# Peer Review of Models Predicting the Fate and Export of PCBs in the Lower Fox River Below DePere Dam

A Report of the Lower Fox River Fate and Transport of PCBs Peer Review Panel

> Administered by the American Geological Institute Alexandria, Virginia

> > **Edited by**

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# Forward

This report represents the results of the AGI peer review panel charged with examining the current state of modeling of the fate and transport of PCBs in the lower Fox River in Wisconsin. AGI created the peer review panel at the request of de maximis, inc., St. Charles, IL, and support for the peer review process was provided by the Fox River Group through de maximis, inc.

The panelists were selected by AGI and the panel chair, Dr. John Tracy. Two meetings of the panel were held. The first meeting on December 10, 1999 was held in Neenah, WI. During that meeting, LTI, the U.S. Fish and Wildlife Service, the U.S. EPA, and the Wisconsin Department of Natural Resources were provided opportunities to present on their activities related to the modeling of the fate and transport of PCBs in the lower Fox River. A second meeting was held on February 3, 2000 in Green Bay, WI. During that meeting, the Wisconsin Department of Natural Resources, US EPA, QEA, and LTI presented details of their modeling efforts to the panel and participated in a roundtable discussion of their efforts.

This report represents a summary of the panel's analysis of the two primary models currently being used to determine the fate and transport of PCBs in the lower Fox River. The first chapter is an overview of the regional geology and history, as well as the development of the issues that have lead to the application of numerical models for the fate and transport of PCBs in the lower Fox River. The second chapter is an analysis of the capabilities of each of the models and how they respond to different components of the fate and transport system within the lower Fox River. Chapter three is a summary and a list of critical issues and recommendations made by the panelists concerning future modeling efforts on the lower Fox River. The fourth section is the list of references. Finally, the appendixes are the original reviewer comments provided by each panelist concerning the models. These comments have only been edited for formatting and represent the individual views and opinions of each panelist.

As editors, Dr. Tracy and I feel that the assertions and conclusions made by the panel are tightly integrated with their supporting thought processes. To this end, we do not believe an executive summary would properly reflect the true tone and intent of this report and that of the peer review panel, and that the synthesis of the reviews provided in chapters two and three best convey the panel's view.

Christopher M. Keane April 14, 2000

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# 1. Introduction

#### 1.1 Overview

The Fox River in northeastern Wisconsin is Green Bay's largest tributary and is recognized as its leading contributor of pollution (Marti and Armstrong, 1990; Swackhamer and Armstrong, 1987). While the Bay and the Fox River suffer from a variety of environmental stresses, it is the extensive contamination by polychlorinated biphenyls (PCBs) that causes the most concern for human and ecological health. Studies indicate that the Fox River is responsible for 95% of the PCB load into Green Bay (WDNR, 1997). PCBs were first introduced into the Fox River in 1954 via wastewater discharge from an Appleton paper mill (Post-Crescent, 1999a). During the next two decades several plants discharged PCBs into the fluvial system causing contamination of water, sediment and biota. Prior to governmental restrictions of PCBs, industries along the Fox River voluntarily discontinued the use of the compound in 1971. By 1976, the compound was legally banned from manufacture. While the U.S. Fish and Wildlife Service initiated legal action in 1989 against paper companies held responsible for PCB contamination, the Wisconsin Department of Natural Resources (WDNR) desired a more cooperative approach between government and industry (Post-Crescent, 1999a).

A study conducted from 1989 until 1990, titled the Lower Fox River/Green Bay Mass Balance Study (GBMBS) hoped to demonstrate the effectiveness of a mass balance approach to managing toxic chemical export into Green Bay. Specific objectives included the measurement of PCB point sources, atmospheric deposition, sediment contamination, and tributary loading, as well as PCB contributions from runoff, groundwater and landfills (Velleux and Endicott, 1994). The need to quantify PCB contamination along the Fox River initiated seven years of sampling as well as the development of a numerical model to help describe PCB fate and transport (WDNR, 1997).

In 1992, the Fox River Coalition (FRC) was formed to address the pressing need of river remediation. This organization consists of approximately 30 entities representing a variety of interest groups such as industry, local government, wastewater treatment facilities, the WDNR and the general public (Post-Crescent, 1999a). From 1992 until 1995, a subcommittee of the FRC was developed to work in conjunction with the Green Bay Remedial Action Plan Science

and Technical Advisory Committee to develop a consensus of technical objectives regarding remediation above and below DePere Dam (WDNR, 1997). Concurrently, the paper mill industry united to form the Fox River Group (FRG). Today the FRG is comprised of seven companies, each of which have been identified by the federal government as responsible for PCB contamination along the Fox River. These companies include P.H. Glatfelter, Fort Howard (now Fort James Corp.), Wisconsin Tissue Mills, Riverside Paper Corp., U.S. Paper Mills Corp., Appleton Papers and NCR, a former owner of Appleton Papers (Post-Crescent, 1999a).

Remediation efforts moved forward in 1997 when several governmental entities, including the WDNR, the U.S. Environmental Protection Agency (EPA), the U.S. Fish and Wildlife Service, the National Oceanic and Atmospheric Administration (NOAA) as well as the Oneida and Menominee tribes, signed an agreement on the management of cleanup efforts along the Fox River (Post-Crescent, 1999a). Currently, the EPA is taking steps to designate the Fox River as a Superfund site by suggesting it be placed on the National Priorities List (NPL), a roster of the nations worst hazardous waste sites (U.S. EPA, 1997). A pilot dredging project of PCB-contaminated sediment began in August 1999 and continues today (Mella and Billings, 1999). This pilot demonstration is largely funded by the FRG, who has paid \$10 million to the Department of Justice as a recognized down payment for remediation (Post-Crescent, 1999a).

## 1.2 Physical Setting

As shown in Figures 1 and 2, the Fox River is located in northeastern Wisconsin. The drainage basin is 6,558 mi<sup>2</sup> (17,000 km<sup>2</sup>) and encompasses portions of Fond du Lac, Winnebago, Calumet, Outagamie and Brown counties. The river begins at Lake Winnebago and continues through Neenah-Menasha, Little Lake Butte des Morts, Appleton, Kimberly, Little Chute, Kaukauna, Wrightstown, Little Rapids, DePere and the metropolitan area of Green Bay. After dropping nearly 170 ft (52 m) over 39 miles (63 km) the Fox River then enters into the Green Bay (Schultz, 1986). Along this route, several small tributaries as well as several industrial/municipal point source discharges enter the Fox River. The flow in the river is generated primarily by spring snow melt and seasonal rains, with the river's discharge being highly regulated by a series of dams with DePere Dam being the last in the system. The DePere Dam marks a critical boundary in terms of sediment and PCB transport. For reference, the "Lower" Fox River is often designated as the 6.8 mile (11 km) section of the river located below

#### DePere Dam.



Figure 1. Map of the Fox River with urban areas and point source discharges marked (adopted from Velleux et al., 1995).

# 1.3 Geology

The geologic time scale subdivides time into several eras from oldest to youngest: Precambrian, Paleozoic, Mesozoic, and Cenozoic (Figure 3). Each of these is divided into Periods. All of the rocks at or near the surface in the Lower Fox valley are Paleozoic (Cambrian, Ordovician, Silurian) in age, and the glacial deposits overlying the rock were left during the Pleistocene. Nonetheless, the Precambrian history of Wisconsin plays a major role in setting the stage for the deposition of rocks that we see at the surface here today.

#### <u>1.3.1 Precambrian Geology</u>

For several billion years, north-central Wisconsin has been at a higher elevation (an arch) than areas to the east, west and south. This has determined the distribution of sedimentary rocks deposited during the Paleozoic and the path of rivers and glaciers in more recent geologic time.

Although no Precambrian rocks are exposed in the Lower Fox valley, they form the basement on which younger rocks have been deposited. For purposes of groundwater studies,

these Precambrian Canadian shield rocks are generally considered to have very low permeability.



**Figure 2.** Map showing the Fox River drainage basin of eastern Wisconsin. (From Martin, 1916, reprinted 1965). Note that the Niagaran Cuesta here is what is commonly called the Niagaran Escarpment today. The asymmetry of the basin is produced by the gently dipping Sinnipee Group dolomite that underlies most of the basin.

#### <u>1.3.2 The Paleozoic Era</u>

Five hundred million years ago, seas advanced onto this part of the continent from the south and west. All of the rocks that are present at the surface and extending several hundred feet

below the Fox River valley are sedimentary rocks deposited in this extensive sea. The sea expanded and contracted numerous times over more than one hundred million years. At times when the sea was shallow sand was deposited. As the sand was buried, it became cemented. Finer silts and clays were carried by currents into deeper water in what is now Michigan and Illinois. The silt and clay produced shale when buried and consolidated into rock.



Figure 3. Geologic time scale. (Modified from Clayton, et al., 1992)

Deep basins continued to develop in Michigan and Illinois throughout much of the Paleozoic, but the East Side of the Wisconsin Arch, where the Lower Fox River is today, remained a shallow shelf. Only occasionally were the seas deep enough here for shale to be deposited. There is very little shale beneath the Fox valley, but the existence of that shale played an important role in determining the shape of the landscape much later, when glaciers covered

the area.

At times during the Paleozoic when the sediment supply from rivers on the continent was diverted to other areas, carbonate sediment in the form of calcareous algae, shells, and by Silurian time, massive coral reefs accumulated. This sediment slowly cemented into limestone (calcium carbonate) and dolomite (calcium-magnesium carbonate).

Periodically, sea level dropped, and the land was exposed to erosion. Streams eroded this surface, forming river valleys across the area, removing some of the previously deposited sandstone and dolomite. These erosional surfaces are called "unconformities." When the sea rose again, sediment filled these valleys, producing an uneven contact between rock types at this unconformity.

Following retreat of the sea in which the Silurian dolomite was deposited, the sea rose again in the Devonian Period (Figure 3). Except in very eastern Wisconsin and beneath Lake Michigan, these rocks have been eroded away. There may have been later marine incursions into Wisconsin, but all evidence of these younger events are erased from the record. From Devonian time until glaciers first covered the surface a million years ago, Wisconsin was a land eroding away much like it is today. Rivers cut valleys below the glacial cover. Little is known of the early drainage history of eastern Wisconsin, but Martin (1916, reprinted 1965) guessed that early streams dominantly drained eastward as shown in Figure 4. Lake Michigan was a river valley in pre-glacial time, much as the Fox River-Lake Winnebago lowland was, because of differential erosion. The Mequoketa Formation is easily eroded. Whatever the pattern of river valleys at the time of an initial glacial advance, the Mequoketa was preferentially eroded by glacial ice coming down the basin. The present Lake Winnebago, Lower Fox River, and Green Bay are located in the deepest part of this lowland. The Upper Fox and its tributaries flow down the dip slope of the Sinnipee dolomite into Lake Winnebago (Figure 4).

To the east of the lowland, differential erosion of the Silurian dolomite has produced the Niagaran escarpment, an asymmetrical ridge, steep on the west and gently sloping eastward to Lake Michigan. This approximately 200-foot-high ridge forms the eastern surface water divide of the Fox River basin (Figure 2). The escarpment forms the backbone of Door County to the northeast and extends across the north side of Lake Huron to Niagara Falls. It was a major control on glacial ice coming into Wisconsin.

#### 1.3.3 The Quaternary Period

Nearly all of the Fox River basin is covered with till deposited directly by glaciers, sand and gravel deposited by streams flowing under and away from the ice, and silt and clay deposited in glacial margin lakes. Need (1985) mapped the glacial deposits in Brown County. No detailed mapping has been done in Outagamie County.

The last glacial advance scoured the rock surface leaving little or no trace of previous glacial deposits, although glaciers have come into the state over the course of the previous 1 million years. All of the deposits known in the area are from the late Wisconsin glaciation (Figure 3), and were deposited by the Green Bay lobe, a mass of ice that advanced into the area



**Figure 4.** Hypothetical preglacial drainage pattern and modern drainage in eastern Wisconsin (from Martin 1916, reprinted 1965).

from the northeast. The ice sheet probably entered the area about 23,000 years ago, and advanced southwestward to the Madison area in a few hundred to thousands of years. The glacier had its maximum extent about 18,000 years ago, and then began to retreat. The retreat was not continuous, but was interrupted by re-advances of the glacier during cool periods (Figure 3). In many cases, these re-advances deposited till of different composition, so the till layer deposited by one advance can be distinguished from that deposited by another advance in the laboratory

and often in the field.

In addition to till, common facies present in the Lower Fox River valley are lake sediments, outwash, and ice-contact stratified deposits. Outwash and ice-contact stratified deposits are stream sediments that are commonly sand and gravel and occur mostly away from the axis of the valley. Need (1985) shows thick sand and gravel beneath at least one Kewaunee Formation unit along the Niagaran Escarpment. The Duck Creek ridges, west of the river, are also composed of sand and gravel (Piette, 1963). Lake sediment is more abundant than stream sediment in the Lower Fox River valley because whenever the glacier edge retreated northeastward, a lake, called Glacial Lake Oshkosh (Thwaites, 1943; Thwaites and Bertrand, 1957), was present in front of the ice. In its early stages, this lake drained into the Wisconsin River at Portage. When ice had retreated far enough to allow drainage out of the Manitowoc River, lake level dropped as this lower outlet carried water into Lake Michigan. Subsequently, the lake level dropped as retreating ice exposed lower outlets on the Door Peninsula. Much of the sediment that was deposited in this lake is silt and clay. This has low permeability, like the Kewaunee Formation till units. Associated with the fine-grained lake sediments are localized beach deposits that are composed of gravel and sand. These long, narrow bodies of highly permeable gravel are not mapped in the subsurface and can create unexpected, high permeability zones in otherwise low permeability sediments.

The Lower Fox River valley is directly underlain by glacial, river and lake deposits. These deposits range from very thin to over 100 feet thick. They range in composition from silty clay to gravel and include substantial amounts of till. Fine-grained sediments dominate in the central part of the valley, although beach gravel in the subsurface is locally important as a permeable avenue for groundwater movement. Coarse gravel deposits beneath clayey till are present along both sides of the valley.

Beneath the glacial and lacustrine cover, Paleozoic dolomite and sandstone dip gently toward the east. The Ordovician Sinnipee Group dolomite (Platteville and Galena formations) is the surface rock under the entire valley. Small, isolated patches of Maquoketa shale may be present, but most is restricted to the base of the Niagaran escarpment. Here, resistant Silurian dolomite forms a prominent ridge along the eastern side of the valley. This east-dipping, resistant dolomite, underlain by easily eroded shale, channeled glacier flow and produced the broad, asymmetrical valley cross section that we see today.

#### 1.3.4 Hydrogeology

The Fox River contains a complex hydrogeologic system of aquifers and confining units. Until 1957, the principal source of water for the Green Bay municipal area was groundwater. In 1957, groundwater levels reached historic lows and the city of Green Bay discontinued pumping and began using water from Lake Michigan. Following recovery of the groundwater system, pumping began again with the growth of other municipalities and today the cone of depression (i.e., lowest point of potentiometric surface) is centered beneath the city of DePere (Brown, 1986). Figure 5 correlates the hydrogeologic units with stratigraphic units for easy reference.





Recharge of water into the groundwater system is the amount of precipitation minus runoff and evapotranspiration. Therefore, recharge occurs during extended periods of rainfall in the spring and fall months. Vertical leakage from the upper aquifer into the deeper St. Peter and Elk Mound aquifers is caused in part by the downward movement of fluid, but is also accentuated by the cone of depression generated by excess pumping in the Green Bay/DePere metropolitan area. Groundwater is also discharged from the upper aquifer into lakes, wetlands, streams and when water is pumped for human use. While the amount of groundwater discharge depends heavily on the factors of evapotranspiration, precipitation, temperature and pumping rates, it represents a continual drain of water from the aquifer (Brown, 1986).

Potentiometric contours indicate that shallow groundwater movement occurs toward the Fox River and Green Bay. Prior to the massive pumping of groundwater along the Fox River (DePere and Green Bay), the deeper aquifers also discharged water into both the Green Bay and the Fox River. Today this in no longer the case (Brown, 1986).

# 1.4 Historical Setting

The location of the Fox River lowland, its surrounding escarpments and subsequent drainage patterns have dictated routes of travel, communication and commerce. Consequently, many of Wisconsin's largest cities are located in the area. Settlement began during the furtrading era as the Fox River proved an important link in the transportation of people and goods between Lake Michigan and the Mississippi River. Travel upon the river and portage around the rapids began with light Indian canoes and later progressed to 30-foot-long French canoes (Schultz, 1986). In 1856, the development of the steamship prompted the U.S. Army Corps of Engineers to improve navigation along the Lower Fox River. Subsequently, a series of 17 locks and dams was completed in 1884 to fully connect the Great Lakes with the Mississippi River system (FRG, 1999; Schultz, 1986).

Before the channel was improved for navigation purposes, the solid bedrock created a series of eight rapids between Neenah-Menasha and DePere with most of the gradient occurring within the 15 miles (24 km) between Lake Winnebago and Kaukauna. Substantial 38-foot (11.6-m) drops occur at Appleton and Little Chute, while a third, larger drop occurred at Kaukauna. Consequently, the Fox River was developed for waterpower beginning with dam construction in the early 1850s at Neenah, Manasha and DePere. Today, no other river in Wisconsin produces as much power in such a short distance (Schultz, 1986).

#### <u>1.4.1 Industrial Development</u>

The abundance of cheap waterpower attracted industry, including flour-milling, the manufacture of wood products and charcoal. The milling industry faded in the 1860s as the industry relocated to Minneapolis (Schultz, 1986). The lumber industry lasted until the late 1800s (FRG, 1999). Appleton and DePere opened smelters for iron ore, which promoted various iron-related industries to migrate into the area (Schultz, 1986). In 1853, the first paper mills appeared in Appleton under the guidance of the Richmond brothers. A Neenah government sawmill was converted into a paper mill in 1865-66, while another mill was built in 1872 by John Kimberly and Charles Clark (FRG, 1999; Schultz, 1986). Over the decades, the paper industry continued to expand into the largest industry along the river. Today, the Fox River valley contains the most concentrated grouping of cities and industry within Wisconsin, and continues to grow as one of the state's foremost industrial regions.

Early in the region's industrial history, environmental stresses were applied to the Fox River Basin. Industrial waste as well as raw sewage was dumped into the Fox River so that by the 1920s the river had a terrible stench. Dissolved oxygen levels plummeted making it difficult for aquatic species to survive. By the 1940s and 1950s, efforts were made to recycle waste materials discharged into the river and municipalities and paper mills began installing primitive wastewater treatment plants (FRG, 1999).

Today, environmental stresses still plague the Fox River system despite both governmental and industrial organizations working to reach and maintain acceptable water quality and biotic standards. While PCBs discharged from point sources into the Fox River ended in 1971, PCBs still remain within the system and are exported into Green Bay where recovery is difficult. Also, non-point pollution from urban and agricultural runoff is continuing to add oil, gas, heavy metals, pesticides, fertilizers and sediment into the system. Continued shoreline development has destroyed wetlands, submerged aquatic vegetation and significantly reduced habitat availability. Exotic species, such as zebra mussels, carp, sea lamprey and purple loostrife have also inundated the area (FRG, 1999). These exotic, or "nuisance," species are not native to the local ecosystem and tend to dominate over the indigenous species to gain vast footholds and offset the natural processes within the ecosystem.

While rock and hardpan river bottoms still constitute much of the river bottom above DePere Dam, active sedimentation occurs along the lower Fox River, where longitudinal channel gradients are diminished, the river is wide, and velocities are slow. The WDNR estimates that nearly 75% of all the deposited solids in the Fox River lie below DePere Dam, creating a river bottom composed mostly of silt and soft mud (FRG, 1999). The active deposition of sediment inhibits navigation, making it necessary to dredge the channel to keep ports open to commercial traffic. The U.S. Army Corps of Engineers reports that 3 million cubic yards of sediment have been removed from 1957 until 1996 and disposed of within the Bayport Disposal Site (FRG, 1999).

To address the variety of environmental problems facing the Fox River, 16 priorities and 120 action plans were initiated by the Lower Fox River/ Green Bay Remedial Action Plan in 1988 (FRG, 1999). While non-point source loading, habitat loss, effects of urbanization, the proliferation of exotic species, and sedimentation are still a priority today, it can be argued that the risk associated with PCBs is far greater (Post-Crescent, 1999b). A full description of PCBs, their origin, health effects, contaminated regions, mode of transport, and remedial options are discussed below.

#### <u>1.4.2 PCB Contamination</u>

A biphenyl molecule consists of two hexagonal rings, each containing six carbon atoms, which are joined in the middle. Chlorine atoms then attach at any of the 10 remaining sites along the biphenyl molecule to create polychlorinated biphenyl (PCB). Due to the different number and arrangement of chlorine atoms possible, there are 209 known variations of the PCB molecule commonly referred to as PCB congeners. Each congener contains unique physical and chemical properties. It is believed that coplanar PCB congeners, named for their flatter shape, are more toxic to aquatic species than other forms of PCB congeners (FRG, 1999).

PCBs were first synthesized in 1929 and were used from 1929 until 1976 in a variety of products including electric capacitors and transformers, adhesives, textiles, sealants, and newspaper ink (FRG, 1999; Post-Crescent, 1999a). Their commercial appeal resides in their resistance to wear and chemical breakdown (Erickson, 1997). In 1954, PCBs were first used in Appleton for the commercial manufacture of carbonless paper. In the early 1970s, scientists began tracing PCBs as toxins that create reproductive problems in fish-eating birds. In 1971, paper mills in the area voluntarily discontinued the use of PCBs in the manufacturing process due to health concerns. By 1972, the government began placing restrictions on PCB use. Finally,

in 1976, the government completely banned the use of PCBs due to their negative impacts on the nervous, immune, circulatory, hormonal, liver, brain, and skin systems (Post-Crescent, 1999a). The EPA (1996, 1998b) lists the following health concerns potentially related to exposure to PCBs:

- Reproductive function may be disrupted by exposure to PCBs.
- Neurobehavioral and developmental deficits occur in newborns and continue through school-age children who have had in-utero exposure to PCBs.
- Other systemic effects, such as self-reported liver disease and diabetes, and immune system risks may be associated with elevated serum levels of PCBs.
- Increased risk of cancer is associated with PCB exposure.

It is believed that exposure to PCBs may cause the risk of cancer to increase between 100 and 1,000 times what government health scientists consider acceptable. Similarly, child development problems may rise by 170 times.

PCBs are "hydrophobic." This means they resist mixing in water, will dissolve more readily in fats and oils, and swiftly adsorb onto particulate matter. Consequently, to understand the behavior of PCBs it is also necessary to describe the dynamics of sediment onto which PCBs adsorb. This means that the quantification of erosion, deposition, and mode of sediment movement becomes critical to any mass balance analysis of PCBs.

Estimates show that approximately 125 tons of PCBs were released into the Fox River from 1957 until 1971, in large part by paper mills in the surrounding area. Of the initial 125 tons, approximately 34 tons of PCBs remain within the fluvial system. Due to PCBs high affinity for particulate matter, these PCBs reside mostly in the river's bottom sediments and contaminate approximately 11 million cubic yards of material (U.S. EPA, 1998b). Note that only 13% of the 34 tons (9,200 lbs.) of PCBs lies within the bottom sediments between Little Lake Butte des Morts and the DePere Dam. Along this 30-mile stretch, 31 areas of discrete contamination have been identified, with the bulk of PCBs residing within Little Lake Butte des Morts and the slack water just upstream of DePere Dam. The remaining 58,000 lbs. of PCB contamination (87%, 7.8 million cubic yards of sediment) are located within the soft sediment between DePere Dam and the Fox River delta into Green Bay (FRG, 1999). Table 1, taken from WDNR (1997), assigns PCB mass, contaminated sediment volume, and associated surface area to discretized regions

along the Fox River.

River Reach	PCB Mass (kg)	Sediment Volume (m <sup>3</sup> )	Surface Area (m <sup>2</sup> )
LLBDM – Appleton	2,300	900,000	3,000,000
Appleton – Kaukauna	300	100,000	400,000
Kaukauna – Little Rapids	200	400,000	1,300,000
Little Rapids – DePere	1,400	1,000,000	2,700,000
DePere – River Mouth	26,500	6,000,000	5,000,000
Totals	30,700	8,400,000	12,400,000

#### Table 1. Estimates of PCB Contaminated Sediment (WDNR 1997).

It is believed that the long term export of PCBs into Green Bay depends on the more heavily contaminated sediments found below DePere Dam. The majority of surface sediments range from less than 3 ppm up to 10 ppm PCB contamination. A few isolated hot spots do occur, with PCB concentrations occurring between 10 and 30 ppm. On average, surficial sediments have PCB levels of 2.7 ppm (FRG, 1999; WDNR, 1997).

Preliminary model results suggest that during the 1980s, contaminated sediment originating upstream of the dam was transported for temporary storage below the dam and subsequently resuspended to become the principal source of PCB loading into the bay (Velleux et al., 1995). Given that Lake Winnebago is not a PCB source and point discharges are nearly negligible, it is hypothesized that the loading of contaminated sediments into the lower portions of the river will decline in the future. On the other hand, the lower Fox River is still heavily contaminated with PCBs. This may be due to the fact that the initial PCB sediment levels were much higher than the upper river and that there has been a flux of contaminated material from upstream (Velleux et al., 1995).

Given the depositional nature of the Lower Fox River, the burial of contaminated sediment with less contaminated sediment is occurring. Sediment cores taken below DePere indicate that 85% of the PCB contamination is buried below 1 foot of cleaner sediment that has entered the river environment from upstream of the dam (FRG, 1999). Table 2 shows the range in PCB concentrations (WDNR, 1997). Note that while these data show an obvious trend of increasing PCB contamination with depth, it does not appear that any significant reduction has occurred in contamination levels between 1989 and 1996. These data also indicated that PCB levels span a significant range from below detection all the way up to a very toxic 400 ppm,

suggesting high spatial variability sensitive to sample location.

<b>Depth of Core</b>	Low (ppm)		High (ppm)	
	1989	1995	1989	1995
<= 60 cm	< 0.05	< 0.05	84	91
Deep cores	< 0.05	< 0.05	110	400

Table 2: WDNR reported PCB levels found in sediment below DePere dam (WDNR 1997).

The Remedial Investigation and Feasibility Study being conducted by the WDNR seeks to establish PCB levels in sediments low enough to protect human and ecological health. Guidelines established by the DNR suggest that sediment concentrations should equal 0.25 ppm. This standard would remove most of the risk to wildlife and allow unlimited consumption of sport fish. Limitations would still need to be placed on subsistence fisherman who rely on a heavy diet of carp. DNR hopes to obtain these goals within 20 years (Post-Crescent, 1999b).

The erosion of material from the channel bottom is influenced by a variety of factors including the age of the settled material, sediment size/type, armoring, and shear stress (Velleux and Endicott, 1994). Freshly deposited material is often more easily suspended than older, more compacted material. The size fraction can complicate understanding resuspension, with larger particles being more difficult as compared to smaller particles. However, small clay particles also resist due to preferential settling and electrical chemical bonding that makes them cohesive. Sediment armoring can also occur through the differential erosion of the more erodable sediment, thus leaving behind a coarser fraction of material that protects the bed from further erosion. Nonetheless, of all the factors dictating erosion, the most important is shear stress. Shear stress occurs at the sediment-water interface in the direction of flow and increases with increased velocity to promote channel bed erosion (Velleux and Endicott, 1994). Consequently, sediment resuspension has a highly non-linear relationship with river discharge.

Controversy arises over the relationship between resuspension along the Lower Fox River and the flow regime. Modeling efforts conducted by the WDNR propose that significant amounts of sediment and PCBs are resuspended when flows along the Fox River are high. Scouring is believed to occur primarily along the deeper, central portion of the river (FRG, 1999; Velleux and Endicott, 1994; Velleux et al., 1995). On the other hand, the FRG argues that erosion along the Lower Fox River is not sensitive to stream flow. It suggests that the river's insensitivity to discharge is caused by several factors. First, the river does not undergo wildly fluctuating river flows, even during a rare flood. The 100-year event is estimated to be only 25% higher than its 10-year flood (U.S.G.S., 1992). This may in part be due to the river's highly regulated nature. It may also be attributed to its wide channel, which may reduce stream velocities enough to inhibit the formation of large shear stresses even during flood events. Finally, the FRG argues that the Lower Fox River is depositional, as demonstrated by the massive dredging efforts conducted by the U.S. Army Corps of Engineers to keep navigation routes open (FRG, 1999).

As already described, water column concentrations of PCBs depend heavily on the concentration of suspended sediments in the water column. Unfortunately, water column data are limited, but it does appear that measured PCB concentrations at the Fox River mouth have not changed much between 1989 and 1995 (WDNR, 1997). Note that it is necessary to compare water samples collected during similar seasons and flow regimes. Water column concentrations range from less than 10 ng/L (ppt) to approximately 160 ng/L. These levels exceed water quality standards imposed at 0.49 ng/L for warm water fisheries and 0.15 ng/L for the Great Lakes (WDNR, 1997).

Estimates of average annual transport of PCBs into Green Bay have been made using the GBMBS data on sediment loading from 1989-1990. Data indicate that approximately 117,000 tons of sediment were transported into the Lower Fox River from 1989 until 1990. Of this total, it is believed 99,000 tons of material initiated upstream of DePere Dam while the remainder fluxed in from tributaries. Model calculations estimate that 83% (97,000 tons) of this sediment settled below DePere while the remaining 17% was transported into the bay (FRG, 1999). Ranges of annual PCB export vary significantly from 350 lbs. to 600 lbs. (Limno-Tech 1999a) in large part due to disagreement on the degree of erosion occurring downstream of DePere Dam and influence of higher magnitude flood events in moving contaminated sediment (U.S. EPA 1998b; FRG, 1999; U.S.G.S, 1998).

Human exposure to PCBs is primarily through the consumption of fish. The Great Lakes Sport Fish Consumption Advisory recommends that one not eat fish with PCB concentrations greater than 1.89 mg/kg (ppm). Environmental endpoints, or objectives for biological integrity that will guide remediation efforts, aim for 0.023 ppm PCB concentrations in fish to protect the most sensitive species, mink (WDNR, 1997). Due to the possible serious health risks associated with PCBs, fish consumption advisories have been enacted along the Fox River since 1976.

According to data presented by the WDNR (1997), the average PCB concentrations in Walleye fillets taken from Little Lake Butte des Morts declined substantially (from approximately 2 to 3 mg/kg (ppm) in 1976 when active wastewater discharges were reduced, to 0.6 ppm in 1985). Consumption guidelines correspondingly improved from no consumption of Walleye to a rate of one meal per month. While PCB concentrations in Walleye are still decreasing, the rate of decline has slowed down. This may reflect the shift in the source of PCBs from industrial point sources to the slow release of PCBs from contaminated bottom sediments. Today, Walleye have mean concentrations of 0.2 ppm, which still corresponds to a limited diet of one meal per month. Fish obtained below DePere Dam have not shown much recovery and continue to present significant human health and ecological risk. For example, 20-inch Walleye still have contamination levels of approximately 2 ppm (6 meals/year), while 15-inch Walleye show levels dipping below 1 ppm (1 meal/month) (WDNR, 1997).

#### **1.5** Remediation Alternatives

There are three primary strategies that can be employed to lower the environmental and health risk associated with PCB-contaminated sediments in the Lower Fox River: (1) natural recovery; (2) dredging of sediments; or (3) capping of sediments. Each of these strategies could be used independently or conjunctively, with the goal being to find the mixture of strategies that proves to have the optimal cost-benefit.

The natural recovery strategy entails no actions that would disturb the river bottom sediments, but the PCB concentrations in the sediments, the water column, and environmental receptors would continue to be monitored to ensure that the risk associated with the PCB-contaminated sediments is lessening over time. When fully operational, the natural recovery strategy involves the healing of surficial sediments, primarily by the combined processes of natural capping by clean solids from the watershed, sorption of PCB on this new material, in-situ degradation by biotic and abiotic processes, burial at depth, and slow release of minute fractions to the water column. There is some evidence that suggests the depositional nature of the Lower Fox River below DePere dam is promoting burial of very contaminated sediments, thereby isolating the overlying water column and biota from future exposure to PCBs (FRG, 1999).

However, the natural recovery strategy will not result in any substantial reduction in the mass of PCB contamination deep within the river sediments over time, but rather will result in an isolation of the contaminated sediments from the environmental receptors.

The dredging-of-sediments strategy involves the removal of contaminated sediments from the river system. Several different mechanisms can be used to dredge the bottom of a river. The oldest technique is termed "mechanical dredging." Using a "bucket," clamshell or cablearm, this method is very precise and uses little water but often allows sediments to be resuspended into the water column and has low efficiency in recovering very fluid and fluffy bottom sediments. Given that resuspension is the method of bringing PCBs into contact with the overlying water column, and potential export to Green Bay, this is not a feasible option for removing PCB-contaminated sediments from the Lower Fox River. "Hydraulic dredging" involves the use of auger and cutterhead dredge. This method minimizes the resuspension of contaminated sediment but it requires a tremendous amount of water for use. "Pneumatic dredging" utilizes less water than the hydraulic dredge, but it is a poor collector of material in shallow waters. Using the hydraulic dredging method, a pilot dredging project in the Lower Fox River began in August 1999 to test the benefits and/or drawbacks of removing material from the river bottom. The first site is located near Kimberly and is often referred to as Deposit N. The second site is at the Sediment Management Unit (SMU) 56/57. This is a nine-acre site located downstream of DePere Dam and about three miles from the mouth of the Fox River (Mella and Billings, 1999). SMU 56/57 represents one of the more heavily contaminated portions of the river.

The capping-of-sediments strategy may entail covering the channel bottom with several inches to several feet of sand or gravel. An optional underlayer, such as clay or a geotextile, can also be used. Capping would cover portions of the near surface river sediments to provide a clean surface for habitat. In addition, capping would further isolate PCBs from the overlying ecosystem (FRG, 1999). Note that capping of the channel bottom will be effective only if the natural river processes do not create an erosive environment for the bed sediments, or the sediments can be armored to protect them against erosion (U.S. EPA, 1998a).

The consideration of each of these remediation alternatives requires that their impact to the PCB loading to Green Bay, the PCB concentration in the water column, and the PCB concentrations in the near-surface and deep river sediments be predicted several decades into the future. The only mechanism available to provide these predictions is computer simulation. Thus, a number of models have been developed to predict the fate of PCBs in the Lower Fox River system.

## 1.6 Models of the Lower Fox River

At the current time, there are primarily two models being used to predict the fate of PCBs in the Lower Fox River system. The first model, used by the Wisconsin Department of Natural Resources (referred to as the DNR model) to evaluate remediation alternatives in the Lower Fox River from DePere Dam to Green Bay, was developed by Velleux (1992) and Velleux and Endicott (1994). Based on this work, a single domain model was later developed for the entire Lower Fox from Lake Winnebago to Green Bay (Velleux et al., 1995; Velleux et al. 1996), and has been used to evaluate selective sediment remediation strategies for the Lower Fox River (WDNR, 1997). The second model, developed by Limno-Tech, Inc. (1999a), was developed as an alternative model of the fate of PCBs in the Lower Fox River from DePere Dam to Green Bay (referred to as the LTI model). The LTI model uses as its foundation much of the previous DNR modeling work, but modifications were made to the numerical routines related to tracking PCB concentrations in the deep riverbed sediments. Modifications were also made to a number of parameters during the model recalibration exercise and included a particle mixing-sediment water mass transfer element in place of the conventional molecular diffusion process used in the DNR model. The review panel is aware of two other models being developed to predict the fate of PCBs in the Lower Fox River below DePere Dam. A modeling effort has been undertaken by QEA for the United States Fish and Wildlife Service. While no documentation of the QEA model is currently available, a presentation was made on their modeling approach, assumptions, limitations and results during a Peer Review meeting on February 3, 2000, in Green Bay, WI. In addition, Baird and Associates has developed a model referred to as ECOM-SED for part of the Lower Fox River, although no reports or presentation on their modeling effort were available for this panel to review.

In general, the DNR and LTI models employ coarse-scale elements in their formulation and calculations, with a large number of adjustable, or calibration, parameters used in both models. The QEA model, on the other hand, employs finer-scale elements in their model formulation, and also employs a smaller number of adjustable parameters. In both the DNR and LTI models, the  $\varepsilon$ -equation (also referred to as the Lick equation) is used to describe the resuspension of sediments into the water column. Some comments on this equation are necessary to understand its appropriate use and limitations.

The  $\varepsilon$ -equation was proposed to describe results of resuspension experiments done on cohesive sediments in an annular flume at relatively low shear stresses (Lick, 1986). For field work with relatively undisturbed sediments, the Shaker was later developed and used (Tsai and Lick, 1986); experiments with this latter device mimic those in an annular flume and can also be described by the  $\varepsilon$ -equation. A major limitation of both the annular flume and the Shaker is that they can only be used to measure the resuspension of relatively small amounts of sediment. By the very nature of these devices, the amount of resuspension is usually limited to a few millimeters; this typically corresponds to shear stresses less than (and often much less than ) 10 dynes/cm<sup>2</sup> (1 N/m<sup>2</sup>) (McNeil et al., 1996). It should also be understood that both of these devices measure net resuspension, that is, the amount of sediment suspended in the overlying water of the device. This suspended matter results from a dynamic balance between erosion and deposition. In these devices, the surficial layer of the bottom sediments is never swept away, and therefore lower layers are never exposed or eroded, even if they could be at the particular shear stress being tested. In particular, these devices do not take into account bed load or erosion and transport of coarse material.

The  $\varepsilon$ -equation is correct in that the functional form of the equation correctly describes the limited resuspension of fine-grained, cohesive sediments at a particular shear stress. It may be appropriate as a first approximation to the resuspension properties of fine-grained, cohesive sediments at depth, as long as the parameters are estimated properly, from resuspension data. If parameters are obtained from the calibration of field data on the concentration of suspended sediments in the water column, then the prediction of sediment erosion from this equation may be incorrect.

While both the DNR and LTI models utilize the  $\varepsilon$ -equation to simulate the resuspension of sediments into the water column, along with many other similarities, the results of long-term simulations have shown significant differences between these two models. The most significant differences between the DNR and LTI model simulations are in the long-term export of PCBs from the Lower Fox River to Green Bay, where the DNR model predicts 70% more PCBs will be transported into Green Bay than the LTI model. A primary reason for these differences is that the parameters that the DNR and LTI models arrived at during their respective calibration exercises are quite different. This is due, in part, to the fact that neither model is adequately constrained (they are both over-determined). This is a common problem with this kind of water quality model. The model parameters and process representation is not set so there is a range of acceptable values for model calibration coefficients. This means that during the calibration process, model coefficients (and other parameters) are adjusted so the difference between model output and observed calibration data is minimized. This can be referred to as a minimization on the model calibration residual. Determining the values used in the model calibration process and oftentimes the minimization of the model calibration residual requires "modeler" (environmental practitioner) judgment. When the model calibration residual is at the minima and if the adjusted parameters are within an acceptable range, the model is considered calibrated. The problem with this process for over-determined models is best illustrated when one considers the relative magnitude of opposing processes. For example, if a model application has relatively high magnitude resuspension and deposition (e.g., WDNR model), it may be able to predict the same observed total particle mass in the water column and in the sediment compartments as the same model with relatively low magnitude resuspension and deposition (e.g., LTI model), even though these are dominate processes. The difference is in the outcome. In the case of the reduced resuspension/deposition scenario, the benthos-water column coupling is reduced and the sediment compartment is less dynamic (with respect to other sediment-state variables, e.g., PCB). This changes what one would conclude by applying the model. This discussion is oversimplified, but illustrative. A summary of final parameter estimates used in the alternative model (Limno-Tech, 1999d) is given in Table 3. Values used in the WDNR model, along with parameters estimated by (McNeil, 1994), are also presented for comparison.

Due to the differences in both the model parameters and model predictions, a review of these models is necessary to understand the limitations of each model in its ability to predict the fate and export of PCBs in the Lower Fox River below DePere Dam. Thus, the purpose of this report is to provide a technical review of the LTI and DNR models in relation to: (1) their ability to predict the fate and export of PCBs from the Lower Fox River below DePere Dam; and (2)

their utility as decision-making tools to aid in the planning of PCB remediation strategies in the Lower Fox River.

Parameter	DNR	McNeil 1994	LTI
Critical Shear (dynes/cm <sup>2</sup> )	1.0	1.0	1.0
Μ	2.75	2.3	1.4
$A_0$	8.0	1.3	2.92 <sup>a</sup>
Z	0.1 - 2	1.38	1.0
Erosion ( $= 3 \text{ dynes/cm}^2$ )	$50^{\mathrm{b}}$	4.64	7.7
Erosion ( $= 5 \text{ dynes/cm}^2$ )	363 <sup>b</sup>	22.9	20.3
Erosion ( = $15 \text{ dynes/cm}^2$ )	11,349 <sup>b</sup>	408	118

Table 3. Summary of Resuspension Parameters and Erosion Rates (mg/cm<sup>2</sup>)

<sup>a</sup> Note that the a0 value presented in Limno-Tech (1999d) are different than estimates given in Limno-Tech (1999a and 1999b). In Limno-Tech (1999a and 1999b), the equivalent  $a_0$  value is equal to 1.07 for soft muds and 0.349 for silty-sand. No justification for the change was presented.

<sup>b</sup> Erosion estimates are based on Z = 1.

# 2. Review Comments on Existing Models

# 2.1 Introduction

A quantitative model can be used for a variety of purposes, but when it is used to develop plans, or set policy, the model's primary purpose becomes one of translating scientific information into decision-making information that is useful to stakeholders and agencies involved in restoration efforts within the river system. That is, a model becomes the link between the scientific community and the public policy community. This is accomplished by using mathematical and statistical relationships to translate the language of the physical sciences into the language of the social sciences. Thus, modeling plays an important role in aiding the development and evaluation of remediation efforts, but a role that is subservient to the availability of scientific descriptions of the processes within the river system and the information needs of the entities charged with developing and reviewing the efficacy of remediation efforts.

For any environmental system, the ideal modeling tool would be one that could efficiently and accurately predict the effect of any environmental factor or remediation alternative on the future concentrations and loading of the hazardous contaminant of concern. A modeling tool such as this could then be used by agencies involved in decision-making activities within a river system to evaluate an exhaustive list of options and arrive at some consensus on the most effective remediation plans. Rarely are the resources available to develop a model to meet these criteria. However, useful decision-making models can still be developed if the development process focuses on three key issues, these being: (1) model accuracy; (2) model utility; and (3) model acceptance.

The accuracy of a model can be thought of as the ability of the model to predict the behavior of a physical system, given a set of impulses to the system. Thus, to assess the accuracy of a model implies that measurements of both model input and output variables are available. From a scientific perspective, the accuracy of a model can be assessed by comparing the modeled output to the measured output for the physical system. The model accuracy can then be quantified using a norm of the difference between the measured and modeled output. This norm is typically the second norm, which is a measure of the squared deviation between the measured and modeled output. The drawback of this perspective in developing models for natural systems is that, typically, the input data set used to assess the accuracy of competing models only

includes environmental variables. Therefore, the measure of accuracy only reflects the model's ability to predict changes in output due to a limited number of input variables. This can result in a model whose accuracy is suspect relative to understanding the impacts of remediation actions on the river system.

The utility of a model is related to whether the model can provide useful information to decision makers who are developing remediation plans for the river. Models that predict the behavior of an undisturbed river system well, but have no ability to be modified to predict the behavior of a dredged river would have very little utility for developing a sediment dredging remediation plan, unless the dredged voids were filled to the rivers original bathymetry. Thus, for a model to have a high utility it must be able to answer the relevant questions that are posed to it by decision makers.

The acceptance of a model can be thought of as how well the model's use is accepted by different agencies, public interest groups and the scientific community. In many respects, this is the most important issue to address when developing a model to be used as a decision-making tool for any purpose. There is no real quantifiable measure of the degree of model acceptance, other than that none of the constituencies stated above object to its use as an aid in developing and evaluating remediation strategies. If a model is found to have both high accuracy and high utility, it should readily follow that the model would have a high acceptance. However, for a variety of reasons, this may not be the case (Tracy, 1995), since model acceptance is primarily governed by socio-political behavior.

Thus, this review will focus on the first two issues listed above, these being the accuracy and the utility of the DNR and LTI models that predict the fate of PCBs in the Lower Fox River below DePere Dam. Under the first issue, model accuracy, there will be three main topics addressed, these being:

- 1. The deficiencies that exist in each of the model descriptions of the physical processes that determine the fate of PCBs in the Lower Fox River;
- 2. The deficiencies that exist in the numerical solution procedures used in each of the models that describes the fate of PCBs in the Lower Fox River; and
- 3. The robustness of the model calibration procedures for each of the models that describes the

fate of PCBs in the Lower Fox River.

Under the second issue, model utility, the general utility of using each of the models for predicting the impact that remediation alternatives will have on the long-term export of PCBs to Green Bay and the long-term concentration of PCBs in the water column and river sediments will be discussed.

## 2.2 Accuracy of Existing Models

#### 2.2.1 Physical Process Descriptions

Figure 6 provides a schematic representation of the fate of PCBs in a riverine environment. For an environment such as the Lower Fox River below DePere Dam, where the largest mass of PCBs resides in the river sediments, the most significant processes that must be accurately represented are the settling of sediments, the resuspension of sediments, the deposition or erosion of deep sediments, the diffusion of PCBs into the water column, burial at depth and disinternment from depth. As such, both the DNR and LTI models' representation of these processes are discussed below.



**Figure 6**. Schematic representation of major mechanisms governing transport and fate of solids in the Lower Fox River.

#### 2.2.1.1 Sediment Settling

In both the LTI and DNR models, a single variable is used to characterize the settling of suspended solids in the Fox River system. Although this approach might serve as a valid first approximation, the use of a single variable to characterize suspended solids is not adequate for the Lower Fox River system below DePere Dam. Based on the fact that different solid fractions have widely different settling velocities and sorption potential, the solids should at the least be divided into three fractions: coarse inorganics, fine inorganics and fine organics. This breakdown would have two major benefits. First, it would allow the characterization of the different levels of sorption exhibited by each of these types of substrate. Second, it would allow a better representation of sediment-water interactions (i.e., the interplay between settling and scour) because more realistic settling velocities would be employed. An ancillary benefit of using more realistic settling velocities is that it might decrease the need for phenomenological or "apparent" mechanisms such as high "background" resuspension. Such mechanisms are often invoked to allow simpler models to fit observations. In addition, it appears that the abiotic settling rate used in both the DNR and LTI models may underestimate the actual settling rate. A constant abiotic solids settling rate of 1.5 m/day was specified, which (through Stokes law) corresponds to a grain size of about 3 to 4  $\mu$ m. This is much smaller than observed particle sizes.

The settling velocity for biotic solids in the DNR model of the Lower Fox River above DePere Dam was set to a constant rate of 0.05 m/s (Limnotech, 1999a). A settling speed of 0.05 m/sec corresponds to a particle size of 220  $\mu$ m, if the particle were solid and mineral, such as sand. For biotic solids, the densities would be much less (probably two orders of magnitude less) and the size would therefore have to be much greater. For biotic solids, this seems to be a huge settling speed. Since this settling speed was only used in the DNR model of the Lower Fox River above DePere Dam, it is unclear what the impacts of this assumption are on sediment concentrations in the Lower Fox River below DePere Dam. It is possible that this velocity should have been reported as 0.05 m/day and was just a typographical error. However, the value reported for the settling velocity should be confirmed.

#### 2.2.1.2 Sediment Resuspension

As discussed earlier, both the DNR and LTI models utilize the  $\epsilon$ -equation to describe the resuspension of sediments as a function of the shear stress. This resuspension of sediments is

related to the velocity of the overlying water by mechanistic formulations parameterized with laboratory analyses of system sediment (e.g., Gailani et al., 1991; McNeil et al., 1996). This approach should yield a consistent and unambiguous representation of scour under a range of water velocities. Unfortunately, at present the DNR and LTI models either do not adopt this approach or base their results on differing laboratory data. Hence, their scour estimates vary significantly. In addition, the LTI model reports that the maximum velocity in the river channel is approximately 2.5 to 3.0 ft/sec. These velocities correspond to 25 to 38 dynes/cm<sup>2</sup> for method 4 as used in the LTI model (LTI 1999a). However, Figure 4-11 in the same report (LTI, 1999a) shows no shear stresses greater than 15 dynes/cm<sup>2</sup> and the report goes on to further state that for the steady-state simulation all shear stresses are below 15 dynes/cm<sup>2</sup>. This inconsistency in the LTI model must be addressed. In addition, a maximum shear stresses of 15 dynes/cm<sup>2</sup> is very low compared to the work of Gailani et al. (1991).

Limno-Tech (1999a and 1999b) determined values for event-based resuspension parameters from a statistical evaluation of site-specific erosion tests (McNeil, 1994). It appears that some adjustment in the parameters was also made during final model calibration (Limno-Tech, 1999d). Final parameters in the LTI model are presented in Table 3, along with calculated erosion rates for three bottom shear stresses. For comparison, values originally estimated by (McNeil, 1994) are also provided. As shown, the calculated erosion rates for the LTI model (Limno-Tech, 1999d) and for McNeil's estimates (McNeil,1994) are in reasonable agreement with each other (and with Shaker test results) for the lower shear stresses. At a higher shear stress (which would correspond to a high-flow event), however, McNeil's estimated erosion rate is almost four times higher than the calculated rate in the LTI model.

For the LTI model, calculated resuspension rates in the Lower Fox above DePere Dam are considered to be proportional to velocity to the first power (Limno-Tech, 1999a). This corresponds to resuspension being proportional to the bottom shear stress to the one-half power, which seems very low. In model formulations, resuspension rates are more typically considered to be proportional to bottom shear stress to the second or third power. Also, the critical velocity for resuspension is given as 0.6 cm/sec (Limno-Tech, 1999a). This calculates to roughly to a critical bottom shear stress of 10 to 3 dynes/cm<sup>2</sup>, which is a very low value. The resuspension formulation for the Lower Fox River above DePere Dam should be critically reviewed.

Finally, in both the DNR and LTI models, the parameters used to simulate the resuspension of sediments are considered uniform with depth into the bed. It is well known that resuspension/erosion properties of sediments vary greatly and in a non-uniform manner as a function of depth and horizontal location (by orders of magnitude). Because of this, resuspension/erosion properties must be measured as a function of depth at different locations and cannot be simply extrapolated to depth from surficial measurements. In particular, for contaminated-sediment problems in rivers and lakes (as in the Lower Fox River, but also at numerous other locations), it is necessary to know resuspension/erosion properties of sediments at high shear stresses, up to stresses on the order of 50 dynes/cm<sup>2</sup> (5 N/m<sup>2</sup>), and with depth in the sediments, down to a meter or more. Because of the limited usefulness of annular flumes and the Shaker and because of the necessity to measure sediment erosion rates as a function of depth in the sediments and at different locations, Sedflume was devised and constructed and has been used extensively (McNeil et al., 1996; Jepsen et al., 1997, 1998). In particular, erosion rates of sediments in the Fox River were measured by means of Sedflume in July and August 1993. Transport models have been adapted so as to use Sedflume data (Lick et al., 1998; Jones and Lick, 2000). The resuspension velocity was then determined from the observed suspended solids concentration, Cs. Since Cs is a dynamic balance between resuspension and deposition, the "right answer" for Cs can be obtained by arbitrarily changing one or the other variable as long as the second variable is changed accordingly. For example, a particular Cs can be obtained by high values of resuspension and deposition or by low values of resuspension and deposition, as long as they balance to give the observed value of Cs. A consequence of the assumption of low settling speeds (as in the LTI modeling) is that, for calibration, low resuspension velocities and hence low rates and low amounts of erosion are needed. Therefore, the total PCB concentration in the water column must be used as an independent constraint. The release of soluble material, directly from the bed and from particles once in the water column, does not redeposit on the bed, so that the use of a higher-than-realistic resuspension rate will cause exceedences in the water column PCB concentration. This could be one reason the WDNR model overestimates the measured values of PCB concentrations for high flow events.

#### 2.2.1.3 Net Deposition of Sediment

Based on sediment transport computations (Gailani et al., 1991) and bathymetric

measurements, erosion in the DNR model is confined to deeper, mid-channel river sediments during high-flow events, while nearshore sediments are not eroded. According to Figure 4-9 in Limno-Tech (1999d), sediment transport in the DNR model results in net erosion rates of 1-2 cm/yr in a significant portion of the Fox River channel below DePere Dam, while according to the same figure, sediment transport in the LTI model results in net deposition rates of 0-2 cm/yr in the Lower Fox River below DePere Dam. Model specification of net erosion in this portion of the Fox River raises several intriguing questions: Are mechanisms such as intense sediment mixing during high-flow events responsible for contamination of deep sediments in net erosion zones? How has channel dredging and the curtailment of dredging in recent years affected sediment transport patterns and PCB transport in the Lower Fox River? At this time, it is not clear if sufficient information on erosion/deposition rates in the Lower Fox River is available to completely answer these questions. A more complete review of existing information of erosion/deposition rates (e.g., sediment core dating, dredging records, etc.) is needed to determine whether the DNR model or the LTI model provides a more realistic description of erosion/deposition patterns in the Lower Fox River below DePere Dam. In addition, further comparisons of model hindcast results (Velleux et al., 1995) and observed PCB sediment concentrations would be a good next step in these concerns and in judging model performance.

The DNR model computes a net sedimentation of approximately 100,000 Mtons of solids in the Fox River between DePere Dam and Green Bay during the 1989-95 calibration period. Assuming a sediment bulk density of 0.65 g/cm<sup>3</sup> and a sediment surface area of 5 x  $10^6$  m<sup>2</sup> between DePere Dam and Green Bay, a net sedimentation of 100,000 Mtons of solids over the 1989-95 calibration period corresponds to an average sedimentation rate of approximately 0.5 cm/yr. Again, this value seems low compared to reported estimates of 0.6 to 2.5 cm/yr (from radioisotope profiles), 2 to 25 cm/yr (from bathymetry data), and 1 to 4.3 cm/yr (from dredging records) (Limno-Tech, 1999a) In addition, this net sedimentation corresponds to a relatively low solids-trapping efficiency of approximately 10%. For comparison, solids-trapping efficiencies from the previous sediment transport modeling studies of (Gailani et al., 1991) are given as 80% for the 50 percentile flow and a 24% for the 99.7 percentile flow. Since the description of sediment transport processes in the WDNR model draws heavily from the work of (Gailani et al., 1991), the low solids-trapping efficiency for the WDNR model (that is reported in Limno-Tech (1999d)) needs further clarification and proper explanation. Since burial serves as an important mechanism for removing PCBs from the biologically active zone, proper understanding of sedimentation (and solids-trapping efficiency) in the Fox River is critical in projecting the future fate of PCBs. Differences in model sedimentation rates and reported sedimentation estimates need to be critically examined.

#### 2.2.1.4 PCB and Sediment Exchange in the Water Column

In the DNR model, settling and resuspension processes provide a continuous exchange of PCB-contaminated particles between the water column and a 10-cm surficial sediment layer. This implies that particles can settle and be incorporated into the bed during all flow conditions, and that mixing processes in the sediments are sufficiently fast to keep the 10-cm layer reasonably well mixed. At high flows, however, settling particles are less likely to deposit in the bed since they will likely experience a decreased probability of deposition at higher shear stresses. In addition, it is not clear that the assumption of vertically well-mixed surficial sediments is appropriate over short time periods associated with high-flow events. Either a reduced probability of particle deposition or incomplete mixing of surficial sediments will likely result in a decrease in sediment-water column exchange and a decrease in PCB water column concentrations during high-flow events.

An additional sediment resuspension term was used in both the LTI and DNR models to help the models better fit the data. In both models, this term is referred to as "background resuspension." At low and moderate flows, subcritical shear resuspension, defined as background resuspension, is used primarily in calibrating the model to PCB water column data. Background resuspension is expected to have a negligible effect on sediment transport (Velleux et al., 1996). Although both models employ a seasonal varying background resuspension adjustment for calibration, the numerical values used in the DNR model are 1.5 to 3 times higher than those recommended by ECOM-SED. While those in the LTI model are in close agreement (LTI Addendum, 23 Dec. 1999).

The use of background resuspension of particles as a fitting parameter for calibrating chemical flux to the water column in undergoing a change in focus within sectors of the modeling community at this time. Numerous in-bed and across-the-interface processes have been identified that have the theoretical ability to move both particle bound and soluble fractions of
chemical species upward and through the interface very effectively (Thibodeaux, 1996). These processes, which include molecular diffusion with and without sorption, colloid-enhanced Brownian diffusion, erosion, capping, bed-load surface roughness advection and bioturbation, have been ranked numerically as to the magnitude of contribution of trichlorobiphenyl release to the water column (Reible et al., 1991). Erosion and bioturbation were equivalent in magnitude and the most rapid processes behind bed-load transport. Laboratory investigation on the release rates of three PNAs (Reible et al., 1996) and measurements of biodiffusion coefficients using tubificid oligochaets are in agreement with reported field measurements of this parameter (Thour et al., 1995). Sediment profiles of <sup>200</sup>Pb and <sup>234</sup>Th/<sup>228</sup>Th, for example were used to obtain bed particle mixing coefficients. Biodiffusion of particles are 100 to 1,000 times more rapid than molecular diffusion in the transport of soluble material from the bed. In addition, the predicted magnitude variations in the biodiffusion coefficient correspond to the seasonal variability that tracks the water temperature (Thibodeaux, 2000). River models developed and/or are under development contain a non-particle resuspension, seasonally varying soluble PCB release mass transfer process. For the Hudson River, these models include that of QEA for General Electric (QEA, 1999) and that of LTI for EPA (Tams et al., 2000). Both these efforts rely upon the field data collected under low-flow, non-particle resuspension conditions across the Thompson Island pool section of the Hudson River.

It should be noted, however, that background resuspension and biologically enhanced diffusive exchange may have different effects on PCB congener distributions (with background resuspension acting on particulate PCBs and affecting all PCB congeners, and diffusive exchange acting on dissolved PCBs and preferentially affecting low-chlorinated PCBs).

At present, both the LTI and DNR models simulate total PCB. It must be recognized that use of a composite total PCB introduces some uncertainty into the analysis. This uncertainty results from lumping all PCB into a single variable and hence not accounting for the differing properties of the component fractions (e.g., sorption, decomposition kinetics, etc.). Efforts to greatly refine the transport mechanisms must be somewhat tempered by the crudeness of the chemical characterization. This also applies to the uncertainties represented by both the initial conditions and the model-forcing functions. Since the DNR model is calibrated to simulate the transport and fate of total PCBs, it is not possible to distinguish between the biologically enhanced diffusion and background resuspension processes. The use of background resuspension, biologically enhanced diffusive exchange, or some combination of the two appears to be a reasonable approach for calibration of a total PCB model if we can safely assume that congener distributions are not changing in time. Observed congener distributions should be examined to check this assumption. If congener distributions are changing in time, serious consideration should be given to PCB congener-specific (or PCB homologue-specific) modeling.

According to Limno-Tech (1999d), background resuspension rates are given as 4 mm/yr (Dec-Mar) and 36 mm/yr (Apr-Nov). This results in 93.7% of the total resuspension flux in the Lower Fox River below DePere Dam occurring at flows less than 188 m<sup>3</sup>/sec (i.e., as background resuspension). This result is surprising, and we hope that someone with more site-specific knowledge of the Lower Fox River can confirm or refute the validity of this claim. It may be that background resuspension rates, which are obtained from model calibration, are too high. An alternative explanation of the TSS and PCB water column data can probably be obtained by specifying two or more particle size classes, with particles of low settling velocities passing through the Lower Fox River during low-flow periods.

Because the resuspension-deposition model by itself does not fit the data on suspended solids concentration, the LTI model uses a seasonally dependent background, non-flow-dependent solids-resuspension term. This wording of "background resuspension" may be incorrect and misleading. What is observed is low to moderate suspended sediment concentrations under low-flow conditions. The reasons for these "background" concentrations are: that (a) suspended solids generally consist of a wide range of particle sizes from coarse sands to fine-grained (almost colloidal) clays, algal particles and organic colloids from the bed; and (b) fine-grained particles have very low settling speeds and stay in suspension for long periods of time. It is these fine-grained particles being transported through the system with negligible settling that are responsible for the low to moderate suspended sediment concentrations during low-flow conditions. As discussed earlier, a better method to simulate this conditions is through the speciation of solids into separate abiotic and biotic size classes.

#### 2.2.2 Numerical Approximations

A variety of numerical approximations are used in both the LTI and DNR models. Of these, the three approximations that appear to be the most critical in relation to predicting the fate and export of PCBs in the Lower Fox River system are: (1) the tracking of the vertical distribution of PCBs in the river sediments; (2) the representation of the stream bottom topography; and (3) the approximation of the Lower Fox River system boundary conditions below DePere Dam.

The DNR model uses a coarse Eulerian representation to characterize the vertical distribution of PCB in the sediment bed. It includes relatively thick, well-mixed layers to represent the strata just below the surface sediment layer. This representation results in significant numerical mixing that can artificially introduce deep contaminated sediments to the surface. Subsequent resuspension and diffusion can then lead to introduction of buried PCBs into the overlying water column.

Particle mixing via mechanisms such as bioturbation are typically isolated to the surface sediment layer. This surface layer is on the order of approximately 10 to 30 cm or 4 to 12 inches (Berner, 1980). Below this horizon, particle mixing is minimal, as the system is considered to be a compacting or consolidating environment. Bioturbation should be modeled explicitly and (a) the mixing must be restricted to the upper well-mixed layer (not in all layers as it is now), and (b) the thickness of this layer must be accurately determined since the thickness of this layer has a significant effect on long-term PCB fate when bioturbation is invoked as a major mechanism. The importance of bioturbation bed-sediment release process in the Lower Fox River must be established. This can be done by a series of field and laboratory investigations involving radioisotope profiles and box cores. Such work should be performed to verify the parameterization presently employed in the LTI model that characterizes the so-called pore water release soluble quantity.

The LTI model represents the deeper sediment in a Lagrangian fashion that effectively eliminates artificial mixing below the surface layer. Analysis by Limno-Tech suggests that this modification results in a 30% drop in PCB export to Green Bay relative to levels predicted by the previous model.

Although the precise magnitude of the effect of the artificial mixing of river bottom sediment in the DNR model is subject to question, this is clearly an artifact that can and should be corrected. It is important to note that the problem of artificial mixing of the river bottom sediments in the DNR model does not affect sediment transport results, only predictions of PCB

flux to the water column and eventually export from the Lower Fox River system into Green Bay. In addition, this numerical mixing will have a smaller impact on short-term simulation results (e.g., calibration runs), but will have a profound effect on long-term simulation results (e.g., 25-year projections).

For the models to evaluate dredging, they must be capable of predicting how physical manipulation of the bed impacts future deposition of PCBs from upstream sources. In essence, digging a hole in the bottom may create a low-energy void that will be preferentially filled by PCBs carried from upstream sources by future high-flow events. If the remedial strategy involves filling the dredged site with clean fill back to the original level, this could be less of an issue. However, if fill is not used to return the bottom to its original topography, it is uncertain whether the existing models would be capable of simulating future deposition correctly.

The DePere Dam serves as the upper boundary for the LTI model. This means that temporally varying boundary conditions for both solids and PCBs must be specified at this point. However, sparse solids and PCB data are measured at DePere during high flow; this means that the model's more important external forcing function exhibits a significant level of uncertainty. The DNR model uses as input for its prediction in the Lower Fox River below DePere Dam output of the model of the Fox River above DePere Dam for both total suspended solids and PCBs. This is a problematic issue for both calibration and prediction. As they say in the computer industry, "Garbage In, Garbage Out." It would therefore seem prudent to extend the LTI model to a "clean" point upstream of the major deposits and inputs of PCB.

#### 2.2.3 Model Calibration

Supposing for the moment that perfect information regarding solids input were available, the fate of strongly sorbed sediment PCB is dictated by the interplay between settling, scour and burial. Unfortunately, because only two mass balances are available (for the river and the surface sediments), only two of these processes can be estimated independently by calibration to data. Further, the calibration data (in particular the river suspended solids concentration) are quite difficult to observe, particularly under high-flow conditions. As a consequence, both the LTI and DNR models have excess degrees of freedom and can adopt different parameterizations to arrive at comparable fits of short-term (several years) data time series. It is only when long-term predictions (decades) are made that the model predictions diverge because of the differences in the "up-down" characterizations.

To progress beyond this ambiguous state of affairs, it is necessary to constrain one of the "up-down" processes. This is most commonly done by fixing the transfer to the deep compacting sediments. To do this, it is necessary to have adequate observations to establish whether long-term deposition or erosion is taking place at each model segment.

Published work on the Fox River (Velleux and Endicott, 1994; Velleux et al., 1995; Velleux et al., 1996) has focused on PCB water column concentrations for model calibration and for model performance evaluation. Since there is a fair degree of uncertainty in setting sediment-water exchange rates (e.g., settling, background and event-based resuspension, biologically enhanced diffusive exchange) in model calibration, comparisons of model results to PCB water column data do not necessarily constitute a rigorous confirmation of model performance, and further testing of PCB-contaminated sediment projections is needed. In WDNR (1997), a comparison of 1989-95 model simulation results and 1995 observed PCB sediment concentrations is presented in Figure 9 of that report for river sediments below DePere Dam. As shown, model results for the 0 to 10 cm and 10 to 30 cm sediment layer appear to under predict observed values by 40 to 50%. The PCB sediment comparison is clearly not as convincing as the PCB water column results and raises concerns of how well the model is describing the longer-term transport and fate of PCBs in the Fox River. More effort should be given to PCB sediment comparisons in evaluations of model performance.

The DNR model was calibrated to total suspended solids (TSS) and water column PCBs at DePere Dam and at the mouth of the Fox River. Temporal plots (e.g., Figure 4 in Velleux and Endicott (1994); Figure 4 in Velleux et al. (1995); and Figure 7 in WDNR (1997)) and statistical evaluations (e.g., Figures 5 and 6 in Velleux and Endicott (1994); and Figure 8 in WDNR (1997)) show reasonable agreement of model results with field data. It is important to note, however, that the DNR model appears to over predict water column PCB concentrations during high-flow events (e.g., during the May-June 1989 high-flow event as shown in Figure 4 of Velleux et al. (1995) and during the during the April 1998 high-flow event as shown in Limno-Tech, (1999c)). Possible reasons for the model's apparent over prediction of water column PCB concentrations are: (1) difficulty in predicting the timing of the PCB concentration spike and in collecting representative field data during high-flow events; and (2) the model's description of

settling-resuspension, which allows for continuous exchange between suspended solids and a 10 cm surficial layer of PCB-contaminated sediments. Since a large portion of the PCB export to Green Bay is expected to occur during high-flow events (Velleux and Endicott, 1994), proper calibration of the model during high-flow events is a critical concern for using the model for long-term predictions of the fate of PCBs in the Lower Fox River.

Model calibration for the Lower Fox River below DePere Dam was performed using an iterative procedure with settling velocity, background resuspension, pore water-water column exchange, and pore water diffusion between the top two layers treated as adjustable parameters. From this procedure, the settling velocity for total suspended solids is determined to be 1.5 m/day. Background resuspension, pore water-water column exchange, and pore water diffusion between the top two sediment layers are affected by ice cover and bioturbation and are adjusted seasonally. Final values are given as 4 mm/yr (Dec-Mar) and 36 mm/yr (Apr-Nov) for background resuspension; 4 cm/day (Dec-Mar) and 20 cm/day (Apr-Nov) for pore water-water column exchange; and 0.4 cm/day (Dec-Mar) and 2 cm/day (Apr-Nov) for pore water diffusion between the top two sediment layers (Limno-Tech, 1999d). According to Figures 5-1 through 5-6 in Limno-Tech (1999a), the model is calibrated reasonably well for TSS and water column PCBs above DePere Dam. There does, however, appear to be a somewhat consistent under prediction of TSS during high-flow events. Statistical testing should be performed to see if there is any bias in the model-field data comparisons.

The LTI model results compare reasonably well to field data for TSS and PCB water column concentrations at the mouth of the Fox River (Figures 4-5 and 4-6 in Limno-Tech (1999d)). The model, however, appears to under predict TSS during high-flow events. Also, based on material presented by David Glazer (QEA) at the February meeting, PCB water column results at the Fox River mouth are closely linked to PCB concentrations coming over the DePere Dam. Since PCB water column concentrations at DePere Dam were specified based on empirical relationships in the current model simulations (Limno-Tech, 1999d), current model simulations for the Lower Fox River below DePere Dam do not seem to be a critical test of model performance.

Since the primary interest in PCB modeling is PCB mass exposure concentrations and PCB mass export to Green Bay, the use of 'Mean Relative Absolute Error' does not appear to be

an appropriate statistic to judge model performance (e.g., see Tables 4-3 and 4-4 in Limno-Tech (1999d)). The problem with 'Mean Relative Absolute Error' is that it gives relative errors for high and low concentrations equal importance. Errors associated with higher concentrations, however, should be given more weight in determining the model's ability to calculate mass exposure concentrations and mass export.

Comparison of Model Results to PCB Sediment Data: The PCB sediment response in Figure 4-8 (Limno-Tech, 1999d) appears to be largely driven by the specification of the upstream boundary condition for PCBs at DePere Dam. The decrease in computed PCB sediment concentrations is given with a half-life of seven years and is similar to the decrease of PCBs at DePere Dam ( $t_{1/2} = 10$  years). Also, there are no direct comparisons of model results and PCB sediment concentrations presented for the LTI model.

## 2.3 Utility as Decision-making Tools

The final issue that must be addressed for both the LTI and DNR models is "Are the models good enough for use in developing remediation plans for the Lower Fox River below DePere Dam?" To be able to answer this question, the ability of each model to assess the impacts of the three remedial actions discussed earlier in this report must be addressed, these being: natural recovery, dredging, and capping.

Implicit in understanding the impacts of each of these remediation options is the idea that nature is highly variable and, over any extended period of time, there will be periods of low flows followed by short periods of high flows. Most sediment and contaminant transport occurs during periods of high stream flows and winds. Although these periods are infrequent and short lived, they tend to dominate the overall transport of sediment and contaminants (Lick, 1992; Lick et al., 1994). This high variability must be considered in the modeling and its effects calculated accurately. At the current time, there are not substantial enough data sets on PCB and total suspended sediment concentrations during high-flow events in the Lower Fox River to be able to accurately calibrate either model. Thus, neither the LTI nor DNR model can be said to accurately represent the fate of PCBs and sediments during these critical flow periods in the Lower Fox River.

As of now, models by these two groups disagree to more than an order of magnitude as far as depth of erosion is concerned. In a previous review of modeling work of the Lower Fox River by a group of scientists convened by the Fox River Advisory Panel, Science and Technical Advisory Committee, the consensus document summarizing the meeting (Barker and Kennedy, 1998) stated, "Despite our best attempts at modeling ecosystems, there is considerable uncertainty in predicting sediment resuspension and deposition, food chain interactions, and changes in fish tissue PCB concentrations over decades." In regards to predicting the resuspension, deposition and export of sediment and PCBs from the Lower Fox River, this review panel still finds considerable uncertainty exists in predictions provided by both the LTI and DNR models, thereby limiting their utility as decision-making tools at the present time.

## **3.0** Summary and Recommendations

## 3.1 Summary

At present, there is a large data base, several models, and a great deal of associated modeling expertise that has been marshaled to address the Lower Fox River PCB problem. With sufficient modification and scientific cooperation, these frameworks could provide a consistent vision of system response that would prove useful in informing the decision-making process. Unfortunately, the "real" differences among the frameworks are somewhat obscured by the various groups' assumptions, algorithms and calibration protocols. In essence, the models have been verified or corroborated in a somewhat ad hoc fashion that detracts from their credibility.

The intensive study of Fox River PCBs is now moving from an annual to a decadal scale. As a consequence, the system's long-term natural recovery is emerging from the observational "noise" (e.g., the half-life of PCB in fish tissue being on the order of 10 years). By using such information as an additional constraint on the calibration/corroboration process, the individual models should be less likely to arbitrarily "go their own way."

Further, it seems that if improvement is actually occurring with an approximately 10-year half life, perceptible changes might be observable in sediment cores from the inner Green Bay. This might represent an additional constraint on the modelers' long-term analyses. For example, if two models exhibit grossly different claims as to export to Green Bay, one way to assess the correct answer might be to compare these claims to what is actually being deposited in the Bay.

In other words, an observational picture of the "real" long-term response of the Lower Fox River is emerging. Models that reproduce this long-term response would have much greater credibility when employed for extrapolation.

However, at the present time there is not a single "best" model that is ready to perform the decision-making duties required of these models related to evaluating remediation alternatives in the Lower Fox River. However, the modeling groups could modify and recalibrate their frameworks to yield more consistent predictions of the Lower Fox River's future state. This could be accomplished through the use of a consensus modeling approach. The resulting model would be extremely useful in informing decision makers as they weigh alternatives for system cleanup.

#### 3.2 Modeling Recommendations

Regardless of whether a consensus modeling approach is followed, there are many specific recommendations that can be made at the present to time-modify the existing DNR and LTI models to increase their decision-making utility. These recommendations are given below.

- The DNR model should adopt a numerical integration scheme that avoids the artificial mixing of deep sediments into the shallow sediment zone of the river bed.
- The upstream boundary of both the LTI and DNR models should be extended to a section above the beginning of major contaminated sediment deposits in the Lower Fox River.
- Both the LTI and DNR models should employ multiple size classes for solids so as to predict the correct deposition rates. At a minimum, three types of solids should be included, these being: fine inorganic, coarse inorganic, and organic solids.
- Data on particle size distribution for incoming flows (as input data for the model)) and for the outflow (as part of the calibration and verification process) must be obtained. This is crucial for the accurate prediction of solids transport and deposition. At present, no data of this type are available, and these measurements can be accomplished relatively easily. One year of would be useful. With this, even previous data on flows and solids concentrations could at least be interpreted more accurately.
- A mechanistic resuspension mechanism related to water shear based on the most current scientific understanding and laboratory analyses of the Lower Fox River sediments should be employed by both the LTI and DNR models. In addition, the effects of high-flow events on sediment mixing (e.g., as suggested by erosion (and subsequent deposition of sediments) in the SEDFLUME experiments of McNeil (1994) and McNeil et al. (1996)) may require an explicit description of surficial and deeper sediment mixing during high-flow events. These mixing events could potentially play an important role in allowing buried PCBs to re-enter the biologically active zone. Before implementing additional sediment mixing processes in the model, Fox River sediment cores should be re-examined for evidence to confirm that such mixing events have occurred during previous high-flow events.
- Variations in sediment properties (especially erosion rates) with sediment depth and horizontal location must be taken into account. This is necessary to: (a) determine whether a particular location is erosional or depositional; and (b) if it is erosional, to determine to what

depth a large flood will erode the sediments.

- Re-evaluate spatial patterns of sedimentation in the Lower Fox River. Specifically, consider how sedimentation rates may have been affected by the curtailment of channel dredging, and how sedimentation patterns will be affected in the future by remedial dredging projects.
- If dredging operations were to occur, the initial dredging operations should serve the ancillary benefit of an experiment to assess the immediate environmental impact of dredging (i.e., how much sediment PCB is actually liberated from the mechanical act of dredging). Further, if the system were monitored during and immediately following dredging, the results might clarify the additional repercussions of the remedial action.
- There is wide disagreement between the LTI and DNR models related to the action of bottom organisms on sediment particle mixing and sediment-water transport. A review of available information as well as additional measurement of bottom organism density, and depth and magnitude of bioturbation should be conducted to reduce this uncertainty. At present, the model assumes a 10-cm surficial sediment layer that is vertically well mixed by physical processes and/or bioturbation. Actual mixing particles by benthic organisms may not be fast enough to keep the top 10 cm of sediment well mixed over short time periods (e.g., during high-flow events) and a more explicit description of sediment mixing (e.g., 1-cm sediment layers with defined particle mixing rates between each layer) may be necessary.
- All of the models must employ the same data sets during model development, calibration and testing. In particular, some consensus as to the depositional/erosional nature of the river has to be agreed upon. At the present time, there appears to be wide disagreement on characterizing this mechanism amongst the modeling groups. In addition, robust sets of statistical measures for evaluating the performance of the models must be developed and adhered to when judging the utility of the models.
- To date, model calibration and model performance evaluation have focused largely on PCB water column concentrations and sediment-water column exchange rates. Although these efforts have been very useful in addressing PCB export to Green Bay, they do not appear to be sufficient in assessing human and ecological risks in the Fox River. Assuming that PCB concentrations in fish are directly linked to surficial sediment concentrations (e.g., through the use of BSAFs), the model needs to do a more convincing job in projecting PCB

concentrations in the biologically active zone of the Fox River sediments below DePere Dam. Toward this end, the following tasks should be considered.

- All models used for decision making should be subject to sensitivity analysis to assess their robustness and sensitivity to their underlying assumptions, boundary conditions and initial conditions. Such an approach was employed in the QEA model presentation at the February 3, 2000, meeting in Green Bay. The panel found this presentation highly illuminating regarding the effectiveness of the model in explaining the observations.
- At a certain point, some consideration should be given to the computational efficiency of each of the frameworks. Efficiency could prove extremely useful to decision makers by allowing them to rapidly evaluate many scenarios in a cost-effective manner. If highly efficient algorithms could be developed, an uncertainty analysis might be performed to estimate the uncertainties connected with model projections.

# 4.0 References Cited

- Ager, D.V., 1981. *The Nature of the Stratigraphical Record*, John Wiley and Sons, New York.
- Barker, N. and J. Kennedy, 1998. Letter from the Science and Technical Advisory Committee for The Fox River and Green Bay to G. E. Meyer, Secretary, Wisconsin Department of Natural Resources, April 30, 1998.
- Berner, R.A. *Early Diagenesis, A Theoretical Approach*. Princeton University Press, Princeton, NJ.
- Brown, B.A., 1986. "Bedrock geology," In Krohelski, J.T., *Hydrogeology and Groundwater Use and Quality, Brown County, Wisconsin.* Wisconsin Geological and Natural History Survey, Information Circular 57..
- Clayton, Lee, Attig, J.W., Mickelson, D.M., and Johnson, M.D., 1992. *Glaciation of Wisconsin*. Wisconsin Geological and Natural History Survey, Educational Series 36.
- Erickson, M.D., 1997. Analytical Chemistry of PCBs. Lewis Publishers, New York.
- FRG, 1999. Sensible Solutions for the Fox River, Fox River Group.
- Gailani, J.Z., Ziegler, K., and Lick, W., 1991. "Transport of suspended solids in the Lower Fox River." J. Great Lakes Res. 17, pp. 479-494.
- Jepsen, R., J. Roberts, and W. Lick, 1997. *Long Beach Harbor Study*, Rept. to U.S. Army Corps of Engrs., Los Angeles District.
- Jepsen, R., J. Roberts, D. Gotthard, and W. Lick, 1998. *New York Sediment Study*, Rept. to U.S. Army Corps of Engrs., New York District.
- Jones, C. and W. Lick, 2000. "Effects of bed coarsening on sediment transport," to be published, *Estuarine and Coastal Modeling*.
- Klussendorf, J. and Mikulic, D.G., 1989. "Bedrock geology of the Door Peninsula of Wisconsin," In Palmqiuist, J.C., *Wisconsin's Door Peninsula*; Appleton, WI, Perin Press, 12-31.
- Krohelski, J.T., 1986. *Hydrogeology and groundwater use and quality*, Brown County, Wisconsin. Wisconsin Geological and Natural History Survey, Information Circular 57, 42 pp.
- LaBerge, G.L., 1994. *Geology of the Lake Superior Region*. Phoenix, Geoscience Press, 313 pp.
- LeRoux, E.F., 1957. *Geology and groundwater resources of Outagamie County*, Wisconsin: U.S. Geological Survey Water Supply Paper 1421.
- Lick, W., 1986. "Modeling the transport of fine-grained sediments in aquatic systems," *The Science of the Total Environment*, 55, pp. 219-228.
- Lick, W., 1992. *The Importance of Large Events, in Reducing Uncertainty in Mass Balance Models*, Great Lakes Monograph, No. 4.
- Lick, W., J. Lick and C. K. Ziegler, 1994. "The resuspension and transport of fine-grained sediments in Lake Eries," *J. Great Lakes Research*, 29, pp. 599-612.
- Lick, W., C. Jones, and Z. Chroneer, 1998. "A predictive model of sediment transport," *Estuarine and Coastal Modeling*, pp. 389-399.
- Limno-Tech, Inc. and WDNR, 1998. *Model Evaluation Workgroup Technical Memorandum* 1: Model Evaluation Metrics.

- Limno-Tech, Inc. 1999a. Fox River and Green Bay PCB Fate and Transport Model Evaluation, Technical Memorandum 2b Computation of Watershed Solids and PCB Load Estimates for Green Bay.
- Limno-Tech, Inc. 1999b. Fox River and Green Bay PCB Fate and Transport Model Evaluation, Technical Memorandum 2c –Computation of Internal Solids Loads in Green Bay and the Lower Fox River.
- Limno-Tech, Inc. 1999c. Development of an Alternative Suite of Models for the Lower Fox River.
- Limno-Tech, Inc. 1999d. Fox River and Green Bay PCB Fate and Transport Model Evaluation, Technical Memorandum 5a Development oand Application of a Sediment Erodibility Study.
- Marti, E.A. and Armstrong, D.E., 1990. "Polychlorinated biphenyls in Lake Michigan tributaries," *Journal of Great Lakes Research*, 16: 396-405.
- Martin, L., 1916 (reprinted 1965). *The Physical Geography of Wisconsin*. Madison, University of Wisconsin Press.
- McCartney, M.C. and Mickelson, D.M., 1982. "Late Woodfordian and Greatlakean history of the Green Bay Lobe," *Geological Society of America Bulletin*, 93, pp. 297-302.
- McNeil, J., C. Taylor, and W. Lick, 1996. "Measurement of the erosion of undisturbed bottom sediments with depth," *J. Hydraulic Engineering*, 122, pp. 316-324.
- McNeil, J. 1994. *Measurements of the Resuspension and Erosion of Sediments in Rivers*. Ph.D. Dissertation, University of California at Santa Barbara.
- Mella, K. and Billings, C., 1999. "Dredging resumes at deposit N and begins at SMU 56/57," *Fox River Current*, pp. 1-14.
- Mudrey, M.G., Brown, B.A., and Greenberg, J.K., 1982. *Bedrock Geologic Map of Wisconsin*. University of Wisconsin-Extension, Wisconsin Geological Survey map.
- Need, E.A., 1985. *Pleistocene geology of Brown County, Wisconsin*. Wisconsin Geological and Natural History Survey Information Circular 48.
- Piette, C.R., 1963. *Geology of the Duck Creek ridge, East Central Wisconsin*. University of Wisconsin, Madison. M.S. thesis.
- Post-Crescent, 1999a. *Fox River PCB Timeline*. WISinfo Network. Internet Access: wysiwyg://121/http://www.wisinfo.com/postcrescent/pcb/022699-2.html
- Post-Crescent, 1999b. *Three-Part River Study Unprecedented*. WISinfo Network. Internet Access: wysiwyg://118/http://www.wisinfo.com/postcrescent/pcb/022699-3.html.
- QEA, LLC. 1999. *PCBs in the Upper Hudson River. Vol.* 2 A Model for PCB Fate, *Transport, and Bioaccumulation.* Report to General Electric. Albany, NY.
- Reible, D. D., K. T. Valsaraj and L. J. Thibodeaux 1991. Ch. 3 in Handbook of Environmental Chemistry, Vol. 2 Part F, "Reactions and processes," O. Hutzinger (Ed.), Springer-Verlag GmbH. Germany, 1991; pp. 185-228.
- Reible, D.D., V. Popov, K. T. Valsraj. 1996. "Contaminant fluxes from sediment due to turbificid oligochaete bioturbation," *Water Research*, 30, pp. 704-714.
- Schultz, G.M., 1986. *Wisconsin's Foundations: A Review of the State's Geology and its Influence on Geography and Human Activities*. Kendall/Hunt, Board of Regents of the University of Wisconsin System.
- Swackhamer, D.L. and Armstrong, D.E., 1987. "Distribution and characterization of PCBs in

Lake Michigan water," Journal of Great Lakes Research, 13: 24-37.

- TAMS Consultants, Inc., Limno-Tech, Inc. Menzi-Cura and Associates, Inc. and TetraTech, Inc. 200. *Revised Baseline Modeling Report – Hudson River PCBs Reassessment RI/FS – Volume 2D*. Prepared for USEPA Region 2 and USAE Kansas City District, USEPA, NY, NY.
- Thibodeaux, L. J. 1996. *Environmental Chemodynamics*, Chapter 5, John Wiley Publ. N.Y., N.Y.
- Thwaites, F.T., 1943. "Pleistocene of part of northeastern Wisconsin," *Geological Society of America Bulletin*, 54, pp. 87-144.
- Thwaites, F.T. and Bertrand, K., 1957. "Pleistocene geology of the Door Peninsula, Wisconsin," *Geological Society of America Bulletin*, 68, pp. 831-879.
- Thour, S. R, G. Matisoff, P. L. McCall and X. Wang, 1995. *Models for Alteration of Sediments by Benthic Organisms, Final Report.* Project 92-NPS-2, Water and Environment Research Foundation, Alexandria, VA.
- Tracy, J. C., Zarta, D. and Scherer, M., 1995. "Assessment of modeling approaches in developing a water rights administration tool," Published in the *Proceedings of the 1995 American Water Resources Association Annual Meeting and Symposium, Advances in Model Use and Development of Water Resources*, November 5-9, 1995, Houston, TX, pp. 71-80.
- Tsai, C.H. and W. Lick, 1986. "A portable device for measuring sediment resuspension," J. of Great Lakes Research, 12, pp. 314-321.
- U.S. EPA, 1996. *Public Health Implications of PCB Exposures*. The Agency for Toxic Substance and Disease Registry and the U.S EPA Region 5. Internet Access: http://www.epa.gov/region5/foxriver/lower\_fox\_river\_PCB\_Exposures.html.
- U.S. EPA, 1997. *Fact Sheet, U.S. EPA's Superfund Role.* Lower Fox River Cleanup, U.S EPA Region 5, Chicago, IL.
- U.S. EPA, 1998a. Fact Sheet, Contaminated Sediments, U.S. EPA Region 5, Chicago, IL
- U.S. EPA, 1998b. Fact Sheet, PCBs: Lower Fox River Impacts, U.S. EPA Region 5, Chicago, IL.
- U.S.G.S, 1998. *Fox River PCB*. U.S.Geological Survey.
- U.S.G.S., 1992. Flood Frequency Characteristics of Wisconsin Streams. U.S. Geological Survey, 91-4128.
- Velleux, M. and Endicott, D., 1994. "Development of a mass balance model for estimating pcb export from the Lower Fox River to Green Bay," *Journal of Great Lakes Research*, 20, pp. 416-434.
- Velleux, M., Endicott, D., Steuer, J., Jaeger, S. and Patterson, D., 1995. "Long-term simulation of PCB export from the Fox River to Green Bay," *J. of Great Lakes Research*, 21, pp. 359-372.
- Velleux, M. J. Gailani, and D. Endicott, 1996. "Screening-level approach for estimating contaminate export from tributaries," *J. of Environmental Engineering*, 122, pp. 503-514.
- WDNR, 1997. Polychlorinated Biphenyl (PCB) Contaminated Sediment in the Lower Fox River: Modeling Analysis of Selective Sediment Remediation. PUBL-WT-482-97, Wisconsin Department of Natural Resources Bureau of Watershed Management.

# Appendix A

# **Review Comments of Dr. James Bonner**

(Documents referenced in reviews are listed in reference section of main text)

## **Review of Fox River Remedial Strategy Assessment**

**Objectives:** To review and comment on the Fox River Remedial Investigation/Feasibility Study (RI/FS). The specific objectives of this review are to comment on the efficacy of models used as assessment tools in this study.

A Fox River RI/FS meeting was conducted on 2/3/2000 in Green Bay WI to provide a status report and summary for panel reviewers and public. An overview of RI/FS model assessment tools developed by the interested parties was presented. The presentations focused on 3 primary modeling efforts. The first was the QEA model presented of behalf of the Fish and Wildlife. The second was the LTI model presented on behalf of the Fox River Group and the third was WDNR model presented on behalf of the WDNR. (For review prior to this meeting see below.) This meeting was very insightful. I learned new things that were not covered in the literature that I had been sent or material summarized during the previous presentation in Appleton WI. on 12/10/2000.

1) More then one modeling effort has been conducted for the RI/FS on the Fox River.

The RI/FS modeling effort has been an evolving process. The first model was the WDNR model that represents the preliminary assessment. The second was further advanced by LTI and corrected some mathematical problems and refined some of the environmental processes. The LTI modeling incorporated field data regarding sediment erodibility. The third model developed by QEA represented the greatest and most refined environmental process mechanism representation, but, was somewhat limited by the level of data assimilation due to limited fiscal resources. During the meeting it was indicated that a fourth modeling effort was underway but little or no details have been presented.

2) Comment regarding flaw in logic of depositional river directed towards LTI project.

In my first review and during the first meeting I commented to LTI regarding issues with reduced or eliminated sediment resuspension allowing a natural attenuation (complete sequestering of contaminant in sediment) conclusion for the RI/FS. I stated in the first review that in the absence of anthropogenic forcing (e.g. alteration of the river channel due to dredging, restructuring or routing of the channel or flow obstruction by dams and impoundments) that reduced resuspension was not possible (if it was resuspended once to produce a void volume it should be able to be resuspended again). LTI researched this question and provided additional information indicating that the channel had been altered by dredging and channel alteration thus providing some scientific justification for "protected" depositional zones that may resist resuspension while the channel alteration is in place. While, I commend LTI for finding this additional information, this kind of investigation should be continued and further researched to validate LTI conclusions.

3) QEA presented data showing the loading of PCB into the Lower Fox River over DePere Dam is currently approximately equal to the PCB discharged from the month of the Fox River into Green Bay. This information needs to be confirmed, but, if true indicates that no further remediation to the Lower Fox should be attempted until the upper river discharge is significantly reduced. QEA also discussed model uncertainty. Their model applied to the Fox River is probably more constrained then either the WDNR or the LTI model. Despite this fact they showed that they could calibrate their model so that two opposing conclusions could be generated (see discussion below regarding over determined models). This was an important finding and confirmed some of my previous concerns. This indicates that what ever model is chosen it must be viewed as a data assimilation tool and not as a definitive representation of the system. This means that to calibrate and apply these models will require model judgment and consensus regarding model input, forcing functions loading and model coefficients. It needs to be recognized that this kind of tool can only be used to provide course question inquiry. For example one may be able to ask question regarding what impact would occur if all the contaminated material was removed, but one would not be able to ask which areas should be dredged or not dredged. This kind of question requires a more highly constrained model with more accurate process representation.

4) WDNR presented new data regarding ACOE transects. This data was very interesting because it showed that very significant sediment depth at various locations could be scoured (as much as 2-3 meters in some areas). The accuracy and validity of these data is suspect and therefore must be determined. If it turns out to be correct and valid then one would almost certainly have to reconsider a natural attenuation remedial strategy.

#### Review of Fox River Remedial Strategy Assessment Review of effort prior to meeting held 2/3-4/2000

**Objectives:** To review and comment on the Fox River Remedial Investigation/Feasibility Study (RI/FS). The specific objectives of this review are to comment on the efficacy of models used as assessment tools in this study.

**Background:** Mechanistic models (data driven) were developed and applied to assess remedial strategies associated with the Fox River. Two primary modeling efforts were commissioned. The first conducted by Wisconsin Department of Natural Resources (WDNR) and the second conducted by LTI. Both models were generally the same with respect to the representation of PCB and other state variables, environmental processes and forcing functions. The LTI model addressed a problem of numerical dispersion in the WDNR model involving mixing in the sediment compartment. The LTI model when calibrated, validated and applied generated modeling results that indicated that natural attenuation as a remediation option would sequester PCB in the sediment compartment. It was also concluded that sequestered PCB would reduce further environmental contamination by preventing the spread of the PCB. The WDNR model indicated that the PCB would be released from the sediment compartment, transported to Green Bay and Lake Michigan and would thus be available for increased ecological exposure.

General Comments: The LTI modification (redevelopment) of the WDNR model to reduce numeric dispersion involving the sediment compartment is a good solution to this problem and should be implemented in whatever model is used as an remediation assessment tool. A bigger problem lies in the fact that both models, even though similar in construction and conception, generate opposing results. This is due, in part, to the fact that neither model is adequately constrained (they are both over determined). This is a common problem with this kind of water quality model. The model parameters and process representation is not set so that there is a range of acceptable values for model calibration coefficients. This means that during the calibration process model coefficients (and other parameters) are adjusted so that the difference between model output and observed calibration data is minimized. This can be referred to as a minimization on the model calibration residual. Determining the values used in the model calibration process and often times the minimization of the model calibration residual requires "modeler" (environmental practitioner) judgment. When the model calibration residual is at the minima and if the adjusted parameters are within an acceptable range the model is considered calibrated. The problem with this process for over determined models is best illustrated when one considers the relative magnitude of opposing processes. For example, if a model application has relatively high magnitude resuspension and deposition (e.g. WDNR model) it may be able to predict the same observed total particle mass in the water column and in the sediments compartments as the same model with relatively low magnitude resuspension and deposition (e.g. LTI model) even though these are dominate processes. The difference is in the out come. In the case of the reduced resuspension/deposition scenario the benthos-water column coupling is reduced and the sediment compartment is less dynamic (with respect to other sediment state variables e.g. PCB). This changes what one would conclude by applying the model. This discussion is oversimplified, but illustrative. Other problems occur when coefficients for model calibration are chosen such that local rather than global minima are obtained for the model calibration automation can be accomplished with specialized parameter estimation algorithms (essentially an inverse modeling application Ernest et. al., 1996).

Natural attenuation occurs through sequestering and through destruction/transformation of the contaminant of interest. The LTI approach states that the PCB will be sequestered in the sediment compartment and will not be released because the sediments are not erodable. Before one can conclude the PCB will be permanently sequestered in the sediment compartment a few questions have to be asked. The answers to the question will determine if common sense will change this conclusion.

## **Questions & comments:**

- Is PCB in the environment primarily associated with particles?
- Because of its hydrophobic nature most PCB 90-99.9% is particle bound.
- How did the particle bound PCB get into the sediment compartment?

It most likely settled (was deposited) into the sediment compartment (into void volumes). After deposited it is compacted and buried. In some cases the PCB can be mixed (through molecular diffusion in porous media and biological processes and other sediment mixing processes) downward and upward causing a spreading of the contaminant. These latter processes are sometimes considered less significant than burial and compaction.

If the particulate material was deposited into the sediment compartment it had to settle into a void volume. A portion of the water column near the benthos void of sediments. A place for sediments to accumulate.

If void volume existed it had to be produced through some means anthropogenic or natural (e.g. dredging or river scour).

If it was produce by natural means then it stands to reason that it could be reproduced through natural means unless the river hydraulics have been changed dramatically during the period of deposition. By allowing floodwater to accumulate in water reservoirs the amplitude of high and low flow events is normally reduced due to water shed management. However, if sustained flow is greater then the design flow of the reservoir then managers maybe forced to discharge accumulated water in addition to river flow thus increasing the flow amplitude.

In situations where resuspension has and still can occur it stands to reason that the deposits are susceptible to sediment resuspension. This should be considered when applying the models.

Its been said that in order to model water quality one must wiggle your toes in the water. If you subscribe to this then in order to model floods one needs to wiggle toes in the water during the flood. If one does this it will soon be recognized that many hydrodynamic models will not work to predict sediment resuspension in the river. In real floods houses, trees, refrigerators, cars, ice,

concrete blocks etc get dislodged and moved down the river. This kind of material can form temporary dams in the river forcing flows around the obstacles in the river channel. This can cause temporary local high velocities with corresponding high shear stress.

Even under steady "non-catastrophic" flow regimes I have some problems with the hydrodynamic models and therefore water quality models presented. I have focused my review on the resuspension issues. This is probably the most important process related to the natural attenuation option.

## Specific comments: Development and Application of a Sediment Erodibility Study.

- Table 4.2 Max velocity fps 2.83
- Page 20, Paragraph 4.91, statement "Because it has a stronger theoretical basis than Method 4 the Manning shear stress equation, is recommended.
- Using 2.83 fps (max velocity) in Figure 4.7 and method 4 yields approximately 35 dynes/cm2
- Referring back to Figure 3.1 Lick et. al., 1995 data shows Observed data Applied shear stress (0-10 dyne/cm2) range of relevance for lick methods used.
- Leads to Table 3.1 showing max. resuspension potential of 32.9 and 18.8 mg/cm2
- Question #1 is this the resuspension values used 33 and 19??
- Sequence of tables and figures indicate that this could be underestimated (maybe by factor 7X or so).
- Question #2 What would be the outcome of reducing the biotic solids settling velocity significantly and leaving the abiottic constant while dramatically increasing erosion rate.
- Question #3 What out come does this have on the justification of the natural attenuation remedial option.
- Question #4 What is the outcome of using the limited resuspension equation the so called Lick equation for ε. Does this limit the resuspension to a few centimeters as asserted by Lick (personnel communications).
- Question #5 What is the estimate of PCB mass transported to Green Bay and over the Depere Dam. What the estimate of PCB mass in each depositional area in the lower fox river? What is an estimate of PCB mass in the lower Fox River.
- Question #6 Which if any of the hydrodynamic models allow for bathymetry changes (i.e. change in depth due to erosion of the bed)?
- Question #7 If PCB is removed from the Lower Fox river what would happen to PCB that is continuing to load into the Lower Fox river over the Depere dam. Would this material deposit into recently dredge areas (depositional areas).
- Question #8 Is there a historical record which would indicate that there are depositional zones (low energy areas that form sediment voids where contaminated particles can accumulate) that are now not susceptible to resuspension events (dredge areas, areas protected high shear stress flows by river re-routing due to channel modification)

# Appendix B

# **Review Comments of Dr. Steve Chapra**

(Documents referenced in reviews are listed in reference section of main text)

# Review of

# PCB Transport and Fate Models for the Lower Fox River

Prepared by

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for

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This report provides an assessment of models that have been developed to simulate the fate and transport of solids and PCBs in the Lower Fox River. The goal of the analysis is to assess their suitability for environmental decision making. As such, it is essential to define the types of decisions that the models would be used to evaluate. In the broadest sense these can be divided into two types:

- 1) No action. This provides an assessment of the system's natural assimilation over time, primarily due to dispersion and burial.
- 2) Remedial measures. These will be limited to two primary types:
  - a) Sediment capping.
  - b) Sediment dredging

The following critique is generic. However, where necessary, individual models are mentioned. These are the State of Wisconsin model (referred to as the *DNR Model*), the LimnoTech model (referred to as the *LTI Model*), and the Fish and Wildlife model (referred to as the *QEA Model*),

## CRITIQUE

All the models are similar in most fundamental respects. That is, they are based on dynamic water and mass balances, and employ comparable spatial and temporal resolution. Most of the following critique focuses on their differences and how these differences impact on their decision making utility. However, the last critique point, spatial segmentation, relates to all the models.

## Deep Sediment Bookkeeping

The first model developed for the Lower Fox (DNR) uses a coarse Eulerian representation to

characterize the vertical distribution of PCB in the sediment bed. It includes relatively thick wellmixed layers to represent the strata just below the surface sediment layer. This representation results in significant numerical mixing that can artificially introduce deep contaminated sediments to the surface. Subsequent resuspension and diffusion can then lead to introduction into the overlying water.

This artifact is a serious deficiency. Particle mixing via mechanisms such as bioturbation is typically isolated to the surface sediment layer. This surface layer is on the order of approximately 10-30 cm or 4-12 inches (Berner 1980). Below this horizon, particle mixing is minimal as the system is considered to be a compacting or consolidating environment.

In contrast, later models (e.g., LTI) represents the deeper sediment in a Lagrangian fashion that effectively eliminates artificial mixing below the surface layer. Analysis by LimnoTech suggests that this modification results in a 30% drop in PCB export to Green Bay relative to levels predicted by the previous model.

Although the precise magnitude of the effect is subject to question, the numerical dispersion is clearly an artifact that can and should be corrected.

#### Solids Balance and Settling/Scour/Diffusion Calibration

Aside from deep sediment characterization, the other major factor dictating long-term recovery is the solids balance for the Fox River and its underlying sediments. There are two issues that can introduce disparities among the present models: (1) the characterization of long-term deposition/erosion and (2) the representation of scour.



#### Long-term Deposition Versus Erosion

# Figure 1. Schematic representation of major mechanisms governing transport and fate of solids in the Lower Fox River.

Supposing for the moment that perfect information regarding solids input were available, the fate of strongly sorbed sediment PCB is dictated by the interplay between settling, scour and burial (Fig. 1). Unfortunately, because only two mass balances are available (for the river and the surface sediments), only two of these processes can be estimated independently by calibration to data. Further, the calibration data itself (in particular the river suspended solids concentration) is quite difficult to observe, particularly under high flow.

As a consequence, the modelers have excess degrees of freedom and can adopt different parameterizations to arrive at comparable fits of short-term (several years) data time series. It is only when long term predictions (decade) are made that the model predictions diverge because of the differences in the "up-down" characterizations.

In order to progress beyond this ambiguous state of affairs, it is necessary to constrain one of the "up-down" processes. This is most commonly done by fixing the transfer to the deep compacting sediments. To do this, it is necessary to have adequate observations to establish whether long-term deposition or erosion is taking place at each model segment. Once this is done, the calibration is usually sufficiently constrained that the models should yield comparable long-term predictions.

#### Scour Characterization

The second issue related to the solids budget is the actual approach used to parameterize settling and scour. Because it is dependent on solids speciation, settling will be discussed in the following section.

Scour can be related to the velocity of the overlying water by mechanistic formulations parameterized with laboratory analyses of system sediment (e.g., Gailani et al. 1991, McNeil et al. 1996). This approach should yield a consistent and unambiguous representation of scour under a range of water velocities.

Unfortunately, the present models either do not adopt this approach or base their results on differing laboratory data. Hence, their scour estimates vary significantly.

On this basis, I would conclude that any model used for Fox River decision-making should employ a mechanistic scour mechanism based on the most current scientific understanding and laboratory analyses of Fox sediments.

#### Speciation of Solids and PCBs

Speciation, or kinetic segmentation, relates to whether solids and total PCBs are treated as single entities, or are divided into categories based on size or chemical characteristics.

#### Solids Speciation

Although it might serve as a valid first approximation, the use of a single variable to characterize suspended solids is not adequate for this system. Based on the fact that different fractions have widely different (a) settling velocities and (b) sorption potential, the solids should at the least be divided into three fractions: coarse inorganics, fine inorganics and fine organics.

This breakdown would have two major benefits. First, it would allow the characterization of the different levels of sorption exhibited by each of these types of substrate. Second, it would allow a better representation of sediment-water interactions (i.e., the interplay between settling and scour) because more realistic settling velocities would be employed. An ancillary benefit of using more realistic settling velocities is that it might decrease the need for phenomenological or "apparent" mechanisms such as high "background" resuspension. Such mechanisms are often invoked to allow simpler models to fit observations.

#### Total PCB or Congeners.

At present, all the models simulate total PCB. Although it is not suggested that modelers move to further speciate PCB (e.g., into congeners), it must be recognized that use of a composite total PCB introduces some uncertainty into the analysis. This uncertainty results from lumping all PCB into a single variable and hence not accounting for the differing properties of the component fractions (e.g., sorption, decomposition kinetics, etc.). Efforts to greatly refine the transport mechanisms must be somewhat tempered by the crudeness of the chemical characterization. This also applies to the uncertainties represented by both the initial conditions and the model forcing functions.

#### Spatial Segmentation

There are two aspects to spatial segmentation which relate to all the models of the system. These involve (a) the specification of the system boundaries and (b) the characterization of bottom topography.

#### System Boundaries

The DePere Dam serves as the upper boundary of some of the current models. This means that temporally varying boundary conditions for both solids and PCBs must be specified at this point. Since but sparse solids and PCB data are measured at DePere during high flow, this means that the model's more important external forcing function will exhibit a significant level of uncertainty. This is a problematic issue for both calibration and prediction. As they say in the computer industry "Garbage In, Garbage Out." It would therefore seem prudent to extend the models to a "clean" point upstream of the major deposits and inputs of PCB.

#### **Bottom Topography**

In order for the models to evaluate dredging, they must be capable of predicting how physical manipulation of the bed impacts future deposition of PCBs from upstream sources. In essence, digging a hole in the bottom may create a low-energy void that will be preferentially filled by PCBs carried from upstream sources by future high flow events. If the remedial strategy involves filling the dredged site with clean fill back to the original level, this could be less of an issue. However, if fill is not used to return the bottom to its original topography, it is uncertain whether the existing models would be capable of simulating future deposition correctly.

#### MODELING RECOMMENDATIONS

At present, there is a large data base, several models, and a great deal of associated modeling expertise that has been marshaled to address the Lower Fox River PCB problem. I believe that with sufficient modification and scientific cooperation, these frameworks could provide a

consistent vision of system response that would prove useful in informing the decision-making process. Unfortunately, the "real" differences among the frameworks are somewhat obscured by the various groups' assumptions, algorithms and calibration protocols. In essence, the models have been verified or corroborated in a somewhat ad hoc fashion that detracts from their credibility.

Thus, at this juncture, I do not believe that there is a single "best" model that is ready to perform the evaluation tasks at hand. However, I do believe that the modeling groups could modify and recalibrate their frameworks to yield more consistent predictions of the Fox's future state. I believe that a "consensus" model could be achieved that would be extremely useful in informing decision makers as they weigh alternatives for system cleanup.

The following sections outline key steps and modifications that must be implemented to achieve this consensus model.

#### **Minimal Mechanism Level**

I believe that there is a minimum level of mechanism characterization that is necessary before predictions are possible. There are three major suggestions that I believe are necessary. A fourth, although not absolutely necessary, is suggested to make the models more robust. These are:

- Adopt a numerical integration scheme that avoids artificial mixing in the deep sediments.
- Include three types of solids: fine and coarse inorganic and organic.
- Employ a mechanistic scour mechanism related to water shear based on the most current scientific understanding and laboratory analyses of Fox sediments
- Extend the upstream boundary to a location above the beginning of major contaminated deposits and significant sources.

#### **Consistent Data**

The groups must employ the same data sets during model development and testing. In particular, some consensus as to the depositional/erosional nature of the river has to be agreed on. It was incredible to me to witness the disagreement in characterizing this mechanism among the groups. If these differences are real (i.e., they truly reflect a lack of fundamental scientific knowledge regarding the system) and cannot be reconciled, I have no confidence that any model will ever help the decision making process.

However, if as I suspect, the long-terms solids status of the Fox is a comprehensible and quantifiable phenomenon, I believe that models with common representations will be sufficiently constrained that they should be much more consistent and would prove useful for decisions.

The same goes for calibration and corroboration data sets. If common and scientifically sound information were shared, I believe that the models would be much more constrained. Hence, there would be much less disparity among the models and much greater convergence on the truth.

#### **DECISION MAKING EVALUATION**

If the models include the aforementioned mechanism enhancements and are properly calibrated to consistent data, I believe that they could provide useful decision making aids for assessing

each of the decision areas outlined at the beginning of this report.

#### No Action Scenario

These simulations would delineate the system's natural dispersion and burial processes. I believe that with some refinement as outlined above, the models would be capable of answering broad management questions such as, "How would the PCB loading to Green Bay change over the next 20 years if nothing was done?"

This conclusion is backed up by observations. The intensive study of Fox River PCB's is now moving from an annual to a decadal scale. As a consequence, the system's long-term natural recovery is emerging from the observational "noise" (e.g., the half-life of PCB in fish tissue being on the order of 10 years). By using such information as an additional constraint on the calibration/corroboration process, the individual models should be less likely to arbitrarily "go their own way."

Further, it seems that if improvement is actually occurring with an approximately 10-yr half life, perceptible changes might be observable in sediment cores from the inner Green Bay. This might represent an additional constraint on the modelers' long-term analyses. For example, if two models exhibit grossly different claims as to export to Green Bay, one way to assess the correct answer might be to compare these claims to what is actually being deposited in the Bay.

In other words, an observational picture of the "real" long-term response of the Fox is emerging. Models that reproduce this long-term response would have much greater credibility when employed for extrapolation.

#### **Remedial Actions**

#### <u>Capping</u>

This scenario would involve overlaying hotspots with sufficient clean, impermeable material to effectively "bury" the contaminated sediments. The present models would be inadequate to make fine-scale design judgements relative to the engineering aspects of such a solution. However, if it is assumed that the capping could be achieved with some agreed upon level of effectiveness, the models could provide order of magnitude estimates of its long-term impact.

#### **Dredging**

It is anticipated that even after making the aforementioned refinements and modifications, the present models are probably inadequate to assess fine-scale, engineering design questions related to dredging. In addition, as mentioned above, they are also probably inadequate to address the refilling of voids.

However, they should nevertheless be useful in obtaining order-of magnitude estimates of the impact of dredging. Further, sensitivity and bracketing analyses could be implemented to bound these estimates.

Finally, the issue of voids would be obviated if dredging was implemented in a downstream direction as suggested below. In this case, the models would be more useful in assessing the impact of the measures.

## ADDITIONAL SUGGESTIONS

In the course of reading material and listening to discussion on the Lower Fox River PCB problem, the following thoughts occurred to me and are offered as suggestions to further strengthen the use of models.

- If dredging were deemed necessary, it would seem prudent to implement the dredging in a downstream sequence. There would be a number of benefits from such a strategy:
- By working downstream from a "clean" boundary, the issue of recontamination by upstream resuspension and deposition during high flow events would seem to become a moot point.
- As a corollary, it would strengthen the models' utility in assessment of dredging because the issue of preferential refilling of voids (as noted above, a limitation of the current models) would become moot.
- Beyond the immediate benefit to the system, the initial dredging operations might have the ancillary benefit of serving as an experiment to assess the immediate environmental impact of dredging (i.e., how much sediment PCB is actually liberated from the mechanical act of dredging). Further, if the system were monitored during and immediately following dredging, the results might clarify the additional repercussions of the remedial action (What is the fate of the liberated PCB?; Does it make it to Green Bay or is it redeposited in the Fox?).
- Characterize bioturbation. I was surprised to observe that there was such controversy related to the action of bottom organisms on sediment particle mixing and sediment-water transport. A review of available information as well as additional measurement of bottom organism density, and depth and magnitude of bioturbation might be conducted to reduce this uncertainty.
- Model sensitivity and performance. All models used for decision-making should be subject to sensitivity analysis in order to assess their robustness and their sensitivity to their underlying assumptions, boundary conditions and initial conditions. Such an approach was employed in the QEA model presentation at the February 3, 2000 meeting in Green Bay. I found this presentation highly illuminating regarding the true effectiveness of the model in explaining the observations.

Further, at a certain point some consideration should be given to the computational efficiency of each of the frameworks. Efficiency could prove extremely useful to decision makers by allowing them to rapidly evaluate many scenarios in a cost-effective manner. If highly efficient algorithms could be developed, an uncertainty analysis might be performed to estimate the uncertainties connected with model projections

# Appendix C

# **Review Comments of Dr. Kevin Farley**

(Documents referenced in reviews are listed in reference section of main text)

#### **Review of Fox River PCB Models**

# Kevin J. Farley Environmental Engineering Department Manhattan College Riverdale, NY 10471

# March 27, 2000 Second Draft

#### INTRODUCTION

Separate reviews of PCB models developed by the Wisconsin Department of Natural Resources (WDNR) and the Fox River Group (FRG) for the Lower Fox River are presented below.

#### WDNR MODEL

#### Model Overview

Over the last ten years, the Wisconsin Department of Natural Resources (WDNR) has conducted several modeling studies to evaluate the transport and fate of PCBs in the Fox River. In early work, separate models were developed for the Fox River from Lake Winnebago to DePere Dam [Steuer et al., 1995], and from DePere Dam to Green Bay [Velleux, 1992]; [Velleux and Endicott, 1994]. Based on this earlier work, a single domain model was later developed for the entire Lower Fox from Lake Winnebago to Green Bay [Velleux et al., 1995]; [Velleux et al., 1996], and has been used to evaluate selective sediment remediation strategies [WDNR, 1997].

In the current model [Velleux et al., 1995]; [Velleux et al., 1996], the river is divided into 43 water column segments (see Figure 3 in [Velleux et al., 1995]). Sediments underlying the water column segments are divided into "net depositional" and "net erosional" zones, each consisting of a surficial layer (of 10 cm) and three subsurface sediment layers (of 20, 120, 150 cm, respectively).

Advective transport in the Fox River are described based on gaged flow records. (Values for longitudinal dispersion in the river were not specifically discussed in [Velleux et al., 1995]; [Velleux et al., 1996], but values were probably set in the range of 0-75 m2/sec based on a calibration to chloride data (see discussion in [Velleux and Endicott, 1994]).)

Descriptions for sediment transport in the Fox River draw heavily from the work of [Gailani et al., 1991]. The grain size distribution of suspended solids (which is described as percent fine, medium, and coarse material) is given as a function of flow (e.g., see [Gailani et al, 1991] or Table 1 in [Velleux et al, 1996]). The effective settling velocity of suspended solids is described as a weighted average for fine-, medium-, and coarse-grained solids (where fine particles are considered to have negligible settling velocities, medium-size particles are affected by

flocculation and have settling velocities on the order of 10 m/day; and coarse-size particles settle discretely with settling velocities on the order of 100 m/day). According to [Velleux and Endicott, 1994], the resulting settling velocity in the river below DePere Dam averages 1.2 m/day for the Oct 1988-May 1990 simulation period. No mention is made of reduced probability of deposition as a function of increasing bottom shear stresses (e.g., Gessler's function as discussed by Kirk Ziegler (QEA) at the February 2000 meeting).

Initial rates for event-based resuspension are estimated from the epsilon equation,

$$\varepsilon = \frac{a_o}{Z} [\tau - \tau_c]^m$$
 for  $\tau > \tau_c$ 

where ao = 0.008, m = 2.75, Z = 1-20, and c = 1 dyne/cm2, based on previous work of [Gailani et al., 1991]. Net settling-resuspension rates are adjusted as necessary to match the TSS data. Final calibration for gross settling and resuspension is accomplished by adjusting rates to match the water column PCB data [Velleux and Endicott, 1994]. This includes both event-based and background resuspension. The background resuspension rates are generally less than 0.1 mm/day (i.e., less than 3.6 cm/yr) [Velleux and Endicott, 1994], and have a negligible effect on sediment transport. Because of large differences in water column and sediment PCB concentrations, however, background resuspension has a significant effect on PCB transport. Note that in the WDNR model, most resuspended sediment originates in the deeper, mid-channel portions of the river during periods of high flow.

PCB sorption is described by three-phase partitioning between freely-dissolved, DOC, and particulate matter. The DOC is considered a less effective sorbent phase (KDOC = 0.01 KPOC in the water column and KDOC = 0.1 KPOC in the sediment). Sorption to particulate matter is described using the particle interaction model [DiToro, 1985] with x = 9, indicating a weak particle effect [Velleux and Endicott, 1994]. The log Koc value is set at 6.35 based on field data collected at DePere Dam.

Volatilization rates are calculated from liquid and gas phase mass transfer rates and are in the range of 0.08-0.3 m/day [Velleux and Endicott, 1994]. In sensitivity studies, PCB loss by volatilization was not found to be an important removal pathway for the Fox River. The porewater diffusion rate is given as 0.4 cm/day [Velleux and Endicott, 1994]. PCB degradation is not considered to be important.

Numerical simulations for PCB transport and fate in the Fox River are performed using the IPX (In-place Pollutant eXport) modeling framework, which is a modified version of TOXI4.

PCB concentrations in fish are calculated using PCB surficial sediment concentrations and Biota-Sediment-Accumulation Factors (BSAFs) that were derived from 1989-90 and 1995-96 sampling data [WDNR, 1997].

#### Comments

I.

Sediment Bed Handling Routine: [Blasland, Bouck & Lee, 1997], [Limno-Tech, 1998], and [Limno-Tech, 1999c] have done a good job in demonstrating the problem of numerical dispersion between sediment layers in the standard WASP-based bed handling routines within the IPX model. This numerical problem causes artificial vertical transport of PCB mass through the sediment bed when major scour/deposition events occur. This results in a larger transport of PCBs from buried sediments and a larger export of PCBs to Green Bay (see the next to last figure in [Limno-Tech, 1999c].

For the remainder of this review, it is important to note that the problem of numerical dispersion in the IPX model does not affect sediment transport results. For PCBs, I will assume that numerical dispersion in the bed handling routine does not have a large impact on short term simulation results (e.g., calibration runs), but does have a profound effect on long-term simulation results (e.g., 25-year projections).

1. Net Sedimentation (Solids Trapping Efficiency): According to Figure 4-11 in [Limno-Tech, 1999d], the WDNR model computes a net sedimentation of approximately 100,000 Mtons of solids in the Fox River between DePere Dam and Green Bay during the 1989-95 calibration period. This corresponds to a relatively low solids trapping efficiency of approximately 10%. For comparison, solids trapping efficiencies from the previous sediment transport modeling studies of [Gailani et al, 1991] are given as 80% for the 50% ile flow and a 24% for the 99.7% ile flow. Since the description of sediment transport processes in the WDNR model draws heavily from the work of [Gailani et al., 1991], the low solids trapping efficiency for the WDNR model (that is reported in [Limno-Tech, 1999d]) needs further clarification and proper explanation.

Assuming a sediment bulk density of 0.65 g/cm3 and a sediment surface area of 5 x 106 m2 between DePere Dam and Green Bay, a net sedimentation of 100,000 Mtons of solids over the 1989-95 calibration period corresponds to an average sedimentation rate of approximately 0.5 cm/yr. Again this value seems low compared to reported estimates of 0.6-2.5 cm/yr (from radioisotope profiles), 2-25 cm/yr (from bathymetry data), and 1-4.3 cm/yr (from dredging records) [Limno-Tech, 1999a]. Since burial serves as an important mechanism for removing PCBs from the biologically-active zone, proper understanding of sedimentation (and solids trapping efficiency) in the Fox River is critical in projecting the future fate of PCBs. Differences in model sedimentation rates and reported sedimentation estimates need to be critically examined.

2. Spatial Patterns of Erosion/Deposition: Based on sediment transport computations [Gailani et al., 1991] and bathymetric measurements, erosion in the WDNR model is confined to deeper, midchannel river sediments during high flow events while nearshore sediments are not eroded. According to Figure 4-9 in [Limno-Tech, 1999d], sediment transport in the WDNR model results in net erosion rates of 1-2 cm/yr in a significant portion of the Fox River channel below DePere Dam. Model specification of net erosion in this portion of the Fox River raises several intriguing questions: Are mechanisms such as intense sediment mixing during high flow events responsible for contamination of deep sediments in net erosion zones? How has channel dredging and the curtailment of dredging in recent years affected sediment transport patterns and

PCB transport in the Lower Fox River? At this time, it is not clear if sufficient information on erosion/deposition rates in the Lower Fox River is available to completely answer these questions. Further comparisons of model hindcast results [Velleux et al., 1995] and observed PCB sediment concentrations would be a good next step in addressing these concerns and in judging model performance (see comment #6 for further discussion).

3. Model Calibration for TSS and Water Column PCBs: The WDNR model was calibrated to total suspended solids (TSS) and water column PCBs at DePere Dam and at the mouth of the Fox River. Temporal plots (e.g., Figure 4 in [Velleux and Endicott, 1994]; Figure 4 in [Velleux et al., 1995]; and Figure 7 in [WDNR, 1997]) and statistical evaluations (e.g., Figures 5 and 6 in Velleux and Endicott, 1994]; and Figure 8 in [WDNR, 1997]) show good overall agreement of model results with field data. It is important to note however that the WDNR model appears to overpredict water column PCB concentrations during high flow events (e.g., during the May-June 1989 high flow event as shown in Figure 4 of [Velleux et al., 1995] and during the during the April 1998 high flow event as shown in Limno-Tech, 1999c]). Possible reasons for the model's apparent overprediction of water column PCB concentrations are: 1) difficulty in predicting the timing of the PCB concentration spike and in collecting representative field data during high flow events; and 2) the model's description of settling-resuspension which allows for continuous exchange between suspended solids and a 10 cm surficial layer of PCB contaminated sediments (see following comment). Since a large portion of the PCB export to Green Bay is expected to occur during high flow events [Velleux and Endicott, 1994], proper calibration of the model during high flow events is a critical concern.

4. Settling-Resuspension Exchange at High Flows: In the WDNR model, settling and resuspension processes provide a continuous exchange of PCB-contaminated particles between the water column and a 10 cm surficial sediment layer. This implies that particles can settle and be incorporated into the bed during all flow conditions, and that mixing processes in the sediments are sufficiently fast to keep the 10 cm layer reasonably well mixed. At high flows, however, settling particles are less likely to deposit in the bed since they will likely experience a decreased probability of deposition at higher shear stresses. In addition, it is not clear that the assumption of vertically well-mixed surficial sediments is appropriate over short time periods associated with high flow events. Either a reduced probability of particle deposition or incomplete mixing of surficial sediments will likely result in a decrease in sediment-water column exchange and a decrease in PCB water column concentrations during high flow events.

5. Background Resuspension: At low and moderate flows, subcritical shear resuspension, defined as background resuspension, is used primarily in calibrating the model to PCB water column data. Since background resuspension is expected to have a negligible effect on sediment transport [Velleux et al., 1996], other mechanisms (e.g., biologically-enhanced diffusive exchange [Thibodeaux et al., 2000]) could also be employed in describing enhanced rates of PCB transfer from surficial sediments to the water column. It should be noted however that background resuspension and biologically-enhanced diffusive exchange may have different effects on PCB congener distributions (with background resuspension acting on particulate PCBs and affecting all PCB congeners, and diffusive exchange acting on dissolved PCBs and preferentially affecting low chlorinated PCBs). Since the WDNR model is calibrated to simulate

the transport and fate of total PCBs, it is not possible to distinguish between the two processes. The use of background resuspension, biologically-enhanced diffusive exchange, or some combination of the two appears to be a reasonable approach for calibration of a total PCB model if we can safely assume that congener distributions are not changing in time. Observed congener distributions should be examined to check this assumption. If congener distributions are changing in time, serious consideration should be given to PCB congener-specific (or PCB homologue-specific) modeling.

6. PCB Sediment Projections: Published work on the Fox River [Velleux and Endicott, 1994], [Velleux et al., 1995], and [Velleux et al., 1996] has focused on PCB water column concentrations for model calibration and for model performance evaluation. Since there is a fair degree of uncertainty is setting sediment-water exchange rates (e.g., settling, background and event-based resuspension, biologically-enhanced diffusive exchange) in model calibration, comparisons of model results to PCB water column data do not necessarily constitute a rigorous confirmation of model performance and further testing of PCB sediment projections is needed.

In [WDNR, 1997], a comparison of 1989-95 model simulation results and 1995 observed PCB sediment concentrations is presented in Figure 9 for river sediments below DePere Dam. As shown, model results for the 0-10 cm and 10-30 cm sediment layer appear to underpredict observed values by 40-50%. The PCB sediment comparison is clearly not as convincing as the PCB water column results and raises concerns of how well the model is describing the longer-term transport and fate of PCBs in the Fox River. More effort should be given to PCB sediment comparisons in evaluations of model performance.

7. PCB Fish Projections: Model results for walleye show a more rapid decline in PCB tissue concentrations than is suggested by the 1986-1996 field data (Figure 10 in [WDNR, 1997]). This finding is consistent with the underprediction of PCB sediment concentrations discussed above. Further efforts should therefore be directed at properly describing PCB concentrations in sediments. Based on the slow decline in PCB sediment and fish concentrations, the use of field-derived BSAFs appears to be a reasonable approach in modeling PCB tissue concentrations. A more elaborate bioaccumulation model may be necessary in the future (e.g., to assess the effects of walleye feeding in Green Bay as discussed by David Glazer (QEA) at the February 2000 meeting).

#### Summary

The WDNR model provides a good overall description of PCB water column response but appears to overpredict declines in PCB sediment and fish concentrations. Factors which are most likely contributing to these apparent overpredictions in PCB sediment and fish declines include:

- Numerical dispersion in the standard WASP-based sediment bed handling routines within the IPX model (see Comment #1)
- An overestimation of PCB sediment-water column exchange during high flow events (see Comment # 5)

- At this time, revision of the sediment bed handling routines and re-examination of PCB transport processes during high flow events should be given very high priorities.
- Additional work should also be performed on processes related to PCB sediment concentration projections, most notably sediment burial and sediment mixing rates. To date, model calibration and model performance evaluation has focused largely on PCB water column concentrations and sediment-water column exchange rates. Although these efforts have been very useful in addressing PCB export to Green Bay, they do not appear to be sufficient in assessing human and ecological risks in the Fox River. Assuming that PCB fish concentrations are directly linked to surficial sediment concentrations (e.g., through the use of BSAFs), the model needs to do a more convincing job in projecting PCB concentrations in the biologically-active zone of the Fox River sediments below DePere Dam. Toward this end, the following tasks should be considered:
- Re-evaluate spatial patterns of sedimentation in the Lower Fox River. Specifically consider how sedimentation rates may have been affected by the curtailment of channel dredging, and how sedimentation patterns will be affected in the future by remedial dredging projects.
- Re-evaluate sediment mixing behavior. At present, the model assumes a 10 cm surficial sediment layer that is vertically well mixed by physical processes and/or bioturbation. Actual mixing particles by benthic organisms may not be fast enough to keep the top 10 cm of sediment well-mixed over short time periods (e.g., during high flow events) and a more explicit description of sediment mixing (e.g., 1 cm sediment layers with defined particle mixing rates between each layer may be necessary). In addition, the effects of high flow events on sediment mixing (e.g., as suggested by erosion (and I assume subsequent deposition of sediments) in the SEDFLUME experiments of [McNeil, 1994] and [McNeil et al., 1996]) may require an explicit description of surficial and deeper sediment mixing during high flow events. These mixing events could potentially play an important role in allowing buried PCBs to re-enter the biologically-active zone. Before implementing additional sediment mixing processes in the model, Fox River sediment cores should be re-examined for evidence to confirm that such mixing events have occurred during previous high flow events.

#### FRG MODEL

#### Model Overview

The "alternative" models were developed by the Fox River Group (FRG) to describe PCB transport and fate in the Lower Fox River above and below DePere Dam. The primary purpose of the alternative models is to address two perceived inadequacies in the WDNR model:

• Numerical dispersion between sediment layers in the standard WASP-based bed handling routines within the IPX model which cause artificial vertical transport of PCB mass through the sediment bed when major scour/deposition events occur.

• Specification of excessively high sediment resuspension rates to describe PCB transport from surficial sediments to the water column.

For this purpose, the IPX model [Velleux and Endicott, 1994] was modified and applied to the upper (Lake Winnebago to DePere Dam) and lower reach (DePere Dam to Green Bay) reaches of the Lower Fox River. The water column was segmented along the longitudinal axis of the channel, similar to previous modeling work by WDNR. The sediment bed handling routines were modified [Limno-Tech, 1998] to limit numerical dispersion that is inherent in simulating major scour/deposition events in the standard WASP-based bed handling routines. As part of this modification, the sediment bed was segmented into 5 cm layers (with two near surface layers actively considered in the computation and up to twelve deeper sediment layer retained in an archival stack).

For the upper reach (Lake Winnebago to DePere Dam), settling velocity for biotic solids is set at 0.5 m/sec [Limno-Tech, 1999a]. (I believe this is a typo and should be 0.5 m/day.) Settling of abiotic solids is determined through model calibration and is given as 1.5 m/day.

Resuspension rates are determined as a function of excess velocity

$$V_r = \max\left[V_{r_{base}} * \left(\frac{v}{v_{crit}} - 1\right) 0\right]$$

Since field data are not available, parameters were determined from model calibration and are given as: Vrbase (base resuspension) equal to 0.1 mm/yr (Dec-Mar) and 0.5 mm/yr (Apr-Nov) for soft muds, and 0.05 mm/yr (Dec-Mar) and 0.25 mm/yr (Apr-Nov) for silty sands; and vcrit = 0.006 m/sec [Limno-Tech, 1999a]. Pore water exchange rates were also obtained from model calibration and are set at 0.196 cm/day (Dec-Mar) and 39.2 cm/day (Apr-Nov) [Limno-Tech, 1999a]. (It is not clear in the report, so I am assuming that the pore water diffusion rates are used to describe both exchange between the surficial sediment layer and the overlying water and exchange between the top two sediment layers.) All other parameters, including DOC, foc, partition coefficients, and Henry's constants are taken directly from the WDNR modeling work.

For the lower reach (DePere Dam to Green Bay), event-based resuspension is determined from the epsilon equation,

$$\varepsilon = \frac{a_o}{Z} [\tau - \tau_c]^m \qquad \text{for } \tau > \tau_c$$

where bottom shear is calculated from a two-dimensional hydrodynamic model (RMA2-V) and initial estimates of the resuspension parameters are determined from the site-specific data of [McNeil, 1994] as discussed in [Limno-Tech, 1999b]. A summary of final parameter estimates used in the alternative model [Limno-Tech, 1999d] are given in Table 1. Values used in the WDNR model, along with parameters estimated by [McNeil, 1994], are also presented for comparison.
Model calibration for the Lower Fox River below DePere Dam was performed using an iterative procedure with settling velocity, background resuspension, porewater-water column exchange, and porewater diffusion between the top two layers treated as adjustable parameters. From this procedure, the settling velocity for total suspended solids is determined to be 1.5 m/day. Background resuspension, porewater-water column exchange, and porewater diffusion between the top two sediment layers are affected by ice cover and bioturbation and are adjusted seasonally. Final values are given as 4 mm/yr (Dec-Mar) and 36 mm/yr (Apr-Nov) for background resuspension; 4 cm/day (Dec-Mar) and 20 cm/day (Apr-Nov) for porewater-water column exchange; and 0.4 cm/day (Dec-Mar) and 2 cm/day (Apr-Nov) for porewater diffusion between the top two sediment layers [Limno-Tech, 1999d].

Particle mixing between the top two sediment layers is given as 16 cm2/yr [Limno-Tech, 1999d]. All other parameters, including DOC, foc, partition coefficients, and Henry's constants are taken directly from the WDNR modeling work.

Parameter	DNR	McNeil 1994	LTI
Critical Shear (dynes/cm <sup>2</sup> )	1.0	1.0	1.0
Μ	2.75	2.3	1.4
$A_0$	8.0	1.3	2.92 <sup>a</sup>
Z	0.1 - 2	1.38	1.0
Erosion ( $= 3 \text{ dynes/cm}^2$ )	$50^{\mathrm{b}}$	4.64	7.7
Erosion ( $= 5 \text{ dynes/cm}^2$ )	363 <sup>b</sup>	22.9	20.3
Erosion ( = $15 \text{ dynes/cm}^2$ )	11,349 <sup>b</sup>	408	118

**Table 1**. Summary of Resuspension Parameters and Erosion Rates (mg/cm<sup>2</sup>)

<sup>a</sup> Note that the a0 value presented in Limno-Tech (1999d) are different than estimates given in Limno-Tech (1999a and 1999b). In Limno-Tech (1999a and 1999b), the equivalent a0 value is equal to 1.07 for soft muds and 0.349 for silty-sand. No justification fo the change was presented.

<sup>b</sup> Erosion estimates are based on Z = 1.

### Comments

- Sediment Bed Handling Routines: Revisions of the sediment bed handling routines as explained in [Limno-Tech 1999a, 199c] are appropriate to correct the problem of numerical dispersion between sediment layers in the standard WASP-based bed handling routines within the IPX model. These corrections are important and should be incorporated in the Lower Fox River PCB models.
- Settling Velocities above DePere Dam: Settling velocity of biotic solids in the Lower Fox above DePere is given as 0.05 m/sec in [Limno-Tech, 1999a]. This is probably a typo and the settling velocity should be 0.05 m/day. Confirmation is needed.

Resuspension above DePere Dam: Calculated resuspension rates in the Lower Fox above DePere Dam are considered to be proportional to velocity to the first power [Limno-Tech 1999a]. This corresponds to resuspension being proportional to the bottom shear stress to the one-half power which seems very low. In model formulations, resuspension rates are more typically considered

to be proportional to bottom shear stress to the second or third power. Also, the critical velocity for resuspension is given as 0.6 cm/sec [Limno-Tech 1999a]. I calculate this to roughly correspond to a critical bottom shear stress of 10-3 dynes/cm2 which is a very low value. The resuspension formulation for the Lower Fox River above DePere Dam should be critically reviewed.

- Model Calibration for TSS and Water Column PCBs above DePere Dam: According to Figures 5-1 through 5-6 in [Limno-Tech 1999a], the model is calibrated reasonably well for TSS and water column PCBs above DePere Dam. There does however appear to be a somewhat consistent under-prediction of TSS during high flow events. Statistical testing should be performed to see if there is any bias in the model-field data comparisons.
- Net Sedimentation (Solids Trapping Efficiency) below DePere Dam: According to Figure 4-11 in [Limno-Tech, 1999d], the FRG model computes a net sedimentation of approximately 100,000 Mtons of solids in the Fox River between DePere Dam and Green Bay during the 1989-95 calibration period. This result is similar to the WDNR model result (discussed previously) and corresponds to a relatively low solids trapping efficiency of approximately 10%. For comparison, solids trapping efficiencies from the previous sediment transport modeling studies of [Gailani et al, 1991] are given as 80% for the 50% ile flow and a 24% for the 99.7% ile flow.

Again, assuming a sediment bulk density of 0.65 g/cm3 and a sediment surface area of 5 x 106 m2 between DePere Dam and Green Bay, a net sedimentation of 100,000 Mtons of solids over the 1989-95 calibration period corresponds to an average sedimentation rate of approximately 0.5 cm/yr. This value seems low compared to reported estimates of 0.6-2.5 cm/yr (from radioisotope profiles), 2-25 cm/yr (from bathymetry data), and 1-4.3 cm/yr (from dredging records) [Limno-Tech, 1999a]. Since burial serves as an important mechanism for removing PCBs from the biologically-active zone, proper understanding of sedimentation (and solids trapping efficiency) in the Fox River is critical in projecting the future fate of PCBs. Differences in model sedimentation rates and reported sedimentation estimates need to be critically examined.

- Spatial Patterns of Erosion/Deposition below DePere Dam: According to Figure 4-9 in [Limno-Tech, 1999d], sediment transport in the FRG model results in net deposition rates of 0-2 cm/yr in the Lower Fox River below DePere Dam. This description of erosion/deposition in the Lower Fox River is very different than the results of the WDNR model. A more complete review of existing information of erosion/deposition rates (e.g., sediment core dating, dredging records, etc.) is needed to determine whether the WDNR model or the FRG model provides a more realistic description of erosion/deposition patterns in the Lower Fox River below DePere Dam.
- Event-Based Resuspension Rates: [Limno-Tech 1999 a,b] determined values for event-based resuspension parameters from a statistical evaluation of site-specific erosion tests [McNeil 1994]. It appears that some adjustment in the parameters was also made during final model calibration [Limno-Tech 1999d]. Final parameters in the FRG model are presented in Table

1, along with calculated erosion rates for three bottom shear stresses. For comparison, values originally estimated by [McNeil 1994] are also provided. As shown, the calculated erosion rates for the FRG model [Limno-Tech 1999d] and for McNeil's estimates [McNeil 1994] are in reasonable agreement with each other (and with shaker test results) for the lower shear stresses. At a higher shear stress (which would correspond to a high flow event), however McNeil's estimated erosion rate is almost four times higher than the calculated rate in the FRG model.

At this time, it is best to acknowledge that, due to sample variability in shaker test results and the limited range of bottom shear stresses that can be considered in shaker test studies, a large degree of uncertainty exists in specifying resuspension parameters for the Lower Fox River. Based on a statistical analysis, the FRG model parameters should be considered a possible description of resuspension in the Lower Fox River. Based on experience at other sites, however the slope ('m') value of 1.4 appears to be low, and I would suspect that this would result in an underestimation of resuspension during high flow events.

- Background Resuspension Rates below DePere Dam: According to [Limno-Tech 1999d], background resuspension rates are given as 4 mm/yr (Dec-Mar) and 36 mm/yr (Apr-Nov). This results in 93.7% of the total resuspension flux in the Lower Fox River below DePere Dam occurring at flows less than 188 m3/sec (i.e., as background resuspension). I find this result surprising and hope that someone with more site-specific knowledge of the Lower Fox River can confirm or refute the validity of this claim. My sense is that background resuspension rates, which are obtained from model calibration, are too high. An alternative explanation of the TSS and PCB water column data can probably be obtained by specifying two or more particle size classes, with particles of low settling velocities passing through the Lower Fox River during low flow periods.
- Porewater-Water Column Exchange Rates and Porewater Diffusion between Sediment Layers: Porewater-water column exchange rates are given as 4 cm/day (Dec-Mar) and 20 cm/day (Apr-Nov) [Limno-Tech 1999d]. These rates are reasonable based on studies in the Upper Hudson River. Based on these values and the background resuspension rates given above, I calculate that PCB exchange across the sediment-water interface is largely controlled by resuspension. I would therefore expect that the current model calibration is not overly sensitive to specification of porewater-water column exchange rates.
- Model Calibration for TSS and Water Column PCBs below DePere Dam: Model results are calibrated reasonably well to field data for TSS and PCB water column concentrations at the mouth of the Fox River (Figures 4-5 and 4-6in [Limno-Tech, 1999d]). The model however appears to underpredict TSS during high flow events. Also, based on material presented by David Glazer (QEA) at the February meeting, PCB water column results at the Fox River mouth are closely linked to PCB concentrations coming over the DePere Dam. Since PCB water column concentrations at DePere Dam were specified based on empirical relationships in the current model simulations [Limno-Tech 1999d], current model simulations for the Lower Fox River below DePere Dam do not seem to be a critical test of model performance.

- Statistical Measures for TSS and Water Column PCB Calibration: Since the primary interest in Pcb modeling is PCB mass exposure concentrations and PCB mass export to Green Bay, the use of 'Mean Relative Absolute Error' does not appear to be an appropriate statistic to judge model performance (e.g., see Tables 4-3 and 4-4 in [Limno-Tech 1999d]). The problem with 'Mean Relative Absolute Error' is that it gives relative errors for high and low concentrations equal importance. Errors associated with higher concentrations however should be given more weight in determining the model's ability to calculate mass exposure concentrations and mass export.
- Comparison of Model Results to PCB Sediment Data: The PCB sediment response in Figure 4-8 [Limno-Tech 199d] appears to be largely driven by the specification of the upstream boundary condition for PCBs at DePere Dam. The decrease in computed PCB sediment concentrations is given with a half-life of seven years and is similar to the decrease of PCBs at DePere Dam (t1/2 = 10 years). Also, there are no direct comparisons of model results and PCB sediment concentrations presented for the FRG model.

#### **Summary**

The primary purpose of the FRG model was to: 1) correct numerical dispersion problems between sediment layers in the standard WASP-based bed handling routines within the IPX model, and 2) provide a realistic representation of sediment transport in the Lower Fox River using site-specific data. Revisions of the sediment bed handling routines developed by [Limno-Tech 1998] are appropriate to correct problems of numerical dispersion and should be incorporated in the PCB Fox River models. However, it is not clear if changes in sediment transport parameters (and other parameters affecting PCB transfer across the water-sediment interface) provide an appropriate description of TSS and PCB transport in the Lower Fox River for the following reasons:

Due to scatter in experimental results, there is a large degree of uncertainty in eventbased resuspension parameters. Parameters estimated of [McNeil 1994] and those used in [Limno-Tech 1999d] both appear to be within the limits of Shaker test results. Since [Limno-Tech 1999a, b, d] did not present a clear justification for dismissing the estimated parameters of [McNeil 1994], model calibration/simulations should have been performed using both the [McNeil 1994] and [Limno-Tech 1999d] resuspension parameters.

The high rates of background resuspension that were obtained through model calibration are questionable. A more realistic description of TSS and PCB transport below DePere Dam would probably be obtained using two or more particle size classes.

In addition to the comments above, the use of Shaker test data to estimate resuspension behavior should also be questioned. As described by Willy Lick at the December 1999, Shaker test results are representative of erosion of the top few millimeters. This is in contrast to SEDFLUME experimental results [McNeil et al 1996] which indicate that up to 20-30 cm of Lower Fox River sediment could potentially be "reworked" during a storm event exhibiting a bottom shear stress of 11 dynes/cm2? (I am using the term "reworked" and not "eroded" since SEDFLUME results would probably not include the effects of any subsequent settling of suspended sediment or

additional energy dissipation associated with high suspended sediment concentrations (or fluid mud) above the bed.) Such sediment mixing events could potentially play an important role in allowing buried PCBs to re-enter the biologically-active zone. Before implementing additional sediment mixing processes in the model, Fox River sediment cores should be re-examined for evidence to confirm that such mixing events have occurred during previous high flow events.

Lastly, it should be acknowledged that the use of a total PCB model implicitly assumes that the PCB congener distribution is remaining relative constant in time and space. Field data should be analyzed to check the validity of this assumption.

# Appendix D

### **Review Comments of Dr. Louis Thibodeaux**

(Documents referenced in reviews are listed in reference section of main text)

American Geological Institute - Fox River Peer Review Louis J. Thibodeaux, Panelist - January 12, 2000 - DRAFT

Only in the few seconds during lift-off as the rocket traverses the atmospheric boundary layer do these rocket scientist have to deal with the Earth=s natural environment. After that the rocket enters the natural environment of space; a perfect vacuum! In my opinion so called rocket sceince is easy compare to PCB modeling in rivers.

The FRG-model is the most representative of actual conditions in the Fox River. The WDNR-model contains at least three technical difficulties. These are:

- so-called Anumerical dispersion
- no PCB flux verification at high flows
- insignificant pore water diffusion rate

Discussion of each follows.

1) In reviewing the integration/sediment layer accounting algorithms used by each model it is clear that the WDNR model incorrectly allows contaminants at depth to be artificially translocated vertically upward and downward. This is not the way nature works; the model does not mimic in-bed processed at depth in this accounting scheme. I am convinced that this is a definite problem based on document review and oral presentations however, I wish to focus specific attention on difficulties b) and c) noted above.

Supposedly the original WDNR model has undergone an extensive peer review. However a close reading of the original manuscript published suggest otherwise. The next two technical difficulties appear in the original manuscript and were apparently missed by its reviewers.

2) The WDNR-model was not verified for PCBs at high flows. The Asmoking gun≅ in this regard is contained within the first manuscript published (J. Great Lakes Res. 20(2): 416-434, 1994). This document is one of three referred to by James Hahnenberg (letter to Mark Travers, 29, Jan. 1999) as evidences of extensive review given to the WDNR model. The 1994 publication is key in that the later ones, in 1995 and another in 1996, cite it primarily. Any flaws that appear in the 1994 publication reappear in the later ones as well. The following paragraph details what I think is a fatal flow in the original 1994 document that was apparently missed by the reviewer(s) of the manuscript.

In the model results section of the document on pages 426-427 I call this readers attention to the paragraph commencing with Unfortunately and ending at top of next page. In this paragraph the authors write that there is no data verification of high PCB concentration, and that data collected (1989-90) at Fox River mouth cannot verify a major feature of the model prediction for PCB. Nevertheless, in the next sentence the authors write that as estimates the high flow PCB predictions are robust! The meaning of robust in this context eludes me. If the data is not available to test high concentration predictions or verify major features then the model is not robust. In the next section of the same paragraph the authors attempt to heal the lack of direct PCB verification by highlighting that the solids data in being constrained (and that since PCBs are known to be sorbed to solids), therefore follows closely the predicted resuspension and therefore PCB mass balance. This involves a key point missed by the manuscript reviewers. The point is they assumed the fate of PCBs is tied 1-to-1 with solids behavior and this is not correct in the case of the Fox River and other rivers with PCB in bed sediment. (This point is developed and presented later in this review). On page 427 the authors apply the model to PCB congeners but note that the accuracy of the model in this regard is largely the same as for  $\Sigma PCBs$ . Before using the robust model in evaluating the sources, transport and fate pathways for PCBs in the Fox River the author end this key section of the manuscript by suggesting that the high flow events account for nearly 50% of the  $\Sigma$ PCBs export. In summary there is no verification of the model at high flows and the attempt to verify using solids data is based on false assumptions.

3) It is conventional wisdom in some segments of the modeling community that because of the hydrophobic nature of chemicals such as PCBs that tracking particle behavior almost exclusively is the key to the calibration process. Early models, and WDNR in particular as evidence by the information contained in the Velleux and Endicott 1994 G. Lakes J. Great Lakes Research manuscript, suffered this defect to a great extent. Under the model calibration section first line the authors write that the calibration parameters were the dispersion coefficient, the settling velocity and the resuspension velocity. In an earlier section of the manuscript the porewater diffusion rate constant for the dissolved and DOC-bound  $\Sigma$ PCBs was set to 0.40 cm/d. Only the settling and resuspension velocities were spatially or temporally varied in the calibration exercise. The average and ranges of these appear in Table 3, p. 424 of the manuscript.

Because of the type and quantity of data available and the biases of the modelers, as noted above, the TSS data was used foremost and PCBs secondary in the calibration exercise (see Fig. 4). By adjusting resuspension parameters (primarily) and settling parameters the model was calibrated. The TSS and PCB data collected and used was within the low to mid-range flows of the Fox River (See Fig. 10). It is this range that the porewater diffusion process dominates or is as significant as the resuspension process. In fact with a model diffusion rate constant of 0.4 cm/d this model process was contributing insignificant amounts of PCBs to the water column. So, in effect the model was calibrated using particle transport parameters in an attempt to capture a release mechanism that was dominantly or significantly a chemical process. The modelers realized there was a disconnect between resuspension velocity PCB flux at low flows. Midway down first paragraph on page 430 they write:

• At low flow, however, the calibrated resuspension velocities are generally small (less than 0.1 mm/d) but still significantly. This background resuspension substantially influences water column PCB concentrations but has little impact on solids concentrations.

How is it possible for the resuspension velocities to be small and the PCB flux substantial? The writers offer a confusing, water-column solids concentration argument as an explanation, naturally. This section on model results ends with this statement:

• Given that the flux of PCBs released from the sediments by background resuspension is at least one order of magnitude greater than the sum of all other diffuse sources, resuspension is the most likely mechanism for PCB release at low flow.

In effect the modelers torpedoed their own efforts to properly calibrate the model by failing to realize that the so-called porewater diffusion process may become significant at low flows. In all fairness to the developers of the WDNR they were following the conventional modeling wisdom of the period. The same can be said about the reviewers for the 1994 J. Great Lakes Research article.

Only within the last decade have the transport processes within the top 10 cm been elucidated sufficiently to show that they are essentially non-molecular diffusion (See for example, Thibodeaux et al. 1990 Final Report on New Bedford Harbor Bed Sediment, LSU/HWRC, Baton Rouge). The importance of bioturbation and other particle translocation processes within the bed at depth #10 cm are being used in the current generation of mass-balance PCB river models. The FRG model has this process incorporated into its alternative model for the Fox River.

Summary. The WDNR model is badly flawed in at least three aspects as presented above. As a results it does not adequately represent the natural processes in the Lower Fox River so as to be of any use in making realistic predictions of downstream PCB movement. Recent development in the art and science of river-chemical modeling has been incorporated in the FRG alternative model of the Fox River in my opinion. Although not perfect it is the better predictor for assessing the fate of PCBs in the Lower River.

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## Appendix E

## **Review Comments of Dr. Willy Lick**

(Documents referenced in reviews are listed in reference section of main text)

### **Review of Fox River Modeling**

Models of the hydrodynamics, sediment transport, and contaminant transport in the Fox River have been recently developed by WDNR, LTI for the Fox River Group, and QEA for U.S. Fish and Wildlife. The WDNR and LTI models employ coarse scale elements in their calculations, while QEA employs fine scale elements in their calculations. Large numbers of adjustable parameters are used in the WDNR calculations, a smaller number (but still large) in the LTI calculations, while the least number of adjustable parameters is used in the QEA calculations.

WDNR and LTI have been working on this problem for a number of years and have numerous reports describing their work. QEA is seriously underfunded in their work and has only been able to devote small amounts of time to the project. No reports on their work were available; however, they did make an excellent presentation at the second panel review meeting and clearly presented the details of their model, its applications, and potential limitations and restraints on modeling.

An additional model, ECOM-SED, is being developed by Baird and Associates for the Fox River Group. However, no reports or presentations on their modeling effort were given to the panel.

### **Specific Comments**

1. The problem of numerical dispersion in the WDNR modeling of sediment bed dynamics is discussed extensively by LTI. This dispersion should be corrected, and my understanding is that it is, or will soon be, corrected.

Part of the justification for this dispersion may be the effects of bioturbation or other mixing processes in the upper layers of the sediment. If this argument is made, bioturbation should be modeled explicitly and (a) the mixing must be restricted to the upper well-mixed layer (not in all layers as it is now), and (b) the thickness of this layer must be accurately determined since the thickness of this layer has a significant effect on long-term PCB fate when bioturbation is invoked as a major mechanism. The importance of bioturbation must be established if it is used; no arbitrary parameterization to fit data should be allowed.

2. In the WDNR modeling, resuspension/ deposition parameters are adjusted for each spatial cell and with time. Because of this and because data is not available for big events and/or new conditions, their model is not suitable for prediction.

Most of the following comments apply specifically to the LTI alternative models, but similar comments also apply to the WDNR models. Page numbers refer to April 5, 1999 report by LTI unless otherwise specified.

3. P. 24. "The primary solids calibrated parameters for the alternative model above DePere Dam included abiotic solids settling and resuspension." "A constant abiotic solids settling rate of 1.5 meters/day was specified." A settling speed of 1.5 m/d  $\Box$  15 µm/s and (through Stokes law) corresponds to a grain size of about 3 to 4 µm. This is much smaller than observed particle sizes. In general, the deposition speed should be less than the settling speed due to non-deposition of settling particles in a flow. The deposition speed should then be a function of fluid speed as well as particle size. If this is assumed, it should be stated explicitly.

The resuspension velocity was then determined from the observed suspended solids concentration,  $C_s$ . Since  $C_s$  is a dynamic balance between resuspension and deposition, the

"right answer" for  $C_s$  can be obtained by arbitrarily changing one or the other variable as long as the second variable is changed accordingly. For example, a particular  $C_s$  can be obtained by high values of resuspension and deposition or by low values of resuspension and deposition, as long as they balance to give the observed value of  $C_s$ .

Since this is an important point, let me be more specific. Denote the erosion rate by E and the depositional rate by  $p w_s C_s$ , where p is the probability of deposition and is flow dependent,  $w_s$  is the settling speed of the particles/flocs, and  $C_s$  is the suspended solids concentration. The formula for the depositional rate is well-accepted. However, the values for E, p, and  $w_s$  are not well-known and can not be determined theoretically.

In a steady-state local equilibrium, the erosion rate is equal to the deposition rate, i.e.,

$$E = p w_s C_s$$

Rearranging, one obtains

$$C_s = \frac{E}{p w_s}$$

From this, it is easy to see that a numerical model can "predict" the observed value for  $C_s$  with an almost arbitrary value of E, as long as p  $w_s$  is changed accordingly, i.e., such that the ratio of E/p  $w_s = C_s$ . For a predictive model, the values for E and p  $w_s$  can not both be determined from calibration of the model. For a predictive and believable model, both should be determined independently and not fitted to the observations for  $C_s$ .

A consequence of the assumption of low settling speeds (as in the LTI modeling) is that, for calibration, low resuspension velocities and therefore low rates and low amounts of erosion are needed.

This assumption of a low settling speed of 1.5 m/day was also made for the River below DePere Dam (P. 30).

4. P. 13. "The settling velocity for biotic solids was set to a constant rate of 0.05 m/s." A settling speed of 0.05 m/s  $\Box$  5 × 10<sup>4</sup> µm/s and corresponds to a particle size of 220 µm, <u>if the particle were solid and mineral, such as sand</u>. For biotic solids, the densities, as determined relative to the density of water, would be much less (probably two orders of magnitude less) and the size would therefore have to be much greater. For biotic solids, this seems to be a huge settling speed. I have not determined what the consequences of this assumption are. This settling speed for biota solids was only used in the upper Fox River model.

5. P. 18, 30. Because the resuspension-deposition model by itself does not fit the data on suspended solids concentration, "the alternative model includes a seasonally-dependent background, non-flow-dependent solids resuspension velocity," referred to generally as background resuspension.

I believe this wording of "background resuspension" is incorrect and misleading. What is observed is low to moderate suspended sediment concentrations under low flow conditions. The inference that this suspended sediment concentration is due to "background resuspension" is misleading. The reason for these "background" concentrations is that (a) suspended solids generally consist of a wide range of particle sizes from coarse sands to fine-grained (almost colloidal) clays, and (b) fine-grained particles have very low settling speeds and stay in suspension for long periods of time. It is these fine-grained particles being transported through the system with negligible settling that are responsible for the low to moderate suspended sediment concentrations during low flow conditions. The LTI and WDNR models can not predict this phenomena since they only consider one size class of sediment. Multiple-size classes are required (Gailani et al., 1991).

6. P. 25, 30. Again, for purposes of fitting the data, pore water diffusion rates are assumed. Above DePere, they are assumed to be 0.196 cm/d from December through March and 39.2 cm/d for the rest of the year. Below DePere, they are assumed to be 3.92 cm/d (December through March) and 196 cm/d in no-ice conditions. No independent justification for these numbers is given and therefore this is pure curve fitting.

7. Referring to LTI June 1, 1999 report and the calculations of maximum velocities and shear stresses.

Fig. 4.6. Maximum velocity is 2.5 to 3.0 ft/s.

Fig. 4.7. These velocities correspond to 25 to 38 dynes/cm<sup>2</sup> for method 4 (Manning, as used by LTI).

Fig. 4.11. However, Fig. 4.11 shows no stresses greater than 15 dynes/cm<sup>2</sup> and the report states (P. 21) "All the shear stresses for the steady-state simulation are below 15 dynes/cm<sup>2</sup>."

Something isn't quite right.

Also, maximum shear stresses of 15 dynes/cm<sup>2</sup> are low compared to the Gailani et al. calculations.

8. Both WDNR and LTI use the  $\varepsilon$ -equation (also referred to as the Lick equation) to describe sediment resuspension. Some comments on this equation and its use are necessary.

This equation was proposed to describe results of resuspension experiments done on cohesive sediments in an annular flume at relatively low shear stresses (Lick, 1986). For field work with relatively undisturbed sediments, the Shaker was later developed and used (Tsai and Lick, 1986); experiments with this latter device mimic those in an annular flume and can also be described by the  $\varepsilon$ -equation.

A major limitation of both the annular flume and the Shaker is that they can only be used to measure the resuspension of relatively small amounts of sediment. By the very nature of these devices, the amount of resuspension is usually limited to a few millimeters; this typically corresponds to shear stresses less than (and often much less than ) 10 dynes/cm<sup>2</sup> (1 N/m<sup>2</sup>) (McNeil et al., 1996).

It should also be understood that both of these devices measure net resuspension, i.e., the amount of sediment suspended in the overlying water of the device. This suspended matter results from a dynamic balance between erosion and deposition. In these devices, the surficial layer of the bottom sediments is never swept away, and therefore lower layers are never exposed or eroded, even if they could be at the particular shear stress being tested. In particular, these devices do not take into account bed load or erosion and transport of coarse material.

The  $\varepsilon$ -equation is correct in that the functional form of the equation correctly describes the limited resuspension of fine-grained, cohesive sediments at a particular shear stress. It may be alright as a first approximation to the resuspension properties of <u>fine-grained</u>, cohesive sediments at depth as long as the parameters are estimated properly, from resuspension data. If parameters are obtained from the calibration of field data on C<sub>s</sub>, then the prediction of sediment erosion from this equation may be incorrect for the same reasons as noted above in the WDNR and LTI modeling. 9. It is well known that resuspension/erosion properties of sediments vary greatly and in a non-uniform manner as a function of depth and horizontal location (by orders of magnitude). Because of this, resuspension/erosion properties must be measured as a function of depth at different locations and can not be simply extrapolated to depth from surficial measurements.

In particular, for contaminated sediment problems in rivers and lakes (as in the Fox, but also at numerous other locations), it is necessary to know resuspension/erosion properties of sediments at high shear stresses, up to stresses on the order of 50 dynes/cm<sup>2</sup> (5 N/m<sup>2</sup>), and with depth in the sediments, down to a meter or more.

Because of the limited usefulness of annular flumes and the Shaker and because of the necessity to measure sediment erosion rates as a function of depth in the sediments and at different locations, Sedflume was devised and constructed and has been used extensively (McNeil et al., 1996; Jepsen et al., 1997, 1998, 1999). In particular, erosion rates of sediments in the Fox River were measured by means of Sedflume in July and August of 1993. Transport models have been adapted so as to use Sedflume data (Lick et al., 1998; Jones and Lick, 2000).

### Conclusion

Eventually, after all of the reviews, comments, and scientific and non-scientific verbiage, the bottom-line question that must be answered is "Are the models good enough?" The obvious question then is "Good enough for what?" Answer, good enough to quantitatively answer the questions that are the essence of this review, i.e., the following questions.

1. What will the water and sediment quality in the Fox be if nothing is done, i.e., if natural recovery is assumed? Time periods of interest are 5, 25, and 100 years.

2. What will the water and sediment quality in the Fox be if something is done? For example, possible remediations could consist of (a) dredging all or part of the river, (b) capping all or part of the river, or (c) some combination of dredging in some parts of the river, capping some parts of the river, and leaving other parts alone. Time periods of interest are the same as those above.

3. A third question that is now commonly asked (for the Fox as well as for other contaminated sediment sites) is "What will be the effects on water quality of large storms and floods in the river?" This is an important question but the answer to this question should really be included as a necessary part of the answers to the above questions.

Implicit in the answers to any of the above questions is the idea that nature is highly variable and, over any extended period of time, there will be periods of low flows followed by short periods of high flows. As stated by Ager (1981) when writing about the stratigraphic record, "The history of any one part of the earth, like the life of a soldier, consists of long periods of boredom and short periods of terror." Sediment and contaminant transport in rivers and lakes are also like the life of a soldier, with long periods of low to moderate winds and flows, when very little sediment and contaminant transport occurs, and short periods of high winds and flows, when most sediment and contaminant transport occurs (Lick, 1992; Lick et al., 1994). This high variability must be considered in the modeling and its effects calculated accurately.

In a previous review of modeling work on the Fox by a group of scientists convened by the Fox River RAP Science and Technical Advisory Committee, the consensus document summarizing the meeting (Barker and Kennedy, 1998) stated "Despite our best attempts at modeling ecosystems, there is considerable uncertainty in predicting sediment resuspension and deposition, food chain interactions, and changes in fish tissue PCB concentrations over decades." Essentially the group did not believe that the models available then (the WDNR and LTI models) could predict water quality in the Fox and Green Bay accurately enough for remediation purposes.

I was part of the review group then and agree with the above statement. At the present time, I do not believe the WDNR and LTI models can accurately predict water and sediment quality in the Fox either during natural recovery or as modified by remedial actions, especially when the effects of big events are included, as they necessarily must be.

As of now, models by these two groups disagree to more than an order of magnitude as far as depth of erosion is concerned. This does not give one confidence in these models or in modeling. Even if there is consensus on parameters so that the models agree, are they correct, i.e., can they quantitatively answer the questions posed above?

Serious limitations of the models are described above. Modifications and processes which are essential to a truly predictive and quantitative model of sediment and hence contaminant transport are as follows.

1. Resuspension/erosion must be determined independently by means of field experiments, not by calibrating resuspension <u>and</u> deposition simultaneously from suspended sediment data alone.

2. Variations in sediment properties (especially erosion rates) with sediment depth and horizontal location must be taken into account. This is necessary (a) to determine whether a particular location is erosional or depositional and (b) if it is erosional, to determine to what depth a large flood will erode the sediments.

3. Multiple size classes must be included in the model so as to predict the correct deposition rates and hence to properly explain "background resuspension."

4. Data on particle size distribution for incoming flows (as input data for the model) and for the outflow (as part of the calibration and verification process) must be obtained. This is crucial for the accurate prediction of solids transport and deposition. At present, no data of this type is available. One year of data (or even three to six months) would be useful. With this, even previous data on flows and solids concentrations could at least be interpreted more accurately. This measurement is relatively easy to do.

5. QEA's model is a numerically fine-grid, time-dependent model based on mass balance, good descriptions of basic processes, and requires minimal parameters and parameterization. Another similar model might be that due to Baird and Associates (ECOM-SED). QEA's model gave excellent but preliminary results. The uncertainties in the model were due to lack of data on the incoming sediment (particle sizes and sediment concentrations) and the erosion of bottom sediments.

Fine-grid models, such as the QEA model and ECOM-SED, with the proper data have the potential for accurately predicting sediment and PCB transport and therefore answering the questions posed above for the scenarios of natural recovery and potential remedial actions. This type of model should be used by all the principal parties in the Fox River dispute. For this purpose, funds for all models need to be made available on an equitable basis.

The above modifications must be included in the modeling in order to accurately predict water and sediment quality in the Fox during natural recovery and especially as a result of any remedial action. If this is done, then differences between the basic structures of the models will be small, and emphasis can be put on the correct description of the processes and accurate determinations of the parameters used to describe these processes. A much less confrontational atmosphere will result, disagreements on technical matters will be less, and natural recovery and remedial actions can be discussed rationally.