Influence of Humic Acid and Ionic Strength on the Sorption of Pyrene to Carbonaceous Materials

Castan, Stephanie (Universität Wien, Wien, AUT);
Hüffer, Thorsten (Universität Wien, Wien, AUT);
Sigmund, Gabriel (TU München, München, GER);
Hofmann, Thilo (Universität Wien, Wien, AUT)

Combustion-derived carbonaceous materials (CMs) are highly abundant in natural freshwater systems. Here, the strong sorption potential of CMs can influence the transport and fate of organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) that are released by a variety of sources into surface waters. The nature and extent of their interactions may depend on water chemistry parameters such as ionic strength (IS) and the concentration of natural organic matter (NOM) as well as on the properties of the sorbents. As previously reported, NOM sorbed to CMs can inhibit or slow down the sorption of contaminants to these surfaces. This may either be due to a direct competition for sorption sites or the blocking of micropores by NOM, limiting the access for other sorbates such as organic contaminants. Therefore, the aim of this study was to systematically investigate the influence of water chemical parameters and sorbent properties on sorption of CMs.

Biochar (BC) was selected as sorbent representing a pool of naturally occurring CMs and Graphite (Gr) was selected as model sorbent to investigate the effects of surface properties on sorption. The comprehensive characterization of the sorbents included elemental analysis, specific surface area and pore size distribution derived from N_2 and CO_2 physisorption isotherms of the materials. Sorption experiments were performed with pyrene as model sorbate and polyoxymethylene sheets were used as passive sampler. The influence of i) IS, including the comparison of mono-and divalent salts, and ii) sorbent loading with NOM on pyrene sorption behavior to CMs was tested in background solutions with either deionized water (Milli-Q), 0.01 M NaCl or 0.01 M $CaCl_2$, with and without addition of humic acid (HA, Sigma Aldrich) at environmentally representative concentrations (1 mg C L-1). Sorption isotherms were fitted with the Polanyi-Manes model (PMM). Furthermore, the adsorption of HA to the CMs in the different background solutions was quantified by UV-vis absorption at 254 nm. Additionally, particle size and aggregation of the sorbents as well as of the HA in the different solutions were measured.

The preloading of BC with HA in Milli-Q resulted in a reduction of pyrene sorption to the porous BC surface, whereas no difference in sorption was observed for the flat Gr surface. This indicates that the reduction in pyrene sorption to BC is mainly due to pore blockage by HA rather than direct sorption site competition. Physisorption experiments confirmed that HA loading of BC reduced specific surface area and total pore volume of BC, especially in the lower mesopore range (1.5 - 2 nm). Interestingly, the observed effect of sorption reduction only occurred in MQ and NaCl but not in $CaCl_2$. Preliminary results suggest that the aggregation of HA in $CaCl_2$ leads to size exclusion of HA from micropores and thereby does not hinder pyrene to diffuse into the pores. Further experiments are currently conducted to investigate this hypothesis by quantifying the amount of HA sorbed on CMs. Furthermore, also BC was shown to aggregate in $CaCl_2$, which did not have implications on pyrene sorption, but does affect dispersion stability of BC particles.