

ARSENIC CONCENTRATIONS IN U.S. FRESHWATER FISH, 1976-1986: NATIONAL CONTAMINANT BIOMONITORING PROGRAM

T. W. May¹, C.J. Schmitt¹, W.G. Brumbaugh¹, and J.D. Petty¹

¹U.S. Geological Survey, Biological Sciences Division, Columbia Environmental Research Center, 4200 New Haven Road, Columbia, MO 65201

History of the NCBP:

The National Contaminant Biomonitoring Program (NCBP) was maintained for two decades by the U.S. Fish and Wildlife Service to document temporal and geographic trends in concentrations of selected environmental contaminants that may threaten the nation's fish and wildlife resources. The NCBP was initiated in 1967 and consisted of periodic collections of freshwater fish, European starlings, and duck wings, with these samples being analyzed for persistent environmental contaminants. Program goals included providing a database of wholebody fish residues for select organic and inorganic contaminants, and providing information on the success of legislative and regulatory actions intended to reduce environmental concentrations of bioaccumulative toxins as well as effects from changing agricultural practices. The program was successful in achieving these goals, as it demonstrated that by the mid-1980's, regulatory and other actions had successfully reduced the flux of persistent contaminants to the North American environment, with examples being organochlorine pesticides and PCBs. In addition, some inorganics, such as Pb and Hg, exhibited concentration levels in fish lower than at any previous period for which there were reliable data. Thus, there developed a period in which persistent contaminants were declining, but the use of other chemicals, especially those that do not accumulate in biota, were increasing. Increasing reports of fish and avian wildlife kills associated with the use of non-accumulating soft pesticides (organophosphates, carbamates, and pyrethroids) were raising public concerns. In addition, the increasing distribution of herbicides in surface and groundwater of agricultural areas aroused concern about the toxicity of these compounds. Thus, since the NCBP only monitored bioaccumulative contaminants, the program came to be viewed by the U.S. Fish and Wildlife Service as one that could no longer meet its contaminant needs. So, NCBP fish collections were suspended and a new program, called Biomonitoring of Environmental Status and Trends, of BEST, was implemented in place of the NCBP.

NCBP Sample Collection, Preparation, and Analysis:

The NCBP had approximately 100 sampling stations located at key points in major rivers throughout the United States and Great Lakes. The stations were located along the major coastal streams and rivers including the Atlantic coastal streams, Gulf coast streams, Great Lakes and Hudson Bay drainage, Mississippi River system, Colorado River system, Columbia River system, Pacific coast streams, and Alaskan and Hawaiian streams. At each active station, collaborators were asked to collect three composite fish samples, each consisting of 3-5 whole adults of a single fish species, with two samples consisting of a representative bottom feeder, and the other a representative predator species. At the laboratory, samples were generally prepared by homogenization followed by lyophilization. The type of chemical preparation and instrumental analysis varied with the collection set. Chemical preparation included a HNO₃ block digester procedure for the 1976 fish collection, a HNO₃/HClO₄ micro-Kjeldahl procedure for the 1977 collection, a HNO₃/HClO₄/H₂SO₄ micro-Kjeldahl procedure for the 1978-1979

collection, and a dry ash procedure for the 1980-81 and 1986 collections. Instrumental analysis ranged from inductively coupled plasma optical emission spectroscopy for the 1976 collection set to hydride generation atomic absorption spectroscopy for all other collection sets.

Arsenic Geometric Means, 85th Percentiles, and Temporal Trends:

Elemental concentrations were expressed as geometric station means of the whole-body concentrations (ug/g wet weight). Nationally, geometric mean arsenic concentrations declined by more than 50% from 1976-1977 (0.199 ug/g) to 1986 (0.083 ug/g), with most of the decline being from 1976-1979 (0.199 ug/g to 0.129 ug/g). Among NCBP samples, arsenic concentrations have historically been greatest in bloaters and lake trout from Lake Michigan stations, but levels showed a marked decline from 1976-1977 (2.93 ug/g) to 1984 (1.50 ug/g). For Lake Michigan, the greatest single source of As was a facility in Marinette WI on the Menominee River, which empties into Green Bay. A plant which was a major manufacturer of arsenical herbicides methanearsonic acid and cacodylic acid was located on the banks of the river. Waste salt piles from the plant were placed adjacent to the river, and groundwater beneath these piles contained As in excess of 6000 ppm. River sediments in proximity of the piles were 2% As by weight. As a result, it was estimated that the Menominee River contributed between 30-50 tons of As per year to Lake Michigan.

To approximate “normal background” ranges for whole-fish As concentrations, station As means were arranged in order of increasing concentration, and the 85th percentile was arbitrarily used to distinguish stations with “high” arsenic values. While used to distinguish “high” from “normal” As concentrations, the 85th percentile had no meaning with respect to either potential hazards to fishery resources or regulatory statutes. There was no clear trend for arsenic in the 85th percentile concentration, which declined from 1976-1977 (0.38 ug/g) through 1980-1981 (0.22 ug/g), but increased in 1984 (0.27 ug/g) and then decreased slightly in 1986 (0.24 ug/g). Tests for temporal trends at individual stations indicated that arsenic concentrations declined significantly at 21 stations from 1976-1977 to 1986. Among these are stations at which concentrations have historically been the highest (i.e., mean concentrations exceeded the 85th percentile), including stations 102 and 103 (Lake Superior), 21, 104, and 105 (Lake Michigan), and 115 (Lower Colorado River). Over the much shorter time span of 1984-1986, increases in As were seen at four stations (16, 37, 100 and 105) and decreases at three stations (18, 104, 114). Some stations that exceeded the 85th percentile in 1986 have been historically high for As. Examples of this were Lake Superior (stations 22, 102, 103), Lake Michigan (stations 21, 104, 105), Colorado River (station 115), and the Rio Grande River (station 16). At all of these stations, planktivorous fishes are collected: bloaters at Lake Superior and Lake Michigan, striped mullet on the Colorado River, and gizzard shad on the Rio Grande. In addition, the predatory lake trout species found at Lake Superior and Lake Michigan stations feed primarily on alewife, another planktivorous species. Planktivorous taxa of fish tend to accumulate arsenic to a greater degree than other fishes, and the accumulated arsenic can be incorporated into piscivorous fishes that prey upon them. Thus, the occurrence of planktivorous taxa at some sites and the dynamics of the ecosystems in which they occur may confound the interpretation of temporal trends for arsenic.

References

- McKinney, G.L.; May, T.W. 1981. Cadmium, lead, mercury, arsenic, and selenium concentrations in freshwater fish, 1976-1977 – National Pesticide Monitoring Program. *Pesticides Monitoring Journal* 15(1): 14-38.
- Lowe, T.P.; May, T.W.; Brumbaugh, W.G.; Kane, D.A. 1985. National Contaminant Biomonitoring Program: Concentrations of seven elements in freshwater fish, 1978-1981. *Arch. Environ. Contam. Toxicol.* 14: 363-388.
- Schmitt, C.J.; Zajicek, J.L.; May, T.W.; Cowman, D.F. 1999. Organochlorine residues and elemental contaminants in U.S. Freshwater fish, 1976-1986: National Contaminant Biomonitoring Program. *Rev. Environ. Contam. Toxicol* 162:43-104.