Speciation of Heavy Metals in Katrina Sediments from New Orleans, Louisiana

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Abstract. Hurricane Katrina, a Category 4 storm on the Saffir-Simpson scale, struck the Gulf Coast of Louisiana on August 29th, 2005. The storm surge resulted in breaches of the levee system in New Orleans at least at two locations, flooding up to 80% of the city. The floodwater also brought sediment which was left behind once the water receded after a few days. The dry sediment covered large parts of the city. Much of it was made airborne by vehicular traffic and was potentially inhaled.

The sediments from the Lakeview area contained an appreciable amount of clay minerals which were absent in samples from Mid City. The speciation of these metals was quantitatively different in two neighborhoods. In one location metallic copper and zinc were present. A small amount of hexavalent chromium was detected at two sites.

Keywords: Sediments; hurricane Katrina; toxic metals; XANES.
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INTRODUCTION

Hurricane Katrina, a Category 4 storm on the Saffir-Simpson scale, struck the Gulf Coast of Louisiana on August 29th, 2005. The storm surge resulted in breaches of the levee system in New Orleans at least at two locations, flooding up to 80% of the city. The floodwater also brought sediment which was left behind once the water receded after a few days. The dry sediment covered large parts of the city. Much of it was made airborne by vehicular traffic and was potentially inhaled[1].

The flood water was sampled in the Mid-City and Lakeview areas of New Orleans within five days[2]. The concentrations of metals such as iron, zinc and copper in the flood water were often elevated compared to EPA drinking water standards but rarely exceeded the limits. The metal concentrations are that typically expected in urban storm water[2].

Quite a few studies have been reported in the literature related to stormwater composition. In comparison, very few studies have been focused on the sediments deposited by these storms. There are even fewer studies on speciation of the toxic metals in these sediments[3]. More emphasis has usually been applied to the organic contaminant in sediments.

EXPERIMENTAL METHODS

FIGURE 1. Sediment sampling sites in New Orleans, Louisiana.

The sediment samples were obtained from the Lakeview and Mid City areas of New Orleans (Figure 1), from the same locations which were earlier sampled for water[2]. The Mid City samples were

moist, often with free standing water. Some of the samples from the Lakeview neighborhood were obtained several days after the water receded and they were relatively dry.

The sediments contained highly diverse materials, including broken Mardi Gras beads. Very often they contained coarse sand size asphalt particles with embedded quartz grains. The sediments from the Lakeview area contained an appreciable amount of clay minerals, montmorillonite, illite and kaolinite. Clay minerals were not detected in samples from Mid City.

Table 1. Element Concentration Range (ppm)

	Mid City	Lakeview
Chromium	34-8	43-27
Copper	132-38	731-164
Zinc	2342-129	10272-3412

Table 1 provides the concentration ranges for the element that were investigated for this study, except that of iron. Presley et al. [1] reported Fe concentration of around 26,000 ppm in some of the Katrina sediments. The analyses of the water samples from these sites have been provided by Pardue et al. [2]. The ranges for Zn, Cu, and Cr from the Lakeview area are 401-79 ppm, 209-77 ppm, and 67-58 ppm, respectively; the corresponding concentrations from the Mid City area are 1500-733 ppm, 155-106 ppm, and 100-76 ppm, respectively.

X-Ray Absorption Spectroscopy

XAS spectra were collected at the J. Bennett Johnston Sr., Center for Advanced Microstructures and Devices (CAMD), Louisiana State University, Baton Rouge, Louisiana, Double Crystal Monochromator beamline. The ring operated at 1.3 GeV. The current in the ring ranged between 225 and 100 mA. The specimens were analyzed in the fluorescence mode by a Canberra 13-element high purity germanium detector. They were prepared by enclosing the moist sediment between Kapton™ tapes. Germanium 220 crystals were used in the monochromator. The measurements were conducted in air. The K edge XANES spectra of Cr, Fe, Cu and Zn (edge ca. at 8979 eV for Zn) were collected from 200 eV below the edge to up to 20 eV above the edge in 3eV steps; from –20 eV to 60 eV above the edge in 0.3 to 0.4 eV steps; and from 60 eV to 300 eV above the edge in 3 eV steps. The spectra were analyzed by Athena and Artemis [4].

RESULTS AND DISCUSSION

The sediments from the Mid City area shows much more variation in iron speciation compare to those from the Lakeview area (Figure 2). For the latter, the edge position shows very little variation but the white line intensity is more variable. Least squares fitting of the XANES spectra with iron standards of different oxidation states suggests close similarity of the iron compound from Lakeview to that of goethite.

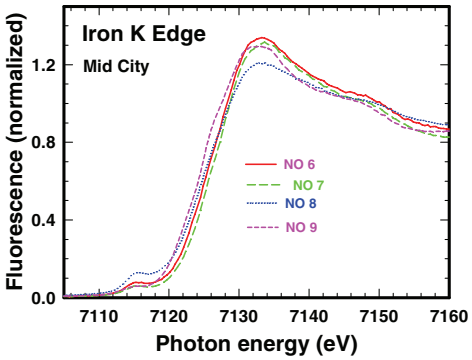

FIGURE 2. Iron K edge XANES spectra of representative sediment samples from Mid City New Orleans.

Table 2. Least Squares Fitting of Iron XANES

		Goethite	Fe II
Mid City NO 8	Weight(%)	0.805 (0.009)	0.195 (0.009)
	E_0	0.234 (0.046)	-0.770 (0.314)
Lakeview 6S	Weight(%)	100.00	
	E_0	-0.972 (0.002)	

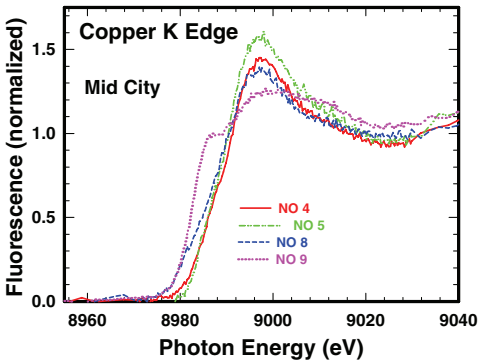

FIGURE 3. Copper K edge XANES spectra of representative sediment samples from Mid City New Orleans.

Copper K edge XANES measurements were made only from the sediments from Mid City (Figure 3). Least squares fitting of the spectra required compounds with various oxidation states. For example, the best fit for NO 9 required 16% metallic copper, 45% Cu +I and 38% Cu +II; for NO 5, the best fit was obtained with a mixture +I and +II oxidation states.

Least squares fitting of the spectra indicated that NO 9 was composed of metallic zinc only (Figure 4); NO 6, in contrast, matched with zinc hydroxide only.

The closest match for spectra with higher intensity white lines was with zinc hydroxide but the match was poor.

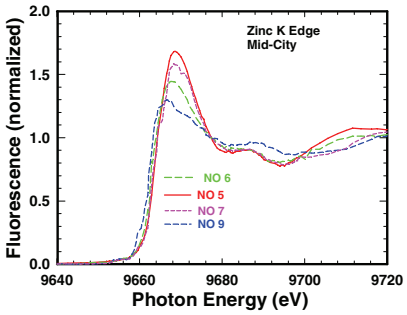

FIGURE 4. Zinc K edge XANES spectra of representative sediment samples from New Orleans.

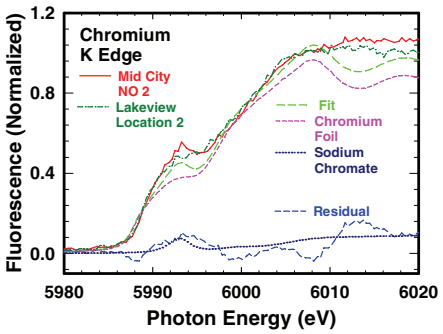

FIGURE 5. Least squares fitting of chromium K edge spectra from two sites in New Orleans.

Table 3. Least Squares Fitting of Chromium K Edge

Location		**Chromium Foil**	**Sodium Chromate**
Mid City NO 2	Weight (%)	0.905(0.024)	0.095(0.024
	E_0 Shift	0.161(0.159)	-0.357(0.541)
Lakeview Location 2	Weight (%)	0.941(0.021)	0.059(0.021)
	E_0 Shift	0.056(0.133)	0.171(0.770)

Chromium K edge spectra from specimens from two sites show a distinct pre-edge peak at around 5993 eV (Figure 5). The peak is more prominent for the sample from Mid City New Orleans. Least squares fitting for these spectra showed the Mid City sample contained ca. 10% by weight of hexavalent chromium or a total of 3 ppm. The amount of hexavalent chromium is less for the Lakeview sample.

There are possibly three of sources heavy metals in Katrina sediments. First, heavy metals are abundant in urban areas. In fact, metals from the pavement, car brakes, atmospheric deposition, etc., ultimately contaminate the surrounding water bodies[5]. Second, the floodwater itself was high in these metals. Third, another potential source is the large number of automobiles which remained immersed in the floodwater for several days. Fourth, the flooding brought in a large amount of sediments from Lake Pontchartrain and the Mississippi River Gulf Outlet. A US Geological Survey of metal concentrations in Lake Pontchartrain found that Zn on the south shore was typically around 150 ppm, Cu 30 ppm and Cr around 80 ppm[6]. The soil and the water bodies in and around New Orleans are high in metals from past industrial activities[7]. The heavy metals are typically concentrated in the fine fraction of sediments. The high clay component in the Lakeview sediments may explain the high Zn concentration[8].

Though very little information is available about speciation of metals from sediments deposited by stormwater there is quite a bit of variation in speciation of the metals at the two sites and even within a single neighborhood. One sample from the Mid City region showed both copper and zinc in reduced (metallic) state but iron appeared in II+ oxidation state. The variation in speciation to some extent represents the variation in the sources themselves. The data presented here from the most unusual conditions created by the hurricane Katrina will be important reference points for monitoring changes in the sediments as a function of time and water/weather conditions.

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