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State of Wisconsin

CORRESPONDENCE/MEMORANDUM

DATE: July 10, 1992 FILE REF: 3200

TO: Mark Giesfeldt - SW/3

FROM: Duane Schuettpelz - WR/2

SUBJECT: Water Quality and Sediment Quality Criteria for the Sheboygan River Superfund Site

The Bureau of Water Resources Management (WRM) is putting forward the following water quality and sediment quality criteria as part of the Superfund process for the establishment of Applicable or Relevant and Appropriate Requirements (ARARs) and To Be Considered (TBC) criteria or guidelines for use in establishing clean-up levels for the Sheboygan River Superfund site. Through the use of the Equilibrium Partitioning (EqP) Approach, Sediment Quality Criteria (SQC) were derived for PCBs for the Sheboygan River and Harbor Superfund project that would protect promulgated Water Quality Criteria in NR 105, Wisconsin Administrative Code, and proposed Great Lakes Initiative Criteria based on toxic PCB congeners as part of Great Lakes Critical Programs Act of 1990.

Protection of NR 105 Water Quality Criteria based on human health concerns will require SQC for total PCBs of 1-14 $\mu g/kg$ (ppb) based on the river segment use classification, total organic carbon (TOC) content of the sediment, and the calculated PCB organic carbon partitioning coefficient (Koc). Additional evaluations of biological effects related to PCBs in aquatic ecosystems and risk characterizations substantiate the low SQC values needed to be protective of all biotic components. The EqP calculated SQC values for total PCBs appear to be lower than background sediment concentrations. Based on available sampling data above the Sheboygan Falls dam, the surficial background concentration for total PCBs in sediment is approximately 50 $\mu g/kg$ (50 ppb). Total PCB clean-up levels for the site will need to be based on the background concentrations of total PCBs in the river sediments based on the considerations made in the following memo.

Using the EqP approach, SQC were also derived for recognized toxic PCB congeners. The toxic PCB congeners have calculated SQC below the background level for total PCBs, therefore special consideration must be given for removal of contaminated sediment and floodplain soils where the more toxic congeners are detected at or below the background concentration of total PCBs and above any toxic congener levels in background site sediments.

ARARs and TBC criteria for the Sheboygan Superfund site will be provided through three submissions. The first submission, which follows, establishes the clean-up criteria for total PCBs and toxic PCB congeners for the Sheboygan River and explains the basic rationale for the establishment of these numbers. Two later submissions, that will follow will discuss establishing SQC for other pollutants of concern, such as metals and polycyclic aromatic hydrocarbon compounds (PAHs), identified in the lower river and harbor portions of the Superfund site.

Assuming no other inputs of PCB contamination to the Sheboygan River system are present, successful remediation of contaminated sediments to a background concentration will likely be protective to the maximum extent possible of the state's Water Quality Criteria and lead to reasonable restoration of the biological integrity of the river system. However, meeting of the Remedial Action Objectives for the site is also contingent upon clean-up of the contiguous contaminated floodplain soils and any contaminated groundwater. The floodplain soils and groundwater could serve as a long term source to recontaminate the water column, biotic, and sediment compartments of the river.

Summary Recommendations

- Clean-up levels of total PCB concentrations in the Sheboygan River and Harbor sediments needs to attain site background levels to be protective of a number of biological endpoints and river uses, and lead to reasonable restoration of the biological integrity of the river system.

- Based on available upstream sampling data, total PCB concentrations in reference background sediment appears to be at a level of 50 μg/kg. Further background sediment sampling is needed to determine the range of variability and maximum probable concentration of total PCBs in reference sediments. Analytical data on Total Organic Carbon content in the sediments is also needed.

- Sediment quality criteria are also recommended for eleven coplanar and monoortho coplanar PCB congeners. As part of the Great Lakes Critical Programs Act of 1990, water quality criteria are proposed under the Great Lakes Initiative (GLI) for the eleven congeners to protect avian and mammalian wildlife populations inhabiting the Great Lakes Basin from adverse effects resulting from ingestion of surface waters and aquatic life taken from surface waters. Based on the GLI proposed water quality criteria for the eleven toxic congeners, sediment quality criteria were developed using an equilibrium partitioning approach. We recommend:

  a. determination of background concentrations of these congeners

  b. determination of congener concentrations within the sediments and on the floodplain soils of the site, and

  c. consideration for remediation of sediments and floodplain soils based on toxic congener concentrations where these toxic congeners of concern are found at elevated levels.

- Sampling data indicates soils and deposited sediments on the floodplain along the Sheboygan River contain elevated levels of PCBs. Clean-up of the concentrations are necessary to prevent transport of contaminated sediments back to the river from erosion or flood events to recontaminate the remediated river channel. We recommend that those contaminated floodplain areas that are prone to frequent flooding or are in the floodway be remediated to background levels comparable to our recommendation for the river channel sediments.

Note: All sediment concentrations of PCBs, Aroclors, and PCB congeners in this and the following paper are expressed on a dry weight basis.

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Application of ambient water quality criteria to the sediment interstitial and interfacial waters protects benthic organisms. For many benthic organisms, concentration response levels attributed to sediment interstitial water concentration matches aquatic toxicity values generated for water column organisms (U.S. EPA 1990b). Additionally, the possible bioavailability of persistent, highly bioaccumulative, organic compounds such as PCBs to any segment of the water column overlying the sediments is lowered with the application of ambient water quality criteria to the aqueous component of the sediment matrix.

Ambient Water Quality Criteria

NR 105, Wis. Adm. Code, contains numerical criteria for PCBs, PAHs, and some metals related to human health (human cancer criteria and human health threshold levels) and wild and domestic animal health (Table 1). NR 105 also contains acute and chronic toxicity criteria for substances to protect fish and aquatic life. It should be noted that it may be necessary to revise the use classifications of the Sheboygan River in the future based on the Great Lakes Water Quality Initiative. The proposed criteria for Total PCBs under the Great Lakes Water Quality based on human health and wildlife protection are 0.003 ng/L and 0.0015 ng/L, respectively. The Initiative would require a revision of the water quality criteria in NR 105. The human cancer criteria in NR 105 establishes the maximum ambient water concentration of a substance, in order to protect humans from an unreasonable incremental risk (10^{-5} risk) of cancer, resulting from contact with or ingestion of surface waters or from ingestion of aquatic organisms taken from surface waters. The wild and domestic animal water quality criterion for PCBs is established to protect animals that utilize waters of the state as a drinking water or foraging source. This criterion was established based on mink toxicity studies. Of all the species tested to date, mink have been identified as the most sensitive to PCB intoxication and as such serves as a sentinel species in monitoring PCB impacts on river systems.

The existing water quality criteria in NR 105 applicable to the use classifications of the reaches of the Sheboygan River discussed above are given in Table 1. The water quality criteria are given for those compounds that were identified in discussions during the Superfund process as being "pollutants of concern" because of their elevated concentrations in the sediments within the boundaries of the Sheboygan River Superfund site.

It is recognized that environmental criteria based on total PCB concentration (without consideration to specific congeners) may not address all biological concerns e.g., food chain contamination, toxicity, and persistence (U.S. EPA, 1990a; Smith et al., 1990; Kubiak et al., 1989; McFarland et al., 1989; Ankley et al. 1991; and Tanabe et al., 1987). It is also recognized that from a toxicological and ecological perspective, some PCB congeners are of more concern than others. Some are important because of structural and toxicokinetic properties similar to those of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). Other PCB congeners that may be found at higher concentrations in sediment than the dioxin-like congeners could have other effects (e.g. neurological) that are more significant. Different combinations of congeners could have different properties (Sonzogni, 1992). By measuring for congeners of concern in sediment, specific baseline information can be established to reference as new health information develops. While there is some understanding of the differences in toxicities, bioaccumulation potential, persistence, and exposure routes of biota to various congeners of concern, more studies are needed, especially on a site-specific basis to fully understand the physical, chemical, and biological factors influencing toxic PCB congener behavior in specific water bodies. Recent recommendations in regulatory evaluations of dredged material have included congener-specific PCB analysis (U.S. EPA/U.S. ACOE, 1991; Clarke et al., 1989).

WDNR believes there is sufficient information available to support the development of specific water quality criteria for some toxic PCB congeners. In early 1991, WDNR proposed PCB congener-specific water quality criteria for inclusion in NR 105, Wis. Adm. Code. The proposed criteria assigned toxicity equivalency factors (TEFs) for 11 toxic coplanar and monoortho coplanar congeners that possess the same mechanism of toxicity and similar molecular structure and activity relationships relative to 2,3,7,8-TCDD. U.S. EPA (1991) has noted that although application of TEFs to PCBs is not as straight forward as it is for polychlorinated dibenzo dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs), it is acceptable for use in wildlife protection. As with dioxins and furans, a TEF scheme for PCBs should be seen as an interim procedure.

The Great Lakes Water Quality Initiative, scheduled for publication in the Federal Register in 1992, establishes TEF values for dioxins, furans and PCBs to be applied to Water Quality criteria protective of wildlife and human health (Table 2). Currently proposed water quality criteria for 2,3,7,8-TCDD under the Great Lakes Water Quality Initiative are a) 0.0086 pg/l for protection of wildlife; b) 0.08 pg/l as a human noncancer value; and c) 0.01 pg/l as a human cancer value. TEFs for PCDDs, PCDFs, and PCBs are applied when establishing wildlife criteria for the congeners within these chemical groups. TEFs are applied when establishing human health criteria for only PCDDs and PCDFs (see Table 2). With congener specific PCB water quality criteria being promulgated based on toxicity equivalencies to 2,3,7,8-TCDD and with increasing knowledge of the significance of even minute amounts of the more toxic PCB congeners being present in environmental matrices, the discussion below puts forward sediment quality criteria for toxic PCB congeners to be considered in the ARAR evaluation process for determining site clean-up levels.

There are site-specific sampling data that indicate some toxic PCB congeners were present at relatively high levels in the sediments of the Sheboygan River (Sonzogni et al., 1991) prior to the pilot study sediment removal and armoring activities. Post-activity levels of these congeners in the sediments are unknown. Given even limited sediment sampling data, 78% of the 36 PCB congeners identified by McFarland and Clarke (1989) as congeners of highest concern were found in the Sheboygan River sediments (Sonzogni et al., 1991; David, 1990; WDNR, unpublished data; and McFarland et al., 1985). Taking the sediment levels of toxic congeners from the Sonzogni et al. (1991) study and applying the Aryl Hydrocarbon Hydroxylase (AHH) enzyme induction potency values for each congener relative to 2,3,7,8-TCDD from Smith et al. (1990), yields the TCDD equivalents given in Table 3 for the eight sediment sampling sites. Surficial background concentrations of PCB congener TCDD-equivalents is approximately 7 or less based on a limited amount of WDNR sampling at other sites.

ARARs and TECs Sediment Quality Criteria for Total PCBs and Toxic PCB Congeners

One concern in developing sediment quality criteria for the clean-up of contaminated sediments in the Sheboygan River is the protection of the promulgated water quality criteria in NR 105, Wis. Adm. Code. The intercompartmental relationships between sediment and water column matrices are discussed above. An equilibrium partitioning model is used to establish a concentration of PCBs in bedded sediment that will be protective of the water quality criteria. The partitioning model assumes that organic carbon measured as total organic carbon (TOC) is the primary sorbent of nonionic hydrophobic compounds in sediments. This EqP model uses the organic carbon partitioning coefficient specific to a compound and the TOC content of a sediment to estimate resulting concentrations of PCBs in the interstitial water and interfacial waters under equilibrium or steady state conditions. By setting the concentration of PCBs in water to the promulgated water quality criteria, the model allows calculation of the appropriate Sediment Quality Criteria (SQC). The EqP approach to establishing SQC is described in a number of U.S. EPA documents (1988, 1989b, 1990a, 1990b). The basic formula for deriving SQC from the EqP approach is shown in Figure 1. U.S. EPA will be publishing criteria in the Federal Register for five compounds using this approach. EPA sediment criteria are designed to protect benthic organisms from levels of chemical substances causing chronic toxicity.

WRM's initial application of the EqP methodology to derive Sediment Quality Criteria based on the human cancer criteria in NR 105, Wis. Adm. Code was for the Moss-American Superfund site which has site-associated PAH contaminated sediments (Schuettpelz memo of 01/09/90). It was indicated in the above memo that it was the WRM's intent to apply the EqP methodology to surface water resources at other Superfund sites where sediments contaminated with non-ionic hydrophobic compounds were an issue.

In regard to the Moss-American Superfund site, section 10.2.4 of the Record of Decision for this site delineated the WRM's intent of establishing SQC for the ARAR evaluation process based on the EqP approach for the protection of NR 105 water quality criteria:

> "In implementing the selected remedy, U.S. EPA has agreed to consider a procedure that is not an ARAR; compliance with Wisconsin SQC as shown. The selected remedy will achieve Wisconsin SQC in order to fulfill the statutory mandate for protectiveness."

Table 4 presents the SQC derived from the EqP approach utilizing water quality human cancer criteria and wild and domestic animal criteria contained in NR 105. The different use classifications of the segments of the Sheboygan River upstream and downstream of the second Kohler Dam result in different SQC for the two stream segments. Additional differences in SQC result from the use of organic carbon partitioning coefficients that were based on the relative proportions of the different Aroclors making up the concentration of total PCB concentrations at the sediment sampling sites in the segments of the river. The SQC at a particular site are determined by the concentration of total organic carbon (TOC) in the sediment. Sampling during the remedial investigation process found TOC content ranged from 0.3 to 3.0 percent in the sediments of the Sheboygan River.

The SQC developed for the toxic PCB congeners are presented in Table 5. These criteria were developed utilizing the EqP approach, the Great Lakes Initiative proposed water quality criteria for 2,3,7,8-TCDD, and applying the TEF for each PCB congener. It is recognized that some PCB congeners of concern, especially the coplanar congeners (#77, 26 and 169) may require more elaborate isolation techniques; however, techniques are available to accurately identify and quantify these congeners even in difficult matrices such as environmental extracts (Armstrong and Sonzogni, 1991; Crecelius et al., 1991).

It should be noted that the SQC in Table 5 are applicable only if individual congeners are present. Where a Water Quality criterion applies to a class of compounds, such as PCB congeners, with varying TEF values that must be considered, there are a number of ways to determine if congener concentrations in sediment are at a level to potentially partition to exceed water quality criteria. Where mixtures of congeners are present in sediment, the SQC values in Table 5 would need to be reduced such that the mixture of congeners is not partitioning to exceed the 2,3,7,8-TCDD Water Quality Criterion based on TEF values. Given the concentration of individual congeners in a mixture at a sediment sampling site, rearrangement of the formula used in the EqP approach allows the calculation of the estimated total partitioned concentration to the water to compare with the water quality criteria (Table 6).

Another approach to address mixtures of toxic PCB congeners in sediments is a Hazard Index (HI) approach (Fed. Reg., 1986) to be taken in relationship to congener-specific SQC. The Hazard Index of a mixture is based on the assumption of dose additivity. This assumption is that the individual compounds in a mixture induce the same effect by similar modes of action. The Hazard Index provides a rough measure of likely toxicity and requires cautious interpretation. As the index approaches unity, concern for the potential hazard of the mixture increases. If the index exceeds unity, the concern is the same as if an individual chemical exposure exceeded its acceptable level by the same proportion. Levels exceeding applicable congener-specific PCB SQC are indicated if the sum of the ratios of TOC normalized PCB congener concentration to the congener-specific SQC (normalized to TOC) is greater than or equal to one. This can be stated mathematically as follows:

$HI \geq 1$ indicates that applicable SQC are exceeded, where:

$$HI = \sum_{i=1}^{n} \frac{PCB_i}{SQC_i}$$

Where: i = toxic congeners that are present and have SQC;

PCB_i = TOC normalized congener concentration in sediment (μg congener/kg OC); and

SQC_i = TOC normalized congener specific SQC (μg congener/kg OC).

Other Considerations in Establishing SQC

In addition to the use of the EqP approach to develop SQC to protect NR 105 promulgated and proposed WQC based on human health and wild and domestic animal health, a number of other mechanisms to establish SQC were also evaluated in order to insure protection of other system biological components and aquatic life endpoints, such as benthic organisms, and fish tissue residue criterion (e.g., U.S. Food and Drug Administration action level [U.S. EPA, 1989a] and Great Lakes Water Quality Agreement Specific Objective [Environment Canada, 1991]). In this evaluation process, use of other partitioning models, (Van Der Kooij et al., 1991; U.S. EPA/U.S. ACOE, 1991), preliminary results from on-site studies, literature and case studies, and criteria and guidance established by a number of regulatory entities (Persaud et al., 1990; Chapman, 1986; Chapman et al., 1987; Wash. Dept. of Ecology, 1991; Long and Morgan, 1990; Van Dillen et al., 1991) from other sites with PCB contaminated sediments were considered. Review of the PCB sediment concentrations related to biological effects from the above sources substantiates the need to attain background-based target clean-up levels.

WRM is developing an assessment policy for contaminated sediments that considers multiple endpoints involving chemical, physical, and biological information in order to assess contaminated sediment sites, to establish clean-criteria, and select appropriate remediation.

Any description of contaminated sediment impacts needs to be based on the range of responses observed or predicted from a number of evaluation tools and methods. The results for multiple evaluation methods/endpoints provides the weight of evidence that substantiates chemical concentrations associated with biological effects and impairments. On a site-specific bases, interdependent endpoints from a number of evaluation methods involving synoptic measures of chemical concentrations, toxicity testing, and infield biological variables. need to be looked at together to relate the information in the form of sediment quality objectives.

By using an integrative assessment approach (Chapman et al. 1992), utilizing multiple evaluation methods/endpoints, remediation decisions are not based on any single calculated method, laboratory or field observation, but a weight of evidence is presented for making a decision.

Relationship of Background PCB Concentrations to SQC and Clean-Up Levels

The calculated PCB SQC values for protection of NR 105 Water Quality criteria and of biotic components, are lower than or similar to background PCB concentrations associated with sediments above the Sheboygan Falls dam. Practicality dictates that the clean-up criteria of contaminated sediments can be established at levels no more stringent than identified representative background concentrations. Clean-up criteria established by background PCB concentrations will be a controlling factor that determines clean-up levels along the impacted river reaches.

Cleanup criteria driven by background concentrations or calculated SQC are meant to be applied to any discrete portion of the sediment deposits in the cleanup area. For example, the clean-up criteria are applicable to each location or station where a sample is collected. If a core is collected, the criteria are applicable to each recognizable strata within the core. Clean-up criteria are not applicable to analytical results from composited sediment samples. For the purpose of evaluating sediment quality within a site unit, the analytical data from individual sample stations with in the site unit need to be reviewed and compared with the background clean-up levels. Therefore, cleanup criteria will be met only when all discrete samples are below established background criteria.

For the site, WRM defines uncontaminated floodplain soil and sediment background levels as the normal concentration of PCBs found at the site prior to its contamination. The upstream samples must be of similar soil type and sediment characteristics and formed under conditions comparable to those found along the impacted reaches of the river. Levels of PCBs in surficial background sites can be expected to have originated from broad regional or ubiquitous sources, primarily atmospheric deposition on the watershed and subsequent transport to the river. Because spatial distribution of PCBs will not be uniform, background concentrations will need to be expressed as a range of concentrations and a maximum probable background determined.

The SQC calculated for the potentially regulated toxic PCB congeners are less than the expected background concentrations for total PCBs. Remediation must consider removal of sediments and floodplain soils containing these toxic congeners even if present at levels less than total PCB background concentrations unless it can be demonstrated that the toxic congeners present are not biologically available and are not available for transport in the system.

Site Specific PCB Sediment Background Concentrations

The Remedial Investigation/Enhanced Screening Report (Blasland and Bouck, 1990) designates that two sediment samples will be collected behind the Sheboygan Falls Dam as background samples. It was indicated that the average PCB concentration of these two samples would be used as a basis of comparison for all sediment and soil data collected for the RI. The results of the two samples (Table 5-1 of the RI) were 1,200 μg/kg and 50 μg/kg with an average of 625 μg/kg.

Additional WDNR sampling of the deposited sediments and sediment trap collections above the Sheboygan Falls Dam generally did not find PCB levels above the detection level of 50 μg/kg in surficial sediments. David (1990) found the following total PCB concentrations in two core samples taken above the Sheboygan Falls Dam:

Sediment Site	Core Depth (cm)	Total PCB Concentration (μg/kg)
A1-1	0-15	35.4
A1-2	15-30	17.6
A1-3	30-45	38.1
A1-4	45-60	86.6
A1-5	60-75	91.6
		Average - 53.9
A2-1	0-15	33.0
A2-2	15-30	23.5
A2-3	30-45	66.3
A2-4	45-60	161.1
A2-5	60-75	58.1
		Average - 62.4

Historically, PCBs have been found in the sediments of the Sheboygan River above the Sheboygan Falls Dam (Kleinert et al., 1978). A single core sample (3 foot length) was taken in the Mullet River sediments at Highway PP in 1978. The sample contained 3,400 μg/kg total PCBs. PCBs were not found above detection (100-200 μg/kg) in sediment samples taken above and below the Plymouth Wastewater Treatment Plant on the Mullet during the 1978 study. However, PCBs were detected in the Plymouth wastewater treatment plant effluent at 9 μg/l and may have been responsible for downstream deposition of PCBs in the sediments behind the Sheboygan Falls Dam. The core sample taken during the RI behind the Sheboygan Falls Dam and reported as 1,200 μg/kg may have penetrated into older sediments containing PCB deposited from previous discharges. These historically deposited, buried PCBs should not be considered in establishing representative background levels for deriving a target cleanup level.

PCB Background in Sediments, Other Sites

The concentrations of PCBs in the top 6 cm of 4 Wisconsin lakes that had no influent tributaries and were distant from urban sources ranged from 4.4 to 50.9 μg/kg with an average of 21.8 μg/kg (Swackhamer and Armstrong, 1986). The only known source of PCBs was atmospheric deposition on the watershed and transport to the water body.

The state of Indiana has compiled data that establishes an average background level of PCBs in stream and lake sediments of 9 μg/kg based on 33 sites. The maximum level of PCBs found at a designated background site was 22 μg/kg (IJC, 1988).

Frank et al. (1981) reported the average whole lake concentrations of PCBs in Lake Michigan sediments (depositional and nondepositional zones) to be 9.7 μg/kg. The depositional basin in the lake off the mouth of the Sheboygan River contained an average of 29.2 μg/kg of PCBs.

Ontario (Persaud et al., 1990) has established a sediment background concentration of 20 μg/kg for PCBs based on an average in the upper Great Lakes basin surficial (5 cm) sediment concentrations.

Table 7 shows the total PCB concentrations in 18 sediment samples from 8 river and harbor sites in Wisconsin collected under a Wisconsin Coastal Zone grant study (WDNR, unpublished). The sampling sites generally range from rivers with no industrial development (sites 2 and 4), to harbor areas with minimal and some industrial development. Based on sampling location, there are intraharbor differences on sediment PCB concentrations (e.g., the Menominee River). Also in Table 7 are: a) the chlorohomolog percentages based on the total weight percent contribution of the congeners; b) the Total Organic Content (TOC) in the sediments at the sample sites; and c) the organic carbon normalized PCB concentrations at each site.

Sites with no industrial development (e.g., 2 and 4) had total PCB sediment concentrations of 24.56 and 33.30 μg/kg, respectively. The organic carbon (OC) normalized values for these two sites are 270 ad 166 μg PCB/kg OC, respectively.

Sites and PCB concentrations at the top of the table represent "clean," relatively unimpacted sites, to more impacted sites at the bottom of the table. Generally "impacted" sites at the bottom of the table have a corresponding low level PCB concentration site within the same harbor or river system. Seventy-two percent of the samples fall within a range of 12.56 to 160.94 μg/kg with a geometric mean of 54.22 μg/kg. The geometric mean PCB content on an organic carbon normalized basis is 1,189 μg PCB/kg OC.

In a study of four Ontario lakes (Macdonald and Metcalfe, 1990) in which atmospheric deposition was the major source of PCB contamination, total congener concentrations (sum of 19 congeners) observed were:

1.	Water	1-2 ng/l
2.	Sediment	10-50 μg/kg (dry weight) 160 to 550 μg PCB/kg OC
3.	Biota from lower trophic levels (zooplankton, golden shiner)	5-10 μg/kg (wet weight)
4.	Fish from upper trophic levels (yellow perch, smallmouth bass)	10-30 μg/kg (wet weight)

PCB Background in Floodplain and Upland Soils

Site Specific

Twenty soil samples were obtained during the RI/Enhanced Screening process from islands and portions of the river bank subject to flooding were downstream from the Tecumseh plant. No upstream background soil or floodplain soil samples were obtained. With the exception of one site that was represented as less than detection (less than <25 μg/kg), the other floodplain soils had PCB levels that ranged from 160-71,000 μg/kg.

Based on a Blasland & Bouck May 1992 Status Report for activities at the Sheboygan River site, sampling done at floodplain location FPL-11 had an initial PCB concentration of 220 mg/kg. Resampling in May 1992 showed levels of 330 mg/kg. If these values are based on composited samples, the areas around an individual sampling station could be higher.

Since overbank flooding occurs along the river, future flood events may transport and return PCB contaminated floodplain soil and sediment particles back to the river channel. We urge that the criteria established for sediment levels of PCBs also be applied to floodplain soils.

Other Sites

Finlay et al. (1976) report means of less than 10-40 μg/kg at background soil sites in the U.S. In Great Britain, soil samples collected from rural and industrial sites contained an average of 33.7 μg/kg of PCBs with a range of 7 to 100 μg/kg (Eduljee et al., 1985). In another study in Great Britain, based on soil samples collected from 84 locations, the general background levels of PCBs were stated as ranging up to approximately 30 μg/kg. Elevated levels were related to urban and industrial areas. The range of concentrations found in 84 samples was 1.9 to 1,208 μg/kg with a mean of 86 μg/kg and median of 23 μg/kg. Sixty percent of the samples fell within the range of 1.9 μg/kg to 36 μg/kg with the mean of 11 μg/kg (Eduljee et al., 1987).

Holsen et al. (1991) measured the dry deposition of PCBs in urban areas during seasonal periods. Dry deposition samples in Chicago averaged 36.8 μg PCB/kg (range 28.5-53.8 μg/kg) of material deposited. The PCB flux measured in Chicago was found to be 3 orders of magnitude higher compared to flux in a nonurban area. Spring deposition samples in the Holsen study were highly correlated with Aroclor 1260 and fall samples were correlated with Aroclor 1242. The depositional homologues show two distinct peaks of concentration for the tri- and hexachlorobiphenyl, which are characteristic of Aroclors 1242 and 1260, respectively.

The above background soil levels of PCB's appear to be comparable to the 50 μ/kg background concentration in sediments. Therefore application of 50 μ/kg for driving cleanup of sediments and floodplain soils would appear to be appropriate. Sampling to establish background PCB levels in floodplain soils of the Sheboygan River will verify that 50 μ/kg is appropriate for the floodplain soils.

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Figure 1
Formulations and Calculations
Used in Deriving Sediment Quality Criteria

A. $SQC = WQC \times K_{oc} \times f_{oc}$

where

SQC = Site specific Sediment Quality Criteria for a pollutant. If the calculated sediment criteria is exceeded, there is a potential for the interstitial water concentration of the pollutant to exceed the Water Quality Criteria. SQC expressed as ug/Kg.

WQC = Water Quality Criteria - can be derived from published aquatic life/water quality criteria or human health criteria documents, or criteria promulgated in regulations or codes (e.g., NR 105, Wis. Adm. Code). EPA (1988) in developing interim SQC uses chronic water quality values because it protects aquatic life from effects due to long-term exposure to contaminated sediments. WQC expressed as ug/L.

K_{oc} = Organic carbon partition coefficient. K_{oc} is a measure of the relative sorption potential for organics. K_{oc} indicates the tendency of an organic chemical to be adsorbed and it is largely independent of soil properties.

$$K_{oc} = \frac{\text{mg adsorbed/Kg organic carbon}}{\text{mg dissolved/L solution}}$$

$$K_{oc} = \text{L/Kg}$$

For nonpolar organic contaminants, the primary sorbent is the organic carbon on the sediment. The higher the K_{oc} value, the greater the affinity for the nonpolar organic compound to concentrate in the organic matter in sediments and in lipid deposits of biota, and the lower the solubility in water.

Where the K_{oc} value is unknown for a compound, the octanol-water partition coefficient can be used as a surrogate to derive a K_{oc} value by use of the following formula (EPA, 1986):

$$\text{Log}_{10}(K_{oc}) = 0.00028 + 0.983 \times \text{Log}_{10}(K_{ow})$$

f_{oc} = Fraction of organic carbon found in sediment samples expressed as a decimal. E.g., a Total Organic Carbon test result of 32,000 mg/Kg = 3.2% = 0.032 Kg C/Kg Sediment.

B. To find the interstitial water concentration (IWC_o) of an organic contaminant to compare with the WQC criteria value, with a known sediment concentration and organic carbon percentage, the following can be used:

$$IWC_o \text{ (ug/L)} = \frac{\text{Sediment Concentration (ug/Kg)}}{K_{oc} \times f_{oc}}$$

Where the IWC_o exceeds the WQC, the SQC value is also being exceeded.

	% TOC	µg PCB/Kg Sediment Site Specific Criteria	
		Minimum Koc	Maximum Koc
Total PCBs	1	4.37	28.1
	2	8.74	56.2
	3	13.12	84.3

<u>Waelderhaus Dam to Harbor</u>

	Organic Carbon Normalized Criteria (µg PCBs/Kg OC)	
	Minimum Koc	Maximum Koc
Total PCBs	1,296.7	6,758.7

	% TOC	µg PCB/Kg Sediment Site Specific Criteria	
		Minimum Koc	Maximum Koc
Total PCBs	1	13.0	67.6
	2	25.9	135.2
	3	38.9	202.8

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Table 5. Calculation of Sediment Quality Criteria for Toxic PCB Congeners Based on the Equilibrium Partitioning Approach and Driven by the Great Lakes Initiative Water Quality Criteria for 2,3,7,8-TCDD

Sediment Quality Criteria (μg/kg)

	Wildlife Sediment TOC	
	1%	3%
Coplanar		
126	0.005	0.015
169	0.03	0.10
77	0.02	0.05
Monortho		
118	0.37	1.10
105	0.30	0.89
123	0.37	1.10
114	0.30	0.89
156	0.99	2.96
157	0.99	2.96
167	1.2	3.65
189	3.3	9.8

Applicable to conditions of the presence of individual congeners and not to be applied to mixtures of congeners.

SQC derivation for toxic PBC congeners:

$$\begin{pmatrix}\text{Toxicity Equivalency}\\ \text{Factor for PCB}\\ \text{Congener [TEF]}\end{pmatrix}\begin{pmatrix}\text{Ambient Water}\\ \text{Concentration for}\\ \text{Congener [AWC]}\end{pmatrix} \leq \begin{matrix}\text{Great Lakes Initiative}\\ \text{Water Quality Criteria}\\ \text{for 2,3,7,8-TCDD (WQC)}\end{matrix}$$

$$AWC = \frac{WQC}{TEF}$$

$$SQC = AWC \times foc \times Koc$$

Where:

SQC = Sediment Quality Criteria
μg Congener/Kg Sediment

AWC = Ambient Water Concentration for congener that cannot be exceeded or 2,3,7,8-TCDD Water Quality Criteria from Great Lakes Initiative will be exceeded based on Congener Toxicity Equivalency Factors

foc = Organic Carbon weight fraction in sediments

Koc = Organic Carbon partitioning coefficient for PCB Congener

Table 6. Method of Comparing Total Estimated Toxic Equivalent PCB Congener Concentrations Partioned to Water From Sediments with Proposed Great Lakes Initiative 2,3,7,8-TCDD Water Quality Criteria

PCB Congener IUPAC No.	Sediment Concentrations µg/Kg[1]	K_{oc}[2] L/Kg	f_{oc} Sediment TOC[1]	K_{oc} x f_{oc}	AWC[3] µg/L	TEF[4]	TEF x AWC
<u>Coplanar</u>							
126		5,888,437				0.1	
169		19,498,446				0.05	
77		1,778,279				0.01	
<u>Monortho</u>							
118		4,265,795				0.001	
105		3,467,369				0.001	
123		4,265,795				0.001	
114		3,467,369				0.001	
156		11,481,536				0.001	
157		11,481,536				0.001	
167		14,125,375				0.001	
189		38,018,940				0.001	

Table 6. (cont.)

Predicted Ambient Water Concentration (AWC) = $\frac{\text{Congener Sediment Concentration } (\mu g/kg)}{K_{oc} \times f_{oc}}$	Sum of TEF x AWC Values	
	Great Lakes Water Quality Initiative 2,3,7,8-TCDD Criteria Human Cancer Value - 0.01×10^{6} µg/L Human Noncancer Value - 0.08×10^{6} µg/L Wildlife - 0.0086×10^{6} µg/L	

[1] Site measured values for the listed congeners. TOC content of the sediment expressed as a decimal fraction (e.g. 2.3% = 0.023).

[2] Organic Carbon Partitioning Coefficients (K_{oc}) values derived from K_{ow} values of Hawker and Connell (1988) and the following formula from Di Toro (1985):

$$Log_{10}(K_{oc}) = 0.00028 + 0.983 \times Log_{10}(K_{ow})$$

[3] Predicted Ambient Water Concentrations (AWC) derived from above formula.

[4] Toxicity Equivalency Factors derived from Safe (1990).

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Table 7. Range of PCB Sediment Concentrations In Reference Sites and Harbor Sites With Varying Degrees of Industrial And Urban Development

River or Harbor Sampling Site[1]	Total PCB Concentration ug/kg[2]	TOC Content %	OC Normalized ug PCB/Kg OC	Chlorobiphenyl Isomer Distribution In Total PCBs At Sample Sites (Weight Percent)							
				Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona
1 KW	12.56	8.48	156	0	9.8	25.7	20.8	32.2	11.5	0	0
2 MI	24.56	9.09	270	5.3	14.3	52.4	17	11	0	0	0
3 SL	31.35	3.82	821	0	1.6	2.1	17.4	43.1	23.2	12.6	0
4 BB	33.30	20.7	161	4.2	12.2	19.3	26.9	12.8	7.9	3.3	13.5
5 AB	39.94	9.15	437	5.0	0	12.2	28	28.5	16.2	8.5	1.5
6 PW	43.25	1.19	3,634	0	9.3	23	26.9	29	8.2	3.5	0
7 PW	50.12	0.63	7,956	0	8.7	22.4	30	28	6.1	4.8	0
8 KE	53.44	4.28	1,249	0	11.9	38	19	19.3	5.9	4.9	1.1
9 MR	65.99	7.50	880	0	5.5	10.1	30.8	24.9	15.3	10.2	3.3
10 MR	79.68	2.63	3,030	0	0	7.7	31.8	32.5	16.2	11.9	0
11 MR	147.41	5.18	2,846	.9	7	18.6	22.5	21	13.8	14.7	1.4
12 SL	147.69	3.50	4,220	1.2	0	4.9	14.4	31.5	26.6	21.4	0
13 MR	160.94	4.51	3,569	0	4.1	11.9	15.9	23.1	21	22.2	1.8
14 SL	463.02	2.87	16,133	.5	7	25.7	27.2	23.4	10.5	5.8	0
15 MR	559.57	3.69	15,164	5.1	10.1	16.8	25	24.6	7.7	10.7	0
16 KE	609.35	2.39	25,496	.5	8.3	42.7	19.1	12.4	5.7	5.3	.4
17 MR	1,107.02	3.51	31,539	.3	4.9	7.4	10.6	21.2	28.7	25.3	1.6
18 BH	1,609.13	1.10	146,285	.1	.4	1.4	12.6	52.8	21.3	11.3	.1

[1] Sampling Site Locations

1.	Kewaunee Harbor	KE-4B	
2.	Mink River	DR-6B	Door County
3.	St. Louis River Hallet Dock #6, Superior - Duluth Harbor	DS-1B	
4.	Bois Brule River Stones Bridge Landing	DS-6B	Douglas County
5.	Allouez Bay Superior-Duluth Harbor	DS-4B	
6.	Port Washington Harbor	OE-2B	
7.	Port Washington Harbor	OE-3B	
8.	Kewaunee Harbor	KE-5B	
9.	Menominee River Above Niagara, USH 141 Bridge	ME-6B	
10.	Menominee River Sturgeon Falls Dam	ME-5B	
11.	Menominee River Mid-Channel Bar	ME-1B	
12.	St. Louis River Minn. Power & light, Superior-Duluth Harbor	DS-2B	
13.	Menominee River 8th Street Slip at Marinette	ME-2B	
14.	St. Louis River Outfall from Western Lake Superior Sanitary District PTW, Superior Duluth Harbor	DS-3B	
15.	Menominee River Boom Landing	ME-4B	
16.	Kenosha Harbor	KA-1B	
17.	Menominee River Off of Ansul Coal Pile	ME-3B	
18.	Bayfield Harbor	BD-5B	

[2] Wisconsin State Laboratory of Hygiene Analysis.

Represents sum of 38 individual and 45 coeluting PCB congeners.

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