



Impact of variable water chemistry on PFOS-goethite interactions under batch and flow-through conditions: experimental evidence and reactive transport modeling

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PFOS fate and transport in the subsurface are significantly impacted by the spatially and temporally variable hydrochemical conditions found in natural environments, which often exhibit strong ionic strength gradients and pH fluctuations [1,2]. Batch and flow-through column experiments are standard methods for characterizing PFOS adsorption and transport behaviors, and their outcomes are often quantitatively interpreted by defining empirically derived solid-water distribution coefficients (e.g., Langmuir and Freundlich equations) [3]. The limitation of these models is that they are strictly system-dependent and cannot precisely assess PFOS removal under varying water chemistry conditions. Thus, there is a need for mechanistic sorption prediction models able to account for varying electrostatic properties of the surface-solution interface in response to changes in pore water chemistry, and that could be implemented in reactive transport simulators for precisely assessing PFOS migration under dynamic hydrochemical conditions in multicomponent systems [4].

In this work, we initially conducted a comprehensive set of adsorption experiments and IR spectroscopy analyses with varying pH and ionic strength conditions to elucidate PFOS binding behavior on goethite surfaces as a function of solution chemistry. The experimental outcomes were quantitatively interpreted by developing a surface complexation model (CD-MUSIC) built on the results of the adsorption experiments and on the molecular-level understanding acquired through IR spectroscopy. Subsequently, a series of one-dimensional flow-through experiments were conducted in fully saturated goethite-coated silica sand columns by injecting a 2 mg/L PFOS pulse with varying NaCl background electrolyte concentrations and collecting PFOS and pH breakthrough curves at the outlet of the domain. PFOS uptake exhibited a complex behavior that was strongly dependent on solution pH and electrolyte concentration and that originated from the co-existence and speciation of two distinct PFOS-goethite surface complexation mechanisms: (i) a hydrogen-bonded complex (HB) and (ii) a weaker outer-sphere complex involving Na⁺ co-adsorption (OS-Na⁺). The non-trivial dependency of PFOS uptake on solution chemistry significantly impacted its transport behavior. Dynamic ionic strength gradients established during the flow-through experiments led to distinct retardation and transport behaviors which were not observed in the experiments performed with constant ionic strengths [5]. PFOS and pH

breakthrough curves were quantitatively described by implementing the developed surface complexation model within the reactive transport simulator PHREEQC-3 coupled with MATLAB through the IPhreeqc module [6,7]. The simulations illuminated the key role of multicomponent transport effects on PFOS mobility and the importance of explicitly accounting for mineral surface charge adjustments in response to changes in water chemistry.

[1] Zhu et al. (2017) *Chemosphere* **168**, 390-398. [2] Blowes et al. (2014) In *Treatise on Geochemistry 2nd Edition* **Vol. 11**, pp 131-190. [3] Johnson et al. (2007) *J. Chem. Eng. Data* **52**, 1165-1170. [4] Cogorno and Rolle (2024) *Env. Sci. Technol.* <https://doi.org/10.1021/acs.est.3c09501>. [5] Cogorno and Rolle (2024) In prep. [6] Charlton and Parkhurst (2011) *Comput. Geosci.* **37**, 1653-1663. [7] Muniruzzaman and Rolle (2016) *Adv. Water Resour.* **98**, 1-15.