

# Metal Speciation in Particulates in the Mississippi River in Louisiana

## Basic Information

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## Publication

1. Ma, Jia, A. Roy, J. Sansalone, J. Pardue, 2005, Partitioning and Particulate-bound Distribution of Phosphorus in Rainfall-Runoff , J. Bennett Johnston Sr., Center for Advanced Microstructures and Devices, Baton Rouge, Louisiana, Annual Users Meeting, April 8th , 2005

## Problem and Research Objectives

### *Phosphorus in stormwater*

As a limiting nutrient for eutrophication in fresh waters, elevated concentrations of phosphorus have been identified in many types of non-point rainfall-runoff discharges from urban areas (EPA, 1993). Having many adverse consequences, eutrophication imposes a high environmental, ecological and health cost on many sectors of economy. For example, it is estimated that the costs of freshwater eutrophication in England and Wales are as high as US \$1.05-1.60 x10<sup>8</sup>/year (Pretty et al., 2003). Phosphorus nominally partitions in urban rainfall-runoff between dissolved and particulate-bound phases (Filippelli, 2002). Results from partitioning analysis between the dissolved and particulate-bound fractions in rainfall-runoff on an event basis indicate that phosphorus can be predominately particulate-bound in urban pavement sheet flow for residence times less than an hour (source areas) at runoff pH levels between 6 and 8 and rainfall pH levels less than 6. In addition to a simple partitioning concept between dissolved and particulate phases, varying species of phosphorus adsorb and distribute across the whole particulate size gradation of particulates in rainfall-runoff. Ranging from less than 1 µm to greater than 9500 µm (Sansalone et al., 1998), particulate and solid matter in rainfall-runoff can be operationally classified as gross solids (> 4750 µm), sediment (> 75 µm), settleable (75 ~ 25 µm) and suspended (< 25 µm) based on the Imhoff settling test convention.

In natural waters and rainfall-runoff, the transport and eventual fate of phosphorus is controlled by reactions with solid surfaces. Characterized by large surface area to solid volume ratios, natural mineral oxides and oxide-coated media can serve as reservoirs for phosphorus with the amphoteric surface. In the presence of water, oxide surfaces such as Al, Ca and Fe are covered with surface hydroxyl groups, protons and coordinated water molecules. This leads to the idea that engineered amphoteric oxide coated surfaces on rainfall-runoff filter media can have large surface areas for adsorption and precipitation processes in a chosen pH range. The phosphorus removal by the oxide surfaces is through the mechanism of adsorption, precipitation, absorption and surface complexation.

Although the effectiveness of oxide coated media in phosphorus removal has been proven on a macroscopic scale in bench scale studies, the types of reactions of phosphate with the oxide coated media are not known. Initially, it was assumed that phosphate reacts with Ca<sup>2+</sup>, Al<sup>3+</sup> to form solid calcium or aluminum phosphate (Moore and Miller, 1994), which is insoluble in the pH range typical of urban rainfall-runoff. Although this assumption has been recognized as oversimplified, little, if any, information about the mechanisms of P fixation on oxide coated media is available, mainly due to the lack of methods sufficiently sensitive to determine the species, or form of P, in the heterogeneous materials.

In this study aluminum oxide coated cementitious media was used for phosphate removal from storm water runoff. The aluminum oxide coating was applied by treating the granules of concrete (about 2 mm diameter) with aluminum nitrate. For one batch of concrete granules, the coating was applied once and for another batch it was applied twice. Column studies were conducted where columns packed with these granules were used to remove phosphate from simulated stormwater at concentrations of 100, 50, 25

and 10 mg/L. A control study with cementitious granules without the aluminum nitrate coating, was also performed.

### *Phytoremediation*

Phytoremediation, the technique of using plants to treat contaminated soils and waters, is being more routinely applied now since its first suggestion in the early eighties (Chaney, 1983). Several army ammunition sites and EPA superfund sites have been treated by phytoremediation. A survey by Baker and others (Baker et al., 2000) showed that 440 plants have been identified which can be used for phytoremediation. A database created by Environment Canada, called PHYTOREM, has more than 770 plants. However, a plant suitable for phytoremediation in one location may not work in others. Introduction of alien plant species in a new environment can also wreak havoc on the local ecology. It is thus important that local plants be tested for phytoremediation.

Chromium contamination is present in more than half of all EPA superfund sites (Wright, 1991). One of the problems associated with chromium contamination is that chromium in the +VI oxidation state can readily dissolve in water and spread the contamination widely. Watercress has shown the ability to uptake thallium and arsenic (LaCoste et al., 2001; Robinson et al., 2003). Watercress, as the name suggests, grows best near a stream or other body of water. This makes watercress perfect for extracting metals out of a poisoned stream or river.

## **Methodology**

### *Phosphorus in Stormwater*

X-ray absorption near edge structure (XANES) was used to determine the phosphorus speciation in a suite of samples of urban rainfall-runoff particulates and oxide coated adsorptive media. The rainfall-runoff particles were divided into three groups in size: 25  $\mu$  m, 75  $\mu$  m and 850  $\mu$  m. Replicate samples were analyzed from each group. Spent adsorptive cementitious media were also analyzed in three groups, according to the procedures they were prepared: uncoated, coated with aluminum nitrate once, and coated with aluminum nitrate twice. These media, used in column studies to treat initial phosphate concentrations of 100, 50, 25 and 10 mg/L, were analyzed in replicate.

### *Phytoremediation*

Watercress was grown from seeds obtained from a commercial source for a three-week period. After the initial growing period the watercress ranged in height of 3.5 cm to 4.5 cm. The watercress was extracted from the soil, and washed with double deionized water to remove any remaining soil from the roots. After removal from the soil, the watercress was placed in a water culture system for one week. The plants were suspended directly in the water, and held in place by the cover of the tank. This setup eliminated the need for a support medium that could have affected the absorption of Cr. Once the watercress was in the hydroponic system, it was transported to a greenhouse on the Louisiana State University campus. The temperature of the greenhouse was  $18.3 \pm 2.8^\circ\text{C}$ . The relativity

humidity within the greenhouse varied depending on the weather. Four tanks were filled with 1.5 liters of distilled water, and all the setups were given the proper amount of hydroponic fertilizer to maintain the watercress. (Three quarters of a gram of  $\text{Na}_2\text{CrO}_4$  were added to two of the tanks, to have a final chromium concentration of 500 part per million (ppm)). During the week, the watercress contaminated with  $\text{Cr}^{+VI}$  showed no signs of growth. In fact, several of the contaminated watercress died. After a week, the watercress was extracted and rinsed with double deionized water to remove any  $\text{Na}_2\text{CrO}_4$  residue from the stems. Following the rinsing, the watercress was left to dry for a week. The dried watercress was then separated into three sections: stems, leaves, and roots.

### *X-ray absorption spectroscopy*

The X-ray absorption spectra were collected at the J. Bennett Johnston Sr., Center for Advanced Microstructures and Devices (CAMD), Baton Rouge, Louisiana, Double Crystal Monochromator beamline. The synchrotron ring operated at 1.3 GeV. The current in the ring typically varied between 200 to 100 mA. The concentrated specimens were analyzed in transmission and those with low concentrations were analyzed in fluorescence by a 13-element high purity germanium detector.

The XANES spectra for phosphorus were collected in the fluorescence mode in a helium path to minimize X-ray absorption. Helium was flowed through the chamber at a pressure adequate enough to displace all the air in the chamber. Indium Antimonide (InSb) crystals were used in the double crystal monochromator. The sample powder was sprinkled on Kapton™ tape and spread thinly with a spatula. The tape was then gently tapped to remove any loose particles. The data collection parameters were: from 2050 eV to 2140 eV at 2.0 eV steps, from 2140 eV to 2180 eV at 0.3 eV steps, and from 2180 eV to 2450 eV at 2.0 eV steps; the integration time in each range was 5, 17, and 5 seconds, respectively. The integration time was varied in inverse proportion to the number of counts. The measurement time for each spectrum was typically two hours.

For chromium, Ge 220 crystals were used in the monochromator. The dried watercress samples were placed on Kapton tape for XAS analysis. Analysis was performed in air, with air also in the ionization chamber(s). The XANES spectra were collected from 200 eV below the edge with 3 eV steps, from 20 eV from the edge to 40 eV above the edge with 0.3 eV steps, and up to 300 eV above the edge with 2 eV steps. The counting time at each step was determined in inverse proportion to the number of counts in that region.

The spectra were normalized with WinXAS (Ressler, 1998). A linear baseline was subtracted through the region without any pre-edge peaks. The normalization line was drawn about 60 eV above the white line through a several hundred eV region.

## **Principal Findings and Significance**

### *Manganese oxide media*

The XAS work related to manganese oxide cementitious media, discussed in last year's report, has been completed. Manuscripts are being prepared from that work for publication.

## Phosphorus in Stormwater

Figure 1 shows the XANES spectra of some common phosphate minerals. The white line A (due to the transition of the excited electron between 1s and  $sp^3$  hybrid and oxygen 2p orbitals (Franke and Hormes, 1995)) appears to be stronger for the iron phosphate (strengite) than the other phosphates. The intensity of this line reported in the literature is somewhat lower (Hesterberg et al., 1999). The white line is wider in the minerals other than strengite. There is a distinct shoulder (B) on the high energy side of the white line for the calcium phosphates (Franke and Hormes, 1995). The calcium phosphates also have a minor oscillation B, and another stronger oscillation, D. The oscillation C is also absent in the iron phosphate.

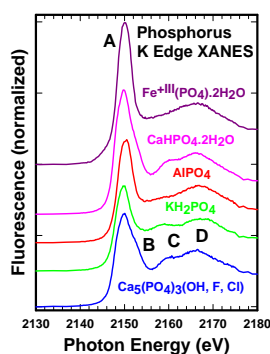


Figure 1  
Phosphorus K edge XANES spectra of some standard phosphate minerals.

Figure 2 shows the phosphorus K edge spectrum in the different fractions of the particulates from storm water. The spectra are noisy because of the very low concentration of phosphorus in the particulates. The 25  $\mu\text{m}$  fraction has a slightly higher peak height. This is possibly due to the difficulty in normalization through the noisy post-edge data range. Otherwise, all the size fractions appear identical. Adsorption of phosphate on ferrihydrite  $\text{Fe}^{\text{III}}_2\text{O}_3 \cdot 0.5(\text{H}_2\text{O})$ , goethite  $\text{Fe}^{\text{III}}\text{O}(\text{OH})$  and boehmite  $\text{AlO}(\text{OH})$  have been studied by Hesterberg and others (Hesterberg et al., 1999; Khare et al., 2004). They observed a statistical difference in the height of the white line of phosphate adsorbed on these minerals, the one for ferrihydrite being stronger than that for boehmite. According to Hesterberg et al. (Hesterberg et al., 1999) phosphate adsorbed onto goethite could be distinguished from the iron phosphate strengite by the lower intensity of the white line, the peak about 3 eV below the white line, the rising edge before the white line, and the stronger oscillation (peak D in Figure 1) at around 15 eV from the white line. A comparison of the spectra of the particulates with those reported in the literature would suggest that the phosphate in the particulates are present as adsorbed species on some iron oxide phases.

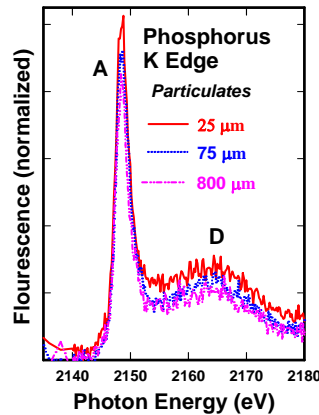


Figure 2

Phosphorus K edge XANES of the particulates collected from stormwater near Baton Rouge

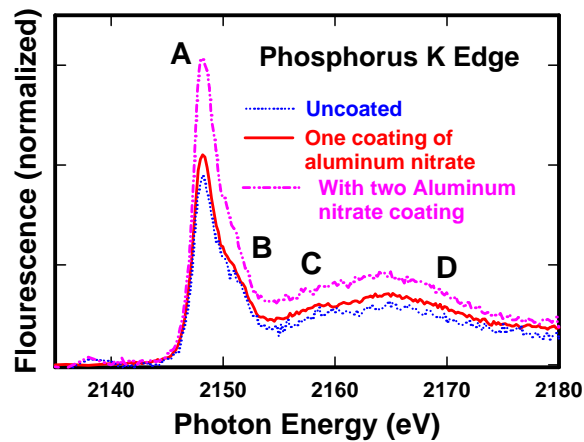


Figure 3

Phosphorus K edge XANES of concrete, with and without aluminum nitrate coating, used for removal of phosphate from stormwater.

Figure 3 shows the spectra of phosphate from the concrete, with and without aluminum nitrate coating, used from phosphate removal from storm water. The spectra of concrete without the coating and just one coating appear very similar. The intensity of the white line (ca. 2150 eV) is somewhat low. There is a bulge on the higher energy side of the white line (peak B from Figure 1) and a minor oscillation is also present around 2160 eV (peak D in Figure 1). A comparison of these spectra with the standards (Figure 1) indicates that these spectra are similar to the calcium phosphates. There is a pronounced difference when two coatings of aluminum nitrate are applied on the concrete. The bulge on the higher energy side of the white line is still visible but the intensity of the white line

is much stronger. It is inferred that in addition to being present as calcium phosphate, some of the phosphate ions are also adsorbed onto the concrete surface.

Because of the low concentration of phosphorus in these specimens, the data collection process is long. The low atomic number of phosphorus also makes measurements difficult as absorption of phosphorus X-rays is high in any tape used to hold the material. It is possible to arrive at quantitative estimates of different phosphate species with least squares fitting of the spectra.

Only preliminary data have been collected so far from the phosphate samples and more is planned. The inferences from X-ray absorption spectroscopy need to be corroborated with the chemistry, phase composition, and microstructure of the particulates and the oxide-coated cementitious media.

### *Phytoremediation*

$\text{Cr}^{+VI}$  has a distinctive pre edge peak at 5993 eV (Figure 4). This pre-edge peak is only present in Cr compounds that are in +VI oxidation state. When the watercress stems and leaves are compared to the  $\text{Na}_2\text{CrO}_4$  standard, it is apparent that there is no  $\text{Cr}^{+VI}$  in the watercress. Not only the pre-edge peak at 5993 eV is absent, the edge has shifted to higher energy. The edge jump for both stems and leaves correspond to that of the +III oxidation state.

The chromium concentrations in different parts of the plant (stems, leaves, and roots) were analyzed by flame atomic absorption spectrometry in replicate (Figure 5).

The two samples of stems had a Cr concentration of 8930ppm, and 11390ppm. The leaves had a lower concentration than the stems with concentration of 5365ppm, and 10120ppm. Finally the two root samples had concentrations of 9480ppm, and 8120ppm. The elevated concentration of Cr in the stems, leaves, and roots shows watercress ability to hyperaccumulate Cr from a hydroponic system.

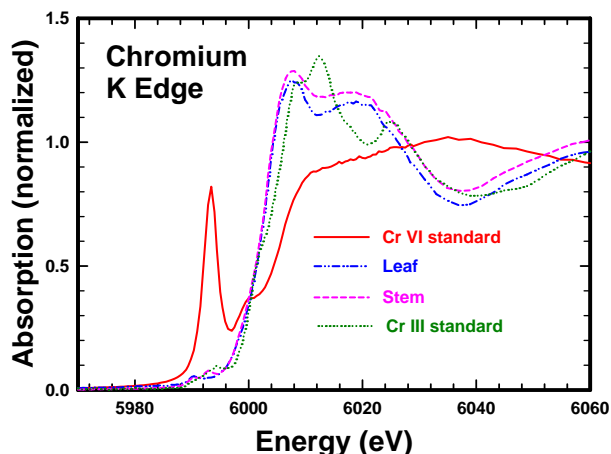


Figure 4

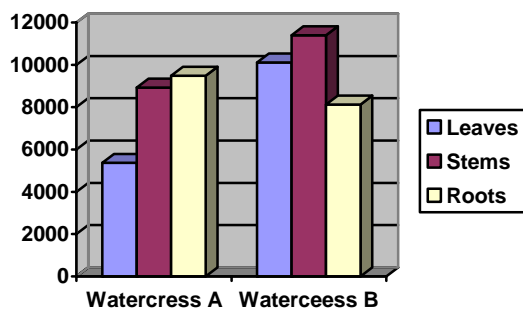


Figure 5

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