

# Identification of Sediment Organic Carbon Location and Association with Polycyclic Aromatic Hydrocarbons (PAHs) in Contaminated Sediment

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## INTRODUCTION

A fundamental long-term issue confronting sediment bioremediation is the lack of understanding of contaminant-sediment interactions and the impacts of such interactions on the failure to achieve treatment goals [1]. Little is known about the mechanisms of PAH and other hydrophobic organic compound sequestration and aging in sediments and the resulting effect on chemical and biological availability [2]. A major factor influencing successful sediment bioremediation is the availability of contaminants to microorganisms for degradation. It needs to be appreciated that contaminants, which are strongly sorbed and not available to microorganisms, may also not be available for a toxic response [3]. Thus, knowledge of how and where PAHs are bound to sediment material is necessary to assess the efficacy of sediment bioremediation and to correlate this knowledge with reductions in availability, mobility, and toxicity. The aim of this study therefore was to investigate those microscale processes that may control the availability of PAHs in sediments.

## RESULTS AND DISCUSSION

Measurements have been conducted at the sub-particle level to understand where PAHs reside on aged sediments and how such locations relate to the presence and nature of sediment organic matter. Infrared microspectroscopy at the NSLS beamline U10B and ALS beamline 1.4 were used to identify organic carbon location in sediment particles. Scanning electron microscopy with wavelength dispersive X-ray analysis was used for elemental microanalysis at Carnegie Mellon University, and microprobe two-step laser desorption laser ionization mass spectrometry ( $\mu\text{L}^2\text{MS}$ ) was used for PAH measurements at Stanford University [4].

Figure 1 presents an example of coincident analysis of two primary types of sediment particles in the 63-250  $\mu\text{m}$  size range in sediment dredged from Milwaukee Harbor. The black carbonaceous particles are found to have 2-3 orders of magnitude more PAHs than silica particles. These black particles are also high in organic carbon, which is indicated by the high IR-absorbance signal for the C-H stretching mode at 2800-3000  $\text{cm}^{-1}$ . SEM spot analysis also indicates a high concentration of elemental carbon. In comparison, the majority of silica particles are high in silicon and oxygen, contain few PAHs and show no IR-absorbance at 2800-3000  $\text{cm}^{-1}$ . These black particles were identified through petrographic analysis to be coal-derived and could be separated by density. Some silica particles in the sediment were found to contain patches of organic matter deposits as shown in Figure 2. IR microspectroscopy analysis of the particle revealed that this region contains organic material, as identified by the C-H stretching mode at 2800-3000  $\text{cm}^{-1}$ . Additional spot analysis for PAHs using the  $\mu\text{L}^2\text{MS}$  revealed high PAH abundance in the regions containing organic matter. These regions were also found to contain clay minerals.

It has been suggested previously that PAHs partition into organic carbon on soils and sediments as a process of aging [5]. However, organic carbon can be present in soils and

sediments in various forms such as humic matter particles, humic matter sorbed on mineral surfaces, detrital debris, vegetative debris, and products of coal and wood use and combustion. Little is known about the relative importance of these different forms of organic carbon in the sequestration of PAHs in sediments. Our investigations reveal that for Milwaukee Harbor sediments, coal-derived particles contribute nearly 62% of total PAHs and constitute only 5% of the sediment by weight. The remaining 38% of the PAHs were found associated with the clay/silt fraction of the sediment. Transmission FTIR spectral analysis of the clay/silt fraction revealed that the organic environment associated with the clay/silt fraction is much more aliphatic in nature than the organic environment of the coal-derived particles. Therefore PAH binding is expected to be different in these two different organic environments.

Desorption kinetic experiments were conducted to evaluate whether PAHs desorb from the different particle types in the sediment at different rates. Separated sediment particles were subjected to aqueous phase desorption experiments with successive additions of an adsorbent resin (Tenax) as the PAH extractant to study the desorption behavior of the PAHs in the sediment. PAHs associated with the coal-derived fractions appeared to be bound very strongly, as only about 8% of the PAHs in this fraction were released over 100 days. Thus, majority of the PAHs associated with this coal-derived fraction may not be bioavailable for degradation nor exhibit a highly toxic response. In contrast, desorption data from the heavier clay/silt fraction indicate a higher availability with nearly 75% of the initial PAHs in this fraction readily desorbing in the first 5 days [6]. In a parallel ongoing biotreatment study we are finding that PAHs associated with the clay/silt fraction are more easily degraded than the ones associated with coal-derived particles. Additionally, PAH removal from the clay/silt fraction provides a significant environmental benefit as shown by large reduction in PAH accumulation in earthworms. The unavailable PAH fraction associated with coal-derived particles in these sediments may pose less environmental risk.

We suggest that complementary microscale measurement techniques presented in this work and others under development can provide a better understanding of physico-chemical mechanisms controlling site-specific bioavailability of contaminants and provide a stronger scientific basis for determining sediment quality guidelines.

## REFERENCES

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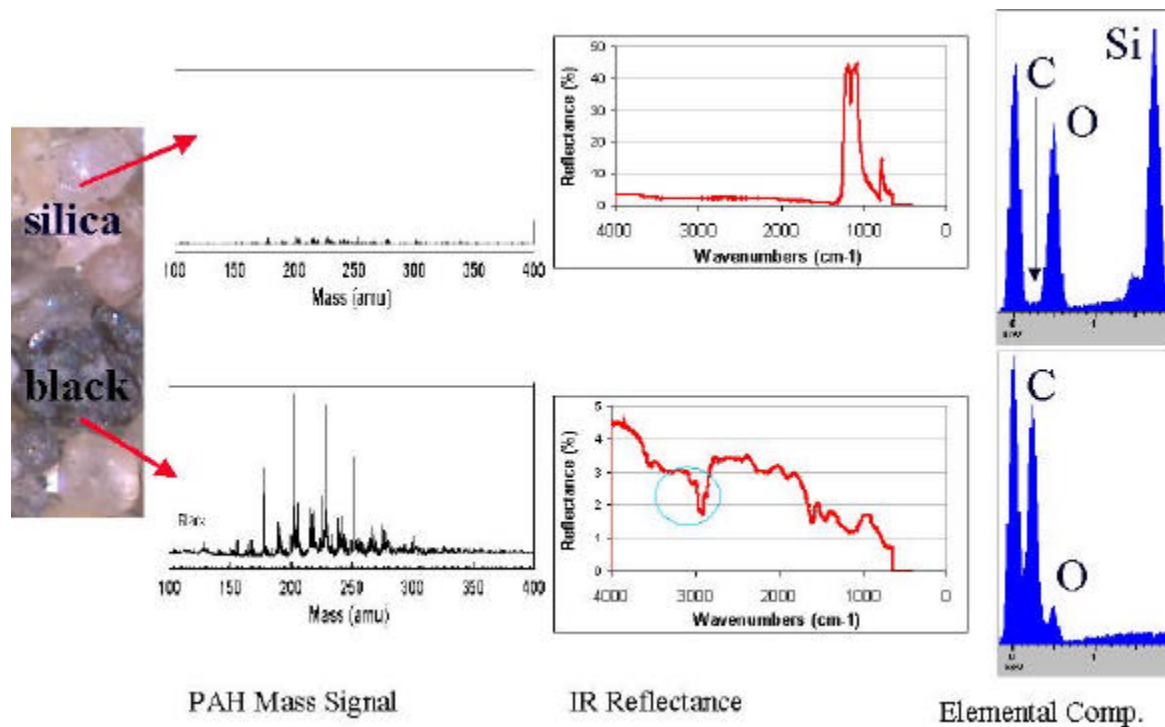


Figure 1. Identification of PAHs, organic matter, and elements on Milwaukee Harbor dredged sediment particles. The above analysis revealed that few black carbonaceous particles had 2-3 orders of magnitude more PAHs than the majority sand, silt, and clay particles.

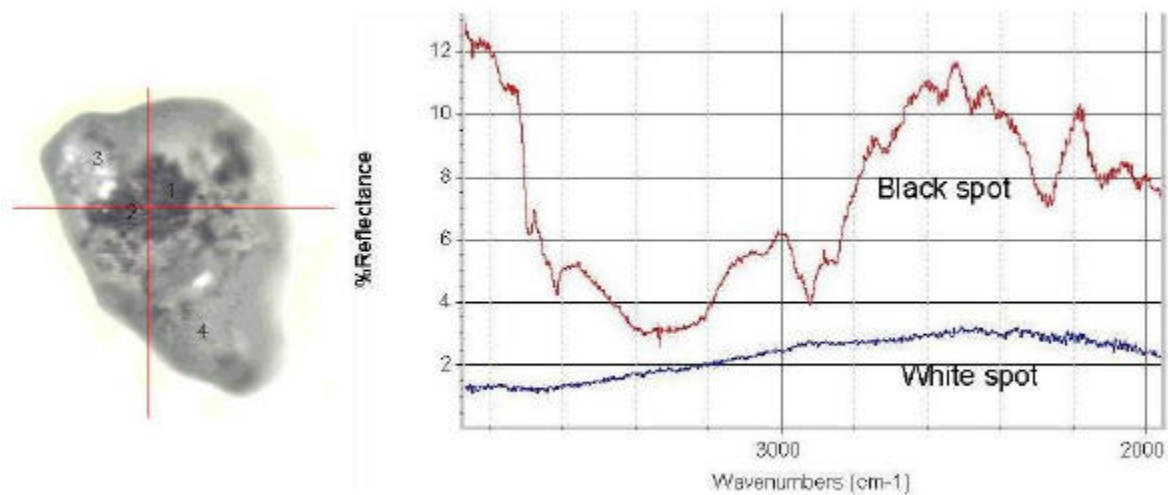


Figure 2. Image of a silica particle having patches of organic matter as identified by the C-H stretching mode at 2800-3000  $\text{cm}^{-1}$  shown in the IR reflectance spectra on the right. Dark spots 1 and 2 in the image on the left also showed higher abundance of PAHs and clay minerals compared to spots 3 and 4.