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Final Project Report on Arsenic Biogeochemistry in the Clinch River and Watts Bar Reservoir

Volume 1: Main Text

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Preface

This study was conducted as a special project of the Clinch River Remedial Investigation, which is tasked with conducting a remedial investigation of the Clinch River and Watts Bar Reservoir by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). The Clinch River Environmental Restoration Program is funded by the U. S. Department of Energy to investigate the possible corrective actions required to rectify the historic releases of hazardous waste and radioactive contaminants into the Clinch River/Watts Bar Reservoir system. The arsenic study was undertaken after preliminary screening of existing data from the Clinch River and Watts Bar Reservoir. As a result of nonconservative screening, arsenic was assigned as a definitely high priority substance for further human health consideration, and the data showed that arsenic concentrations exceeded benchmark criteria for ecological risk assessment. This study investigated the speciation, distribution, and mobility of arsenic in the sediment, pore water, and the water column seasonally over a 3-year period (1990-1992).

Executive Summary

This document reports on the study of arsenic contamination in the Clinch River/Watts Bar Reservoir (CR/WBR) system, downstream from the U.S. Department of Energy's Oak Ridge Reservation (ORR). Arsenic is of particular interest and concern because (1) it occurs commonly in coal-bearing rock and waste products, such as fly ash associated with the burning of coal; (2) it is classified as a Class A carcinogen by the Environmental Protection Agency; and (3) disposal of fly ash, both on and off the ORR, may have contaminated surface water and sediments in the Clinch River and Watts Bar Reservoir.

The present study differs from previous reports on arsenic concentrations in the CR/WBR system because investigators used much more sensitive and precise processing and analytical techniques to measure arsenic species (arsenate, arsenite, and organic arsenic) at levels well below the ecological and human health risk screening criteria. Absolute detection limits with these techniques are approximately 20 to 40 pmol/L, or 0.0015 to 0.003 µg/L. The human health cancer risk value corresponding to a 10^{-4} risk is 4.7 µg/L (62 n*M*). Arsenic concentrations greater than or equal to 11 µg/L (146 n*M*) exceed the hazard index for human health toxicity. Ecological risk values are based on the National Ambient Water Quality Criteria for Protection of Aquatic Life, which is intended to protect most aquatic species from excess exposure. Values of 190 µg/L (2536 n*M*) for arsenite [As(III)] and 8.1 µg/L (108 n*M*) for arsenate [As(V)] exceeded lower ecological screening benchmarks (*Toxicological Benchmarks for Screening Potential Contaminants of Concern for Effects on Aquatic Biota*, 1994, G. W. Suter II and J. B. Mabry, ES/ER/TM-96/R1, Oak Ridge National Laboratory).

Four main sites were sampled quarterly over a 3-year period (1990 through 1992). Sites investigated included lower Watts Bar Reservoir (LWBR) near Watts Bar Dam [Tennessee River kilometer (TRK) 849.6], the Kingston area [Clinch River kilometer (CRK) 1.6], Poplar Creek [Poplar Creek kilometer (PCK) 1.6], and the McCoy Branch Embayment [McCoy Branch kilometer (MBK) 0.3]. Additional sites were investigated in the vicinity of these main stations to determine the distribution of contamination and to identify possible alternative or additional sources of arsenic.

Seasonal increases in dissolved inorganic arsenic in bottom waters in LWBR were attributable to fluxes of dissolved arsenic from sediments during conditions of low dissolved oxygen. The maximum arsenic concentration under low dissolved oxygen conditions was 8.9 n*M* (0.67 µg/L). Surface water arsenic concentrations did not exceed the minimum ecological risk screening concentrations.

Inorganic arsenic levels were elevated in surface waters (0 to 5 m deep) in the Kingston area. Values dropped with depth in the water column and were at their lowest near the sediment-water interface. Surface water arsenic contamination in this area did not appear to originate on the ORR. An arsenic source to the surface water in the Kingston area is suspected.

In Poplar Creek, sediments found deeper than 15 cm were grossly contaminated with arsenic. Sediment pore water values averaged 38,000 n*M* (2,850 µg/L). Surface sediment arsenic concentrations were not different from those observed at Kingston, LWBR, or in Melton Hill Reservoir, upstream. The Poplar Creek site historically received fly ash directly from disposal operations at the K-25 Site on the ORR until 1963. Evidence suggests that deposition and accumulation of cleaner sediment since 1963, in combination with stream-like water flow rates and oxic conditions throughout the water column, may be preventing significant sedimentary release of arsenic to the surface waters in Poplar Creek.

Arsenic concentrations in Rogers Quarry outfall (MBK 1.6) dropped greatly during this study as a result of actions taken to curtail and eventually eliminate fly ash disposal in Rogers Quarry. However, arsenic concentrations in the Rogers Quarry discharge were in excess of both human health and ecological risk screening criteria for all sample collection periods. Arsenic concentrations in surface waters (0 to 2 m deep) decreased with distance downstream in McCoy Branch. Maximum summer values in upper McCoy Branch Embayment (MBK 0.85 and MBK 0.7) exceeded human health risk screening criteria. Winter concentrations were significantly lower. The maximum summer values in lower McCoy Branch Embayment (MBK 0.5 and MBK 0.3) were elevated, but were significantly lower than upper McCoy Branch Embayment and significantly higher than at CRK 60.5, approximately 0.25 km downstream in Melton Hill Reservoir.

Seasonal increases in dissolved inorganic arsenic were observed both in the sediment pore waters and surface waters throughout the McCoy Branch Embayment, downstream from Rogers Quarry. Seasonal change was not observed either upstream (MBK 2) or downstream (MBK 1.6) from Rogers Quarry. Changes in surface water arsenic values in McCoy Branch Embayment may be attributed largely to seasonal changes in sediment pore water chemistry, rather than to changes in Rogers Quarry outflows.

Based on observed concentration differences within the surface sediments and between the surface sediment and overlying surface water, the apparent flux of arsenic from sediment pore waters was greatest by far in upper McCoy Branch Embayment, followed by lower McCoy Branch Embayment, Poplar Creek, and LWBR. Concentrations in excess of risk screening values were observed only in upper McCoy Branch Embayment. The degree to which sediments serve as a source of dissolved arsenic on a seasonal basis should be evaluated more thoroughly by performing arsenic flux calculations at these sites.

The elevated surface water arsenic concentrations in the Kingston area (CRK 8 to TRK 907.2, approximately 8 km) were much more extensive than for McCoy Branch Embayment (MBK 0.85 to the McCoy Branch mouth, approximately 0.85 kilometers). The aerial extent of surface water contamination in the Kingston area is approximately 10 times greater than for McCoy Branch Embayment. If a more extensive investigation were conducted in the Kingston area, it is likely that arsenic concentrations similar to those observed in Rogers Quarry surface waters would also be found for the Kingston contamination source.

Detection limits that were a factor of 20 below the minimum risk screening criteria were achieved for 100% of arsenic speciation data. However, 118 samples for inductively coupled plasma metals analysis were not preserved to analytical specifications, and the analytical holding times for 180 ion chromatography samples were not met. More rigorous preservative testing protocols and more tightly defined analytical statements of work will prevent these problems in the future.

Introduction, background, materials and methods, results, discussion, and conclusions are presented in

Volume 1. The Quality Assurance/Quality Control Summary Report; the listing of water quality and surface water arsenic speciation data by source and site; and the listing of pore water arsenic speciation and particle-to- water distribution coefficients for arsenic, iron, and manganese by source, site, and season are presented in Volume 2.

The Clinch River Environmental Restoration Program is currently completing its second phase of the Clinch River Remedial Investigation, with the intent of performing a baseline risk assessment on the collected data. The data collected for this report will contribute to the baseline risk assessment. Many of the goals of the Clinch River Remedial Investigation were refined using the results of this study.
