U.S. Fish and Wildlife Service
Region 3
Division of Environmental Contaminants

/

INVESTIGATION OF IMPACTS TO FEDERALLY ENDANGERED FRESHWATER MUSSELS OF THE LOWER OHIO RIVER: CHEMICAL AND BIOLOGICAL SURVEY FOR ENVIRONMENTAL CONTAMINANTS ADJACENT TO THE REPUBLIC CREOSOTING HAZARDOUS WASTE SITE NEAR JOPPA, ILLINOIS

Melanie Y. Young

Study Identification Number 90-3-054

U.S. Department of the Interior
Fish and Wildlife Service
4469 48th Avenue Court
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Abstract

A survey for contaminants in bed sediments and freshwater mussels was conducted in the region of the Lower Ohio River adjacent to the Republic Creosoting hazardous waste site near Joppa, Illinois during the 1990 field season. Inorganic and organic chemical analysis was conducted with bed sediments and tissue samples of two freshwater mussel species, Megalonaias gigantea and Quadrula quadrula, collected from selected locations upstream, adjacent to, and downstream from the site. This paper reports the results of the chemical analyses, which suggest that creosote wastes originating from a creosote waste lagoon at the Republic Creosoting facility are currently being transported into the Ohio River adjacent to the site.

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Introduction

Republic Creosoting hazardous waste site was a railroad tie creosoting facility located near the Village of Joppa, Illinois, which is currently under ownership of Union Pacific Railroad, Omaha, Nebraska. The facility was in operation from the early to mid-1920's, up until its abandonment in 1945 (CH2M Hill 1988; U.S. Environmental Protection Agency 1987). During this time period timber, which was processed for use as railroad ties, was treated with creosote and held on site to cure before being shipped out. Extensive areas on the former facility grounds currently show significant contamination due to creosote-associated organic and inorganic chemicals. Areas that have been previously identified as contaminated include a 2-acre lagoon with a depth in excess of four feet which was used to store creosote wastes, and surface soils located throughout the site that were associated with various treatment, processing and storage areas.

A site assessment conducted in 1988 by a contracted Union Pacific Railroad representative, CH2M Hill (1988), identifies significant concentrations of benzo(b)fluoranthene and zinc on site, and above background levels of cadmium (CH2M Hill 1988). Other polycyclic aromatic hydrocarbon compounds that have been identified on site at extremely high concentrations include naphthalene (550 ppm), 2-methylpropylene (1,800 ppm), acenapthalene (110 ppm), dibenzofuran (1,400 ppm), fluorene (2,200 ppm), phenanthrene (6,000 ppm), anthracene (5,500 ppm), fluoranthene (3,800 ppm), pyrene (2,400 ppm), benz(a)anthracene (870 ppm), chrysene (1,500 ppm), xylene (110 ppm), and benzo(a)pyrene (240 ppm), (U.S. Environmental Protection Agency 1987). The hydrocarbons above include some high molecular weight, carcinogenic polycyclic aromatic hydrocarbons as well as some low molecular weight compounds.

The site is currently identified as a hazardous waste site by the Illinois Environmental Protection Agency - Division of Land Pollution Control, and the U.S. Environmental Protection Agency (U.S. Environmental Protection Agency 1987). Due to the various contaminants found on site in combination with the presence of a tributary which serves as a primary discharge point of the creosote waste lagoon, there was the potential for contamination of a small creek (Bayou Creek) which drains the tributary, which in turn empties into the Ohio River. A need was identified to determine the potential for adverse impacts to federally endangered freshwater mussel species as

well as other benthic and pelagic organisms inhabiting the portion of the Lower Ohio River adjacent to the site.

There are historical and recent records of two federally endangered freshwater mussel species from the Lower Ohio River near the vicinity of Joppa, Illinois and Bayou Creek. Freshwater mussel beds have recently been identified upstream from the confluence of Bayou Creek and the Ohio River (Williams and Schuster 1989). The pink mucket pearly mussel (Lampsilis orbiculata), has been previously identified in mussel beds located from Ohio River mile 944 to 950 (Ahlstedt 1985). Another federally endangered species, the orange-footed pearly mussel (Plethobasis cooperianus), has historically been identified in beds at various locations from Ohio River mile 940 to 965 (Ahlstedt 1984), and recently near river mile 967.2 (Miller et al. 1986). Of critical interest to the present study, a live specimen of the orange-footed pearly mussel was identified in the Ohio River just upstream of Joppa, Illinois and the Republic Creosoting hazardous waste site, at approximately river mile 949.2 near the Illinois shoreline, during a 1992 freshwater mussel survey of the Lower Ohio River (Havlik 1992).

As creosote-contaminated aquatic environments have previously been demonstrated to be highly toxic to a wide variety of aquatic organisms (Eisler 1987; Tagtz et al. 1983; U.S. Fish and Wildlife Service 1990), and bioaccumulation of creosote compounds in general, and specifically polycyclic aromatic hydrocarbons, from contaminated aquatic environments has been demonstrated with marine bivalves (Cossa et al. 1983; DeLeon et al. 1988), the present study was undertaken to develop baseline data on organic and inorganic contaminants in bed sediments and biota at selected aquatic sites adjacent to the Republic Creosoting hazardous waste site. Recent freshwater mussel surveys have reported a decrease in freshwater mussel species diversity as well as numbers of mussel beds in this general region of the Lower Ohio River (Williams and Schuster 1989). The purpose of this study was to assess the extent of adverse impacts that may have occurred from the Republic Creosoting hazardous waste site to federally endangered mussel species located in the vicinity of the site in the Lower Ohio River.

Study Area Description

The study area consists of the Republic Creosoting waste site, Bayou Creek, and the Lower Ohio River in the vicinity of Bayou Creek. The study area is located in Massac County in southern Illinois near the Village of Joppa, and is illustrated in Figure 1. The creosote waste lagoon at the site is shown in Figure 2. There is a network of drainages in the general vicinity of the site, and only one of these drainages, the western drainage, flows in a westerly direction toward and then away from the site, eventually draining into the Ohio River via Bayou Creek. This western drainage forms the southern tributary after its confluence with a discharge from the creosote waste lagoon, and the southern tributary joins with Bayou Creek. The creosote lagoon on site essentially discharges through a culvert to this southern tributary to Bayou Creek. This southern tributary is approximately 500 feet in length and follows a steep gradient down to the creek. The confluence of Bayou Creek and the Ohio River is approximately 600 feet downstream from the confluence of the creek and the southern tributary. The total stream length from the creosote waste lagoon on site to the Bayou Creek/ Ohio River confluence is approximately 1,200 feet. Bayou Creek empties into the Ohio River at approximately river mile 950.7.

The sampling locations for bed sediments and freshwater mussels are shown in Figure 3 and listed in Table 1. A total of 11 sites were sampled in the study area. There were two reference sites in Bayou Creek, the first site (RC-5) was located approximately 350 feet upstream from the confluence of the southern tributary creosote lagoon drainage and Bayou Creek, the second site (RC-6) was located 1,600 feet north of the confluence of the southern tributary and Bayou Creek. This second Bayou Creek reference site was also located north of the entrance of a small farm pond which was located immediately north of Joppa Road just outside of the Village of Joppa, Illinois. It served as a second upstream reference site with which to evaluate any impacts the small farm pond might have had on bed sediments along the entire length of Bayou Creek. Samples were collected from four sites in the Ohio River, spanning approximately three river miles from Ohio River mile 949.3 to 952.3. These sites were located upstream, adjacent to, and downstream of the creosote tie yard and the mouth of Bayou Creek. The upstream site, RC-10, served

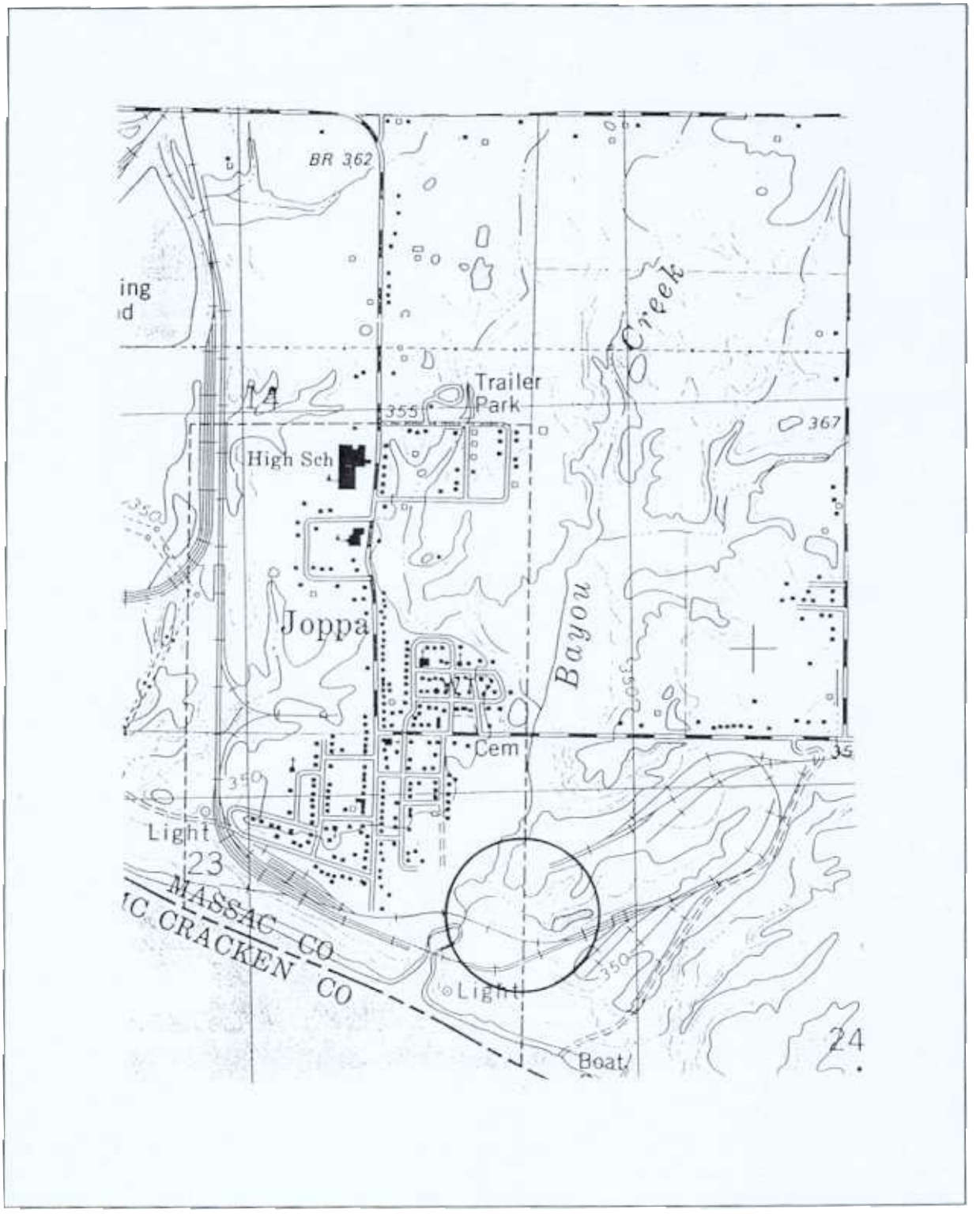

Figure 1. Republic Creosoting study area.

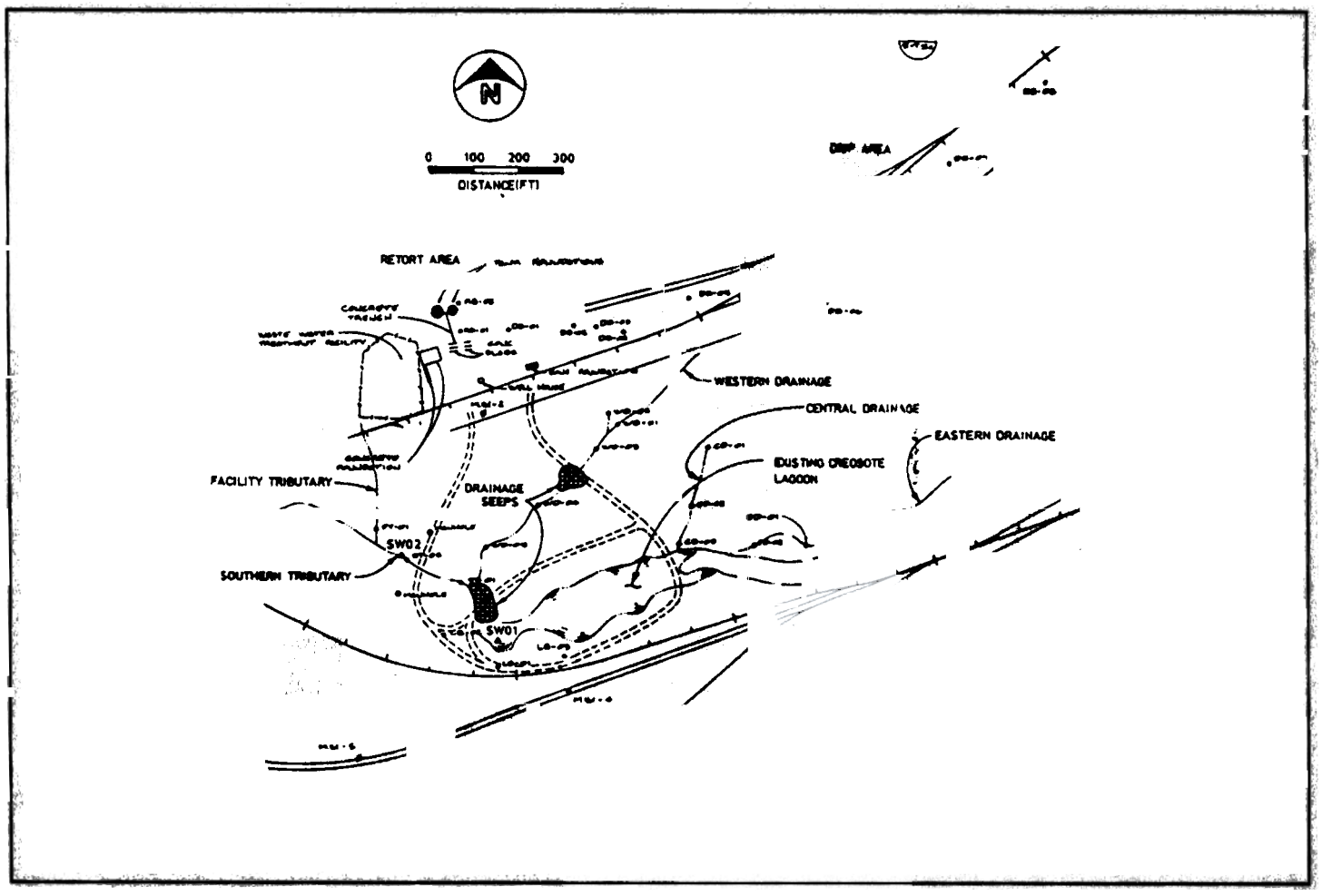

Figure 2. Creosote waste lagoon (CH2M Hill 1988).

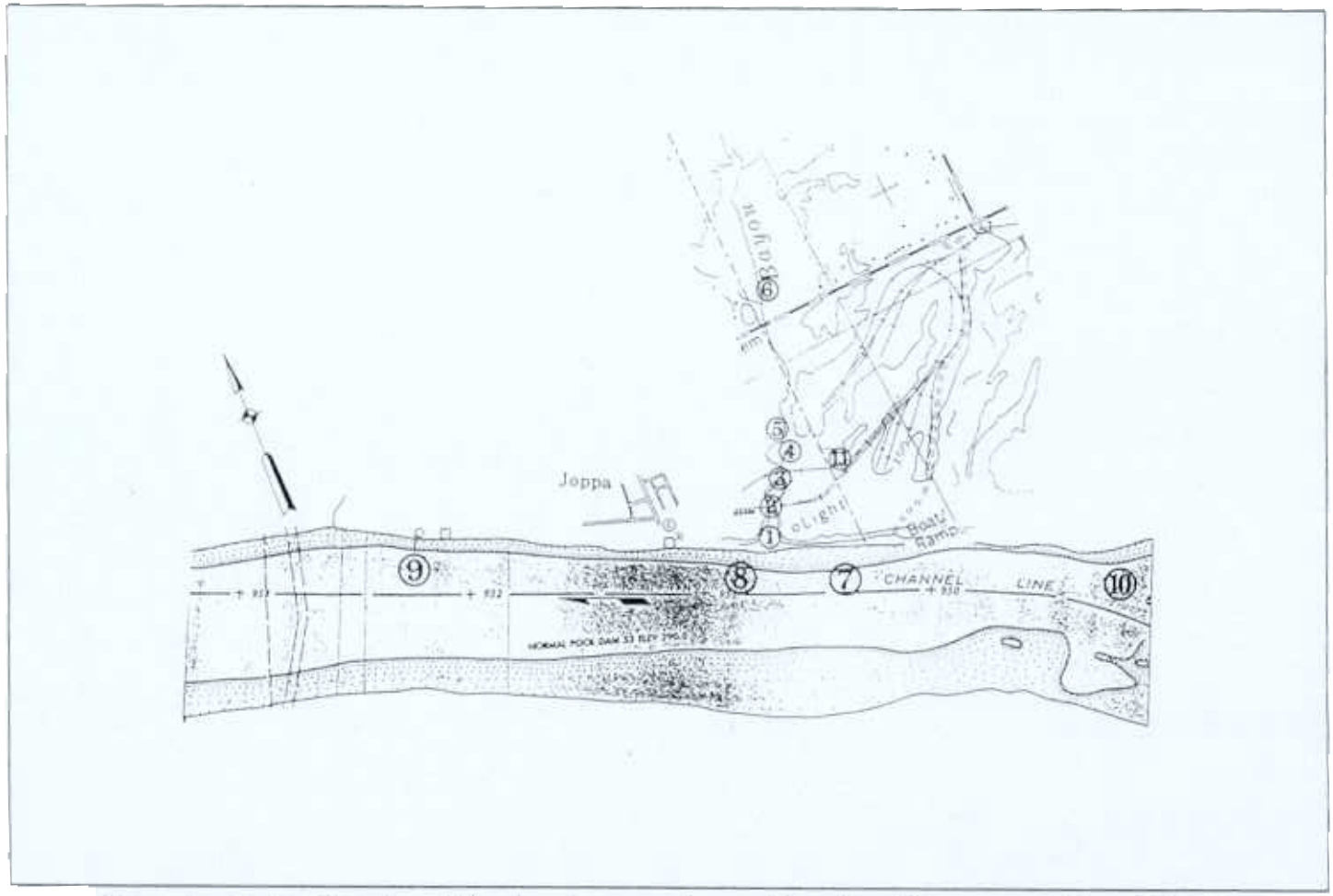

Figure 3. Bed sediment and freshwater mussel sampling sites (sites are numbered

Table 1. Republic Creosoting 1990 survey sampling sites

Sample Location	Sample Number	Sample Type	Samples Collected
Confluence of Bayou Creek and Ohio River	RC-	Bottom sediments	1 (composite)
250 feet upstream on Bayou Creek	RC-2	Bottom sediments	1 (composite)
550 feet upstream on Bayou Creek (below S. tributary from creosote waste lagoon)	RC-3	Bottom sediments	1 (composite)
Lower end of S. tributary from creosote waste lagoon	RC-4	Bottom sediments	1 (composite)
350 feet upstream from confluence of S. tributary and Bayou Creek (reference site)	RC-5	Bottom sediments	1 (composite)
400 feet north of Joppa Road on Bayou Creek (reference site)	RC-6	Bottom sediment	1 (composite)
Ohio River - RM 950.3 directly adjacent to creosote tie yard	RC-7	Bottom sediments, mussels	3 (composites)
Ohio River - RM 950.9 downstream of Bayou Creek	RC-8	Bottom sediments, mussels	3 (composites)
Ohio River - RM 952.3 downstream of Joppa, Illinois	RC-9	Bottom sediments, mussels	3 (composites)
Ohio River - RM 949.3 upstream of creosote tie yard (reference site)	RC-10	Bottom sediments, mussels	3 (composites)
Creosote lagoon/ S. tributary confluence (positive control)	RC-11	Bottom sediments	1 (composite)

as the reference site for the Ohio River samples. One additional sampling site was selected to serve as a positive control (RC-11), which was an area that was sampled at the culverted confluence of the creosote lagoon discharge and the southern tributary to Bayou Creek at the very top of the steep gradient. This site, which represented as close an approximation to a positive control as possible without actually entering and sampling the creosote lagoon itself, was selected to provide comparative information on the maximum concentrations of creosote-associated wastes present immediately outside of the fenced boundaries of the lagoon.

Bayou Creek appears to originate approximately two miles north of its confluence with the Ohio River, and its direction of flow is generally southwesterly towards the river. However, the lower 200 feet of Bayou Creek has a mechanically widened streambed, which was dredged sometime during the mid-1900's to create a barge loading inlet. This inlet was created in order to permit Ohio River barge traffic into the creek to approach a coal loading tipple trestle which spans the inlet and leads to rail lines on the Republic Creosoting facility tie yard. Water levels in this lower portion of Bayou Creek partially fluctuate with water levels of the Lower Ohio River watershed, and may be influenced by such factors as local and regional precipitation, as well as mechanically regulated pool levels.

Methodology

Sample Collections

Bottom sediment samples were collected at 11 sampling locations adjacent to the creosote waste lagoon on Bayou Creek, and in the Ohio River near Joppa, Illinois (Table 1, Figure 3) during two sampling trips conducted in August and November of 1990. One composite bottom sediment sample, which was comprised of three to five subsamples, was collected at each site. Bottom sediments were collected primarily with an Ekman dredge sampler with 6" x 6" x 6" chamber dimensions. Sediment samples were also collected by hand with a stainless steel spoon and pan. The subsamples collected from each site were placed in acetone-rinsed stainless steel containers and thoroughly mixed, then proportioned into 1000 ml chemically-cleaned borosilicate glass jars with Teflon™-lined lids. The sampling equipment was rinsed with acetone between each sample site location. The sample containers were labeled and stored temporarily at ambient temperature in the field, then later returned to the field office and stored at -20° C, prior to shipment under ice to contracted analytical facilities.

Indigenous freshwater mussels were collected for whole soft tissue analysis from the Ohio River adjacent to the Republic Creosoting facility. The freshwater mussel samples were collected by brailing with two 16-foot crowfoot bars during two sampling trips conducted in August and November of 1990. Two species, Quadrula quadrula and Megalonaias gigantea, were collected from each of four different sampling locations. Approximately 20 individual specimens of each species were collected from each sampling location, and each set of 20 individuals collected from each location comprised one composited sample for chemical analysis. Since the size of an individual mussel specimen may be correlated with whole body contaminant concentration (Boyden 1974; Hinch and Stephenson 1987; Naimo et al. 1992), adults of similar size were collected for each of the eight composites. The mussels were kept in plastic buckets, separated by sampling site, which were filled with river water in the boat during sample collections, and then transferred to 60-quart insulated coolers (also separated by sampling site) filled with river water and aerated with battery operated aquarium pumps for transport back to the field office. Upon return

to the field office, the mussels were maintained alive for approximately one week in filtered, aerated, dechlorinated tap water, without substrate, to allow for depuration of sediments and other particulate matter from the organisms' digestive tracts. After the depuration period, each specimen from each sampling site was dissected and its soft tissues were removed and stored in separate 40 ml chemically cleaned borosilicate glass jars with Teflon-lined lids, draining off excess moisture. Each specimen sample jar was labeled as to the species, specimen identification number, total length and approximate age, and sampling location, and then immediately stored at -20° C, prior to shipment under ice to the analytical facility.

Chemical Analysis

Bed sediments and freshwater mussel samples were analyzed for trace elements, polycyclic aromatic hydrocarbons, organochlorine pesticides and polychlorinated biphenyls (PCBs).

Bed sediments were chemically and physically characterized by percent moisture, total organic carbon (TOC) content, and grain size analysis. Determinations were made by Environmental Trace Substances Research Center, Columbia, Missouri. Percent moisture determinations were made by oven-drying a pre-weighed homogenized aliquot of the sample in a Fisher Isotemp oven at 103-105° C, and then reweighing the dried sample. Total organic carbon analysis was made using a dry oxidation method. The sample was treated with 10% HCL to remove the inorganic carbon prior to TOC analysis, with concurrent blank preparation. The samples were oven-dried at 100° C for at least one hour, and then analyzed using a standard curve prepared with a set of potassium hydrogen phthalate standards, which also received the same preparation as the samples. The micrograms of organic carbon determinations in each sample were made using this potassium hydrogen phthalate standard curve. Results were reported by the analytical facility in units of percent concentration. The limits of detection for a 4 mg sample was 0.1%. The accuracy and precision of the analysis was measured by method blank sample analysis, spike recovery analysis, standard reference material analysis, and duplicate sample analysis by the analytical facility. Grain size analysis determinations were made according to the methods described by Folk (1980), which generally involves separation of the sand from the sediment sample, followed by

pipette analysis of silt and clay.

Chemical residue analysis for the trace elements was performed by Research Triangle Institute, Research Triangle Park, North Carolina. Sediment and biota samples were homogenized and analyzed for 20 trace elements, using Inductively Coupled Plasma (ICP) emission spectroscopy, with preconcentration for selected elements for the biological samples. ICP measurements were made using a Leeman Labs Plasma Spec I sequential spectrometer. Selenium concentration determinations were made using graphite furnace atomic absorption spectroscopy. Graphite furnace atomic absorption measurements were made using a Perkin Elmer Zeemen 3030 atomic absorption spectrophotometer with an HGA-600 graphite furnace and an AS-60 autosampler. Mercury concentration analysis was made using cold vapor atomic absorption. Cold vapor atomic absorption measurements were made using an Instrumentation Laboratory Model 251 atomic absorption spectrophotometer. In addition to the ICP analysis which included cadmium, cadmium was also measured by graphite furnace atomic absorption spectroscopy. The accuracy and precision of the chemical analysis was measured by method blank sample analysis, spike recovery analysis, standard reference material analysis, and duplicate sample analysis by the analytical facility. The estimated analytical detection limits varied according to the particular analyte, and is presented with the tabulated data. Quality assurance and quality control was monitored by the U.S. Fish and Wildlife Service, Patuxent Analytical Control Facility, Laurel, Maryland and was reported as acceptable for all analytes.

Chemical residue analysis for the organic compounds was performed by Mississippi State Chemical Laboratory at Mississippi State University, Mississippi Sate, Mississippi. Sediment and biota samples were analyzed for polycyclic aromatic hydrocarbons, organochlorine pesticides and PCB arochlors.

Sediment and biota samples were homogenized and analyzed for 14 polycyclic aromatic hydrocarbons. The aromatic hydrocarbons were fractionated by initially extracting the sediment samples with acetone and petroleum ether. The hydrocarbon residues were partitioned from the extraction into petroleum ether, and then double rinsed and concentrated prior to transfer to a silica gel column. Biota samples analyzed for aromatic hydrocarbons were initially homogenized and digested in aqueous potassium hydroxide and extracted with methylene chloride, dried and

reconstituted in petroleum ether prior to transfer to a silica gel column. An aliphatic fraction was separated from the hydrocarbon residue by eluting the aliphatic fraction from the column with petroleum ether. The aromatic fraction was eluted from the silica gel column using methylene chloride/petroleum ether and methylene chloride, successively. The aromatic hydrocarbon fraction was concentrated, subjected to gel permeation chromatography for clean-up, and then quantified by capillary column flame ionization gas chromatography and florescence high performance liquid chromatography.

Sediment and biota samples were analyzed for 21 organochlorine pesticides and four PCB arochlors. Sediment samples were initially homogenized and extracted with acetone and hexane, and the residues partitioned into the hexane portion were washed, concentrated and then transferred to a Florisil mini-column, where the residues were eluted from the column in two primary elution fractions. Biota sample homogenates analyzed for organochlorine pesticides and PCBs were initially ground and mixed with anhydrous sodium sulfate, and then extracted in hexane using the soxhlet extraction method. The extract was concentrated to dryness for percent lipid determinations, and then extracted with acetone saturated with petroleum ether. Petroleum ether-partitioned, concentrated residues were eluted in a Florisil column, and then separated into two fractions with diethyl ether/petroleum ether. Additional fractionation of PCBs from other organochlorines was performed by silicic acid column chromatography. Organochlorine and PCB residues in each set of fractions were quantified by packed column electron capture gas chromatography.

For the organic analysis of sediments, the accuracy and precision of the analysis was measured by reagent and matrix blank sample analysis, spike recovery, and duplicate sample analysis, with confirmation of selected samples by gas chromatography/ mass spectrometry by the analytical facility. For the organic analysis of biota samples, the accuracy was measured by reagent and matrix blank sample analysis and spike recovery, with confirmation of selected samples by gas chromatography/ mass spectrometry. The lower level of detection for the polycyclic aromatic hydrocarbon analysis was 0.01 ppm for both sediment and tissue samples. The lower level of detection for the organochlorine compound analysis, with the exception of toxaphene and PCBs, was 0.01 ppm for both sediment and tissue samples. The lower limit of detection for toxaphene and the PCB arochlors was 0.05 ppm. Quality assurance and

quality control for both sediment and biota analysis was monitored by the U.S. Fish and Wildlife Service Patuxent Analytical Control Facility, Laurel, Maryland, and was reported as acceptable for all analytes.

Results

Table 2(a) summarizes the analytical results for each site for the trace element, polycyclic aromatic hydrocarbon and organochlorine chemical analysis of bed sediments samples which were collected adjacent to the Republic Creosoting hazardous waste site. All bottom sediment sample analytical results were transformed to dry weight, based on the percent moisture determinations provided by the analytical facilities. The actual results of the analysis of bed sediment samples are tabulated in Appendix A (Tables 3 - 6). Table 3 shows the results of the total organic carbon and grain size analysis determinations for bottom sediments collected from each site. The samples from all of the sites are relatively uniform in percent moisture content. Samples from three sites, two along Bayou Creek, and one collected from the southern tributary, had lower than average organic carbon contents' (on a dry weight basis). With respect to the grain size determinations, all of the Ohio River samples had the highest percent sand fractions and the second lowest percent clay fractions, as a group

The results of the trace element chemical analysis of bottom sediments samples for each site is shown in Table 4. Three trace elements, zinc, cadmium and mercury, are substantially elevated above background levels (represented by sites RC-5, RC-6, and RC-10) at both the positive control site at the creosote lagoon/southern tributary confluence (RC-11) and the site just downstream from that located in the southern tributary (RC-4). Zinc is the primary trace element which appears to originate from the creosote lagoon and is found in elevated concentrations in bed sediments all the way out to the Ohio River. The slightly lower concentrations of metals that appear uniformly across all inorganics at site RC-3 are likely due to the low organic carbon content and the low percent clay fraction which physically characterizes the sample collected at that site. Cadmium and mercury are also somewhat elevated in Ohio River sediments, relative to Bayou Creek reference site (RC-5, RC-6) sediments.

The results of the polycyclic aromatic hydrocarbon analysis of bottom sediments is presented in Table 5. The majority of the 14 polycyclic aromatic hydrocarbons analyzed are elevated in bed sediments with respect to the lower southern tributary site RC-4, the positive control site RC-11, and background reference sites RC-5 and

Table 2(a). Summary of the Republic Creosoting 1990 bottom sediment chemical residue analysis results for trace elements, polycyclic aromatic hydrocarbons, and organochlorines by general sampling locations (data summarized from Appendix A). "Elevated" indicates elevation of one or more analytes in a particular parameter class over background sample residue analysis. "Not detected" indicates analytical parameters were not detected upon chemical analysis. "Background" indicates analytical parameters were significantly depressed with respect to downstream sample residue analysis.

Sample Location	Trace Elements	Polycyclic Aromatic Hydrocarbons	Organochlorines
Creosote lagoon southern tributary	Elevated	Elevated	Not Detected
Bayou Creek (downstream from southern tributary)	Elevated	Elevated	Not Detected
Bayou Creek reference site	Background	Background	Not Detected
Ohio River (downstream from the creosote lagoon)	Elevated	Slightly Elevated	Not Detected
Ohio River reference site	Background	Background	Not Detected

RC-6. All Bayou Creek bed sediment samples, in particular, are substantially elevated in polycyclic aromatic hydrocarbons with respect to control and reference samples.

The results of the organochlorine analysis is presented in Table 6. Generally, no organochlorine pesticide compounds were detectable in bottom sediments adjacent to the Republic Creosoting site.

Table 2(b) summarizes the analytical results for each site for the trace element, polycyclic aromatic hydrocarbon, and the organochlorine chemical analysis of freshwater mussel tissue, from specimens collected in the Ohio River adjacent to the Republic Creosoting hazardous waste site. Tables 7, 8, and 9 (Appendix B) contain the analytical chemical results for the soft tissue analysis of the two freshwater mussel species that were collected, M. gigantea and Q. quadrula. The analytical results are presented both in units of mg/kg dry weight [Tables 7(a), 8(a), 9(a)], and in units of mg/kg wet weight [Tables 7(b), 8(b), 9(b)]. Tables 7(a) and (b) show the results of the analysis of trace elements for each sample. Samples of both species which were collected at site RC-10 represent reference samples collected above the region of the Ohio River directly adjacent to the creosote waste lagoon. The freshwater mussel sampling sites correspond directly to the bed sediment sampling sites described in Table 1, and shown in Figure 3. Two elements, zinc and cadmium, appear to be elevated significantly in mussel soft tissues with respect to the RC-10 reference site. M. gigantea in particular, appears to have accumulated higher concentrations of these metals, as well as others, when compared with the zinc and cadmium concentrations for Q. quadrula. (Some fluctuations in metal concentrations across sampling locations for either species might be due to slight variations in total sample weight.) Several other elements (aluminum, barium, boron, cobalt, chromium, iron, manganese, lead, and strontium) show some elevation at site RC-7 only, and then decrease at sites RC-8 and RC-9. Mercury appears to be at background levels at all sites with the exception of RC-9 for Q. quadrula. The concentration of mercury increases by an order of magnitude in Q. quadrula tissue samples for this site furthest downstream. This particular sample was collected in the vicinity of a coal-fired power plant because a sufficient number of specimens originally could not be located upstream of the plant, and the elevation of mercury in these mussel tissue samples was later determined to be due principally to the proximity of the sample location to the coal

Table 2(b). Summary of the Republic Creosoting 1990 freshwater mussel tissue chemical residue analysis results for trace elements, polycyclic aromatic hydrocarbons, and organochlorines by general sampling locations (data summarized from Appendix B). "Elevated" indicates elevation of one or more analytes in a particular parameter class over background sample residue analysis. "Not detected" indicates analytical parameters were not detected upon chemical analysis. "Background" indicates analytical parameters were significantly depressed with respect to downstream sample residue analysis.

Sample Location	Trace Elements	Polycyclic Aromatic Hydrocarbons	Organochlorines
Ohio River (downstream from the creosote lagoon)	Elevated	Not Significantly Elevated	Not Significantly Elevated
Ohio River reference site	Background	Background	Not Detected

power plant. Additional mussel samples collected upstream of the plant that were collected and analyzed subsequent to this first collection demonstrated lower mercury concentrations in tissues (unpublished data). Several elements appear to be relatively constant in concentration in mussel tissue samples throughout all four Ohio River sites. These trace elements are: antimony, beryllium, molybdenum, nickel, selenium, silver, tin, and vanadium.

Tables 8(a) and (b) shows the results of the freshwater mussel tissue analysis for polycyclic aromatic hydrocarbons, and Tables 9(a) and (b) the results of the analysis for organochlorines. Only trace amounts of one polycyclic aromatic hydrocarbon, phenanthrene, and one organochlorine, trans-nonaclor, were detected in one freshwater mussel tissue sample (M. gigantea) at one of the four sites sampled in the Ohio River, the upstream reference site RC-10.

Discussion

Upon comparative analysis of the concentrations of inorganic and organic chemicals in bed sediments collected along Bayou Creek and the Ohio River, the data demonstrates that contaminants originating from the Republic Creosoting hazardous waste facility are entering the Ohio River. With respect to the trace elements, zinc and cadmium were found to be significantly elevated at a few locations in Bayou Creek. Zinc was found to be elevated in the Ohio River downstream from Bayou Creek. Both of these elements were elevated in creosote waste lagoon samples and soil samples collected on site previously (CH2M Hill 1988). Table 2(c) shows a comparison of maximum and background zinc and cadmium concentrations adjacent to the Republic Creosoting site, with local and regional background concentrations and regional sediment quality criteria. Although the concentrations of cadmium, both in Bayou Creek and the Ohio River, are not significant in terms of these other comparative concentrations, the zinc concentrations in both Bayou Creek and the Ohio River are in excess of regional background concentrations, as well as regional and national sediment quality criteria for the protection of benthic aquatic organisms in general. Though proportionally smaller concentrations of polycyclic aromatic hydrocarbons were found in bottom sediment samples collected from the Ohio River as compared with Bayou Creek samples, it is evident that the migration of aromatic hydrocarbons from the creosote waste lagoon out into the Ohio River follows a generally declining progression which parallels the progressive pattern in zinc concentrations in bed sediments along the same route. The combination of the two chemical analytes (PAHs and zinc) along this pathway provides a confirmational marker of the migration of contaminants from the creosote waste lagoon out into the Ohio River.

The trace element analysis of freshwater mussel tissue shows several trends that are similar to the trends in the trace element analysis of bed sediments from the Ohio River. Two elements, zinc and cadmium, were elevated in freshwater mussel tissues of both species analyzed. Zinc was also elevated in bed sediments at the same Ohio River sampling sites that it was observed elevated in mussel tissue samples, with respect to upstream reference samples. Figure 4 describes the general trend in zinc concentrations in freshwater mussel tissue samples collected upstream, adjacent to,

Table 2(c). Comparison of maximum concentrations (mg/kg dry weight) of zinc and cadmium detected in bed sediments in and adjacent to Bayou Creek and in the Ohio River downstream from the Republic Creosoting hazardous waste site, with local (on-site) and regional background concentrations and available sediment quality criteria for the protection of benthic aquatic organisms.

Location:	Bayou Creek		Ohio River	
	Zinc	Cadmium	Zinc	Cadmium
Maximum Concentration	794.0	0.575	132.0	0.616
Background Concentrations:				
Local	21.7	<0.02	96.8	0.816
Illinois	50.3[1]	<0.5[1]	50.3[1]	<0.5[1]
Sediment Quality Criteria	<90.0[2] 120.0[3] 130.0[4]	 0.6[3] 1.7[4]	<90.0[2] 120.0[3] 130.0[4]	 0.6[3] 1.7[4]

[1]Kelly and Hite (1984); lowest average background concentrations in Illinois stream sediment samples statewide.

[2]U.S. Environmental Protection Agency (1977); zinc classification range for Great Lakes harbors sediments characterizing non-polluted sediments (90-200=moderately polluted; >200=heavily polluted).

[3]Jaagumagi (1992); lowest effect level concentration at which the majority of benthic organisms are unaffected.

[4]Long and Morgan (1991); apparent effects threshold above which statistically significant biological effects occur, specifically in reference to a marine bivalve larvae bioassay.

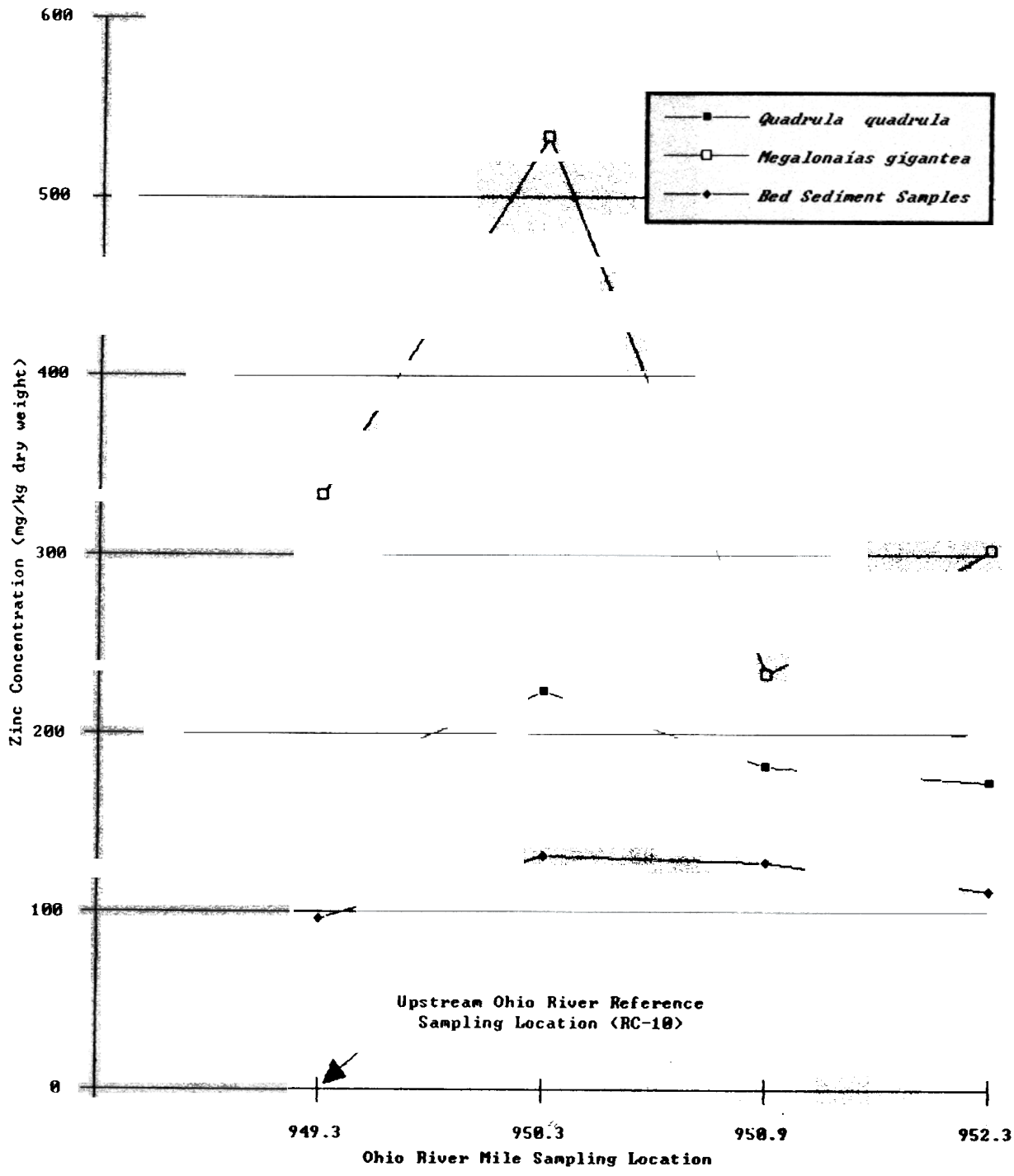

Figure 4. Line graph of the concentrations of zinc (mg/kg dry weight) in freshwater mussel tissue samples collected from the Ohio River upstream, adjacent to, and downstream from the Republic Creosoting hazardous waste site.

and downstream from the Republic Creosoting facility

Freshwater mussels are generally accepted as ideal biomonitoring species in metal-contaminated environments (Adams et al. 1981; Foster and Bates 1978; Schmitt et al. 1987). With respect to studies pertaining to the genera Megalonaias and Quadrula, the results of a study conducted by the U.S. Army Corps of Engineers (1984) involving analysis of soft tissues of M. gigantea, Quadrula spp. and Amblema plicata for PCBs indicated that among the three, M. gigantea represented the best species for long-term monitoring. However, the use of several species of the genus Quadrula in the Corps' study might have introduced excessive variation in the analytical results such that this genus initially appeared less suitable as a species for biomonitoring for environmental contaminants. In the present study, M. gigantea also appears to be a more sensitive biomonitor than Q. quadrula for trace elements. The higher concentrations of cadmium and zinc in M. gigantea soft tissue samples at each site, when compared to Q. quadrula, might be reflective of an inter-species difference, with an enhanced physiological capacity for M. gigantea to bioconcentrate trace elements.

Conversely, the lack of accumulation of polycyclic aromatic hydrocarbons in either species of freshwater mussel tissue might reflect either the absence of sufficient and/or bioavailable concentrations of PAHs in the immediate environment of the collected specimens, or a lack of ability to bioaccumulate and bioconcentrate significant concentrations of PAHs over a long time period. Heit et al. (1980) report significant accumulation of trace elements in all freshwater mussel tissue samples of three species of Unionidae mussels (Lampsilis radiata, Elliptio complanatus, and Anodonta grandis) collected from a region highly contaminated with both trace elements and PAHs, but only partial detection of PAHs in the same mussel tissue samples analyzed. In the present study, other physiological mechanisms may be in operation as well, similar to the capacity of some aquatic vertebrates to metabolize parent PAH compounds (Eisler 1987). With this mechanism, any bioaccumulated PAHs may be metabolized relatively quickly and completely enough such that analysis for only the parent PAH compounds in biological samples might prove meaningless. However, the data obtained from the present study suggests that PAHs and organochlorines were not significantly elevated enough in the Ohio River bed sediments to bioaccumulate in mussel tissue, since the background and downstream

samples did not vary significantly, and were comparatively cumulatively much lower in concentration than the Bayou Creek and southern tributary samples.

With respect to the effects of the contaminants originating from the creosote lagoon waste site on biota, specifically freshwater mussels, it may be anticipated that metals in general (Foster and Bates 1978), and particularly the concentrations of zinc present, would have significantly more of an adverse effect on mussel resources than the polycyclic aromatic hydrocarbons (Fuller 1974; Havlik and Marking 1987). Several trace elements, specifically cadmium, chromium, nickel, zinc, copper and mercury, are all known to be toxic to freshwater mussels during early juvenile stages of development (Keller and Zam 1991), as well as at the adult stage (Havlik and Marking 1987). The bioavailability zinc in the Ohio River bed sediments and water column in the vicinity of the Republic Creosoting facility has been demonstrated through the bioaccumulation of substantial quantities of this metal in soft tissues of the adult freshwater mussels collected and analyzed during the present study. The highest zinc concentration detected in freshwater mussel tissue was 533.0 mg/kg dry weight in M. gigantea. The highest cadmium concentration was 2.88 mg/kg in Q. quadrula. Naimo et al. (1992) studied trace element concentrations in Amblema plicata plicata in the upper Mississippi River, and reports maximum zinc concentrations of 203 ug/g dry weight, and cadmium concentrations of 1.25 ug/g, both in samples collected from areas influenced by industrial and domestic inputs. Zinc and cadmium concentrations in freshwater mussel tissues from heavily polluted environments might generally range from 300 to 700 ug/g dry weight for zinc, and 1.4 to 5.5 ug/g dry weight for cadmium [Mathis and Cummings 1973; Anderson 1977(a); Anderson 1977(b)]. Thus, both the zinc and cadmium concentrations that were detected in freshwater mussel tissue samples collected from adjacent to the Republic Creosoting site appear to be indicative of a contaminated environment. Although there is a physiological requirement for zinc in freshwater mussels [Anderson 1977(b); Wurtz 1962], it is an element that is considered to be highly toxic in excessive quantities (Fuller 1974; Wurtz 1962). Also, a physiological competitive interaction between zinc and cadmium with respect to gill tissue membrane transport sites has been investigated in the freshwater mussel Anodonta cygnea (Hemelraad et al. 1987), which serves to effectively reduce cadmium uptake in the presence of zinc. This physiological competitive interaction may also exist in the two federally endangered species of concern in the present study, and under field conditions, may render zinc the more

hazardous of the two metals when both are present (and particularly when zinc is present in significantly higher quantities).

At the present, the concentrations of zinc in Ohio River bed sediments appear to be detrimental to the survival of at least juvenile freshwater mussels, based on the sediment quality criteria described in Table 2(c). Whether the concentrations of this particular metal are in fact high enough over the short term to affect viability of juveniles probably would best be tested by controlled laboratory and/or in-situ studies with juvenile mussels, which was an aspect not incorporated into the present study. However, the concentrations of zinc in bed sediments in Bayou Creek and the Ohio River are well above the range of concentrations previously determined to be toxic to juvenile mussels of the genus Anodonta (Keller and Zam 1991). Keller and Zam report a mean 96-hour LC 50 for zinc of 0.438 mg/L, and for cadmium of 0.107 mg/L, in moderately hard freshwater. These investigators also report the results of toxicity tests utilizing zinc in combination with cadmium; in both short (48-hour) and long term (96-hour) tests, zinc was found to be more toxic to juvenile freshwater mussels in the presence of cadmium.

In its present condition, the site should be remediated to the extent that contaminated sediments be removed from Bayou Creek. This is because the contaminants in the creek, which are assumed to have been present on site since at least the 1940s, are at relatively high levels (with respect to the positive control and reference sites), and, if not remediated, will continue to be a source of contaminant loading to that region of the Ohio River. The metals, in particular, would not be anticipated to degrade to any extent over time, as might some of the low molecular weight aromatic hydrocarbons. Anthracene, although characterized as a low molecular weight hydrocarbon (Eisler 1987) is known to be highly phototoxic to aquatic invertebrates and vertebrates (Holst and Giesy 1989; Landrum et al. 1987; Oris and Giesy 1986), and was found in very significant concentrations in Bayou Creek, along with many other phototoxic PAHs. (Oris and Giesy 1987). Any of these phototoxic PAHs that are present could possibly adversely affect fish that may be encysted with the glochidia of freshwater mussels. Also, the analytical results indicate that this region of Bayou Creek and the Ohio River is relatively free from organochlorine pesticide and PCB contamination in bottom sediments or biota. This indicates that there are no anthropogenic sources of organochlorine compounds in this vicinity. This also suggests that adverse impacts to

aquatic organisms due to metals and aromatic hydrocarbons originating from the Republic Creosoting hazardous waste site have historically been the only source of contaminant pressures on biota, particularly the freshwater mussel resources, in this region. As long as the former facility and the adjacent tributaries leading from the site remain un-remediated, it would be anticipated that the only contaminant pressures on mussel resources in this region will continue to originate from this site, possibly irreversibly impacting freshwater mussel diversity in this section of the Ohio River. Other major water bodies that formerly supported diverse freshwater mussel populations are currently showing moderate to severe declines in freshwater mussel resources and changes in species composition, principally or at least partially due to anthropogenic sources of contaminants (Hornbach et al. 1992; Nalepa et al. 1991; Starrett 1971).

Some considerations with respect to future studies at the Republic Creosoting hazardous waste site might include laboratory toxicity testing with juvenile freshwater mussels. Another study of environmental contaminants at a creosote waste site has demonstrated that bioassay analysis of contaminated site material is actually advantageous in defining site clean-up parameters, due to the typical complexity of chemical contamination present at such sites (Athey et al. 1989), which is a characteristic that is also quite evident at the Republic Creosoting hazardous waste site (CH2M Hill 1988). It is also very important to note that juvenile freshwater mussel toxicity testing efforts have only very recently been undertaken, and the sediment quality criteria described in Table 2(c), although extremely valuable in identifying a benchmark for target zinc contaminant levels in bottom sediments for the protection of benthic organisms, do not specifically take into consideration the effects of zinc on juvenile freshwater mussels, because the currently still limited scientific data with respect to juvenile freshwater mussels has only recently been available. The Republic Creosoting hazardous waste site represents a circumstance where a locally important species has a more sensitive life-stage than currently available criteria take into consideration and/or are protective of. Therefore, site-specific quality criteria should be developed for a site such as this to ensure the survival of the species of particular concern with respect to this study. Additional bioassays at this facility should take the form of acute and/or chronic exposure bioassays with juveniles of indigenous species phylogenetically related to the two federally endangered species of concern, L. orbiculata and P. cooperianus. The analysis should be conducted with bottom

sediments (or sediment pore water extractions) collected from Bayou Creek and the Ohio River. This approach should provide ecologically relevant, site-specific data as to the toxicity of contaminated sediments at the site to the particular freshwater mussel species of concern.

Literature Cited

Adams, T. G., G. J. Atchison and R. J. Vetter. 1981. The use of the three-ridge clam (Amblema perplicata) to monitor trace metal contamination. Hydrobiologia 83:67-72.

Ahlstedt, S. 1985. Recovery plan for the Pink Mucket Pearly Mussel, Lampsilis orbiculata. U.S. Fish and Wildlife Service, Atlanta, Georgia. 47pp.

Ahlstedt, S. 1984. Recovery plan for the Orange Footed Pearly Mussel, Plethobasis cooperianus. U.S. Fish and Wildlife Service, Atlanta, Georgia. 47pp.

Anderson, R. V. 1977(a). Concentration of cadmium, copper, lead, and zinc in six species of freshwater clams. Bull. Environ. Contam. Toxicol. 18(4):492-496.

Anderson, R. V. 1977(b). Concentration of cadmium, copper, lead, and zinc in thirty-five genera of freshwater macroinvertebrates from the Fox River, Illinois and Wisconsin. Bull. Environ. Contam. Toxicol. 18(3):345-349.

Athey, L. A., J. M. Thomas, W. E. Miller and J. Q. Word. 1989. Evaluation of bioassays for designing sediment cleanup strategies at a wood treatment site. Environ. Toxicol. Chem. 8:223-230.

Boyden, C. R. 1974. Trace element content and body size in molluscs. Nature 251:311-314.

CH2M Hill. 1988. Phase I Initial Site Assessment, Joppa Tie Yard Site, Joppa, Illinois. Draft Final Report prepared for Union Pacific Railroad, Omaha, Nebraska. 37pp.

Cossa, D., M. Picard-Berube, and J. P. Gouygou. 1983. Polynuclear aromatic hydrocarbons in mussels from the estuary and northwestern Gulf of St. Lawrence, Canada. Bull. Environ. Contam. Toxicol. 31:41-47.

Literature Cited (cont.)

DeLeon, I. R., J. B. Ferraio and C. J. Byrne. 1988. Bioaccumulation of polynuclear aromatic hydrocarbons by the clam, Rangia cuneata, in the vicinity of a creosote spill. Bull. Environ. Contam. Toxicol. 41:872-879.

Eisler, R. 1987. Polycyclic aromatic hydrocarbon hazards to fish, wildlife and invertebrates: a synoptic review. U.S. Fish and Wildlife Service Biological Report 85. 81pp.

Folk, R. L. 1980. Petrology of sedimentary rocks. Hemphill Publishing Co., Austin, Texas. 182 pp.

Foster, R. B. and J. M. Bates. 1978. Use of freshwater mussels to monitor point source industrial discharges. Environ. Sci. Technol. 12(8):958-962.

Fuller, S. L. H. 1974. Clams and mussels (Mollusca: Bivalvia). In: Pollution Ecology of Freshwater Invertebrates. C. W. Hart and S. L. H. Fuller (eds. Academic Press, New York. Pages 215-273.

Havlik, M. E. 1992. A survey for unionid mollusks (Mollusca: Bivalvia: Unionidae) from Ohio River mile 938.9 to 981.0, between Paducah, KY and Cairo, IL. Final Report for U.S. Army Corps of Engineers, Louisville District, Louisville, Kentucky. Contract No. DACW27-92-B-0049.

Havlik, M. E. and L. L. Marking. 1987. Effects of contaminants on naiad mollusks (Unionidae): a review. U.S. Fish and Wildlife Service Resource Publication 164. 20pp.

Heit, M., C. S. Kleisek and K. M. Miller. 1980. Trace element, radionuclide, and polynuclear aromatic hydrocarbon concentrations in unionid mussels from Northern Lake George. Environ. Sci. Technol. 14(4):465-468.

Hemelraad, J., H. A. Kleinveld, A. M. de Roos, D. A. Holwerda and D. I. Zandee. 1987. Cadmium kinetics in freshwater clams. III. Effects of zinc on uptake and distribution of cadmium in Anodonta cygnea. Arch. Environ. Contam. Toxicol. 16:95-101.

Hinch, S. G. and L. A. Stephenson. 1987. Size and age-specific patterns of trace metal concentrations in freshwater clams from an acid-sensitive and a circumneutral lake. Can. J. Zool. 65:2436-2442.

Holst, L. L. and J. P. Giesy. 1989. Chronic effects of the photoenhanced toxicity of anthracene on Daphnia magna reproduction. Environ. Toxicol. Chem. 8:933-942.

Hornbach, D. J., A. C. Miller, and B. S. Payne. 1992. Mussels in the upper Mississippi River. Malacological Review 25:119-128.

Jaagumagi, R. 1992. Development of the Ontario provincial sediment quality guidelines for arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel and zinc. Water Resources Branch, Ontario Ministry of the Environment. 10pp. + Appendices.

Keller, A. E. and S. G. Zam. 1991. The acute toxicity of selected metals to the freshwater mussel, Anodonta imbecilis. Environ. Toxicol. Chem. 10:539-546.

Kelly, M. H. and R. L. Hite. 1984. Evaluation of Illinois stream sediment data: 1974-1980. Illinois Environmental Protection Agency, Division of Water Pollution Control. IEPA/WPC/84-004. 105pp.

Landrum, P. F., J. P. Giesy, J. T. Oris, and P. M. Allred. 1987. Photoinduced toxicity of polycyclic aromatic hydrocarbons to aquatic organisms. In: Oil in Freshwater: Chemistry, Biology, Counter Measure Technology. J. H. Vandermeulen and S. Hrudey (eds.). Pergamon Press, New York. Pages 314-328.

Long, E. R. and L. G. Morgan. 1991. The potential for biological effects of sediment-sorbed contaminants tested in the national status and trends program. NOAA Technical Memorandum NOS OMA 52. 175pp.

Mathis, B. J. and T. F. Cummings. 1973. Selected metals in sediments, water, and biota in the Illinois River. Jour. Wat. Poll. Control Fed. 45 (7):1573-1583.

Miller, A. C., B. S. Payne and T. Siemsen. 1986. Description of the habitat of the endangered mussel Plethobasis cooperianus. The Nautilus 100(1):14-18.

Naimo, T. J., D. L. Waller and L. E. Holland-Bartels. 1992. Heavy metals in the threeridge mussel Amblema plicata plicata (Say, 1817) in the upper Mississippi River. J. Freshwater Ecology 7(2):209-217.

Nalepa, T. F., B. A. Manny, J. C. Roth, S. C. Mozley and D. W. Schloesser. 1991. Long-term decline in freshwater mussels (Bivalvia: Unionidae) of the western basin of Lake Erie. J. Great Lakes Res. 17(2):214-219.

Oris, J. T. and J. P. Giesy. 1986. Photoinduced toxicity of anthracene to juvenile bluegill sunfish (Lepomis macrochirus): photoperiod effects and predictive hazard evaluation. Environ. Toxicol. Chem. 5:761-768.

Oris, J. T. and J. P. Giesy. 1987. The photo-induced toxicity of polycyclic aromatic hydrocarbons to larvae of the fathead minnow (Pimephales promelas). Chemosphere 16(7):1395-1404.

Schmitt, C. J., S. E. Finger, T. W. May, M. S. Kaiser. 1987. Bioavaulability of lead and cadmium from mine tailings to the pocketbook mussel (Lampsilis ventricosa). In: Proceedings of the workshop on die-offs of freshwater mussels in the United States. R. J. Neves (ed.). Sponsored by the U.S. Fish and Wildlife Service and the Upper Mississippi River Conservation Committee. Pages 115-142.

Starrett, W. C. 1971. A survey of the mussels (Unionacea) of the Illinois River: a polluted stream. Illinois Natural History Survey Bulletin, Vol. 30, Article 5. Natural History Survey Division, Urbana, Illinois.

Tagtz, M. E., G. R. Plaia, C. H. Deans and E. M. Lores. 1983. Toxicity of creosote-contaminated sediment to field and laboratory-colonized estuarine benthic communities. Environ. Toxicol. Chem. 2:441-450.

U.S. Army Corps of Engineers. 1984. Chemical analysis of sediments and mussel tissue, Pool 15, Upper Mississippi River. Brice, Petrides and Donohue. 32pp

U.S. Environmental Protection Agency. 1977. Guidelines for the pollutional classification of Great Lakes harbor sediments. 7pp.

U.S. Environmental Protection Agency. 1987. Potential Hazardous Waste Site - Site Inspection Report: Republic Creosote. ILD-0989607097. 14pp. + Attachments.

U.S. Fish and Wildlife Service. 1990. Biota investigation of freshwater streams possibly affected by Southern Maryland Wood Treating Superfund Site. Publication No. AFO-C90-05. Prepared by E. Block, Annapolis Field Office, U.S. FWS, for the U.S. Environmental Protection Agency.

Literature Cited (cont.)

Williams, J. C. and G. A. Schuster. 1989. Freshwater mussel investigations of the Ohio River mile 317.0 to mile 981.0. Kentucky Dept. Fish and Wild. Res. 57pp.

Wurtz, C. B. 1962. Zinc effects on fresh-water mollusks Nautilus 76(2):53-61