CONCENTRATIONS OF ORGANIC COMPOUNDS IN BED SEDIMENT IN THE MISSISSIPPI EMBAYMENT STUDY UNIT

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INTRODUCTION

In 1991, the U. S. Geological Survey (USGS) began the National Water-Quality Assessment (NAWQA) Program to describe current water-quality conditions in a large part of the nation's streams, rivers, and aquifers. The purpose of the NAWQA Program is to characterize current water-quality conditions, to observe any changes in water-quality over time, and to improve the understanding of natural and anthropogenic factors that influence water-quality. The study incorporates more than 50 of the nation's largest river basins and aquifer systems; one of these basins is the Mississippi Embayment (MISE) Study Unit.

In 1995, as a part of the MISE Study Unit evaluation, the USGS collected bed sediment from 15 sites that represented a variety of land use and streams throughout the study unit (fig.1). More than 85 percent (median value) of the land in the MISE study unit is used for agriculture and includes row crops, grain crops, pasture/hay, and other grasses. The remaining land is used for forestry, wetlands, or open water.

The sampling of bed sediment is important because the chemistry of bed sediment can provide insight about the environment surrounding a stream. In addition, it is important to understand how the concentrations of potential toxins attached to sediment could be available to biotic communities and how they could cause environmental effects. The concentrations for 32 organic compounds were analyzed in this study. This paper focuses on the compounds present in concentrations above the reporting limit that also have applicable guidelines.

DATA COLLECTION AND ANALYSIS

At each of the 15 sampling sites, 10 wet depositional zones likely to have recently deposited fine-grained sediments were sampled along a 500-m reach of stream. The 10 zones were chosen to represent a variety of depositional areas including left and right bank and center channel as well as varying water depths. In wadeable streams, sediment was collected in the depositional area by using a Teflon spatula. In non-wadeable streams, bottom samples were collected from a bridge or boat by lowering a mechanical sampler, called a Young grab, to the streambed by a rope. Only the fine surface material scraped from the top 1-cm of sample was used. At each site, a sediment sample from the 10 zones within the reach was composited. Then an aliquot of the sample was filtered through a 2.0-mm stainless-steel sieve into a 1,000-mL glass jar, which had been previously rinsed with methanol. allowed to air dry, and wrapped in aluminum foil. The sample was worked through the sieve with the aid of a Teflon spatula without the use of any water (Shelton and Capel 1994).

After collection, samples were then prepared for shipping to the USGS National Water Quality Laboratory for analysis. The samples were placed in protective sleeves, packed in ice, and shipped by overnight carrier no more than three days after collection (Shelton and Capel 1994). The sediment samples were then dried, and a subsample was Soxhlet-extracted with dichloromethane, cleaned up by gel permeation chromatography, solvent-exchanged to hexane, fractionated using alumina/silica adsorption chromatography, and analyzed by gas chromatography with electron capture detection. Surrogates of known concentrations were added to the samples to determine the effectiveness of the extraction analysis. These surrogates consisted of compounds with structures similar to target analytes but that were not expected to be present in the sampling environments. Extracted concentrations can be compared with the known initial concentrations to determine the accuracy of analysis and monitor for errors in the procedure (Foreman et al. 1995).

GUIDELINES AND STANDARDS

The concentrations of organic compounds found in bed sediment were compared to available guidelines and standards including the Canadian Sediment Quality Guidelines (SQG) and the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends (NS&T). By comparing concentrations to available national trends, the impact of certain concentrations can be more clearly understood and interpreted.

The Canadian SQG's recommend a minimum effect level called an interim sediment quality guideline (ISQG) and a value suggesting a probable effect level (PEL). These guidelines are derived by using compiled chemical and biological data to create sets of effects and no-effects data in which a lower level effects guideline (ISQG) and a higher level effects guideline (PEL) are determined (Canadian Council of Ministers of the Environment 1999). Nowell et al. (1999) describe the Canadian ISQG and PEL as being equivalent with the Florida Threshold Effect Level (TEL) and Florida PEL, respectively. The TEL represents the geometric mean of the concentrations from the lower 15th percentile of the effects data and 50th percentile from the no-effects data, which are the concentrations in which toxic effects were rarely seen. The PEL represents the geometric mean of the concentrations from the 50th percentile of the effects data and 85th percentile of the no-effects data, which are the concentrations in which toxic effects were frequently seen (Nowell et al. 1999).

The NOAA NS&T ERL (effects range low) and ERM (effects range mediam) are derived through compiled studies of contaminants with varying concentrations along with their subsequent biological effects. The ERL represents the concentrations in the lower 10th percentile of available effects data in which adverse effects are first detected. The ERM represents the concentrations in the median of available effects data in which concentrations are at or above the point when adverse effects are first detected (Nowell et al. 1999).

RESULTS AND DISCUSSION

Bed sediments were analyzed for over one hundred constituents including organic compounds, semi-volatile compounds, and trace elements. In this report, the focus is on organic compounds. Bed sediments are important sampling agents especially when testing for many of the organic compounds used as pesticides. The chemical properties of organochlorine compounds cause them to be resistant to degradation and to be hydrophobic. Therefore, they concentrate in bed sediment, and when digested by aquatic biota these compounds bioaccumulate. Bed sediments can subsequently be used to determine the presence of organochlorine compounds more effectively than testing the water column alone (Nowell et al. 1999).

The 32 organic compounds that were analyzed for measurable concentrations, along with their laboratory reporting limits, maximum and median concentrations, and the percentage of sites at which they were detected are listed in table 1. Only nine of the 32 compounds were detected in samples from at least one of the sites. Of those nine compounds, four had available guidelines with which to compare concentrations: *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT, and dieldrin. The remaining detected compounds that did not have available guidelines were as follows: hexachlorobenzene, mirex, *o,p'*-DDD, *o,p'*-DDE, and *o,p'*-DDT. Dieldrin concentrations did not exceed guidelines.

The only detected compounds with available guidelines found at concentrations which exceeded the laboratory reporting limits were *p,p'*-DDT and its metabolites (fig. 2). Therefore, the remaining focus of this report will be on *p,p'*-DDT and its metabolites. DDT was used as an insecticide from 1939 until it was banned in 1972. DDT is a hydrophobic organochlorine compound that has low water solubilities, strong tendencies to sorb to soil and to bioaccumulate, and long soil half-lives. It breaks down into two metabolites, DDD and DDE. both with low solubility and long half-lives. DDT has a half-life of 15 years, and DDD and DDE each have a half-life of 15.5 years. As a result, DDT and its metabolites have the potential to stay in the environment for decades. Since DDT and its metabolites have such longevity in the environment, bioaccumulation is a continual problem (Nowell et al. 1999).

Seven sites had concentratons of at least one of either DDT or its metabolites exceed the Canadian ISQG and PEL, and the NOAA NS&T ERL and ERM. These seven sites are: Tensas River at Tendal, LA; Yazoo River below Steele Bayou near Long Lake, MS; Bayou Macon near Delhi, LA; Steele Bayou East Prong near Rolling Fork, MS; Big Sunflower River near Anguilla. MS; Bogue Phalia near Leland, MS; and Cassidy Bayou at Webb, MS. These sites are located in a grouping near the junction of the Louisiana, Arkansas, and Mississippi borders (fig. 1).

The U.S. Environmental Protection Agency (USEPA) has classified this area as one of the Areas of Probable Concern (APC) for Sediment Contamination (USEPA 1997a). This area is considered an APC because it is "a watershed that contains 10 or more Tier 1 sampling stations" (USEPA 1997b)," where a site is considered "Tier 1" if *p,p'*-DDD, *p,p'*-DDE, and *p,p'*-DDT are present in amounts greater than or equal to 8.51,15, and 7 parts per billion (ppb), respectively (Nowell et al. 1999). Also, "at least 75 percent of all sampling stations [in the area] have been classified as Tier 1 or Tier 2 (USEPA 1997b).

Other studies have shown similar results. The USGS and the USEPA began a study called the Pesticide Monitoring Network in 1975 to examine the use and concentration of pesticides in the environment. Results of the data collected between 1972 and 1982 indicated "the highest median concentrations of total DDT in bed sediment. . . were observed at sites along the lower Mississippi River" and that the elevated concentrations "observed at sites in the Delta States and Southeast regions are consistent with the high agricultural use of DDT plus DDD in these regions" (Nowell et al. 1999). A USEPA study further supports the idea of agricultural sources by indicating the "agricultural land use was correlated with the extent of sediment contamination with organochlorine pesticides in APC watersheds, especially in those with more than 75 percent of land area devoted to crop production" (USEPA 1997a)."

The historic use of DDT in the MISE Study Unit along with the persistence and bioaccumulation of DDT causes it to be a predominant contaminant in sediments. It appears that concentrations of DDT and its metabolites generally increase with a southward trend in the alluvial plain region of the MISE area (figs. 2, 3). One hypothesis for this trend is that the lower Yazoo basin serves as a sump in which sediments are deposited, given time to settle out and therefore, increase concentrations of the compounds. A second hypothesis is that the geology of the area causes a higher clay concentration to exist in this region than elsewhere. Higher clay concentrations, due to recent alluvial deposition, cause organic compounds such as *p,p'*-DDT and its metabolites to sorb more readily because of a strong attraction between the compounds and the clay minerals.

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Table 1. Organic compound target analyte median and maximum concentrations compared to laboratory reporting limits along with the percentage of sites concentrations were detected at the reporting limits [Concentrations, in parts per billion]

Organic Compound	Reporting Limit	Maximum	Median	Percent Detects
Aldrin	1	-------	-------	0
Chloroneb	5	-------	-------	0
Dacthal	5	-------	-------	0
*Dieldrin	1	2	<1	6
*Endrin	2	-------	-------	0
Heptachlor	1	-------	-------	0
*Heptachlor epoxide	1	-------	-------	0
Hexachlorobenzene	1	11	<1	6
Isodrin	1	-------	-------	0
*Lindane	1	-------	-------	0
Mirex	1	2	<1	6
Oxychlordane	1	-------	-------	0
Pentachloroanisole	1	-------	-------	0
*Polychlorinated biphenyls	50	-------	-------	0
*Toxaphene	200	-------	-------	0
alpha-Endosulfan	1	-------	-------	0
alpha-HCH	1	-------	-------	0
beta-HCH	1	-------	-------	0
cis-Chlordane	1	-------	-------	0
cis-Nonachlor	1	-------	-------	0
cis-Permethrin	5	-------	-------	0
o,p'-DDD	1	10	<1	46
o,p'-DDE	1	3	<1	13
o,p'-DDT	2	18	<2	40
o,p'-Methoxychlor	5	-------	-------	0
*p,p'-DDD	1	52	2	60
*p,p'-DDE	1	99	4	73
*p,p'-DDT	2	18	<2	46
p,p'-Methoxychlor	5	-------	-------	0
trans-Chlordane	1	-------	-------	0
trans-Nonachlor	1	-------	-------	0
trans-Permethrin	5	-------	-------	0

* These compounds have available guidelines

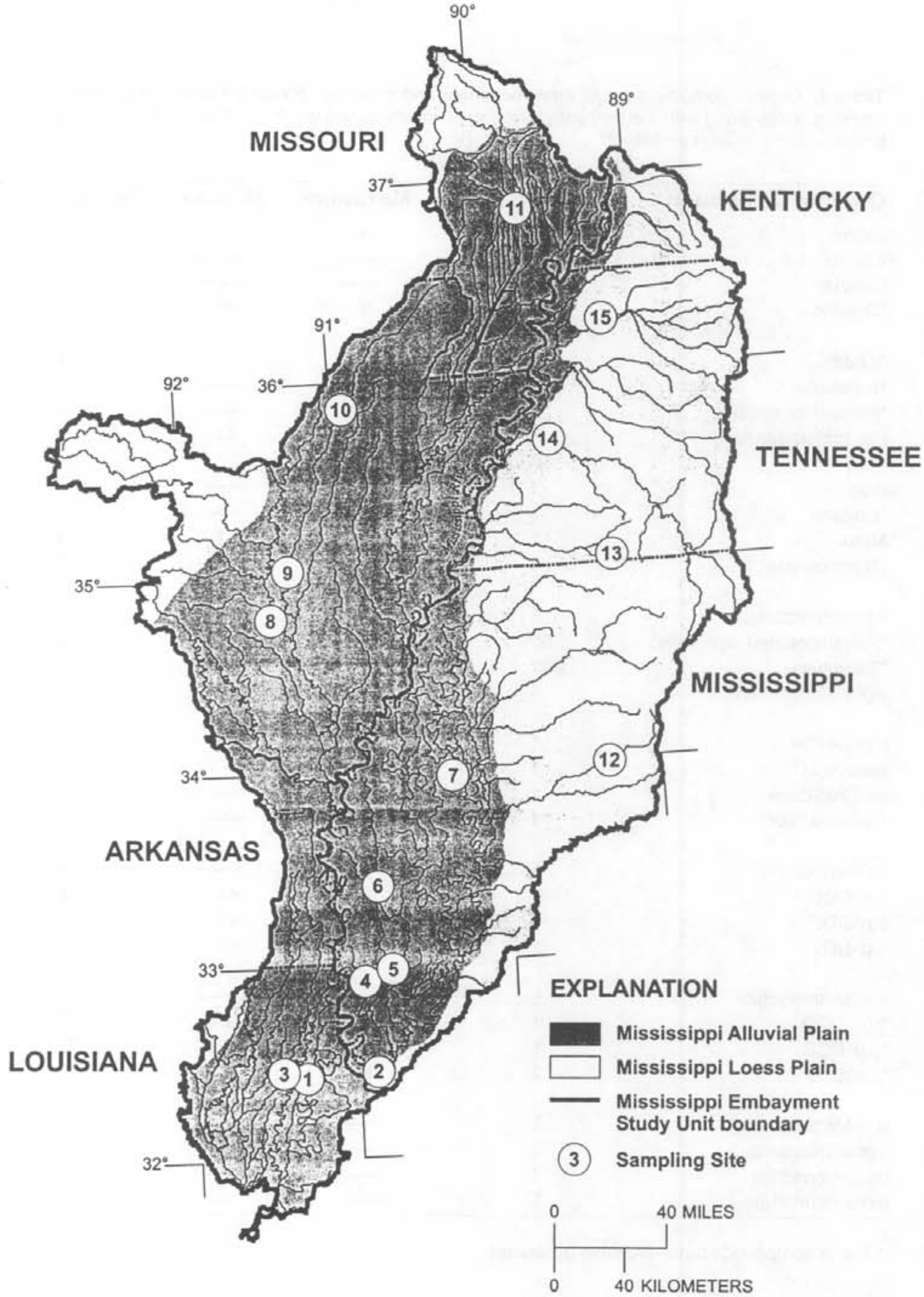

Figure 1. MISE Sudy Unit divided into the alluvial plain and loess plain.

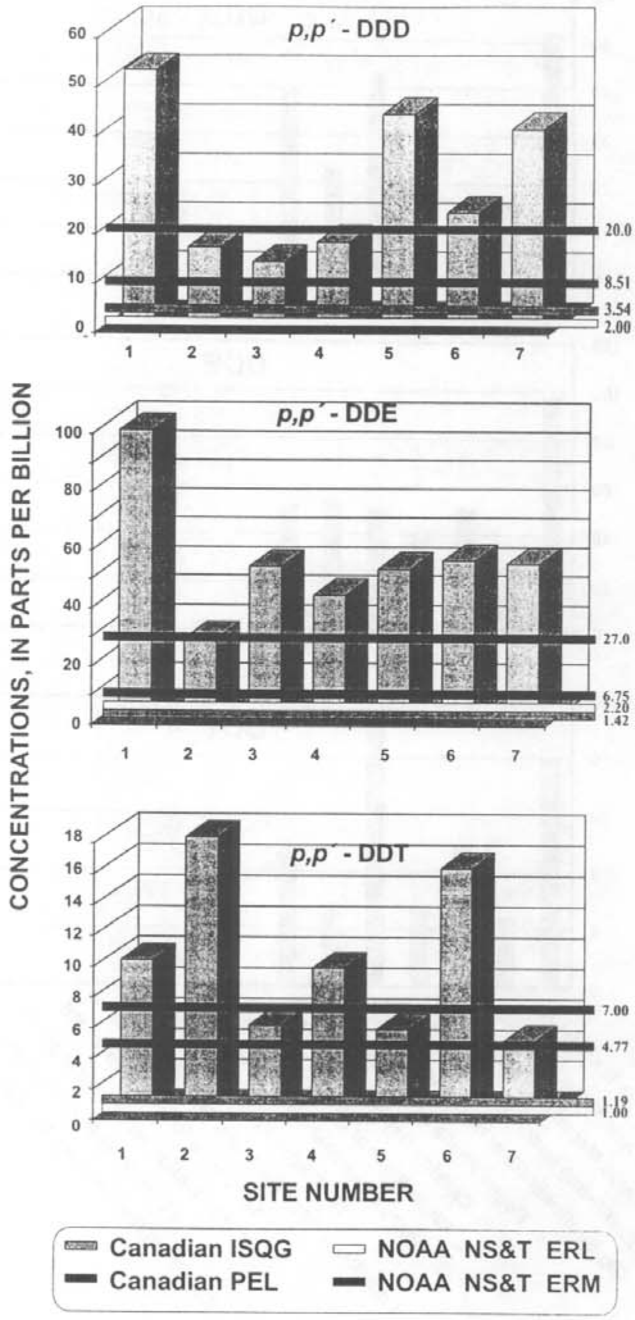

Figure 2. Concentrations of DDD, DDE, and DDT in bed sediment compared to various guidelines.
[For site locations, see figures 2 and 3]

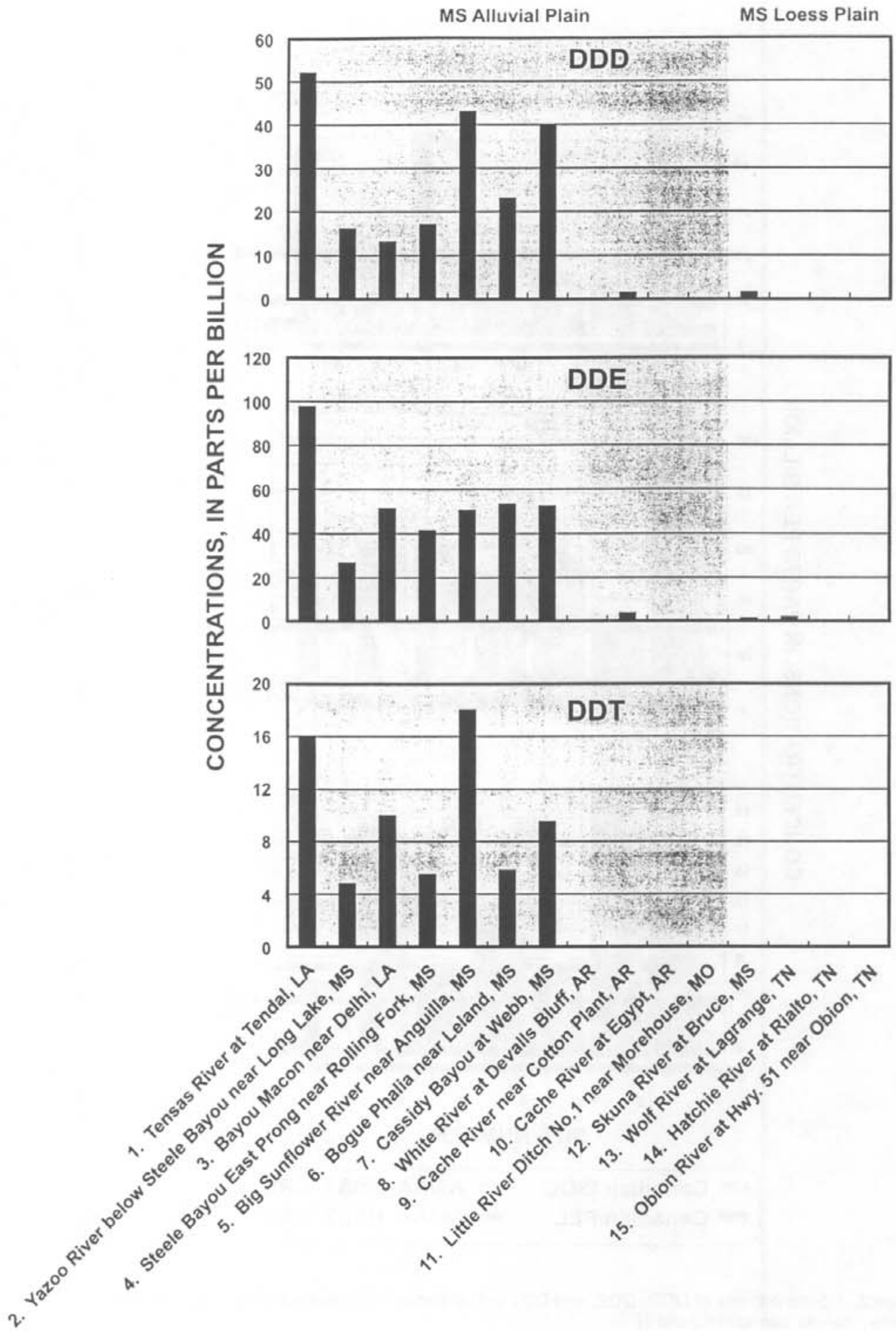

Figure 3. Concentrations of *p,p'*- DDT and metabolites in the Mississippi alluvial plain and loess plain.