Metadynamics based molecular dynamics simulation and experimental study of the adsorption of per- and polyfluoroalkyl substances on smectite clay surfaces

JENNIFER WILLEMSEN*, IAN C. BOURG

Princeton University, Princeton, NJ 08544, USA
(jarw@princeton.edu, bourg@princeton.edu)

Per- and polyfluoroalkyl substances (PFASs) are persistent, bioaccumulative contaminants harmful to human health. High levels of PFASs have been detected in water and soils and a fundamental understanding of PFAS adsorption is essential for developing effective remediation strategies and predicting the fate and transport of these contaminants. Previous research on PFAS asdsorption in soils has indicated the importance of both soil organic mattter and clay minerals as adsorbents but the underlying mechanisms are not fully understood. This research focuses specifically on PFAS interactions with smectite clays, one of the predominant minerals in temperate soils.

To understand these interactions, we use molecular dynamics simulations to model a stack of flexible smectite clay sheets with cleaved edges in contact with a bulk aqueous reservoir containing PFAS molecules and reconstruct the associated free energy landscape. Simulation results are obtained for multiple PFASs with different anionic head groups and fluorinated alkyl chain lengths including perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), perfluorobutane sulfonic acid (PFBS), and hexafluoropropylene oxide dimer acid (HFPO-DA) and are compared to collected experimental batch adsorption and x-ray diffraction results. In addition, various aqueous chemistry conditions are examined to study the effect of salinity and coordinating cation type (K, Na, Ca) on adsorption. The simulation output provides atomistic-level insights that help discern mineral-organic interaction mechanisms and conformations (i.e. cation bridging, hydrophobic partitioning), and aid in the interpretation of experimental data. In particular, we calculate the free energy, enthalpy, and entropy of adsorption, the affinity of the PFASs for different clay adsorption sites (interlayer, edge, external basal surface) and examine the effects of clay surface charge density.