

Chapter 6. Sediment Chemistry Analyses

6.1. Introduction

Sediment chemistry is closely linked to the water quality of the overlying water body. Many water-borne pollutant and nutrient species are predominately associated with particulate matter that can settle and become sediment. Fine-grained silt or clay sediments have the potential to sorb or otherwise sequester greater quantities of pollutant species than sand-sized sediments because of their higher surface area. Because fine-grained sediments tend to accumulate behind dams, dam removal options must consider the quality of the exposed sediments. Moreover, dissolved oxygen (DO) is usually rapidly depleted (within millimeters or mm to a few centimeters or cm) below the sediment-water interface of fine-grained sediments resulting in significant sediment oxygen demand (SOD), which helps to depress DO concentrations in the overlying water column. The resulting anoxic conditions can also drive the development of steep chemical gradients for various pollutant and nutrient species with the result that sediment-water exchange can constitute a significant component of nutrient or pollutant budgets for a water body.

This chapter focuses on description and analysis of the sediment chemistry data compiled for the Fox River database (FoxDB). The major sediment chemistry data sources are described and summarized to identify significant spatial, temporal, and chemical data gaps.

6.2. Data Sources

There are four main sources of sediment chemistry data in the FoxDB. Data obtained from the U.S. Environmental Protection Agency (USEPA) Legacy STORET system originated from the routine or intensive monitoring programs of the Illinois EPA or IEPA (USEPA, 2003g). Data exist for 30 mainstem and 29 tributary stations over a total period of record from 1974 to 1996, although most stations were sampled on only one or two dates over this period. These data can be selected from the FoxDB by querying Project Code 21ILSED. Surficial sediments (~0-3 cm depth) were analyzed for a variety of inorganic and organic species, including Total Phosphorus (total P) and Total Kjeldahl Nitrogen (TKN). Since the early 1980s, sediment samples have been wet sieved to less than 63 microns (μm) prior to analysis. Short (1997) compared data for sieved and unsieved stream sediments from Illinois from IEPA data for 12 chemical parameters. Chemical Oxygen Demand (COD) was the only parameter for which mean sieved and unsieved concentrations were statistically different, and COD was dropped from analyses in 1991.

A pilot project of the U.S. Geological Survey (USGS) National Water Quality Assessment (NAQWA) Program was conducted in the upper Illinois River basin in 1987, and results have been summarized in several publications (Colman and Sanzolone 1991, 1992; Fitzpatrick et al., 1995, 1998). Data specific to the Illinois portion of the Fox River basin consist of 24 stations on the mainstem of the Fox River and 54 tributary stations. Surficial sediments (~0-3 cm depth) were collected in September and October 1987. These data can be selected by querying Project Code 2 in the FoxDB. Mainstem samples were wet sieved ($< 63 \mu\text{m}$) in the

field, while tributary samples were dry sieved in the laboratory. These streambed sediments were analyzed for 46 elements. A comparison between wet and dry sieving methods was conducted at 21 sites. Wet sieved concentrations were higher than dry sieved concentrations by up to 17 percent for most elements (Colman and Sanzolone, 1992).

In a recent USGS NAQWA investigation, sediment sampling was conducted at 46 sites in the Fox and Des Plaines River basins between 1999 and 2001 (Adolphson et. al., 2002). Surficial sediments were sampled at 14 tributary stations in the Illinois portion of the Fox River watershed in July 2000 and analyzed for 46 elements. Wet sieving (< 63 μm) was performed in the field prior to analysis. These data can be selected by querying Project Code 11 in the FoxDB.

Santucci and Gephard (2003) collected both surficial and cored sediments between August and September 2000. Samples from both above and below 12 mainstem dams (Algonquin to Dayton) were analyzed for an extensive suite of inorganic and organic constituents (80 total). These data can be selected by querying Project Code 12 in the FoxDB. Sediment samples apparently were not sieved prior to analysis, and the cored samples were homogenized and treated as a single composite sample. The geographical coverage of these four major sediment chemistry datasets is presented in Figure 6.1.

6.3. Sediment Quality Analyses

Despite the incompleteness of the current sediment chemistry dataset, comparing the four primary datasets against each other and with respect to location in the watershed (upstream to downstream, mainstem vs. tributaries) serves to establish similarities and differences among data sources and locations. A few such examples are provided below. The original reports and publications that present and discuss these data can be consulted for more information about individual datasets. It is possible to roughly assess the relative degree of sediment contamination in the basin with the data at hand by comparison to published sediment quality guidelines for certain contaminants. These guidelines are best viewed as screening criteria, most appropriately used to help establish if additional more detailed chemical or sediment toxicity studies are warranted. At present, there are no enforceable sediment concentration standards for streams in Illinois, or in any other state.

6.3.1. Total Phosphorus and Total Kjeldahl Nitrogen

Total phosphorus (P) and total Kjeldahl nitrogen (TKN) concentrations for mainstem Fox River sediments are presented as a function of decimal latitude (a surrogate for location along the river) in Figures 6.2 and 6.3. Three major data sources contain total P data, and two contain TKN data. A preliminary assessment of USEPA (2003g) data revealed no discernible differences in either total P or TKN concentrations from samples collected at the same site at different times. Hence, all sampling dates for this dataset are included in the figures. The lower and upper horizontal dotted lines in the figures refer to the “elevated” and “highly elevated” concentrations, respectively, for total P and TKN given in Short (1997). These concentrations are based on an

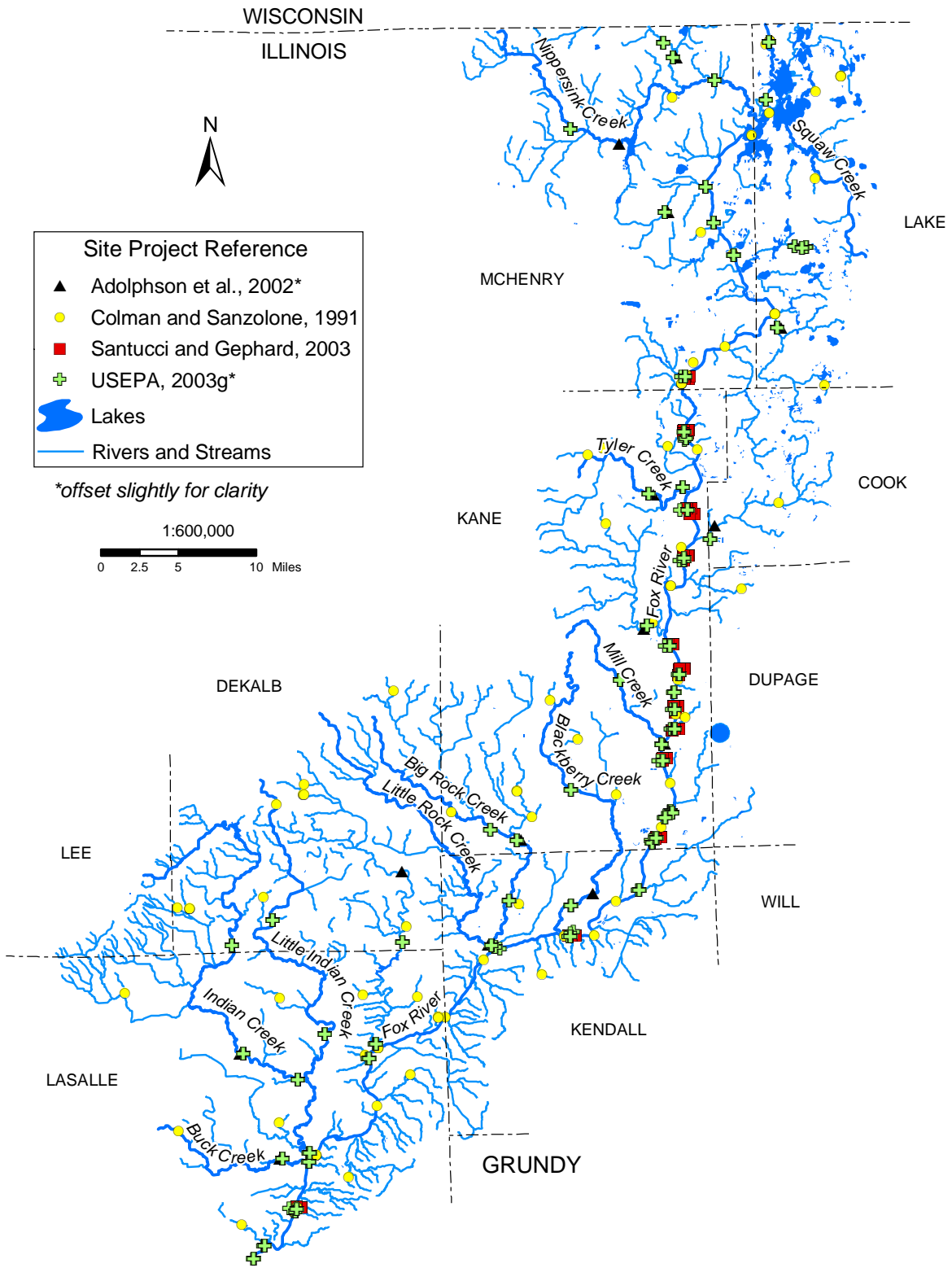


Figure 6.1. Fox River watershed major sediment chemistry datasets

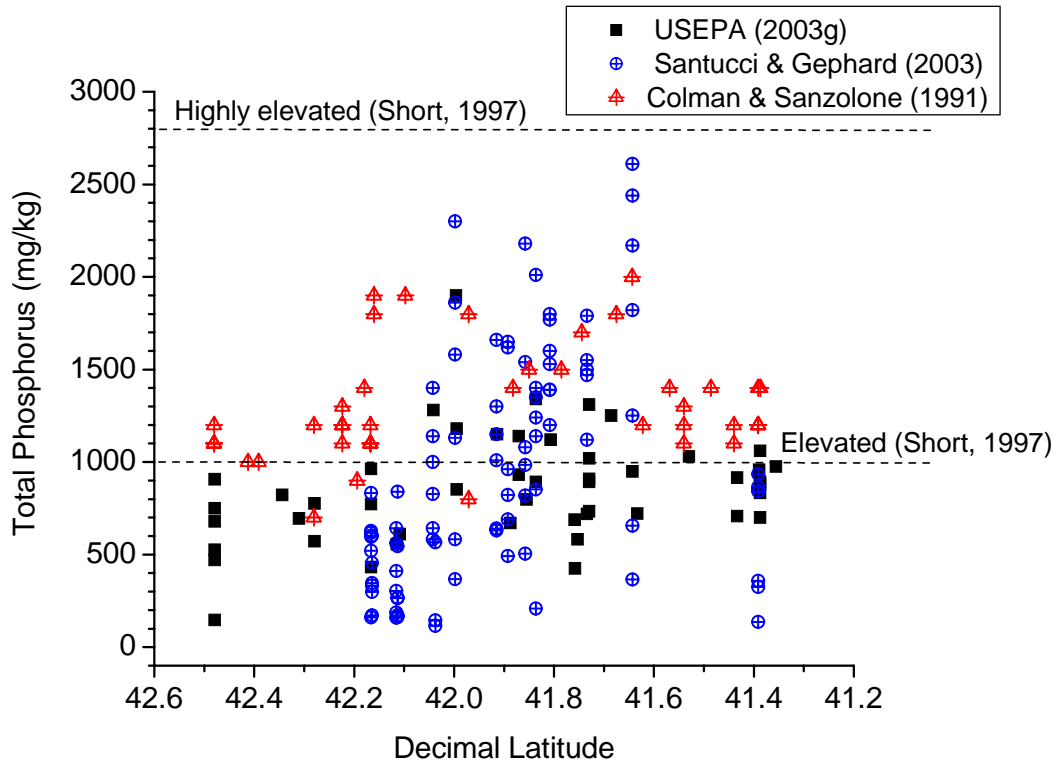


Figure 6.2. Fox River total P concentrations against decimal latitude

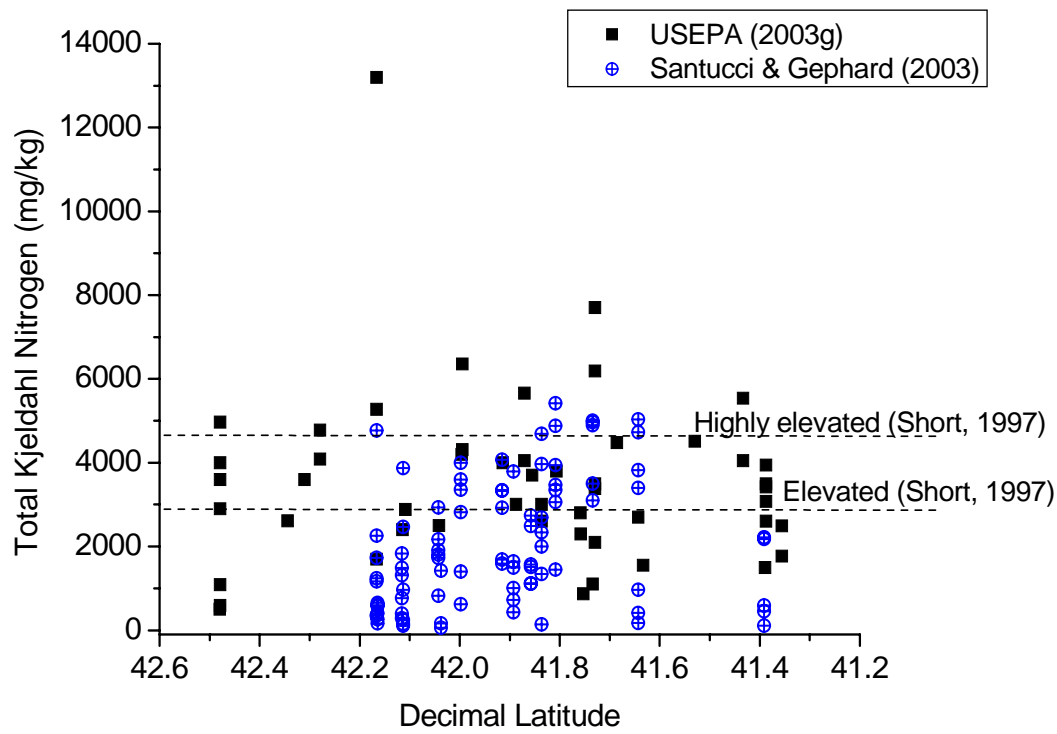


Figure 6.3. Fox River TKN concentrations against decimal latitude

analysis of sieved stream sediment data for Illinois between 1982 and 1995 from the Legacy STORET system. “Elevated” and “highly elevated” refer to those concentrations of a particular constituent that equal or exceed the 85th and 98th percentiles, respectively, (along the normal distribution curve) of the samples included in the analysis.

The figures reveal that neither total P nor TKN vary in any discernible way from upstream to downstream (north to south) along the Fox River. Moreover, no total P values exceed the “highly elevated” value of 2800 milligrams per kilogram (mg/kg) total P, while roughly 20 percent of the TKN concentrations exceed the “highly elevated” value of 4680 mg/kg TKN. This indicates that Fox River sediments are moderately enriched in total P and organic nitrogen, which agrees with the conclusions given by Santucci and Gephard (2003).

Figures 6.4 and 6.5, respectively, present statistical (“Box and Whisker”) plots of the total P and TKN data. Mean and median sediment total P concentrations in the Fox River mainstem are higher than concentrations in its tributaries. This difference is especially apparent in the Colman and Sanzalone (1991) dataset, although in this instance at least part of this difference could result from the fact that the Fox River samples were wet sieved while the tributary samples were dry sieved. For TKN, the USEPA (2003g) median Fox River concentration is somewhat higher than the pooled tributary concentration, but mean concentrations are more alike. However, Fox River mean and median TKN values from Santucci and Gephard (2003) are lower than even the USEPA (2003g) tributary values.

Figures 6.6 and 6.7 compare above dam and below dam total P and TKN concentrations from the Santucci and Gephard (2003) study. Mean and median concentrations for both total P and TKN were higher in above dam pools. This difference also was noted by Santucci and Gephard for many of the chemical constituents analyzed in their study, and is not too surprising. These pools contain a larger percentage of finer grained sediments that trap more pollutants than do stream reaches immediately downstream.

6.3.2. Total Mercury and Copper

Figure 6.8 presents total mercury (Hg) concentrations for Fox River sediments as a function of decimal latitude. These same data are summarized as “Box and Whisker” plots in Figure 6.9. The horizontal dotted lines on these figures refer to the “Probable Effect Concentration” (PEC) for Hg (lower line, 1.06 mg/kg) from MacDonald et al. (2000), and the “highly elevated” value (1.4 mg/kg) from Short (1997). Figure 6.10 compares total sediment Hg concentrations for above and below dam locations for each dam site in the Santucci and Gephard (2003) study. Figure 6.11 compares total Hg concentrations for Fox River sediments with those of tributary streams.

Total sediment Hg concentrations frequently exceed available sediment quality guidelines above six dams. However, exceeding these criteria does not directly imply that sensitive sediment-dwelling organisms are being adversely affected. The PEC values from MacDonald et al. (2000) are based on “weight of evidence” observations from carefully controlled (primarily laboratory) studies that assessed the toxicity of contaminants to certain aquatic species.

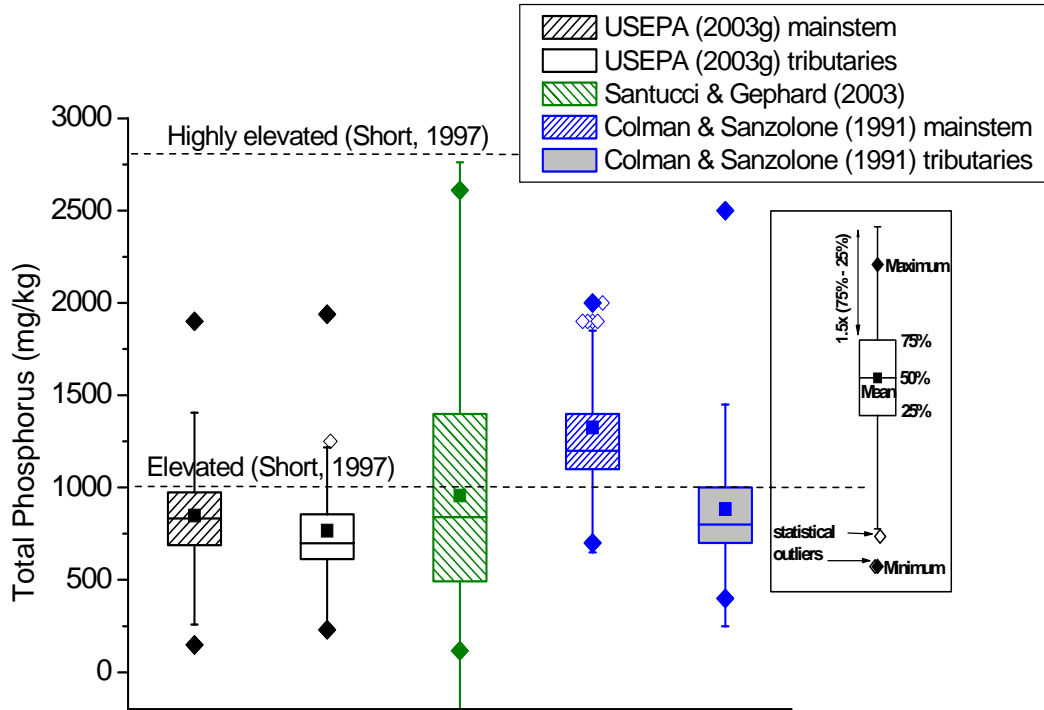


Figure 6.4. Box and whisker plot comparison of mainstem (hatched boxes) and tributary total P concentrations, with a partial key for the box plots in the inset

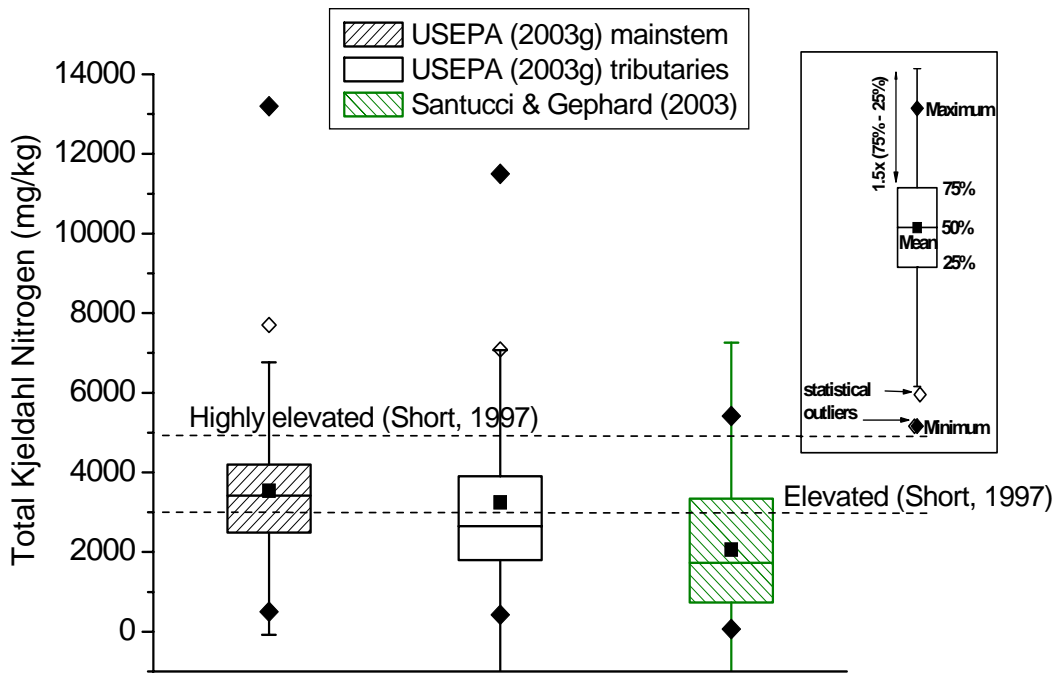


Figure 6.5. Box and whisker plot comparison of mainstem (hatched boxes) and tributary TKN concentrations

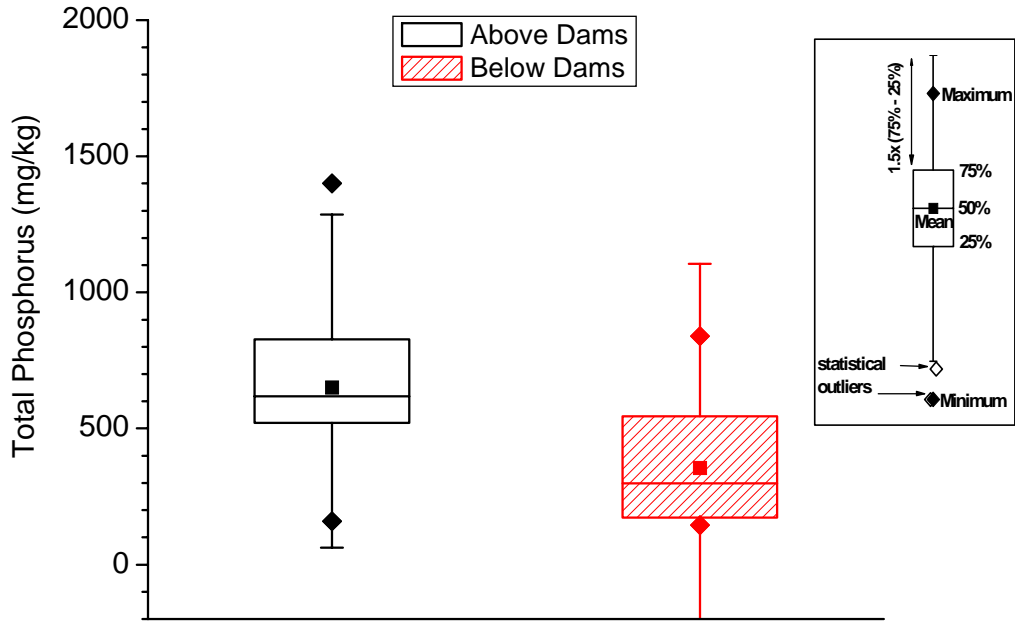


Figure 6.6. Box and whisker plot comparison of above and below dam total P concentrations from Santucci and Gephard (2003)

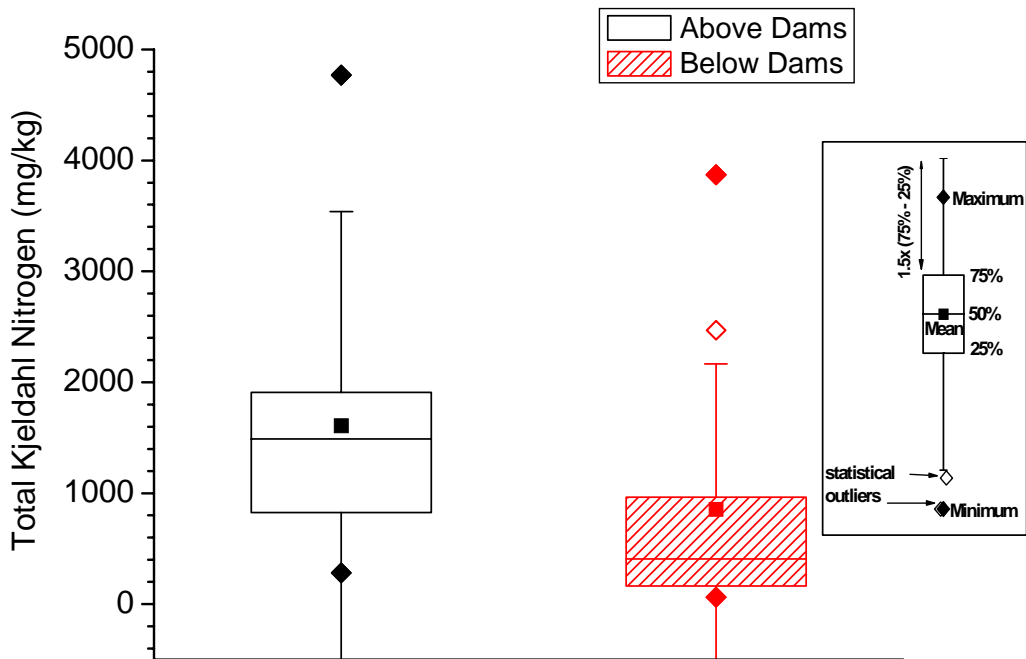


Figure 6.7. Box and whisker plot comparison of above and below dam TKN concentrations from Santucci and Gephard (2003)

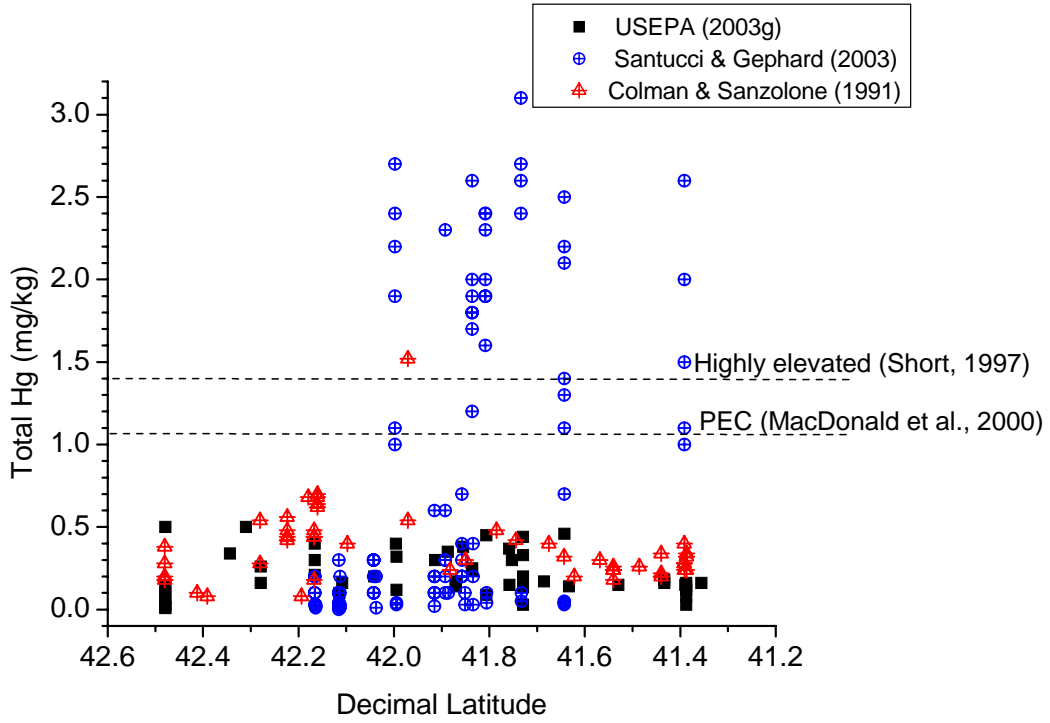


Figure 6.8. Fox River total Hg concentrations against decimal latitude

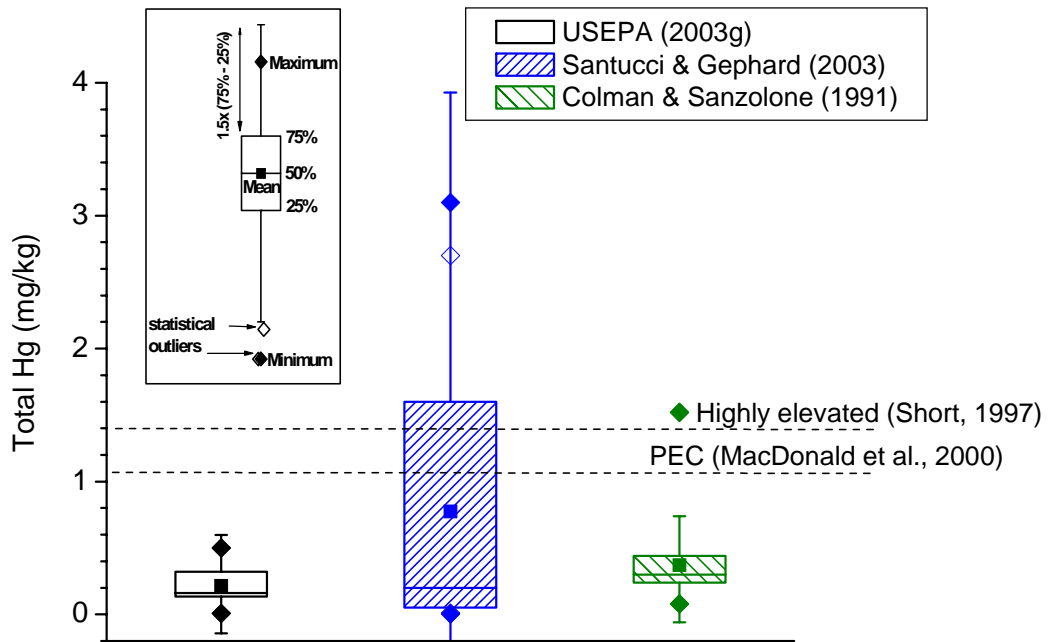


Figure 6.9. Box and whisker plot comparison of total Hg concentrations in Fox River sediments

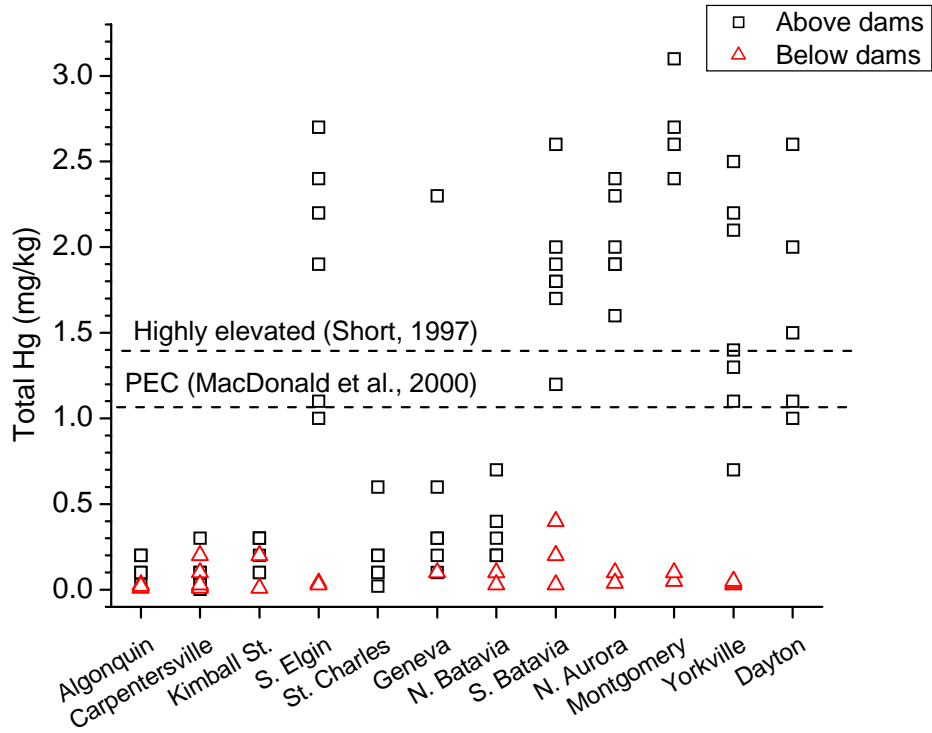


Figure 6.10. Comparison of above dam and below dam total Hg concentrations for the Fox River from Santucci and Gephard (2003)

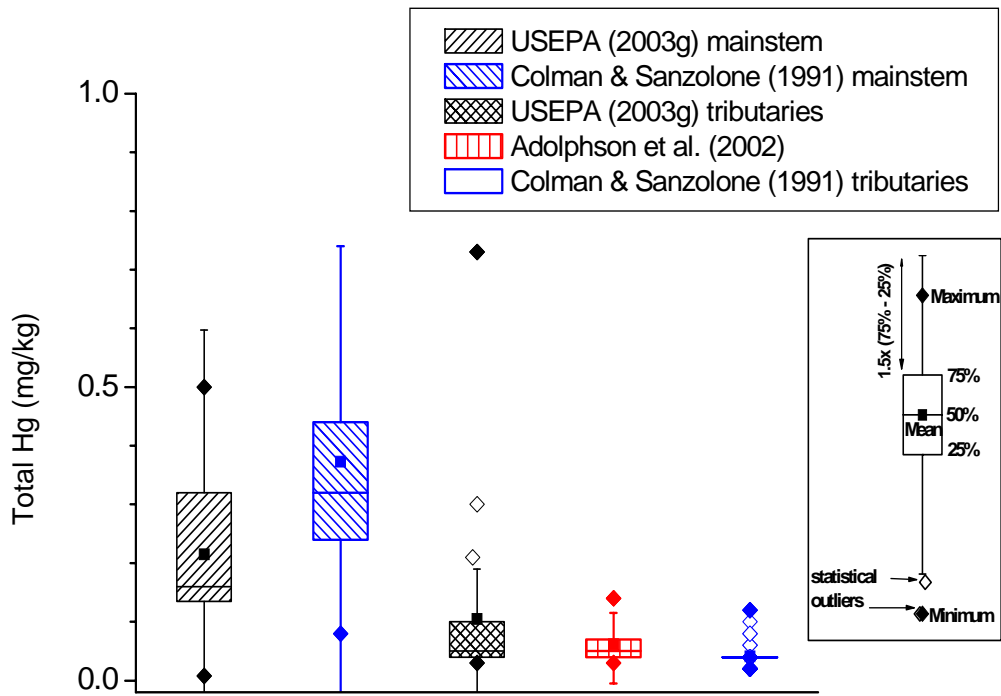


Figure 6.11. Box and whisker plot comparison of mainstem and tributary total Hg concentrations

Many other experts advocate that it is the specific form or bioavailability of a chemical contaminant that determines toxicity, rather than its total concentration. This is certainly the case for Hg where methyl mercury (MeHg) is known to be a particularly toxic and bioaccumulative form of Hg. The MeHg concentrations have apparently not been measured in Fox River sediments. A recent USGS study (Krabbenhoft et al., 1999) gives one value for Nippersink Creek sediments (0.08 nanograms per gram or ng/g), which is about 1 percent of the total Hg concentration (8.7 ng/g) measured at the same site. Of the contaminants measured for which sediment quality guidelines have been advanced, the total Hg concentrations found by Santucci and Gephard (2003) most often exceed these guidelines. This certainly merits further investigation. Given that no USEPA (2003g) and only one Colman and Sanzalone (1991) Fox River total Hg value exceeds 1 mg/kg, a logical first step would be to verify the Santucci and Gephard results by a check of the field and laboratory procedures.

Mean and median total Hg concentrations were considerably lower in sediments collected in Fox River tributaries (open boxes in Figure 6.11) than those in the Fox River itself (cross-hatched boxes). It is also worth noting that these tributary values are similar to the Nippersink Creek value (0.087 mg/kg) found by Krabbenhoft et al. (1999) with the benefit of state-of-the-art “ultra-clean” sampling and analysis techniques for Hg. These techniques, as fully described in Olsen and DeWild (1999), minimize potential contamination sources during the collection and analysis of environmental samples for Hg. Water column total Hg and MeHg concentrations at this Nippersink Creek location derived using these “ultra-clean” techniques were 1.42 ng/L, and 0.04 ng/L, respectively.

Sediment concentrations for total copper (Cu) are compared in Figure 6.12. In this instance only a very few Fox River samples exceed the MacDonald et al. (2000) PEC value for Cu (149 mg/kg), or the “highly elevated” Cu value (170 mg/kg) from Short (1997). Comparison of data from the same general sources (USEPA, 2003g; Colman and Sanzalone, 1991) shows that mean and median Cu concentrations are considerably lower in Fox River tributary sediments than in the mainstem. However, mainstem mean and median Cu concentrations from the Santucci and Gephard (2003) study are more comparable to the tributary concentrations. The concentrations of other potential metal contaminants in the database (e.g., zinc and cadmium) follow similar patterns. That is, sediment concentrations are higher in the Fox River than in its tributaries, with relatively few samples exceeding available sediment quality guidelines.

6.3.3. Organic Pollutants

Only USEPA (2003g) and the Santucci and Gephard (2003) study contain data for possible organic contaminants, and only USEPA (2003g) contains data for tributary sediments. An examination of the available USEPA data indicates that the vast majority of measured concentrations are near or below method detection limits. The Santucci and Gephard (2003) study analyzed for a much more extensive suite of potential organic contaminants in sediments. Some pesticide and polyaromatic hydrocarbon (PAH) compounds, particularly from above dam pools, exceeded the PEC values of MacDonald et al. (2000), but not as frequently as for Hg. The Santucci and Gephard dataset also includes sediment concentrations for several alkylphenol compounds, which are potential endocrine disruptors. Very little is known about the fate,

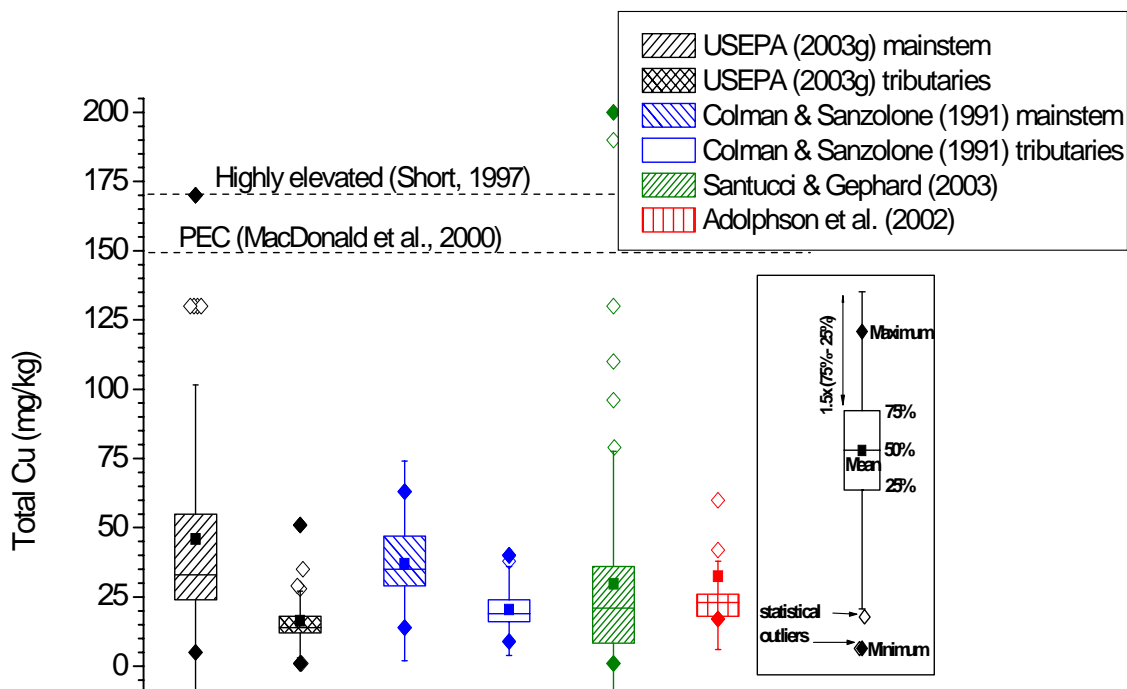


Figure 6.12. Box and whisker plot comparison of mainstem and tributary total Cu concentrations

transport, or toxicity of these and similar compounds in natural water bodies, although reconnaissance studies are beginning to appear (Kolpin et al., 2002).

6.4. Limitations and Data Gaps

Geographic coverage is quite extensive between these major datasets, especially along the Fox River itself (Figure 6.1). Temporal coverage, however, is very inadequate as only one major dataset (USEPA 2003g) contains data for stations sampled at more than one time. Moreover, even this data set is limited to one or two sampling dates for most stations. Cored, sectioned, and dated sediments could be used to help determine historical temporal trends in sediment and water quality, but such data appear to be lacking within the Fox River watershed. The Santucci and Gephard (2003) dataset is the only one that includes sediment core data, but the cores were homogenized and treated as a single sample. In any case, the lack of adequate temporal coverage diminishes the significance of the geographical coverage.

Other limitations of the sediment chemistry dataset concern the type of data currently available. As mentioned above, the current dataset contains no sectioned core data, and most data refer to surficial sediments. In addition, two of the four major datasets (Colman and Sanzalone, 1991; Adolphson et al., 2002) contain no data on possible organic contaminant concentrations. Because these datasets were exclusively (Adolphson et al., 2002) or predominately (Colman and Sanzalone, 1991) concerned with tributaries, available data for possible organic contaminants in tributary sediments are much less extensive than for Fox River sediments.

Another limitation is that available sediment chemistry data are of very limited utility for water quality modeling purposes. The SOD, which is driven primarily by the microbial respiration of organic matter at or near the sediment-water interface, contributes to DO depletion observed during the summer months in impounded reaches of the river. Butts and Evans (1978) measured SOD rates in the Fox River between 1.0 and 4.8 grams per square meter per day ($\text{g/m}^2/\text{day}$). These measurements should be updated and supplemented by complementary measurements for water quality modeling purposes. Complementary measurements could include pore water concentrations of important nutrient species to help assess the impact of bed sediments on nutrient budgets. In addition, potentially toxic species such as ammonia and hydrogen sulfide typically exist in much higher concentrations in anoxic sediment pore waters than in oxic overlying waters, and this can adversely affect sensitive sediment-dwelling organisms. No sediment pore water data were located for the Fox River or its tributaries for inclusion in the FoxDB.

6.5. Summary

The geographic coverage of the sediment chemistry data within the FoxDB is good, especially along the mainstem. Temporal coverage, however, is poor. Only the data collected by the IEPA and maintained by the USEPA in their STORET system contains data for sediments collected more than once at the same location. Even in this instance, temporal coverage is not complete enough to even attempt to discern temporal trends in sediment quality. With the available data, however, several general conclusions can be drawn. First, tributary sediment quality is generally better than that along the mainstem. This trend is more distinct for potential metal contaminants (e.g., Hg and Cu), and less distinct for total nutrient concentrations (total P and TKN). A similar trend probably holds for many potential organic contaminants, although only the USEPA (2003g) dataset contains organic contaminant data for tributaries. Fortunately, most analyses indicate concentrations near or below method detection limits.

Along the mainstem, the Santucci and Gephard (2003) data reveal higher concentrations of total nutrient, metal and organic contaminant concentrations in above dam pools than in stream reaches immediately downstream. Fortunately, even in above dam pools, most constituents are present at concentrations below available sediment quality guidelines in most samples. Total Hg concentrations appear to be an exception to this trend, with elevated Hg concentrations predominating in six above dam pools.

The available dataset is generally inadequate to aid water quality modeling efforts. For example, sediment-water exchange of nutrients could be significant under low-flow conditions in above dam pools and upstream in the Fox Chain of Lakes. Nutrient data for sediment pore waters would help to assess the significance of this component, but none are available. Other gaps in the available sediment chemistry dataset include:

- The lack of sufficient data to assess any temporal trends.
- No data from sectioned and preferably dated sediment cores.
- Relatively poor coverage of organic contaminant data for tributary sediments.