Importance of carbonaceous materials on sorption of phenanthrene by sediments

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Increasing studies indicate strong sorption of hydrophobic organic contaminants (HOCs) to carbonaceous materials such as black carbon (BC), coal, and kerogen in soils and sediments, which is possibly the reason for recent observations of elevated geosorbent-water distribution ratios, slow desorption, limited uptake, and restricted bioremediation. We evaluated the role of environmental BC and coal-like materials in the sorption of phenanthrene to polluted sediments from Hudson River and Balrimore Harbor, and tried to predict the fate and transport of PAHs and HOCs that are currently introduced to aquatic systems.

Organic petrographic analysis and wet chemical extraction method indicated that carbonaceous particles primarily composed of coal, coke, charcoal, soot, pitch, cenospheres, and wood. In the sediments, carbonaceous particles contributed 3-9% of the total mass and 60-90% of the PAHs.

Sorption isotherms of phenanthrene were determined for the original sediment (with organic matter, native sorbates, and BC), sediment from which >90% of the native sorbates were stripped (only OM and BC), and sediment combusted at 375 ^{o}C (only BC). It is shown that nonlinear sorption to carbonaceous materials can completely dominate total sorption of PAHs. The sorption isotherms of the original and stripped sediments were almost linear (Freundlich coefficient or $n > 0.9$), whereas the isotherm of the BC remaining after the sediment combustion was highly nonlinear ($n = 0.55$).

Phenanthrene sorption to BC in the combusted sediment was found to exceed the total PHE sorption in the original and stripped sediments. Competition between the added phenanthrene and the native PAHs and/or OM may explain this difference. This implies that it may not be possible to use a BC-water sorption coefficient measured in combusted sediment to estimate total sorption to the original sediment. Because sorption is a central process affecting contaminant behavior and ecotoxicity, understanding this process can strongly contribute to risk assessment and fate modeling.

[1] Cornelissen *et al*. (2005) *EST* **39**, 6881-6895.
[2] Connelissen & Gustafsson (2004) *EST* **38**, 148-155.

Pelagosite climate record and the role of cyanobacterial biomineralization

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Pelagosite is a dark, shiny, pisolitic mineral encrusting rocky coasts exposed to sea spray. X-ray diffraction and optical microscopy showed that pelagosite is aragonite with 2-3 micron thick alternating dark-light laminae. Assuming that the laminae represent yearly accretions, we produced time series through sections several hundred microns thick. Fourier trasform power spectra show frequency peaks that match El Niño Southern Oscillation, North Atlantic Oscillation, and sun spot cycles. Power spectra are also consistent with instrumental climate data (yearly precipitation and mean annual temperature) continuously recorded at one of the sample sites since 1859. We conclude that pelogosite is a precise geochronometer for assessing neotectonic movements of rocky coasts, and a faithful recorder of Holocene climate cycles. A potential role for biology in the precipitation of pelagosite crusts is suggested by its growth on carbonate rocks with strong chemical corrosion textures. Molecular biological analyses of pelagosite crusts indicate that they are intimately associated with *Xenococcus*, a poorly known cyanobacterial genus previously found to colonize rocks in the littoral zone of California. A role for *Xenococcus* metabolism and/or cell surface chemistry in nucleating aragonite is suggested by previous studies of carbonate biomineralization, and is currently under investigation using microbial culturing, natural abundance stable isotope analyses, electron microprobe analysis, and syncrotron-enabled approaches including Scanning Transmission X-ray Microscopy (STXM).