## ARSENIC CONCENTRATIONS IN FISH COLLECTED AS PART OF THE BIOMONITORING OF ENVIRONMENTAL STATUS AND TRENDS PROGRAM'S LARGE RIVER MONITORING NETWORK. **G.M. Dethloff**<sup>1</sup>, C.J. Schmitt<sup>2</sup>, and T.M. Bartish<sup>3</sup>.

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The Biomonitoring of Environmental Status and Trends (BEST) Program identifies, monitors and assesses the effects of contaminants on the Nation's biological resources. The goals of BEST are to: measure and assess the effects of contaminants on selected species and habitats throughout the Nation; conduct synthesis activities and research directed at providing new biomonitoring methods for operational applications; and deliver effective and efficient tools to DOI Bureaus for assessing contaminant threats to species and lands under their stewardship. The BEST Program uses measures of both chemical concentration and biological responses to evaluate the effects of environmental contaminants on biota and habitats. Biological responses are evaluated by measuring biochemical, physiological, morphological, and histopathological endpoints in organisms.

One aspect of BEST is to monitor contaminants and their effects in fish from large rivers of the Nation. This network builds on experiences from the National Contaminant Biomonitoring Program (NCBP), which measured contaminant concentrations in fish from over 100 locations nationwide during the period 1967-1986. The objectives of this network are to: identify the types of biological effects of contaminants and their distribution; provide comparative, benchmark data for biomarker response variables; determine temporal trends in organism-level responses, tissue concentrations, and fish health parameters; and provide support for more intensive research and investigation efforts. BEST is monitoring large rivers because they are conduits and receptors of chemical contaminants, are important biologically, and are relevant to DOI information needs. Rivers often reflect the land use occurring in the watershed and are a significant regional transport mechanism for contaminants. Large rivers support backwater, wetland, and riparian habitats and the organisms associated with those habitats; provide migration corridors for waterbirds, shorebirds, raptors, songbirds, and migrating anadromous fishes such as salmon and striped bass; and provide spawning and nursery areas for some anadromous and federally-listed species.

In 1995 and 1997, BEST collected fish from 72 sites in the Mississippi River (Figure 1), Columbia River (Figure 2), and Rio Grande (Figure 3) basins for analysis of organochlorine compounds, elemental contaminants, and a suite of biological effect measures. The sampling was conducted at historic NCBP sites to assess trends in contaminant concentrations in tissues from those sites. Sampling was also conducted at National Water Quality Assessment (NAWQA) sites in the Eastern Iowa Basins and Mississippi Embayment study units, and at National Stream Quality Accounting Network (NASQAN) sites in the Columbia and Rio Grande basins. The NAWQA sites were sampled to compare large river results (as indicated by the NCBP sites) with those from lower order streams. NASQAN sites were sampled to evaluate water column data on contaminants with the biological effects data of BEST. Fish species targeted for collection were common carp (*Cyprinus carpio*) and largemouth bass (*Micropterus salmoides*), and, in the Columbia River basin, largescale sucker (*Catostomus macrocheilus*). At some locations, alternative species were collected when the target species were not present. Fish

were composited for tissue analysis, with composites comprised of 10 individuals and separated by species and sex. Results are presented for arsenic concentrations. The presence of arsenic in the environment can be linked to releases from industrial sources and the use of pesticides and defoliants that include this element.

Overall, stations sampled in the 1995 and 1997 did not have high As concentrations. With two exceptions (both in the Columbia River), geometric station means did not exceed 0.25 µg/g. The maximum single sample (composite) concentration recorded was 0.56 µg/g. All three basins had a similar maximum value ( $0.52-0.56 \mu g/g$ ). In the Arkansas-Red River sub-basin, the Ohio River sub-basin, and the Lower Mississippi sub-basin of the Mississippi River basin, all stations or all stations but one had one or more composites with detectable As. Composites with no detectable As were collected at all 12 NAWQA sites (primarily carp). Relatively high individual concentrations were found at stations in the Arkansas-Red River and Lower Mississippi subbasins. While no area in the Rio Grande basin appeared to be more heavily contaminated than any other, it is notable that all stations had at least one composite with detectable As. There also did not appear to be a geographic trend in contamination in the Columbia River basin. As for temporal comparisons to concentrations in the historic NCBP database, there was some indication that As concentrations were slightly greater in 1995 and 1997 when compared to samples from the 1980s. Some of this may be the result of different species with different accumulation patterns being collected in different sampling periods. However, in cases where the same species were collected at a site, increases were often noted.

In the 1995 collection in the Mississippi River basin, As was detected (detection limits = 0.12-0.3  $\mu$ g/g) in 46 composites (28% of the total composites collected) at 22 of the 46 stations sampled. It was not detected at the reference site (Station 400). Relatively high concentrations (0.30-0.52  $\mu$ g/g) were found at Stations 78, 79, 29, 15, 80, 26, 76, and 75 (Lower Mississippi and Arkansas-Red River sub-basins). One of these composites was a carp composite, two were white bass (*Morone chrysops*) composites, and the remaining eight were largemouth bass composites. Geometric mean As concentrations did not exceed 0.24  $\mu$ g/g at any station. Historically, As accumulation has not been great at stations in the Mississippi basin with the exception of Station 69. However, Station 69 was not sampled in 1995. Relative to 1986 (the final NCBP collection), geometric mean concentrations of As were slightly higher in 1995. Decreases of note (0.05-0.1  $\mu$ g/g) occurred at Stations 32 and 70. In comparisons within taxa at stations sampled in 1986 and 1995, As concentrations decreased in carp and largemouth bass at Station 70, increased in brown trout (*Salmo trutta*) at Station 84, increased in goldeye (*Hiodon alosoides*) at Station 85, and increased in white sucker (*Catostomus commersoni*) at Station 74.

In the Columbia River sampling of 1997, 16 composites (25% of the total composites collected) from nine of 16 stations contained detectable As concentrations (detection limits = 0.05-0.3  $\mu$ g/g). The range of detected As concentrations was 0.14-0.56  $\mu$ g/g. The highest concentrations (> 0.5  $\mu$ g/g) were measured in composites of male carp, male largescale sucker, and female largemouth bass from Stations 96, 504, and 505, respectively. In the basin, carp had a slightly higher geometric mean than *Micropterus* species, largescale sucker, northern pikeminnow (*Ptychocheilus oregonensis*) and rainbow trout (*Oncorhynchus mykiss*); these other species had very similar geometric means. Geometric mean As concentrations exceeded 0.25  $\mu$ g/g only at Stations 502 (0.29  $\mu$ g/g) and 96 (0.37  $\mu$ g/g). In the historic NCBP database, no composite As concentrations for 1980-86 exceeded 0.5  $\mu$ g/g. Concentrations greater than 0.2 were only detected at Stations 44, 46, and 98. In 1997, Station 96 had consistently higher composite

concentrations than in previous collections. However, species collected in 1997 did not match those collected previously. Species matches at stations in the final NCBP collection (1986) and in 1997 only occurred at Stations 43 and 117. Largescale sucker from Station 117 had similar As concentrations for the two collections whereas large scale sucker and smallmouth bass (*Micropterus dolomieui*) from Station 43 had higher As concentrations in 1997.

As concentrations exceeded detection limits (0.04-0.15  $\mu g/g$ ) in 38 composites (80.9% of the total composites collected) from all ten stations sampled in the Rio Grande basin in 1997. The range of detected As concentrations was 0.04-0.55 µg/g. The highest concentrations (0.3-0.55  $\mu g/g$ ) occurred in composites from Stations 65, 512, and 514; three composites were of carp whereas the other two were of largemouth bass and white bass. The species geometric mean for carp equaled that of channel catfish (Ictalurus punctatus) and was similar to that of white bass and Micropterus species. Arsenic concentrations in all northern pike (Esox lucius) composites were below detection limits. Geometric mean As concentrations at all stations were  $\leq 0.24 \,\mu g/g$ . In NCBP collections from 1980-86, As concentrations in all carp and largemouth bass composites at Stations 16, 63, and 65 were  $\leq 0.27 \ \mu g/g$ . Concentrations at Station 64 were <0.10 but only brown trout and white suckers were collected. White bass and whiper (Morone spp.) from Station 65 contained As concentrations between 0.3 and 0.6  $\mu$ g/g. These concentrations did not differ greatly from those measured in 1997. Historically, concentrations were elevated (>  $0.3 \mu g/g$ ) in gizzard shad (*Dorosoma cepedianum*) from Stations 16, 63, and 65, but this species was not targeted in 1997. Concentrations of As increased from 1986 to 1997 in the few species/stations that matched. Concentrations increased in largemouth bass at Station 16 and carp at Stations 63 and 65.

The detected concentrations of As in freshwater fishes collected in 1995 and 1997 (0.04-0.56  $\mu g/g$ ) are not considered a hazard to the fish or to piscivorous fishes or wildlife.







Figure 2.



Figure 3.