# Project Summary

**Title:** Investigation of PFAS adsorption by selected Wisconsin aquifer sediments

**Project I.D.:** DNR-239

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**Background:** Per- and polyfluoroalkyl substances (PFAS) are a large class of synthetic organic chemicals that are widely used in a variety of applications. Due to their diverse structure and widespread use, PFAS have been detected in waterways across the U.S. As human exposure to PFAS has been linked to cancer, elevated cholesterol, obesity, immune suppression, and endocrine disruption, the occurrence of PFAS in the natural environment is raising public health concerns. Specifically, PFAS contamination has been reported in numerous Wisconsin groundwater aquifers. Since PFAS tend to be stable in the natural environment, the transport and fate of PFAS within the groundwater system is directly related to their adsorption onto the aquifer materials which in turn is strongly dependent on the compositions and properties of the aquifer materials. As a result, site-specific investigation would be required to reliably predict the subsurface transport of PFAS. To the best of our knowledge, however, the adsorption of PFAS onto aquifer materials relevant to Wisconsin aquifer settings has remained largely unexplored.

**Objectives:** The overall objective of this project was to investigate the adsorption behavior of PFAS onto several representative Wisconsin aquifer materials collected from sites susceptible to PFAS contamination. The sites were selected for their geographical coverage, their different aquifer material composition, and their proximity to known and possible PFAS sources. Our central hypothesis was that PFAS adsorption onto aquifer materials would depend on both PFAS structure and aquifer material composition, and longer-chain PFAS would show stronger adsorption affinity with aquifer materials than those of shorter-chain PFAS.

**Methods:** Aquifer materials of varied compositions were collected from five representative locations across Wisconsin in the counties of Dane, La Crosse, Marinette, Waukesha, and Washington. For comparison purpose, dolomite samples were also collected from a quarry located in Sussex, WI and was ground to granules before use. Six representative PFAS with different carbon chain lengths and end functional groups were selected for investigation, including perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluoroheptanoic acid (PFHpA), perfluorohexanesulfonic acid (PFHxS), and perfluorobutanesulfonic acid (PFBS). Detailed adsorption isotherm experiments were performed to determine the aquifer material-water partition coefficients ($K_d$) of PFAS. Specifically, experiments were conducted with the six PFAS mixture in a representative groundwater matrix and a range of environmentally relevant concentrations (nominally 100 – 5000 ng/L for each PFAS). Furthermore, the measured $K_d$ values were applied to a one-dimensional (1-D) transport model to illustrate the impact of PFAS adsorption on PFAS transport in groundwater aquifer.

**Results and Discussion:** Aquifer materials mainly consisted of dolomite ($CaMg(CO_3)_2$) and/or quartz ($SiO_2$), and the relative abundance of the two minerals were substantially varied among

different aquifer materials. In general, PFAS adsorption onto aquifer materials could be described by the linear isotherm model, suggesting the relatively constant adsorption affinity between PFAS and aquifer materials under environmentally relevant conditions. PFAS adsorption was highly dependent on aquifer material composition, particularly dolomite content. Aquifer materials of higher dolomite content showed significantly stronger affinity with PFAS than those of lower dolomite content. Compared to dolomite content, other parameters of aquifer material such as contents of $SiO_2$, Al, and Fe, cation exchange capacity (CEC), anion exchange capacity (AEC), and porosity played a less substantial role in PFAS adsorption. Furthermore, PFAS adsorption was also strongly related to PFAS structure. Longer-chain PFAS had higher adsorption affinity with aquifer materials than those of shorter-chain PFAS, and perfluorinated sulfonic acids were more strongly adsorbed onto aquifer materials than perfluorinated carboxylic acids. Octanol-water distribution coefficient ($D_{ow}$) could be considered a good indicator to correlate PFAS structure with their adsorption onto aquifer materials. An empirical model was established based on multilinear regression of the experimental data to determine $log\ K_d$ of PFAS onto aquifer materials based on dolomite content of aquifer material and $log\ D_{ow}$ of PFAS.

**Conclusions and Implications:** This project suggested that dolomite played an important role in PFAS adsorption onto aquifer materials. Aquifer materials with high dolomite content may show more significant retention of PFAS and stronger retardation on PFAS transport in comparison to materials with low dolomite content, and thus reduce the likelihood and extent of PFAS contamination of the groundwater. It is worth mentioning that while this project primarily investigated the adsorption of six representative PFAS, the adsorption affinity of other relevant anionic PFAS onto aquifer materials may be readily predicted based on their $log\ D_{ow}$ values. The fundamental information obtained from this project can help provide a quantitative understanding of the fate and transport potential of PFAS in impacted groundwater aquifers in Wisconsin, which can be used to develop improved strategies for remediation of PFAS-contaminated sites, and guide general PFAS management practices in groundwater in Wisconsin. Considering the complexity of aquifer settings, combined experimental and modeling efforts are recommended to improve the understanding of PFAS adsorption and transport behavior in various complex aquifer systems.

**Related Publications/Presentations:**

Zhao Y., Min X., Xu S., Wang Y. Adsorption of per- and polyfluoroalkyl substances by aquifer materials: the important role of dolomite. *Environmental Science & Technology Letters*, **2023**, 10, 931-936, DOI: 10.1021/acs.estlett.3c00583

Zhao Y., Grosskopf B.C., Min X., Henderson Z.D., Xu S., Wang Y. Adsorption of PFAS by aquifer materials: Implications on PFAS transport in groundwater. 265th American Chemical Society National Meeting, March 26-30, **2023**, Indianapolis, IN and online.

Zhao Y., Grosskopf B.C., Min X., Henderson Z.D., Xu S., Wang Y. Investigation of PFAS adsorption onto aquifer materials in Wisconsin. Wisconsin AWRA 2023 Annual Meeting, March 16-17, **2023**, Wisconsin Dells, Wisconsin.

Zhao Y., Grosskopf B.C., Min X., Henderson Z.D., Xu S., Wang Y. Adsorption of perfluoroalkyl acids onto aquifer materials with varied composition. The 2023 Emerging Contaminants in the Environment Conference (ECEC23), April 18-19, **2023**, Champaign, IL and online.

**Key Words:** PFAS; Adsorption; Aquifer material; Groundwater; Dolomite; Transport

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