-gas extraction wastewaters are located upstream of the Conemaugh River Lake including the Josephine Brine Treatment facility where radium concentrations above radioactive waste disposal threshold regulations have been found in the sediments downstream. Waste from conventional oil and gas operations has been accepted at the centralized waste treatment plants upstream of the Conemaugh River Lake since 1995, while unconventional waste was only accepted at these facilities between 2005 and 2011. Additionally, there are high sediment accumulation rates and sedimentation in the lake is well-structured allowing for temporal resolution of contaminants entering the lake. This sampling location was selected for all of the reasons listed above, however, the results of this study are also applicable to other watersheds with similar amounts of shale-gas development and/or oil and gas wastewater treatment facilities. Quantification of the impacts and possible toxicity within the watershed could have significant repercussions with respect to oil and gas wastewater management in the future.

During this study, the sediment record of the Conemaugh River Lake was analyzed for evidence of impacts from upstream centralized wastewater treatment plants treating oil and gas wastewater. In order to do this, intact sediment cores were collected from several locations in the Conemaugh River Lake. Sediment sampling was selected to provide a more comprehensive, time-composited approach for environmental assessments. Sediment is deposited in lakes over time and an age model was used to determine the age of sediment at each depth. Contaminants discharged from centralized wastewater treatment plants associate with solids in the stream and eventually accumulate in sediments. As a result, the impacts of oil and gas extraction on the sediment and in the watershed can be determined with respect to time.

The sediments that were collected were analyzed for organic contaminants known to be elevated in shale-gas wastewaters, including surfactants, biocides and petroleum derived hydrocarbons. The sediment cores were divided by depth and an age model was used to determine the age of sediment at each depth, as mentioned previously. Contaminants were extracted from the sediment using a liquid-solid extraction method where an acetone-hexane solvent was used to remove chemicals from the soil (Figure 1). This solvent solution was then analyzed for contaminants including surfactants, biocides and petroleum-derived hydrocarbons. Petroleum-derived hydrocarbons were analyzed using gas chromotography coupled with mass spectrometry (Figure 2). Surfactants and biocides were analyzed using liquid chromatography-time-of-flight mass spectrometry.

Results showed that at least three types of surfactants were present in the sediment including nonylphenol ethoxylates (NPEs), C-14 alkylated polyethlene glycols (PEGs) and polypropylene glycols (PPGs). Nonylphenol ethyoxylates are commonly used by the oil and gas industry and are known to breakdown into nonylphenol, an endocrine disrupting compound. C-14 PEGs are not considered toxic, but are commonly used by the oil and gas industry and therefore a good indicator of oil and gas impacts on the sediment. Analysis also revealed a range of petroleum derived hydrocarbons in the sediment including many polyaromatic hydrocarbons (PAHs) such as fluoranthene, a known carcinogen and one of the EPA's 16 priority pollutant PAHs. Benzo(a)pyrene, which is also a PAH and a carcinogen was also found in the sediment and has been found in well water in Dimock, PA, an area that was previously polluted by unconventional oil and gas activity. Other petroleum-derived hydrocarbons were also found including nonadecane, heptadecane and 1-hexadecene, all of which have been found in produced water from unconventional oil and gas operations. Biocides were not found in the sediment samples likely because glutaraldehyde, one of the most commonly used biocides, degrades in a few weeks while other biocides, such as didecyl dimethyl ammonium chloride (DDAC) likely bind strongly to the sediment.

The results from the petroleum derived hydrocarbon analysis, including fluoranthene, pyrene, nonadecane and heptadecane, showed an increase during the time period (2005-2011) in which unconventional oil and gas wastewater was accepted to the wastewater treatment plants. Figure 3 shows the results for the two PAHs, fluoranthene and pyrene. Data on the volume of unconventional and conventional wastewater treated each year was obtained from the Pennsylvania Department of Environmental Protection and the peak in petroleum-derived hydrocarbons is associated with the year in which the largest volume of unconventional wastewater was treated. A peak in NPE and C-14 PEG surfactants was also seen during the 2005-2011 time period, showing that the concentration of these surfactants increased as the volume of wastewater treated increased. Both fluoranthene and pyrene are also a by-product of coal combustion, which is why they are also present prior to 1995. NPEs and other surfactants are also present prior to 1995 because surfactants are used in a variety of household products including detergents and shampoos.

These results show that the historic impacts of unconventional oil and gas extraction can be detected within sediment profiles. As a result of the larger volumes of water used and the different geological formations that are targeted in unconventional versus conventional extraction, the impacts of these two industrial activities can potentially be differentiated. These results can be used to inform regulations on the treatment of this wastewater in the future. In fact, in early June, the EPA finalized a rule that banned the disposal of hydraulic fracturing waste at centralized wastewater treatment plants, effectively preventing this practice from happening again. As with many regulations involving the oil and gas industry, this new rule has been very controversial. The results of this study will provide further evidence for why such a rule is probably needed.

As a result of this study, a proposal was submitted in conjunction with Drs. William Burgos, Nathaniel Warner and Patrick Drohan from Pennsylvania State University to the NSF Geobiology and Low-Temperature Geochemistry Program titled “Collaborative Research: Impact of Oil & Gas Wastewater Disposal on Lake and River Sediments.” Additionally, the results of this study, along with the results obtained by our collaborators at Penn State will soon be submitted to a peer-reviewed journal.