DEPARTMENT OF NATURAL RESOURCES
NORTH CENTRAL DISTRICT

FROM: Jim Kreitlow

DATE: 4/14/95

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___S. Ironside, Friendship
___J. Zimmermann, WI Rapids

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___B. Baker-WR/2
___J. Bode-WR/2
___E. Boebel-WR/2
___L. Kosmond, WR/2
___C. Ledin-WR/2
___L. Liebenstein-WR/2
___B. Wallace-WR/2
___T. Janisch-WR/2
___D. Schuettpelz-WR/2
___D. Valvassori-WR/2
___T. Lohr, WR/2
___M. Turville-Heitz, WR/2
___J. Amrhein-WR/2

___T. Bainbridge-SD
___D. Weisensell-LMD
___A. Bernhardt-WCD
___S. Fix-SD
___Planner-NWD
___M. Jones-SED
___T. Smith-NWD
___C. Koperski-WD
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COMMENTS:

Evaluation of Sediment Quality In Military Creek Associated With The Site Assessment for the C.M. Christiansen Wood Treatment Facility

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April 1995

Summary of Sediment Quality Evaluation for Military Creek Associated with the C. M. Christiansen Wood Treatment Facility

Along with the dioxin/furan data provided to us in the Khazae to Parkinson memo of June 21, 1994, I have also taken a look at sediment and soil data for inorganics and organics provided to us in a Khazae to Antonek memo of March 21, 1994. It is my understanding the site sampling was performed by the Site Assessment program to collect contaminant specific data to score the site for placement on the Superfund National Priorities List. My evaluation focused primarily on the sediment concentrations of pentachlorophenols (PCP) and dioxins and furans. However, data on PAHs, metals and organic compounds in sediment samples were also reviewed and some comments made.

It needs to be noted that all the concentrations reported out on the data sheets for all parameters in soils and sediments that

accompanied the above two mentioned memos are on a wet weight basis and need to be converted to a dry weight basis to make standard evaluations and comparison Total solids information is provided for each sample to do this conversion.

Unfortunately, EPA does not believe that obtaining particle size analysis or TOC information for sediments contributes to the purpose of collecting contaminant data for site scoring purposes. I don't know what elements are in their scoring system but I believe particle size and TOC information is needed to do any risk-type of evaluation to provide information on potential partitioning behavior between environmental compartments, estimate bioavailability type of substrate conditions and habitat for stream biota, and potential for off-site transport of contaminants related to the hydrodynamics of the stream. Based on the Kreitlow sediment sampling in 1992 we do have some idea of particle size distribution and TOC levels but it is not at the same sample sites for the Site Assessment.

For the sediments, core samples were taken (0-2 ft at S-20, S-21; 0-1 ft at S-22, S-23;) and a trowel sample was taken at S-24 because of the hard bottom.
The core samples were composited for analysis. With compositing lengths of core, any information on elevated levels of contamination present in particular strata or segments is lost. The elevated concentrations in the strata will be diluted by mixing in uncontaminated material from other strata. It would be important to know if the contaminated strata lies at the top of the sediment surface which makes up the biologically active zone (as much as 15 cm) and where interchange with the overlying creek water can occur, or if the contaminated strata lies buried under a clean cap of naturally deposited sediment. If the contaminated strata is 6 inches thick and the remaining 18 inches of material in a 2 foot core is uncontaminated, the actual concentration of contaminants in that 6 inches could be 4 x that reported based on the analysis of the entire composited 2 foot core. If the contamination

lies in the top 6 inches of sediment this could be important for evaluating the risks and biological impacts of the site. This should be kept in mind in the discussion that follows.

In the summary that follows, there may be references to tables and ~~text~~ the text that follows that more fully explains the data and interpretations.

The site soil data shows significant levels of pentachlorophenols and elevated levels for a number of pesticides. Dioxin and furan analysis was not done for plant site soils. We requested dioxin and furan analysis for sediments. ~~Test~~ Sediment sample S-22 that had a pentachlorophenol and concentration of 2.5 mg/kg had a corresponding 2,3,7,8, substituted furan and dioxin isomer TCDD-Equivalent ~~▲~~ of 2504 pg/g. ~~Based on ratio of TEF to TCDD-EQ for the sediments, the soil sample at S-11 that had 87,000 mg/kg would potentially have to be occurrence of TCDD EQ of 8,338,200 pg/g.~~

The PCP/TCDD-EQ ratio in sediments is controlled by a number of weathering conditions in the aquatic system. Some site soils had PCB concentrations of up to 193,000 mg/kg, or more than 19% PCP. The co-occurrent TCDD-EQ concentrations must be significant. Based on the potential for TCDD-EQ to be extremely high, it would seem that scoring for listing the site should have considered this in addition to pentachlorophenol. ~~Considerations~~.

Site soils and groundwater may continue to be sources of contamination of the Creeks in the future through surface water runoff and any channels or pipes from the property that enter the Creek. Site ~~soil~~ sediment remediation and appropriate controls must proceed remediation work.

Evaluation Summary of Dioxin and Furan Data

1. The reported detection limits for ~~some of~~ the 2,3,7,8-substituted dioxin (PCDD) and furan ~~congeners~~ (PCDF) congeners were in cases two to three orders of magnitude too high and did not yield any information. For site investigations involving aquatic systems, detection limits for the furan and dioxin congeners of concern need to be in the range of 0.5 – 1.0 pg/g (see Table 3).

2. The dioxins and furans in the Military Creek sediments were dominated by the following congener in order of concentrations found:
   a. OCDD
   b. OCDF
   c. 1,2,3,4,6,7,8 HpCDD
   d. 1,2,3,4,6,7,8 HpCDF

   The predominant concentrations and relative proportions of these four congeners are characteristic of the fingerprint proportions of these congeners as impurities in the manufactured PCP product (Tables 16 – 20).

3. Applying the standard Toxic Equivalency Factors to all quantified congeners, yields the following 2,3,7,8-TCDD Equivalents (TCDD-EQ) expressed as pg TCDD-EQ / g:

Military Creek Sediment Sample Site	Dioxin Contributed TCDD-EQ pg/g	Furan Contributed TCDD-EQ pg/g	Total TCDD-EQ pg/g
*S-20 (Reference)	1.41	0.92	2.33
S-21	650	333	983
S-22	1611	893	2504
S-22 DUP	1190	623	1813
S-23	28.8	8.2	37
S-24	34	14	48

* High detection levels for Military Creek did not allow establishment of reference site values. The values used are from a typical unimpacted waterbody in Wisconsin.

On average, almost 70% of the TCDD-EQ concentration is contributed by the 1,2,3,4,6,7,8-HpCDD and OCDD congeners, which is again characteristic of the dioxin and furan fingerprints in manufactured PCP.

The TCDD-EQ concentrations in samples S-21, S-22 and S-22 DUP represent the highest levels found in any sediments sampled to date around the state. The next

highest levels are found in the lower Fox River below the De Pere dam where the sediments have been impacted from paper mill effluents. TCDD-EQ levels in the lower Fox average 210 pg/g with a maximum of 441 pg/g.

The Military Creek situation is unique in that the TCDD-EQ concentrations ~~is~~ are being largely contributed by the higher chlorinated congeners that have the lowest TEF values. The large concentrations are responsible for this.
While the most toxic congener 2,3,7,8-TCDD, was not detected due to the abnormally high detection limits, the fingerprint for manufactured PCP indicates none would be expected to be found even at an acceptable detection level. The PeCDDs/Fs and HxCDDs/Fs would be expected to be present but at low concentrations, much below the detection limits reported for the analysis. That they were missed because of the high detection limits achieved, the low levels would only contribute a small amount to the total TCDD-E compared to the OCDD, OCDF ~~and~~ HpCDF and HpCDF

may not be that important as

4. Using a simple model, the sediment pore water concentrations were predicted based on the sediment concentrations of each dioxin and furan congener of concern (Tables 23-27). (p. 32) The model is:

$$C_{pw} = \frac{C_{sed}}{K_{OC} \times f_{OC}}$$

An organic carbon partition coefficient specific to each congener was used. Sediment TOC was assumed to be 5%. Once the pore water concentration was calculated it was multiplied by the congener-specific TEF value to find the TCDD-EQ concentration. The TCDD-EQ value for all congeners in the pore water was totaled. The total ~~The~~ TCDD-EQ concentrations for all congeners in pore water at each sampling site are as follows:

Sediment Sample	Total Estimated TCDD-EQ In Sediment Pore Water pg TCDD-EQ/L
S-21	0.649
S-22 DUP	2.0
S-22	1.38
S-23	0.01
S-24	0.017

A criteria to compare these values against is the ambient water quality criteria in NR 105. Criteria applicable to a Cold Water Community Use application for Military Creek is appropriate to protect human health. The criteria value is 0.03 pg/L. While it is not appropriate to compare surface water quality criteria with pore water concentrations, the contaminants in the pore water will diffuse out of the pore to the overlying surface waters. Their ultimate concentrations there will depend on the creek flows, mixing, water volume etc. Generally, some portion of the water column immediately above the sediment surface will have elevated levels of contaminants in solution if sediment contamination is at the surface. Even if ~~soil~~ contaminant concentrations where reduced by an order of magnitude from the pore water to the overlying surface waters by dilution at sites S-22 and S-22 DUP, they would still potentially exceed the 0.03 pg/L criteria.

The Great Lakes initiative ~~for~~ Water Criteria development document

has the following water quality criteria for 2,3,7,8-TCDD:

Wildlife Protection - 0.0031 pg/L

Human Cancer Criteria - 0.0085 pg/L

Human Non Cancer Criteria - 0.067 pg/L

Pore water concentrations at the military Creek site would have to be reduced by 3 orders of magnitude or more to get below the above criteria levels at S-22 and S-22 DUP.

5. See page 39 for model used to predict fish uptake of dioxins and furans from water by applying a BCF factor and predicting release from sediments. Model shows no problems.

6 See page 44 for model used to predict fish uptake from water and food chain. Use of a Bioavailability Index. Model shows potential problems from predicted fish tissue residue concentrations of furans and dioxins.

7. Pentachlorophenol concentrations in sediment indicate potential problems to benthic invertebrate Community. (page 46)

8. No metals problems in sediments. Maybe be PAH problems related to potential impact to benthic organisms. (page 56) (page 57)

9. Pesticides and other organics need further assessment. (page 60

Converting Wet Weight Concentrations to Dry Weight Concentrations

Concentrations for the 2,3,7,8-substituted PCDD and PCDF isomers reported in the Khazae to Parkinson memo of 6/21/94 are on a wet weight basis and need to be converted to a dry weight basis for comparison of results from site-to-site and with other statewide and literature data. The percent solids content for each sample is reported as below:

Sample	% Solids	Conversion Factor (CF)
S-20 Background	12	8.33
S-21	32	3.13
S-22	57	1.75
S-22 DUP	50	2.00
S-23	66	1.52
S-24	20	5.00

The conversion factor to go from wet to dry weight concentrations is derived by $\frac{100}{\%\text{ Solids}} = CF$

$CF \times \underset{\text{Concen.}}{\text{Wet Weight}} = \underset{\text{Concen.}}{\text{Dry Weight}}$

Table 1 shows dry weight sediment concentrations for the 2,3,7,8 substituted isomers based on the above formula. The concentrations in Table 1 are reported in units of pg/g (ppt or ng/kg

Detection Limits

A number of isomers were not found above the reported detection limits of the contract laboratory. Table 2 shows where the isomers were reported as non-detected and the detection limit. Since these detection limits are based on wet weight it probably is appropriate to apply the sample conversion factor from above to derive a dry weight detection limit. Table 3 shows this conversion to dry weight detection limits. It is noted that these detection limits are high meaning biosignificant 2,3,7,8 substituted isomers as well as 2,3,7,8 TCDD may be present but not being measured. Suitable detection limits for the important

PCDD and PCDF 2,3,7,8 substituted isomers are shown in the far right column of Table 3. These detection levels were achieved by a laboratory doing sediment analysis for the isomers associated the Lehr paper mill sludge landfill on Kankakee Creek, a tributary to the Fox. This is a site that was undergoing an ERR program investigation. It is noted that these suitable detection limits are 2-3 orders of magnitude lower than those achieved for the Military Creek sediments. To do a thorough evaluation of potential impacts on aquatic biota and risks associated with toxicologically significant isomers of dioxins and furans, detection limits of 0.5-1.0 pg/g dry weight should be established in the data quality objectives for a sampling project.

Calculation of 2,3,7,8 TCDD toxic equivalency (TCDD-EQ) based on the Toxic Equivalency Factor (TEF) specific value X the measured 2,3,7,8 substituted dry weight concentration

Table 4 shows the TEF adjusted concentration for each 2,3,7,8 substituted dioxin and furan isomer, a total for all substituted dioxin and furan isomers, and total TCDD-Equivalents (TCDD-EQ) for each of the 6 samples. The duplicate sample, S-22 DUP (S-25) is looked at as a separate sample.

Table 5 shows the percent contribution of each 2,3,7,8 substituted isomer to the total TCDD-EQ.

Because of the high detection limits and inability to measure approximately 60% of the isomers in the samples, the total potentially concentrations of dioxins and furans in Table 1 and total TCDD-EQ in Table 4 are on the low end of the range of potential concentrations

in the sediments. On summary, the Total TCDD-EQ concentrations in the sediment samples are shown below:

Sample Site	pg TCDD-EQ / g sediment
S-20 Background	High DL's, Not determined
S-21	983
S-22	2504
S-22 DUP	1813
S-23	37
S-24	48

On Table 5 it should be noted the relatively high TDDD-EQ contribution in each sample coming from the 1,2,3,4,6,7,8 HpCDD and OCDD isomers:

	% TCDD-EQ CONTRIBUTION TO TOTAL	
	Ave.	Range
1,2,3,4,6,7,8 HpCDD	28.8%	22.1 — 37.3
OCDD	31.3%	23.2 - 40.5
TOTAL	Ave. 69%	

Almost 70% of the Total TCDD-EQ from the 5 sediment sample is due to the above 2 isomers. The % TCDD-EQ. contribution from the isomers is comparable in samples S-21, S-22, and S-22Du. The contribution increases in S-23 and S-24. The difference is that in the latter samples is that the total PCDD and PCDF isomer concentrations are less.

Total 2,3,7,8 substituted isomer concentrations versus total dioxin and furan concentrations

Table 6 shows the number of positional isomers in each dioxin and furan chlorohomolog group (Total 210) and the number of 2,3,78 substituted isomers in each group (total 17). Measuring only the substituted isomers and totaling them accounts for only a fraction of the total furan and dioxin isomers that may be present in sediment. The concentrations and relative proportions of isomers present depends on the original source(s), degree of weathering etc. In some cases, concentrations are reported for the furan and dioxin chlorohomolog groups, and not for individual isomers.

Background Perspective

Tables 7-15 presents a perspective on concentrations of the chlorohomolog groups and TCDD-EQ at a cross section of soil and sediment sites, both relatively unimpacted (ubiquitous sources primarily air transport) and various degrees of impact. All values are reported in units of pg/g (ppt) dry weight or pg TCDD-EQ/g dry weight.

The toxicological significance of the Military Creek sediment samples in terms of TCDD-EQ can be seen by comparing Table 4 values with Table 15 values, especially those for Wisconsin sediment sample results. The comparison is as follows:

TOTAL TCDD-EQ
(pg TCDD-EQ / g)

- Unimpacted Reference Site Sediments — 0.15 – 2.45
- Peterwell and Castle Rock Flowages On Wisconsin River Impacted From Paper Mill Discharges — 30.86 — 77.97
- Fox River Below De Pere Dam Impacted From Paper Mill Discharges — 21 – 441, $\bar{x} = 210$
- Military Creek Sediments — 37 – 2504

Individ. – 983
2504
1813
37
48

$\bar{x} = 1077$

Based on existing statewide sediment data, Military Creek has the highest TCDD-EQ concentration of any known site in the state. The concentrations may be even greater based on the high detection levels for some of the isomers of concern as discussed above.

As some additional perspective on the Military Creek TCDD-EQ concentrations, Wisconsin's landspreading program for paper mill sludges sets the following concentration limits for spreading based on the following land uses:

	TCDD-EQ
Silviculture	10 pg/g
Agriculture	1.2 pg/g
Agriculture with Grazing	0.5 pg/g

The levels are established based on foodchain uptake and risks posed to exposed wildlife.

The relatively large concentrations of the following should be noted based on Table 1 values:

OCDD
OCDF
1,2,3,4,6,7,8-HpCDD
1,2,3,4,6,7,8-HpCDF

These high concentrations are reflected in the % contribution to the Total TCDD-EQ for each sample even though their TEF values are relatively low. A comparison of typical reference site ~~concentrations~~ chlorohomolog group concentrations with the maximum concentrations of the above isomers in the Military Creek sediments is as follows:

	Reference Site Sediments pg/g	Maximum Concentrations In Military Creek pg/g
OCDD	560	577,500
OCDF	50	115,500
1,2,3,4,6,7,8 HpCDD	70 *	64,750
1,2,3,4,6,7,8 HpCDF	20 □	24,500

* Total 2 isomers

□ Total 4 isomers

Identifying Dioxin and Furan Sources in Sediment to Pentachlorophenol Through Fingerprinting

Technical grade or manufactured pentachlorophenol has been documented to contain dioxin and furan impurities formed during the manufacturing process. Tables 16-20 summarizes various literature data that establishes the chlorohomolog, 2,3,7,8 substituted isomer concentrations and TCDD-EQ of the isomers in the manufactured pentachlorophenol product. Note the concentrations in these tables are reported in mg/kg or ug/kg that reflects pure, undiluted, unweathered pentachlorophenol product. The relative concentrations and proportions of the chlorohomolog groups, ~~isomers found in the Wheeler Creek sediment.~~

isomers and contributions of the isomers to the TCDD-EQ in the Military Creek sediments ~~is reflected~~ (Tables 1 and 5) reflects the predominance of the OCDD, OCDF, 1,2,3,4,6,7,8 HpCDD, and 1,2,3,4,6,78-HpCDF in the manufactured pentachlorophenol product. Some changes in relative proportions may have occurred from the pentachlorophenol product and its release into Military Creek because of weathering (physical, chemical, and biological).

It is noted that the most toxic PCDD and PCDF isomer, 2,3,7,8-TCDD has not been detected in the manufactured product. The literature seems to verify this noting only very low levels have been found in only a few instances in the manufactured product.

It is also noted in Table 17 that a number of substituted dioxin and furan isomers are found at very low levels in the pentachlorophenol product. As shown in table 3 these are the same ones that had relatively high detection levels. Because of their low concentration they will not contribute to the overall TCDD-EQ for the sample in any large amounts compared to the above four isomers - [illegible] that have dominant concentrations. For other sites and other sources of dioxins and furans, it may be important to achieve the low detection levels of 0.5 - 1.0 pg/g for these isomers.

Fate, Bioavailability, and Significance of the Presence of 2,3,7,8-Substituted PCDD and PCDF Isomers in Sediments of Military Creek

No corresponding Total organic carbon or particle size analysis was done on the sediment samples from ~~Pen~~ Military Creek. Both parameters are useful for evaluating partitioning behavior, sorbance, and potential transport within the aquatic system.

The field sheets describe the general sampling locations. Water depths at the sample sites is not clearly described.
S-20 is the upstream reference site.
S-21, S-22, and S-22 DUP are upstream of Co. Hwy E and adjacent to or near the impacted plant property.

S-23 and S-24 are downstream of the property and Co. Hwy E. S-24 is at the mouth of the Creek at the lake.
The most TCDD-EQ contaminat sites are at S-21, S-22, and S-22 DUP. ~~It is unknown if~~ S-22 is a field duplicate. ~~and~~ Th ~~what~~ distance it was taken from S-22.) S-23 and S-24 is are much less contaminated unknown by dioxins and furans (and subsequently TCDD-EQ) The levels at S-23 and S-24 below Co. Hwy are only approximately 2% of the levels at the sediment sample sites above Co. Hwy E.

Apparently the following core lengths were composited at each sample site ~~to yield~~ for analysis:

S-20	2 ft.
S-21	2 ft.
S-22	1 ft.
S-23	1 ft
S-24	2-5 in. taken b trowel due to

Compositing cores of any lengths loses the ability to determine if high concentrations of contaminants are confined to particular strata related to a period of discharge or if they are relatively homogenous throughout the whole core. If the contaminants are confined to a strata, it is important to know if these strata are at the sediment surface where they will be inhabited by benthic macroinvertebrates and interchange with the overlying water can occur or if the contaminated strata are buried under overlying clean sediments at a distance to be isolated from biota and the overlying creek water.

While the 2,3,7,8 substituted isomers have similar structure and activity relationships related to toxici compared to 2,3,7,8-TCDD,

the overall degree of chlorination of the isomers will be reflected in different partitioning and solubility characteristics. The 2,3,7,8 substituted isomers will behave differently than 2,3,7,8-TCDD once released to the environment. The in situ TCDD-EQ concentration of the isomers in sediment will not stay the same as the isomers move into other environmental compartments.

Table 21 shows the relative characteristics of the PCDD chlorohomolog groups compared to TCDD. Generally, the higher the chlorination, the greater the hydrophobicity or absorbance to organic carbon in the sediments or particulate matter. Strong absorption reduces bioavailability. The PCDDs and PCDFs can be recalcitrant to microbial degradation.

BCF's based on lab measurements in environment, such high lipophilic compounds will be adsorbed to particulate and dissolved organic carbon

Despite the theoretical relative BCF and lipophilicity assigned to the higher chlorinated compound in Table 21, the hepta- and octa-isomers can have low BCFs and accumulation in lipids. This may be due to factors affecting membrane transport such as increase in molecular size with increasing chlorination or solubility. Preferential metabolism of certain isomers has also been suggested.

Table 22 shows the Biota-Sediment Accumulation Factor (BSAF) or Bioavailability Index calculated for Carp exposed to sediments from the Petenwell Flowage. From Table 15, it can be seen that the Petenwell Flowage is moderately contaminated with 2,3,7,8-TCDD and substituted isomers. On a TCDD-EQ basis

The BSAF value is the lipid normalized concentration of an isomer in fish divided by the organic carbon normalized concentration in sediments

Table 22 shows that generally as the degree of chlorination increases, the isomer is less likely to move from the sediment into the water or food and bioaccumulate in the fish or if they are taken up by the fish they are preferentially metabolized or not absorbed because of molecular size and are depurated. ~~Apparently no levels of TCDF or CDD are bioaccumulated and only low levels are of HpCDD and HpCDF are bioaccumulated~~ These are isomer groups that predominated in the Military Creek sediments. On a site specific basis, the concentrations are so high in the sediments that exposed aquatic organisms may take up greater amounts than taken up from the Petenwell sediments. At the high end, the OCDD and HpCDD concentrations are approximately 28x and 14x higher, respectively in Military Creek sediments compared to Petenwell sediments.

Predicting Water Concentrations of the Measured Dioxins and Furans in Sediments

A simple model used to predict the concentration of non-polar hydrophobic organic compounds in sediment pore water based on their concentration in the solid phase is:

$$C_{pw} = \frac{C_{sed}}{K_{oc} \times f_{oc}}$$

where: C_{pw} = Concentration in sediment pore water ug/l

C_{sed} = Dry weight concentration in sediment ug/kg

K_{oc} = Organic carbon partitioning Coefficient l/kg

f_{oc} = Weight fraction of organic carbon in sediments

The predicted pore water concentration if achieved in situ may result in diffusion of the partitioned compound to the overlying surface water. The concentration achieved in the ~~surface~~ surface water depends on the ~~hydrodynamic~~ hydrodynamic conditions of the site, that is flow, mixing, dilution, stagnant standing water etc. On a conservative basis, a closed system can be assumed where at equilibrium the surface water concentration approaches the pore water concentration. The K_{OC} value specific to the PCDD or PCDF isomer must be known and the TOC concentration for the sample must be known.

To use the above formula on the PCDDs and PCDF data for the Military Creek sediments the K_{OC} values from a study in the literature were used (Table 2
A TOC value of 5% was
used.

The calculated pore water concentrations for each PCDD and PCDF isomer and total concentration is shown in Tables 23-28. An additional factor was incorpated into the pore water concentration value. Each of the isomers has a specific TEQ value that is used to determine TCDD-equivalence for the concentration of that isomer. This TEQ value was multiplied by the pore water concentration. For each sample, the calculated TCDD-EQ water concentration for each isomer was totaled. A basis for comparison with sample pore water TCDD-EQ is the ambient water quality criteria value for 2,3,7,8-TCDD in NR 105. The comparison of these values are as follows:

← $C_W \times TEQ$

SEDIMENT SAMPLE	TOTAL Estimated TCDD-EQ IN SEDIMENT PORE WATER pg TCDD-EQ / liter
S-21	0.649
S-22	2.0 [Dissolved]
S-22 DUP	1.38
S-23	0.01
S-24	0.015
• NR 105 Ambient Water Quality Criteria for Cold Water Community (Trout Stream) 2,3,7,8-TCDD	0.03 pg / liter [Dissolved + Particulate Associated]
• Proposed Criteria in Great Lakes Initiative	0.0031 pg / liter

If the TOC value or TOC content in the sediment is less than 5%, the calculated TCDD-EQ values ~~calculated~~ above for pore water would be greater. Dilution of pore water concentrations of PCDDs/Fs as it diffuses into the overlying surface waters will probably occur with the amount of dilution

dependent on the site. The greatest concentrations will be in some zone immediately above the sediment-water interface. The amount of exceedance of the predicted TCDD-EQ pore water concentrations of the NR 105 ambient water quality criteria is as follows:

Sample Site	Exceedance Factor
S-21	21.6 x
S-22	66.7 x
S-22 DUP	46.0 x
S-23	0
S-24	0

The NR 105 criteria are applicable to the total 2,3,7,8-TCDD present in water which includes both dissolved and particulate associated 2,3,7,8-TCDD. The above partitioning formula only predicts the dissolved fraction in pore water. 80% of the 2,3,7,8-TCDD can be associated with particulate matter, leaving 20% in the dissolved phase.

If the 80:20 mix is applied to the water quality criteria means that 80% of the criteria value or 0.024 pg can be

allocated to particulate phase and 20% or 0.006 pg can be allocated to the dissolved phase.

Comparing the predicted dissolved water PCDD/F concentrations to the 0.03pg/L criteria value is underprotective because a large portion of the PCDD/Fs could be in a particulate phase. The model predicted dissolved concentrations should be compared to a fraction of the criteria that is attributable to an estimated portion in the dissolved state or 20% x.03pg = 0.006 pg. Based on comparing the predicted dissolved from the model with estimated dissolved fraction of the criteria, the calculated exceedance factor for pore water concentrations compared with dissolved portion criteria is.

Sample Site	Exceedance Factor
S-21	108x
S-22	333x
S-22 DUP	230x
S-23	1.67x
S-24	2.5x

One additional consideration that needs to be made is that the NR 105 criteria are based on the toxicity of the 2,3,7,8 TCDD isomer alone and do not provide for TEF considerations or presence of the 2,3,7,8 substituted isomers.

To derive the criteria for 2,3,7,8-TCDD in water for human health protection, backcalculations from fish concentrations were used based on BCF/BAF values specific to 2,3,7,8-TCDD. The TCDD-EQ values calculated above for pore waters / surface waters are based on mixtures of different isomers. While the TCDD-EQ in water to 2,3,7,8-TCDD for the mixtures can be calculated, once in water they will not behave similarly to 2,3,7,8-TCDD in terms of partitioning behavior, solubility, or have the same BCFs. The behavior of the mixture of isomers can't be predicted from how 2,3,7,8-TCDD behaves. Each isomer will behave differently. ~~There can be an order of magnitude difference between the BCF for 2,3,7,8-TCDD and OCDD and HpCDDs (table 29).~~

The Great Lakes Water Quality Initiative uses a Bioaccumulation Equivalency Factor to account for the potential differences in uptake of the different substituted congeners. The Bioaccumulation Equivalency factors are in the table on the following page.

Total 2,3,7,8-TCDD toxicity equivalence concentration = Pore Water Concentration x TEF x BEF

If the resulting concentration exceeds the 2,3,7,8-TCDD criteria in the Great Lakes Initiative, either 0.0085 pg/L or 0.067 pg/L a potential problem exists. The resulting pore water concentrations with the BEF applied as follows:

Sediment Sample	TOTAL Estimated TCDD-EQ IN SEDIMENT PORE WATER THAT CONSIDERS DIFFERING BIOACCUMULATION OF EACH CONGENER IN FISH pg TCDD-EQ liter
S-21	0.14 *
S-22	0.55 *
S-22 DUP	0.37 *
S-23	0.0027 +
S-24	0.0043 +

* Exceed NR 105 and GLI criteria
+ Exceeds GLI HCC

Table 1
Toxicity Equivalency Factors for CDDS and CDFs

Congener	TEF
2,3,7,8-TCDD	1.0
1,2,3,7,8-PeCDD	0.5
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.001
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
OCDF	0.001

Table 2

Bioaccumulation Equivalency Factors for CDDs and CDFs

Congener	BEF
2,3,7,8-TCDD	1.0
1,2,3,7,8-PeCDD	0.9
1,2,3,4,7,8-HxCDD	0.3
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.05
OCDD	0.01
2,3,7,8-TCDF	0.8
1,2,3,7,8-PeCDF	0.2
2,3,4,7,8-PeCDF	1.6
1,2,3,4,7,8-HxCDF	0.08
1,2,3,6,7,8-HxCDF	0.2
2,3,4,6,7,8-HxCDF	0.7
1,2,3,7,8,9-HxCDF	0.6
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.4
OCDF	0.02

Consideration of BCF Factors in Sediment Partitioning Model

BCF values, uptake from water alone, derived from Muir et al. 1985 and Muir et al. 1986.

Fish Species	Isomers	BCF
Fathead Minnow	1,2,3,4,6,7,8 HpCDD	51[illegible]
Fathead Minnow	OCDD	2222

* BCF for whole fish Samples

The partitioning model to be used is:

$$\text{Fish Tissue Residue Concentration} = \left(\frac{\text{Sediment Concentration}}{foc \times Koc}\right)\left(BCF\right)$$

Muir, D.C. et al 1985. Bioconcentration of Four Chlorinated Dioxins by Rainbow Trout and Fathead Minnows. In: Aquatic Toxicology and Hazard Assessment: Eighth Symposium. ASTM Technical Publications

Muir, D.C. et al. 1986. Bioconcentration and Depuration of 1,3,6,8-TCDD and OCDD by Rainbow Trout and Fathead Minnows. Environ. Tech. Chem. 5: 261-270

Considerations:

- Assume BCF for OCDF and 1,2,3,4,6,7,8 HpCDF are the same as corresponding dioxin isomers.
- foc and Koc considerations made above
- Assume predicted pore water concentrations equal overlying surface waters especially near sediment-water interface area.
- Assume contaminated area in Creek makes up the largest daily use area for the fish. Average sediment concentrations from 5 samples in Military Creek
- Assume measured contaminants are in top 5-10 cm of sediment

	Ave. Sediment Concer
1,2,3,4,6,7,8 HpCDD	26.62 ug/Kg
OCDD	278 ug/Kg
1,2,3,4,6,7,8 HpCDF	10.6 ug/Kg
OCDF	52.7 ug/Kg

	Pore Water pg/L	BCF	Whole Fish pg/g	TEF	TCDD-EQ in fish-tissue pg TCDD-EQ/g
1,2,3,4,6,78 HpCDD	8.4	515	4.32	.01	.04
OCDD	69.9	2226	155.6	.001	.156
1,2,3,4,6,7,8 HpCDF	2.6	515	1.34	.01	.01
OCDF	41.9	2226	93.3	.001	.093

Fish Tissue Levels Used in Great Lakes Initiative To Derive WQC to protect mammals Consuming fish

Otter — 0.89 pg/g
Mink — 0.67 pg/g

— May have been revised upward in latest version GLI

TCDD-EQ - 0.30 pg/g In Whole Fish Exposed To Military Creek Sediments

TCDD-EQ - 10 pg/g For Fish Advisories Protection human Health

The above only accounts for 4 of the 11 2,3,7,8 substituted isomers found in the Military Creek sediments however it does include those with the greatest concentrations. If BCFs were available to calculate tissue residues for the others, they would not contribute substantially to the total TCDD-EQ concencentration in fish tissue.

Because surface water concentrations will generally not equal pore water concentrations and fish will not spend all their time in the contaminated area of the Creek, the actual TCDD-EQ concentration in fish will be less than 0.30 pg/g. The levels ~~of~~ in fish tissue are predicted not to exceed the 10 pg/g that triggers fish advisories.

While this seems to indicate, uptake ~~from water~~ of the dissolved fraction of PCDDs/Fs from water is not an important route of exposure and uptake for fish, uptake through the food chain may be. Evidence from mesocosm studies suggests the major pathway for uptake of higher chlorinated PCDDs/Fs is the food chain. If present in water, a high proportion of the isomers are associated with DOC. This reduces direct uptake of PCDDs/Fs by invertebrates and fish from water. Uptake from water may also be limited by steric effects and low bioavailability due to

strong absorbance to organic particles. Biota ingesting or filtering contaminated particles at the sediment-water interface high high PCDD/F concentrations in tissue. The highest bioavailability indexes were achieved by fish and crayfish feeding on PCDD/F contaminated benthic organisms.

Consideration of All Routes of Uptake of PCDDs/Fs To Fish in Military Creek

The use of the Bioavailability Index of Kuehl et al. (1987) provides a way of considering uptake of the 2,3,7,8 substituted isomers ~~from~~ by fish from ~~water~~ a number of routes namely from the water and from food. The Bioavailability Indexes are based on exposing carp to sediments from the Petenwell Flowage. The Kuehl BI values are shown in Table 22 for some of the isomers. They are based on the following formula:

$$\frac{\text{pg/g lipid}}{\text{pg/g OC}} = \text{BI}$$

	Ave. Sediment Concentrations ①	Assumed Sediment TOC	Organic Carbon Normalized Concentration pg/g OC
1,2,3,4,7,8 HxCDD	140 pg/g	5 %	2800
1,2,3,6,7,8 HxCDD	1016 pg/g	5 %	20320
1,2,3,4,6,7,8 HpCDD	26,616 pg/g	5 %	532 320
OCDD	277,976 pg/g	5 %	5,559,520
1,2,3,6,7,8 HxCDF	336 pg/g	5 %	6720
1,2,3,4,6,7,8 HpCDF	10,608 pg/g	5 %	212,160
OCDF	52,690 pg/g	5%	1,053,800

① In Averaging, any concentrations reported at detection level, assumed to be 0. (Table 1)

	Organic Carbon Norm. pg/g OC	× BI =	Lipid Normalized Concen. pg/g lipid	× Fish at 8% Lipids pg/g
1,2,3,4,7,8 HxCDD	2800	0.035	98	7.84
1,2,3,6,7,8 HxCDD	20320	0.035	711	56.9
1,2,3,4,6,7,8 HpCDD	532,326	0.0048	2555	204.4
OCDD	5559520	0.00047	2613	209.0
1,2,3,6,7,8 HxCDF	6720	0.037	249	19.9
1,2,3,4,6,7,8 HpCDF	212160	0.0033	700	56
OCDF	1,053,800	0.0022	2318	185.4

	Fish at 8% Lipid pg/g fish	× TEF =	TCDD-EQ pg/g
1,2,3,4,7,8 HxCDD	7.84	.1	0.78
1,2,3,6,7,8 HxCDD	56.9	.1	5.7
1,2,3,4,6,7,8 HpCDD	204.4	.01	2.04
OCDD	209.0	.001	0.21
1,2,3,6,7,8 HxCDF	19.9	.1	2.0
1,2,3,4,6,7,8 HpCDF	56.0	.01	0.56
OCDF	185.4	.001	0.19

Predicted Total TCDD-EQ – 11.48
In Fish Tissue
Exposed To
Military Creek
Sediments

The predicted fish tissue concentration for fish exposed to the Military Creek sediments is 11.48 pg TCDD-EQ/g

This slightly exceeds the 10 pg/g level used to issue fish advisories for human health

The 11.48 pg TCDD-EQ/g exceeds the fish tissue residue values used in the Great Lakes Criteria Development document to derive WQC protective of mammals consuming fish in their diet. The fish tissue residue values are 0.89 pg/g to protect otter and 0.67 pg/g to protect mink.

Pentachlorophenol Concentrations on Military Creek Sediments

Previously provided analytical data for Military Creek sediments show the following PCP concentration at the sample sites along with the reported % solids:

Sample Site	Wet Weight ug/Kg	% Solids
S-20	ND (800)	10
S-21	1400	35
S-22	1300	53
S-22 DUP	1600	54
S-23	70	46
S-24	ND (800)	18

It is noted that the % solids reported above are different from the % solids reported for the same sample numbers involved with dioxin/furan samples discussed earlier. This may be due to multiple cores taken at a site with different cores submitted for chemical analysis.

It is not certain if the above PCP concentrations are reported on a wet weight or dry weight basis. I suspect ~~on a~~ they are on a wet weight basis given the lab provided information that the Contract required quantification limits (CRQL) listed in a table are based on wet weight. The reported detection limit of 800 ug/kg for PCP is in this table and therefore is wet weight based. As was done for dioxins and furans above the reported concentrations must be multiplied by a conversion factor to yield a dry weight basis.

Sample Site	Wet Weight ug/kg	Conversion Factor	Dry Weight ug/Kg
S-20	ND (800)	10	ND (8000)
S-21	1400	2.86	4004
S-22	1300	1.89	2457
S-22 DUP	1600	1.86	2976
S-23	70	2.17	152
S-24	ND (800)	5.56	ND (4448)

The unacceptably high dry weight detection limits for PCP at S-20 (8000 ug/kg) and S-24 (4448 ug/kg) should be noted. Biologically significant levels can be present at much lower concentrations.

A point of reference for the PCP concentrations in Military Creek sediments is the attached Feb. 7, 1990 memo to NCD regarding PCP contamination at another site. The memo provides a methodology to calculate a sediment value for PCP that would be protective of aquatic organisms from chronic toxicity. An important component of the calculation is to have the TOC content of the sediments at the sample site. TOC was not analyzed for. The Kreitlow 1992 sampling of the sediments in Military Creek found the following TOC concentrations and particle size fractions:

Kreitlow Sample Site	Percent TOC	Sand	Silt	Clay
⑥ G-1-92 Reference Site	22.4	22	51	27
⑥ G-2-92 Foot bridge below Pole Drying Area	1.14	93	3	4
⑥ G-3-92 Below Hwy E	12.6	37	51	12
⑥ G-4-92 100 ft above Confluence of N. Twin Lake	1.37	94	4	2

G-2 and G-4 are dominated by fine sand or larger size particles

G-1 and G-3 are dominated by the fine fraction (clays + silt.

On average, the TOC content is approximately 10%. Based on the attached memo, at 10% TOC, the concentration of PCP in sediments cannot exceed 1424 ug/kg or benthic organisms exposed to sediment pore water or organisms in the overlying water will potentially subject to chronic toxicity.

These PCP concentrations are exceeded by approximately 2-3 x at sites S-21, S-22, and S-22 DUP. If the TOC concentrations are lower at specific sample sites, the exceedance of the calculated sediment objective concentration could be even greater.
The assumption is that the measured PCP concentrations were in the surface strata of the core or homogenously distributed throughout the core and not buried under clean strata in a lower contaminated strata.

The State of Washington Sediment Quality Standards establish a concentration of 690 ug/kg for PCP to prevent adverse impacts to benthic and aquatic organisms. This value backs up the above calculated method to prevent chronic toxicity based on water quality standards in NR 105.

State of Wisconsin

CORRESPONDENCE/MEMORANDUM

51

DATE: February 7, 1990 FILE REF: 3200

TO: Larry Maltbey - NCD

FROM: Bruce Baker - WR/2

SUBJECT: Sediment Quality Criteria for Pentachlorophenol Related to the Semling-Menke Company Contaminated Groundwater Inflow to the Wisconsin River

At the request of NCD, the in-place pollutant staff have developed sediment quality criteria for pentachlorophenol. The developed criteria along with procedures and rationale for the criteria are attached. Sediment quality criteria are based on an approach U.S. EPA has developed and is refining that applies an equilibrium partitioning method for deriving criteria for nonpolar hydrophobic organic compounds. Because pentachlorophenol dissociates in natural waters depending on pH, adjustments were made in the partitioning model in an attempt to address for this physicochemical factor.

The sediment quality criteria are based on water quality standards in NR 102 and NR 105, Wisconsin Administrative Code. Assuming no other inputs of contaminants through groundwater inflow, successful remediation of in-place pentachlorophenol in the sediments to the levels of the attached criteria would allow promulgated state surface water standards to be met. Pentachlorophenol levels in the sediments above the calculated criteria could potentially be toxic to benthic organisms that inhabit the sediment pore water or the pentachlorophenol could potentially be released to the overlying water column at concentrations that would exceed surface water quality standards.

Also, attached is applicable literature related to pentachlorophenol characteristics and distribution in the environment.

Remediation of PCP-contaminated river bank sediments should be preceeded by the cleanup and/or discontinuation of the contaminated groundwater flow toward the river. Removal of contaminated surficial sediments, bedded sediments and possibly underlying substrata materials and replacement with clean natural materials may need to be considered. A necessary buffer zone needs to be created to ensure PCP in deeper strata and soils does not continue to be transported to the sediment-water interface. The armoring or placement of an impenetrable barrier over the impacted river bottom area either alone or in conjunction with excavation and clean fill replacement is another approach to consider. The armoring of the bottom sediments should provide a more substantial barrier than only riprapping placement to prevent transport and release of PCP from and through the sediments to the overlying water column.

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Attachments

cc: Bill Jaeger - NCD
Kevin Kessler - WR/2
Lyman Wible - AD/5

Comments on Approach Taken to Derive Sediment Quality Criteria for Pentachlorophenols

52

Sediment quality criteria were developed for pentachlorophenol (PCP) utilizing an equilibrium partitioning approach (EQP). The approach was developed and is currently under review by U.S. EPA. The approach is based on the established characteristics of organic compounds to partition between an organic solvent and water at a constant ratio. This physicochemical relationship is extrapolated to natural conditions by relating the sorption of organic compounds to sediment particles containing organic carbon present in organic matter.

That portion of the organic chemical compound that is partitioned to the sediment pore water is related to surface water quality criteria. It is assumed that benthic organisms have the same sensitivity to the organic compound as water column organisms used to develop the toxicological data base for water quality criteria. Water quality criteria are used to derive sediment quality criteria in the EQP approach.

The organic carbon partition coefficient value (K_{oc}) for a specific organic compound can be found experimentally or derived from the octanol water partition coefficient values (K_{ow}). The K_{ow} value is a proportionality constant characteristic of a specific compound and can be found in standard chemical references and technical papers. Any K_{oc} and K_{ow} value used needs to be assessed if references report different K_{ow} or K_{oc} values.

U.S. EPA has applied the EQP approach to only neutral, nonpolar hydrophobic compounds. The partitioning of these compounds between sediments and sediment pore waters has been demonstrated to be dependent on the organic carbon content of the sediment, with little or no dependence on or effects by any other physical or chemical factors. Sediment criteria that can be referenced or normalized to one factor such as organic carbon content can apply across a wide variety of sediment types and variable physical and chemical conditions found in the sediment environment.

The EQP approach used to describe the sorption of neutral hydrophobic organic chemicals by natural sorbents is applicable only to a limited agree to organic compounds which dissociate or ionize at natural pH values, unless appropriate considerations are made. Phenolic compounds dissociate based on pH. Chlorinated phenols are hydrophobic weak acids. Because of this characteristic, calculation of water quality criteria for PCP is based on consideration of the natural pH present in surface waters.

The K_{ow} value for PCP in most standard chemical reference text and technical papers is a value of 5.01. This value does not appear to consider the pH - dissociation relationship and assumes a total undissociated PCP concentration in the solution. Predictions of the overall distribution ratios based on simple partitioning of nondissociated species are generally in error. One study that examined the apparent octanol-water portion coefficient of PCP as a function of ph found the following relationships:

53

Procedures and Values Utilized in Calculating Sediment Quality Criteria For Pentachlorophenol in the Wisconsin River; Semling - Menke Co., Merrill; Contaminated Groundwater Inflow

1. Water Quality Standards for Pentachlorophenol (PCP) that Apply to the Wisconsin River Based on NR 102 and NR 105, Wis. Adm. Code

   a) Human Threshold Criteria - 840 ug/L

   b) Threshold Concentration Causing Taste and Odor in Water - 30 ug/L

   c) Chronic Toxicity Criteria (CTC)

   $CTC = e^{(V(pb) + \ln CCI}$
   pH Wisconsin River at Merrill - 7.0
   $CTC = e^{(1.005 \times 7.0 - 4.9779)}$
   * CTC = 7.82 ug/L

   * PCP CTC of 7.82 ug/L is the most stringent value, therefore it was used to derive the sediment quality criteria for pentachlorophenol applying the formula in the attached Figure 1.

2. To derive the particle organic carbon normalized partition coefficient (Koc) needed for the formula in Figure 1 to calculate sediment quality criteria, the above discussed Kow value (PCP octanol/water partition coefficient) of Log Kow = 3.32 was used in the following formula (also in Figure 1):

   Log_{10} Koc = 0.00028 + 0.983 Log_{10} Kow
   = 0.00028 + (0.983) (3.32)
   = 0.00028 + 3.26
   = 3.26028
   Koc = 1821 liters/Kg OC

3. Insertion of the above Koc value and the Water Quality Standard into the Figure 1 formula are as follows:

Sediment Quality Criteria (ug PCP/Kg OC)	=	WQS (ug/L)	x	Koc L/Kg OC

   Sediment Quality Criteria = 7.82 ug/L x 1821 L/Kg OC
   = 14,240 ug PCP/Kg OC

4. To derive site specific sediment quality criteria, the 14,240 ug PCP/Kg OC value needs to be multiplied by the concentration of Total Organic Carbon (TOC) found in sediment samples taken from the Wisconsin River in the area that is being impacted by the groundwater inflow that is

54

contaminated with PCP. The TOC value is the foc component in the Figure 1 formula needed to calculate site specific sediment quality criteria. Analytical results for TOC can be reported as a percent or concentration. Some interrelationships of expressing TOC values are as follows based on an example concentration:

10,000 ppm TOC = 10,000 mg TOC/Kg sediment =

1% of sediments due to particle organic carbon weight fraction = 0.01 kg OC/Kg sediments = foc

5. Applying the formula

Sediment Quality Criteria = 7.82 ug/L x 1821 L/Kg x foc (Kg OC/Kg sediments)

and using a range of foc values that are representative of the TOC concentrations that may be present in the Wisconsin River sediments, the following site specific sediment quality criteria were calculated:

Percent Total Organic Carbon In Sediment Samples	Site Specific Sediment Quality Criteria (ug PCP/Kg Sediment - dry weight)
0.5	71.20
1.0	142.40
2.0	284.80
3.0	427.21
4.0	569.61
5.0	712.01
6.0	854.41
7.0	996.82
8.0	1,139.22
9.0	1,281.60
10.0	1,424.00

PCP analytical results from sediment samples can be directly compared with the sediment quality criteria in the table based on TOC content of the samples. The comparison will determine whether or not the PCP levels in the sediments meet the sediment criteria.

The site specific calculated sediment quality criteria are above the Method Detection Limit of 20 ug/Kg reported by the State Laboratory of Hygiene.

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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 are 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). U.S. 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 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.

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

K_{oc} = liters/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 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. (U.S. 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=0.032 Kg of C/Kg sediment.

B. To find the interstitial water concentration (IWCO) 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 (see tables 6-19):

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

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

Sediment levels of metals at the study site sampling locations (S-21, S-22, S-23 and S-24) do not appear to be different from the reference site levels. Lead levels at S-21 (46.3 mg/Kg) and S-24 (31.1 mg/kg) are elevated above reference site level (10.3 mg/Kg) but may be natural variability with no site input. Information on particle size would be useful to do site-to-site comparisons. Apparently, EPA believes that obtaining particle size information and TOC information does not contribute to the purpose of collecting contaminant data for site scoring purposes.

We believe particle size and TOC information is needed on site for doing any risk-type of evaluation to determine potential partitioning behavior, bioavailable substrate habitat and transport of contaminants off-site.

Polycyclic Aromatic Hyarocarbons (PAHs)

A number of PAH compounds were reported at estimated concentrations on the sediment samples. Total PAH concentrations are given below at the sample sites:

	Total PAH ug/Kg (Dry Weight)
S-20 (Reference)	16,300
S-21	10,322
S-22	4,692
S-22 (DUP)	4,165
S-23	5,082
Ontario SQG Lowest Effect Level	2,000

It must be noted that it appears that all the data reported out for the samples from this site appears to be on a wet weight

basis and must be converted to dry weight based on the percent solids information given for each sample. The PAH concentration data above has been converted to dry weight. The metals data above has not been converted to a dry weight basis and should be for a more definitive site-to-site comparisons between reference site and study sites to see if there has been any enrichment.

The above total PAH concentration in sediments at 16,300 ug/Kg ~~appears~~ for the reference site would appear high based on the setting and what has been ~~been~~ found at comparable sites. The 16,300 ug/Kg value represents a value that would be expected in a developed urban area with lots of roadway and parking area runoff, heavy traffic, and smokestack emissions. Is the reference site far enough upstream so as not to be influenced by the C.M. Christiansen site? It is noted that site soil samples contain relatively high PAH levels. It is not unexpected that the creek sediments at the study sites

(S-21 – S-24) have elevated PAHs originating from site runoff, but PAH levels should not be elevated at the reference site. Total PAH levels at an unimpacted reference site for the Military Creek setting should not exceed 500 ug/kg and certainly not 1000 ug/kg. There is nothing in the watershed upstream except large areas of wetland.

Based on the Ontario Sediment Quality Guidelines, the Lowest Effect Level for total PAHs in sediment is 2000 ug/kg. As levels increase above this, more and more benthic organisms will be impacted in terms of growth, reproduction and survival. Based on the Military Creek Total PAH sediment levels that range from 5,000 to 10,000 ug/kg, some adverse impacts to benthic organisms may be occuring.

Pesticides and Other Organics

The analytical results for pesticides report estimated concentrations for 1 to 3 pesticides in the sediment samples. The results are qualified as to make the accuracy of the results uncertain. Values are given for Endrin, 4-4'-DDT, and Endrin aldehyde.

It is noted that analytical results for site soils report out results for 19 pesticides. Why aren't results reported out for 19 pesticides in sediment rather than 3? Tables present only detected target compounds?

As with all results for sampling associated with this project, the pesticide results are reported out in wet weight, and to be revaluated, must be ~~reported~~ converted to a dry weight basis.

It is noted that there were significant levels of a number of pesticides at soil sample sites S-11 with elevated concentrations for a number of pesticides at soil sample sites S-12, S-13, S-14, S-15, and S-19. Why weren't all of these analyzed for in the sediments such as aldrin, 4,4'-DDD, beta-BHC, gamma-chlordane, Endrin Ketone, and others. Not detected

The Notes on Organic Qualifiers accompanying the Khazae Jan. 20, 1994 memo on page 4 indicates that there may be a number of organic compounds with estimated concentrations found in sediments. However there are no sheets that report the actual estimated concentrations associated with specific compounds. Detected compounds cannot be distinguished from non detected compounds in the list. Comparisons cannot be made with reference site values to determine if any of the study site values are elevated or significant.

Table 1. Reported Wet Weight Sediment Concentration Converted To Dry Weight

	pg/g (ng/Kg / ppt) Dry. Weight							
	Background S-20	S-21	S-22	S-22 DUP	S-23	S-24		
2,3,7,8-TCDD	ND	ND	ND	ND	ND	ND		
1,2,3,7,8-PeCDD	ND	ND	ND	ND	ND	ND		
1,2,3,4,7,8-HxCDD	ND	ND	400	300	ND	ND		
1,2,3,6,7,8-HxCDD	ND	970	2450	1660	ND	ND		
1,2,3,7,8,9-HxCDD	ND	380	910	700	ND	ND		
1,2,3,4,6,7,8-HpCDD	ND	25350	64750	40000	1380	1600		
OCDD	ND	259790	577500	520000	14590	18000		
TOTAL Dioxin Isomer		286,490	646,010	562,660	15,970	19,600		
2,3,7,8-TCDF	ND	ND	ND	ND	ND	ND		
1,2,3,7,8-PeCDF	ND	ND	ND	ND	ND	ND		
2,3,4,7,8-PeCDF	ND	ND	ND	ND	ND	ND		
1,2,3,4,7,8-HxCDF	ND	940	2630	1660	ND	ND		
1,2,3,6,7,8-HxCDF	ND	310	790	580	ND	ND		
2,3,4,6,7,8-HxCDF	ND	530	790	780	ND	ND		
1,2,3,7,8,9-HxCDF	ND	ND	750	380	ND	ND		
1,2,3,4,6,7,8-HpCDF	ND	10020	24500	17000	520	1000		
1,2,3,4,7,8,9-HpCDF	ND	1060	3150	1940	ND	ND		
OCDF	ND	53210	115500	88000	2740	4000		
TOTAL Furan Isomer		66,070	148,110	110,340	3,260	5,000		
TOTAL FURan + Dioxin Isomers		352,560	794,120	673,000	19,230	24,600		
ug/Kg ppb (ng/g)		352.56	794.12	673.00	19.23	24.60		

Table 2. Reported Detection Limits For Isomers and Sites Where Not Detected Based On Wet Weight

	Method Detection Limits pg/g Wet Weight							
	Background S-20	S-21	S-22	S-22 DUP	S-23	S-24		
2,3,7,8-TCDD	ND (34)	ND (35)	ND (53)	ND (28)	ND (47)	ND (25)		
1,2,3,7,8-PeCDD	ND (74)	ND (79)	ND (150)	ND (87)	ND (97)	ND (50)		
1,2,3,4,7,8-HxCDD	ND (76)	ND (180)			ND (120)	ND (59)		
1,2,3,6,7,8-HxCDD	ND (73)				ND (120)	ND (58)		
1,2,3,7,8,9-HxCDD	ND (71)				ND (120)	ND (56)		
1,2,3,4,6,7,8-HpCDD	ND (48)							
OCDD	ND (380)							
2,3,7,8-TCDF	ND (17)	ND (23)	ND (43)	ND (30)	ND (39)	ND (21)		
1,2,3,7,8-PeCDF	ND (41)	ND (52)	ND (74)	ND (110)	ND (61)	ND (33)		
2,3,4,7,8-PeCDF	ND (43)	ND (55)	ND (130)	ND (120)	ND (65)	ND (35)		
1,2,3,4,7,8-HxCDF	ND (45)				ND (86)	ND (46)		
1,2,3,6,7,8-HxCDF	ND (40)				ND (80)	ND (42)		
2,3,4,6,7,8-HxCDF	ND (46)				ND (92)	ND (47)		
1,2,3,7,8,9-HxCDF	ND (53)	ND (140)			ND (110)	ND (54)		
1,2,3,4,6,7,8-HpCDF	ND (45)							
1,2,3,4,7,8,9-HpCDF	ND (62)				ND (120)	ND (73)		
OCDF	ND (74)							

Table 3. Wet Weight Detection Limits Converted To A Dry Weight Basis.

	Method Detection Limits pg/g Dry Weight							
	Background S-20	S-21	S-22	S-22 DUP	S-23	S-24		Lehr Landf
2,3,7,8-TCDD	ND (283.22)	ND (109.55)	ND (92.75)	ND (56.0)	ND (71.44)	ND (125.0)		ND (0.3
1,2,3,7,8-PeCDD	ND (616.42)	ND (247.27)	ND (262.5)	ND (174.0)	ND (147.44)	ND (250.0)		ND (0.4
1,2,3,4,7,8-HxCDD	ND (633.08)	ND (563.4)			ND (182.40)	ND (295.0)		ND (0.15
1,2,3,6,7,8-HxCDD	ND (608.09)				ND (182.40)	ND (290.0)		ND (0.3
1,2,3,7,8,9-HxCDD	ND (591.43)				ND (182.40)	ND (280)		ND (0.69
1,2,3,4,6,7,8-HpCDD	ND (399.84)							ND (0.96
OCDD	ND (3165.41)							
2,3,7,8-TCDF	ND (141.61)	ND (71.99)	ND (75.25)	ND (60.0)	ND (59.28)	ND (105)		ND (0.61
1,2,3,7,8-PeCDF	ND (341.53)	ND (62.76)	ND (129.5)	ND (220.0)	ND (92.72)	ND (165)		ND (0.36
2,3,4,7,8-PeCDF	ND (358.19)	ND (172.15)	ND (227.5)	ND (240.0)	ND (98.8)	ND (175)		ND (0.54
1,2,3,4,7,8-HxCDF	ND (374.85)				ND (130.72)	ND (230)		ND (0.79
1,2,3,6,7,8-HxCDF	ND (333.20)				ND (121.6)	ND (210)		ND (0.38
2,3,4,6,7,8-HxCDF	ND (383.18)				ND (139.84)	ND (235)		ND (0.4
1,2,3,7,8,9-HxCDF	ND (441.49)	ND (438.2)			ND (161.20)	ND (270)		ND (0.37
1,2,3,4,6,7,8-HpCDF	ND (374.85)							ND (0.62
1,2,3,4,7,8,9-HpCDF	ND (516.46)				ND (182.4)	ND (365)		ND (0.96
OCDF	ND (616.42)							ND (0.89

Table 4. Calculation of TCDD-Equivalencies Using TEF For 2,3,7,8 Substituted TCDD and TCDF Isomer

pg TCDD-EQ/g Dry Weight

	Background S-20	S-21	S-22	S-22 DUP	S-23	S-24		
2,3,7,8-TCDD	ND	ND	ND	ND	ND	ND		
1,2,3,7,8-PeCDD	ND	ND	ND	ND	ND	ND		
1,2,3,4,7,8-HxCDD	ND	ND	40	30	ND	ND		
1,2,3,6,7,8-HxCDD	ND	100	250	170	ND	ND		
1,2,3,7,8,9-HxCDD	ND	40	91	70	ND	ND		
1,2,3,4,6,7,8-HpCDD	ND	250	650	400	13.8	16		
OCDD	ND	260	580	520	15	18		
Dioxin Isomer EQ		650	1611	1190	28.8	34		
2,3,7,8-TCDF	ND	ND	ND	ND	ND	ND		
1,2,3,7,8-PeCDF	ND	ND	ND	ND	ND	ND		
2,3,4,7,8-PeCDF	ND	ND	ND	ND	ND	ND		
1,2,3,4,7,8-HxCDF	ND	90	260	170	ND	ND		
1,2,3,6,7,8-HxCDF	ND	30	79	58	ND	ND		
2,3,4,6,7,8-HxCDF	ND	50	79	80	ND	ND		
1,2,3,7,8,9-HxCDF	ND	ND	75	38	ND	ND		
1,2,3,4,6,7,8-HpCDF	ND	100	250	170	5.2	10		
1,2,3,4,7,8,9-HpCDF	ND	10	30	19	ND	ND		
OCDF	ND	53	120	88	3	4		
Furan Isomer EQ		333	893	623	8.2	14		
TOTAL TCDD-EQ		983	2504	1813	37	48		

Table 5. Percent Contribution of Individual Isomers To Total TCDD-EQ

	% Contribution of 2,3,7,8 Substituted Isomers To TOTAL 2,3,7,8-TCDD EQUIVALENTS							
	Background S-20	S-21	S-22	S-22 DUP	S-23	S-24		
2,3,7,8-TCDD	ND	ND	ND	ND	ND	ND		
1,2,3,7,8-PeCDD	ND	ND	ND	ND	ND	ND		
1,2,3,4,7,8-HxCDD	ND	ND	1.6	1.7	ND	ND		
1,2,3,6,7,8-HxCDD	ND	10.2	10.0	9.4	ND	ND		
1,2,3,7,8,9-HxCDD	ND	4.1	3.6	3.9	ND	ND		
1,2,3,4,6,7,8-HpCDD	ND	25.4	26.0	22.1	37.3	33.3		
OCDD	ND	26.5	23.2	28.7	40.5	37.5		
Total Percent		66.2	64.4	65.8	77.8	70.8		
2,3,7,8-TCDF	ND	ND	ND	ND	ND	ND		
1,2,3,7,8-PeCDF	ND	ND	ND	ND	ND	ND		
2,3,4,7,8-PeCDF	ND	ND	ND	ND	ND	ND		
1,2,3,4,7,8-HxCDF	ND	9.2	10.4	9.4	ND	ND		
1,2,3,6,7,8-HxCDF	ND	3.1	3.2	3.2	ND	ND		
2,3,4,6,7,8-HxCDF	ND	5.1	3.2	4.4	ND	ND		
1,2,3,7,8,9-HxCDF	ND	ND	3.0	2.1	ND	ND		
1,2,3,4,6,7,8-HpCDF	ND	10.2	10.0	9.4	14.1	20.8		
1,2,3,4,7,8,9-HpCDF	ND	1.0	1.2	1.1	ND	ND		
OCDF	ND	5.4	4.8	4.9	8.1	8.3		
Total Percent		34.0	35.6	34.2	22.2	29.1		

Table 6. Possible Number of Positional PCDD and PCDF Isomers and Number of 2,3,7,8 Substituted Isomers Per Chloronomolog Group

Levels of Chlorine Substitution	Number of Positional Isomers	Number of 2,3,7,8-Substituted Isomers
PCDD		
Mono- (MCDD)	2	0
Di- (DCDD)	10	0
Tri- (TrCDD)	14	0
Tetra- (TCDD)	22	1
Penta- (PeCDD)	14	1
Hexa- (HxCDD)	10	3
Hepta- (HpCDD)	2	1
Octa- (OCDD	1	1
TOTAL	75	7
PCDF		
Mono- (MCDF)	4	0
Di - (DCDF)	16	0
Tri - (TrCDF)	28	0
Tetra - (TCDF)	38	1
Penta - (PeCDF)	28	2
Hexa - (HxCDF)	16	4
Hepta - (HpCDF)	4	2
Octa - (OCDF)	1	1
TOTAL	135	10

Table 7. Atmospheric Deposition As A Source of PCDDs and PCDFs To Sediments. ① Siskiwit Lake, Isle Royale

pg/g

Sediment Depths	0-0.5 cm	5-6 cm	8-9 cm (1940 levels)
TCDD	26	12	<0.4
PeCDD	12	11	<0.4
HxCDD	10	8	<0.4
HpCDD	70*	46*	4.5
OCDD	560	396	54
Σ PCDD	678	467	59.7
TCDF	15	18	<0.4
PeCDF	5	2	<0.4
HxCDF	2	2	<0.4
HpCDF	20.2*	8.6*	1.9*
OCDF	4	3.2	1.1
Σ PCDF	46.2	33.8	4.2
Σ PCDD+PCDF	724.2	500.8	63.9

* HpCDD - Sum of 2 isomers
HpCDF - Sum of 3 isomers

1. Czuczwa, J.M., B.D. McVeety, and R.A. Hites. 1984. Polychlorinated-p-dioxins and Dibenzofurans in Sediments from Siskiwit Lake, Isle Royale. Series (7)

Table 8. Typical Background Site Soil Concencentrations of PCDDs and PCDFs and 2,3,7,8 TCDD In 65 samples Throughout Great Britain.[1]

pg/g Dry Weight

	Mean	Std. Dev.	Range	Median
TCDD	9.4	11	<0.5-69	6.0
2,3,7,8-TCDD	<0.5	0.5	<0.5-2.1	<0.5
PCDD	6.6	8.4	<0.5-46	4.6
HxCDD	38	27	2.8-165	31
HpCDD	66	46	7.5-234	55
OCDD	191	162	29-832	143
Σ PCDD	311.5			
TCDF	25	32	<0.5-237	16
PCDF	23	27	<0.5-185	17
HxCDF	41	32	4.3-212	32
HpCDD	26	27	1.5-138	15
OCDF	27	33	<2.0-144	15
Σ PCDF	142			
Σ PCDD + PCDF	453.5			

1. Creaser, C.S., A.R. Fernandes, A. Al-Haddad, S.J. Harrad, R.B. Homer, P.W. Skett, and E.A. Cox. 1989. Survery of Background Levels of PCDDs & PCDFs in UK Soils. Chemosphere 18: 1-6: 767-776.

Table 9. Semirural Soil Levels of Chlorohomolog PCDDs and PCDFs Groups and Associated TCDD-EQ In Those Groups ①

	1846		1986	
	Sum Isomers pg/g	pg TCDD-EQ / g	Sum Isomers pg/g	pg TCDD-EQ / g
TCDD	0.86	0.048	1.6	0.058
PeCDD	2.53	0.07	3.8	0.14
HxCDD	5.1	0.077	8.6	0.14
HpCDD	5.8	0.028	13.0	0.063
OCDD	13.0	0.013	25.0	0.025
Σ PCDD	27.29	0.24	52.0	0.42
TCDF	8.5	0.079	9.0	0.1
PeCDF	10.1	0.47	10.8	0.48
HxCDF	7.7	0.23	9.1	0.25
HpCDF	4.8	0.27	6.0	0.045
OCDF	2.9	0.003	5.2	0.005
Σ PCDF	34.0	0.82	40.1	0.88
Σ PCDD + PCDF	61.29	1.06	92.1	1.3

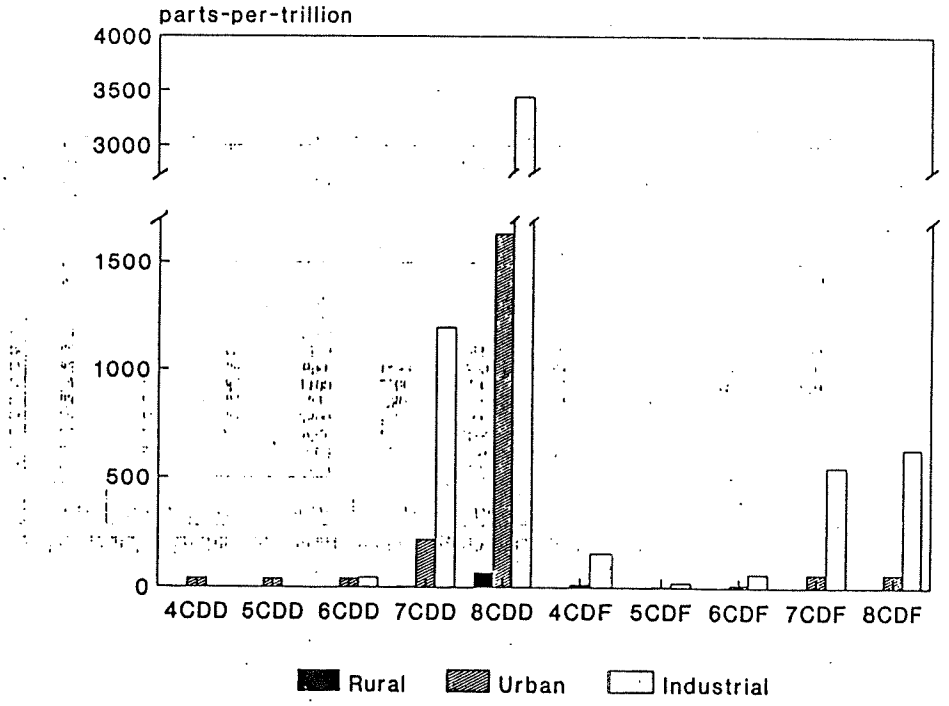
① Kjeller L., K.C. Jones, A.E. Johnston, and C. Rappe. 1991. Increases in the Polychlorinated Dibenzo-p-dioxin and furan Content of Soils and Vegetation Since the 1840's.

Table 10. Total PCDDs and PCDFs and Congener Group Profiles In Rural, Urban, and Industrial Soils ①

Mean and Standard deviation values for total PCDD and PCDF (pg/g) and TEQ (pg TCDD-EQ/g

	Total PCDD+ PCDF (pg/g)	Total TEQ (pg TCDD-EQ/g)
Rural ($n=30$)	73 ± 150	0.4 ± 0.6
Urban ($n=47$)	2075 ± 3608	11.3 ± 21.8
Industrial ($n=20$)	8314 ± 9955	40.8 ± 33.1

Figure 1. Mean congener group profiles.



Birmingham, B. 1990. Analysis of PCDD and PCDF Patterns in Soil Samples: Use in the Estimation of the Risk of Exposure. Chemosphere 20(7-9): 807-814.

(10)

Table 11. PCDDs and PCDFs In Sediments Associated With Harbor Areas Along The Elbe River, Germany

pg/g Dry Weight

	Bunthaus Harbor	Geesthacht	Tespe Harbor
TCDD	120	140	270
PeCDD	20	20	100
HxCDD	130	170	210
HpCDD	2670	2760	1410
OCDD	8540	7970	4660
Σ PCDD	11,480	11,060	6,650
TCDF	1190	2160	1820
PeCDF	750	1730	740
HxCDF	1880	1880	1680
HpCDF	3750	2510	5910
OCDF	7020	8520	11,030
Σ PCDF	14,590	16,800	21,180
Σ PCDD+ PCDF	26,070	27,860	27,830
pg TCDD-EQ / g	127	138	156

Götz, R. et al. 1993. Polychlorinated-p-dioxins (PCDDs), Dibenzofurans (PCDFs), and other Chlorinated Compounds in the River Elbe. Chemosphere (11)

Table 12. Results For PCDD and PCDF Homolog Group Analysis For Little Menomonee River Sediment During Remedial Investigation For Superfund.

pg/g

	302	303	305	308
Dibenzo-p-dioxins	ND (20)	ND (13)	ND (6.7)	ND (45)
Tetrachloro -	ND (19)	ND (17)	ND (10)	ND (24)
Pentachloro -	ND (68)	450	ND (37)	ND (56)
Hexachloro -	ND (100)	8700	ND (16)	ND (39)
Heptacloro -	1200	11000	ND (42)	ND (100)
Octachloro -	— *	—	—	—
Σ PCDD	1200	20,150	<105	<219
Dibenzofurans				
Tetrachloro -	ND (20)	ND (13)	ND (6.7)	ND (45)
Pentachloro -	ND (86)	550	ND (22)	ND (52)
Hexachloro -	230	8400	ND (16)	ND (83)
Heptachloro -	750	22000	ND (99)	ND (53)
Octachloro -	ND (1700)	8800	ND (140)	ND (200)
Σ PCDF	980	28,950	<284	<383
Σ PCDD + PCDF	2180	49,100	<389	<602

2,3,7,8 TCDD

* OCDD not reported

(2)

Table 13 Sediment Sample Analysis For PCDDs and PCDFs Chlorohomolog Groups In Wisconsin River, Wausau pg/g *

	Above Dam	Below Dam	So. Pine Island	So. Blue Gill Is.			
Dibenzo-p-dioxins							
Tetrachlor -	ND(0.64)	ND (1.2)	ND (2.7)	ND (1.9)			
Pentachloro-	ND (0.63)	ND (0.69)	ND (2.1)	ND (1.2)			
Hexachloro -	19.2	ND (1.7)	12.8	18.8			
Heptacloro -	133	5.1	73.6	122			
Octachloro -	1010	84.5	520	927			
Σ PCDD	1163.5	93.19	611.2	1070.9			
Dibenzofurans							
Tetrachloro -	26.7	ND (0.90)	11.9	31.7			
Pentachloro -	17.8	ND(0.81)	13.4	23.7			
Hexachloro -	47.2	4.1	21.4	31.7			
Heptachloro -	79.0	5.8	33.6	68.8			
Octachloro -	47.4	4.3	15.5	35.4			
Σ PCDF	218.1	15.91	95.8	191.3			
Σ PCDD+PCDF	1381.6	109.1	707	1262.2			

+ Not corrected for % Recovery of internal standard

+ Sites sampled in Wisconsin River at Wausau

(2)

Czuczwa, J. M. and R. A. Hites. Dioxins and
Table 14. Dibenzofurans in Air, Soil, and Water

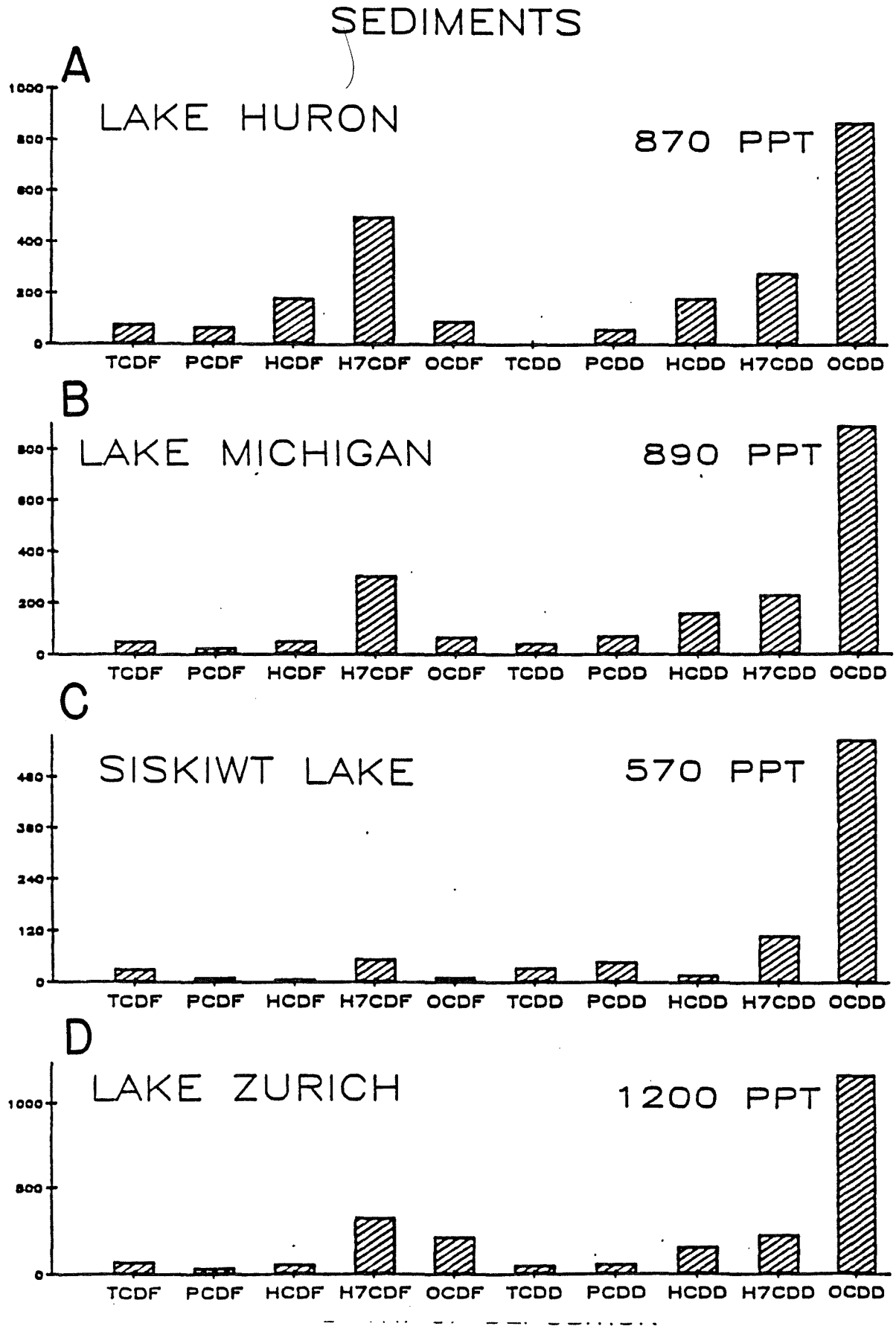


Table 15. Lehrer Landfill and Kankapot Creek

	Upstream Reference	Landfill Drainage Ditch					
	S-11	S-24	S-12	S-16	S-13	S-14	S-15
2,3,7,8-TCDD	ND(0.37)	ND(0.36)	ND(0.66)	ND(0.49)	ND(0.58)	ND(0.86)	ND(0.
Dioxin Isomer EQ	1.28	1.73	1.49	0.29	0.32	0.14	0.68
Furan Isomer EQ	0.44	0.61	0.37	0.07	0.07	0.33	0.11
TOTAL TCDD-EQ	1.72	2.34	1.86	0.36	0.39	0.47	0.79

Wisconsin Data ~ Sediments

Wisconsin Reference Sites	Rainbow Flowage On Wis. River Outstanding Resource Water			Lake Sediments Western District Hatfield Lake	Bass Lake	
2,3,7,8-TCDD	ND(0.27)	ND(1.78)		ND(2.18)	ND(1.31)	
Dioxin Isomer EQ	1.62	1.41		0.14	0.20	
Furan Isomer EQ	0.83	0.92		.012	0.03	
TOTAL TCDD-EQ	2.45	2.33		0.15	0.23	

Literature Data

Great Britain Soils	Soil Samples, Semi-Rural Site Great Britain 0-23cm (Kjeller et al. 1991)						
	1846	1986					
2,3,7,8-TCDD	0.048	0.058					
Dioxin Isomer EQ	0.24	0.42					
Furan Isomer EQ	0.82	0.88					
TOTAL TCDD-EQ	1.05	1.30					

Sweden Baltic Sea Sediments	Sediment Samples Taken In Baltic Sea 100-125 mi off Swedish Coast" Referenced in Rappe et al. 1989 as background levels		
2,3,7,8-TCDD	1.4	1.0	Est. that Scandinavian pulp and paper mills contribute 300,000-400,000 tons of chlorinated organic materials to coastal water annually. Levels in Baltic Sea at left even though removed from coasts may be influenced
Dioxin Isomer EQ	8.46	5.91	
Furan Isomer EQ	12.08	9.02	
TOTAL TCDD-EQ	20.54	14.93	

Table 15 (cont't)

Europe Soils	Soils From Various Parts of Europe (Rappe et al. 1987)			
	Rural		Urban	
2,3,7,8-TCDD	<2.0	<0.2	2.4	0.84
Dioxin Isomer EQ	0	0.014	15.94	29.12
Furan Isomer EQ	1.65	1.07	33.52	160.62
TOTAL TCDD-EQ	1.65	1.09	49.46	189.74

Wisconsin Fox River Sediments	Fox River – 10 Sediment Samples From Below De Pere Dam To Mouth of Green Bay (Ankley et al. 1993)											
2,3,7,8-TCDD	7.4	4.5	1.1	3.4	4.2	4.0	ND (1.4)	2.4	4.2	2.2		
Dioxin Isomer EQ	384	222	45	205	270	333	17	73	201	49		
Furan Isomer EQ	57	46	7	48	44	46	4	12	28	12		
TOTAL TCDD-EQ	441	268	52	253	314	379	21	85	229	61		

Wisconsin	From Above Study			
	Sediment Samples From Green Bay		Background Site For Study East River	
2,3,7,8-TCDD	2.0	2.0	0.5	
Dioxin Isomer EQ	38	31	2.6	
Furan Isomer EQ	11	11	1.7	
TOTAL TCDD-EQ	49	42	4.3	

Table 15 (cont)

Sediments from Petenwell and Castle Rock Flowages On Wis. River Below Wis. Rapids Input from Consolidated and Nekoosa Paper Mil.

Wisconsin	A	B	C
2,3,7,8-TCDD	40.6	36.3	15.7
Dioxin Isomer EQ	60.82	50.49	23.27
Furan Isomer EQ	17.15	10.99	7.59
TOTAL TCDD-EQ	77.97	61.48	30.86

Table 16. Tetra- to Octa CCD and CDF in Manufactured Pentachlorophenol (1)

	mg/Kg	% Contribution To TOTAL PCDD+PCDF	mg/Kg	% Contribution To TOTAL PCDD + PCDF
TCDD	.0019	.0002	.0004	.00003
PeCDD	.0065	.0006	.0152	.0012
HxCDD	1.7	0.16	3.3	0.26
HpCDD	154	14.2	198	15.60
OCDD	733	67.6	790	62.2
ΣPCDD	888.7	81.9	991.3	78.06
TCDF	.0008	.00007	.0004	.00003
PeCDF	0.141	0.013	0.343	0.03
HxCDF	4.3	0.40	13.9	1.09
HpCDF	74	6.81	127	10.0
OCDF	118	10.87	137	10.79
ΣPCDF	196.4	18.1	278.2	21.94
ΣPCDD+PCDF	1085.1	100%	1269.5	100%

Hagenmaier, H. and H. Brunner. 1987. Isomerspecific Analysis of Pentachlorophenol and Sodium Pentachlorophenate for 2,3,7,8-Substituted PCDD and PCDF at Sub-PPB Levels. Chemosphere 16(8-9): 1759-1764.

Table 17. 2,3,7,8 - Substituted Tetra- to Hepta-CCD and CDF In Pentachlorophenol

	PCP PRODUCT # 1			PCP PRODUCT # 2			
	ug/Kg	ug TCDD EQ/Kg	% TCDD EQ Contrib	ug/Kg	ug/TCDD EQ/Kg	% TCDD EQ Contrib	
2,3,7,8-TCDD	<0.03	.03	.002	<0.05	.05	.002	
1,2,3,7,8-PeCDD	1.0	0.05	.03	2.0	0.1	.04	
1,2,3,4,7,8-HxCDD	<1.0	.1	.007	<1.0	.1	.003	
1,2,3,6,7,8-HxCDD	83.1	8.3	0.55	1480	148	5.47	
1,2,3,7,8,9-HxCDD	28.0	2.8	0.18	53	5.3	0.20	
1,2,3,4,6,7,8-HpCDD	112,000	1,120	73.8	138,000	1,380	51.1	
OCDD	133,000	133	8.76	790,000	790	29.2	
Σ PCDD	245,113	1264.7	83.33	929,536	2324.5	86.02	
2,3,7,8-TCDF	<0.1	.01	.0007	<0.1	.01	.0004	
1,2,3,7,8-PeCDF	0.5	0.025	.002	0.2	.01	.0004	
2,3,4,7,8-PeCDF	1.5	.75	.05	0.9	.45	.02	
1,2,3,4,7,8-HxCDF	125	12.5	.82	163	16.3	.60	
1,2,3,6,7,8-HxCDF	<1.0	.1	.007	<1.0	.1	.004	
2,3,4,6,7,8-HxCDF	—	—	—	—	—	—	
1,2,3,7,8,9-HxCDF	32	3.2	.21	146	14.6	0.54	
1,2,3,4,6,7,8-HpCDF	11,280	112.8	7.42	19,940	199.4	7.38	
1,2,3,4,7,8,9-HpCDF	637	6.37	0.41	980	9.80	0.36	
OCDF	118,000	118	7.77	137,000	137	5.07	
Σ PCDF	130,077	253.76	16.71	158,231	377.7	13.98	
Σ PCDD+PCDF	375,190	1518.5	100	1,087,777	2702.2	100	

Hagenmaier, H. et al 1987.

Table 18. Percent Weight Contribution of 2,3,7,8-Substituted Isomers To Chlorohomolog Groups of PCDDs and PCDFs in Manufactured Pentachlorophenol

	% Weight Contribution
2,3,7,8-TCDD	1.57
1,2,3,7,8-PeCDD	15.38
1,2,3,4,7,8-HxCDD	.06
1,2,3,6,7,8-HxCDD	4.88
1,2,3,7,8,9-HxCDD	1.64
1,2,3,4,6,7,8-HpCDD	72.72
OCDD	100
2,3,7,8-TCDF	12.5
1,2,3,7,8-PeCDF	0.36
2,3,4,7,8-PeCDF	1.06
1,2,3,4,7,8-HxCDF	2.91
1,2,3,6,7,8-HxCDF	.02
2,3,4,6,7,8-HxCDF	—
1,2,3,7,8,9-HxCDF	.74
1,2,3,4,6,7,8-HpCDF	.02
1,2,3,4,7,8,9-HpCDF	15.2
OCDF	100

Based on Hagenmaier, H. et. al 1987

Table 19 Impurities (mg/Kg PCP) in different manufactured PCP products ①

	1	2	3	4	5	6	7
% PCP Content	84.6	88.4	98	90.4	ns	87	86
Dibenzo-p-dioxins							
Tetrachlor -	<0.1	<0.05	<0.05	<0.05	<0.2	<0.001	<0.01
Pentachloro-	<0.1	ns	ns	ns	<0.2	ns	ns
Hexachloro -	8	4	<0.5	1	9	3.5	5
Heptacloro -	520	125	<0.5	6.5	235	130	150
Octachloro -	1380	2500	<1.0	15	250	600	600
Σ PCDD	1908.2	2629	—	—	494.4	733.5	
Dibenzofurans							
Tetrachloro -	<4	ns	ns	ns	<0.2	ns	ns
Pentachloro -	40	ns	ns	ns	<0.2	0.2	ns
Hexachloro -	90	30	<0.5	3.4	39	10	ns
Heptachloro -	400	80	<0.5	1.8	280	60	ns
Octachloro -	260	80	<0.5	<1.0	230	150	ns
Σ PCDF	794	190	—	—	549.4	220.2	
Σ PCDD+PCDF	2702.2	2819.0			1043.8	953.7	

1. Adapted from World Health Organization. 1987. Environmental Health Criteria 71. Pentachlorophenol

Table 20. Per Cent Contribution of Dioxin and Furan Chlorohomolog Groups To Manufactured Product (1)

	1 %	2 %	3 %	4 %	5 %	6 %	7 %
Dibenzo-p-dioxins							
Tetrachlor -	0.003	0.002	—	—	.02	—	
Pentachloro -	0.003	—			.02	—	
Hexachloro -	0.3	0.14			0.86	0.37	
Heptacloro -	19.2	4.4			22.5	13.6	
Octachloro -	51.1	88.7			24.0	62.9	
Total Percent	70.6	93.2			47.4	76.9	
Dibenzofurans							
Tetrachloro -	0.15	—			0.02	—	
Pentachloro -	1.5	—			0.02	0.02	
Hexachloro -	3.3	1.1			3.7	1.1	
Heptachloro -	15.0	2.8			26.8	6.3	
Octachloro -	9.6	2.8			22.0	15.7	
Total Percent	29.4	6.8			52.6	23.1	

1. From data in Table 20.

Table 21. Relative Partition Coefficients of PCDDs

Homolog	Relative lipophilicity	Relative BCF	Relative Soil Partition Coefficient	Relative Aqueous Solubility
OCDD	700	300	700	0.001
HpCDD	100	70	100	0.007
HxCDD	30	20	30	0.04
PeCDD	5	4	5	0.2
TCDD	1	1	1	1.0
TrCDD	0.2	0.2	0.2	5
DCDD	0.04	0.06	0.04	30
MCDD	0.007	0.01	0.007	100

Moore, J. W. and S. Ramamoorthy. 1984. Organic Chemicals in Natural Waters. Springer-Verlag. New York.

Table 22. Bioavailability Index For 2,3,7,8 Substituted PCDD and PCDF Isomers Based On Carp Uptake Exposed To Petenwell Flowage Sediments

	BSAF or Bioavailability Index	BF (BSAF Normalized to TCDD
2,3,7,8-TCDD	0.27	1.0
1,2,3,7,8-PeCDD	0.060	0.22
1,2,3,6,7,8 and 1,2,3,4,7,8 HxCDD	0.035	0.13
1,2,3,4,6,7,8-HpCDD	0.0048	0.018
OCDD	0.00047	0.0017
2,3,7,8-TCDF	0.06	0.22
2,3,4,7,8-PeCDF	0.28	1.04
1,2,3,6,7,8-HxCDF	0.037	0.14
1,2,3,4,6,7,8-HpCDF	0.0033	0.012
OCDF	0.0022	0.008

Kuehl, D.W. et al. 1987. Bioavailability of PCDDs and PCDFs From Contaminated Wisconsin River Sediment To Carp. Chemosphere 16(4): 667-679.

Table 23. S-21

	Sed c						
	ug/kg	Koc	x	foc	=	Wc	x TEF
2,3,7,8-TCDD	—	—	—	—	—	—	—
1,2,3,7,8-PeCDD	—	—	—	—	—	—	—
1,2,3,4,7,8-HxCDD	—	—	—	—	—	—	—
1,2,3,6,7,8-HxCDD	.97	25,118,864		.05	1,255,943		$.07 \times 10^{-6}$
1,2,3,7,8,9-HxCDD	.38	3,981,072		.05	199,054		$.19 \times 10^{-6}$
1,2,3,4,6,7,8-HpCDD	25.4	63,095,734		.05	3,154,786		$.08 \times 10^{-6}$
OCDD	260	79,432,823		.05	3,971,641		$.07 \times 10^{-6}$
2,3,7,8-TCDF	—	—	—	—	—	—	—
1,2,3,7,8-PeCDF	—	—	—	—	—	—	—
2,3,4,7,8-PeCDF	—	—	—	—	—	—	—
1,2,3,4,7,8-HxCDF	.94	25,118,864		.05	1,255,943		$.07 \times 10^{-6}$
1,2,3,6,7,8-HxCDF	.31	25,118,864		.05	1,255,943		$.02 \times 10^{-6}$
2,3,4,6,7,8-HxCDF	.53	25,118,864		.05	1,255,943		$.04 \times 10^{-6}$
1,2,3,7,8,9-HxCDF	—						
1,2,3,4,6,7,8-HpCDF	10.0	79,432,823		.05	3,971,641		$.025 \times 10^{-6}$
1,2,3,4,7,8,9-HpCDF	1.06	5,011,872		.05	250,594		$.042 \times 10^{-6}$
OCDF	53.2	25,118,864		.05	1,255,943		$.042 \times 10^{-6}$

Total TCDD-EQ = $0.649 \times 10^{-}$ ug/l
Concentration in water

Table 24.

	Sedc	S-22			
	ug/Kg	Koc x	foc =		Wc x TEF
2,3,7,8-TCDD					
1,2,3,7,8-PeCDD					
1,2,3,4,7,8-HxCDD	0.4	25,118,864	.05	1,255,943	$.03 \times 10^{-6}$
1,2,3,6,7,8-HxCDD	2.45	25,118,864	.05	1,255,943	$.19 \times 10^{-6}$
1,2,3,7,8,9-HxCDD	0.91	3,981,072	.05	199,054	$.45 \times 10^{-6}$
1,2,3,4,6,7,8-HpCDD	64.8	63,095,734	.05	3,154,786	$.21 \times 10^{-6}$
OCDD	578	79,432,823	.05	3,971,641	$.15 \times 10^{-6}$
2,3,7,8-TCDF					
1,2,3,7,8-PeCDF	—				
2,3,4,7,8-PeCDF	—	25,118,864	.05	1,255,943	
1,2,3,4,7,8-HxCDF	2.63	25,118,864	.05	1,255,943	$.2 \times 10^{-6}$
1,2,3,6,7,8-HxCDF	.79	25,118,864	.05	1,255,943	$.06 \times 10^{-6}$
2,3,4,6,7,8-HxCDF	.79	25,118,864	.05	1,255,943	$.06 \times 10^{-6}$
1,2,3,7,8,9-HxCDF	.75	3,981,072	.05	199,054	$.37 \times 10^{-6}$
1,2,3,4,6,7,8-HpCDF	24.5	79,432,823	.05	3,971,641	$.06 \times 10^{-6}$
1,2,3,4,7,8,9-HpCDF	3.15	5,011,872	.05	250,594	$.13 \times 10^{-6}$
OCDF	116	25,118,864	.05	1,255,943	$.09 \times 10^{-6}$

Total TCDD-EQ = 2×10^{-6} ug/L
Concentration in water

Table 25.

	Sed_C	S-22 DUP			
	ug/kg	K_{OC} X	f_{OC} =		$W_C \times TEF$
2,3,7,8-TCDD	—	6,309,573	.05	315,479	—
1,2,3,7,8-PeCDD	—	6,309,573	.05	315,479	—
1,2,3,4,7,8-HxCDD	.30	25,118,864	.05	1,255,943	$.02 \times 10^{-6}$
1,2,3,6,7,8-HxCDD	1.66	25,118,864	.05	1,255,943	$.13 \times 10^{-6}$
1,2,3,7,8,9-HxCDD	.70	3,981,072	.05	199,054	$.35 \times 10^{-6}$
1,2,3,4,6,7,8-HpCDD	40	63,095,734	.05	3,154,786	$.13 \times 10^{-6}$
OCDD	520	79,432,823	.05	3,971,641	$.13 \times 10^{-6}$
2,3,7,8-TCDF	—	6,309,573	.05	315,479	—
1,2,3,7,8-PeCDF	—	6,309,573	.05	315,479	—
2,3,4,7,8-PeCDF	—	25,118,864	.05	1,255,943	—
1,2,3,4,7,8-HxCDF	1.66	25,118,864	.05	1,255,943	$.13 \times 10^{-6}$
1,2,3,6,7,8-HxCDF	.58	25,118,864	.05	1,255,943	$.04 \times 10^{-6}$
2,3,4,6,7,8-HxCDF	.78	25,118,864	.05	1,255,943	$.06 \times 10^{-6}$
1,2,3,7,8,9-HxCDF	.38	3,981,072	.05	199,054	$.19 \times 10^{-6}$
1,2,3,4,6,7,8-HpCDF	17	79,432,823	.05	3,971,641	$.05 \times 10^{-6}$
1,2,3,4,7,8,9-HpCDF	1.94	5,011,872	.05	250,594	$.08 \times 10^{-6}$
OCDF	88	25,118,864	.05	1,255,943	$.07 \times 10^{-6}$

Total TCDD-EQ Concentration in water 1.38×10^{-6} ug/

Table 26.

	Sed_C	S-23			
	ug/Kg	K_{OC} X	f_{OC}	=	$W_C \times TEF$
2,3,7,8-TCDD	—	6,309,573	.05	315,479	
1,2,3,7,8-PeCDD	—	6,309,573	.05	315,479	
1,2,3,4,7,8-HxCDD	—	25,118,864	.05	1,255,943	
1,2,3,6,7,8-HxCDD	—	25,118,864	.05	1,255,943	
1,2,3,7,8,9-HxCDD	—	3,981,072	.05	199,054	
1,2,3,4,6,7,8-HpCDD	1.38	63,095,734	.05	3,154,786	$.004 \times 10^{-6}$
OCDD	14.6	79,432,823	.05	3,971,641	$.003 \times 10^{-6}$
2,3,7,8-TCDF	—	6,309,573	.05	315,479	
1,2,3,7,8-PeCDF	—	6,309,573	.05	315,479	
2,3,4,7,8-PeCDF	—	25,118,864	.05	1,255,943	
1,2,3,4,7,8-HxCDF	—	25,118,864	.05	1,255,943	
1,2,3,6,7,8-HxCDF	—	25,118,864	.05	1,255,943	
2,3,4,6,7,8-HxCDF	—	25,118,864	.05	1,255,943	
1,2,3,7,8,9-HxCDF	—	3,981,072	.05	199,054	
1,2,3,4,6,7,8-HpCDF	.52	79,432,823	.05	3,971,641	$.001 \times 10^{-6}$
1,2,3,4,7,8,9-HpCDF	—	5,011,872	.05	250,594	
OCDF	2.74	25,118,864	.05	1,255,943	$.002 \times 10^{-6}$

Total TCDD-EQ = 0.01×10^{-6} ug/L
Concentration in water

Table 27.

S-24

	Sed_C ug/Kg	K_{OC} X	f_{OC} =		$W_C \times TEF$
2,3,7,8-TCDD		6,309,573	.05	315,479	
1,2,3,7,8-PeCDD		6,309,573	.05	315,479	
1,2,3,4,7,8-HxCDD		25,118,864	.05	1,255,943	
1,2,3,6,7,8-HxCDD		25,118,864	.05	1,255,943	
1,2,3,7,8,9-HxCDD		3,981,072	.05	199,054	
1,2,3,4,6,7,8-HpCDD	1.6	63,095,734	.05	3,154,786	$.005 \times 10^{-6}$
OCDD	18	79,432,823	.05	3,971,641	$.005 \times 10^{-6}$
2,3,7,8-TCDF		6,309,573	.05	315,479	
1,2,3,7,8-PeCDF		6,309,573	.05	315,479	
2,3,4,7,8-PeCDF		25,118,864	.05	1,255,943	
1,2,3,4,7,8-HxCDF		25,118,864	.05	1,255,943	
1,2,3,6,7,8-HxCDF		25,118,864	.05	1,255,943	
2,3,4,6,7,8-HxCDF		25,118,864	.05	1,255,943	
1,2,3,7,8,9-HxCDF		3,981,072	.05	199,054	
1,2,3,4,6,7,8-HpCDF	1.0	79,432,823	.05	3,971,641	$.002 \times 10^{-6}$
1,2,3,4,7,8,9-HpCDF	—	5,011,872	.05	250,594	
OCDF	4.0	25,118,864	.05	1,255,943	$.003 \times 10^{-6}$

Total TCDD-EQ = 0.015×10^{-6} ug/L
Concentration in Water

Table 28. Organic Carbon Partion Coefficients (Koc) For 2,3,7,8, Substituted PCDD and PCDF Isomers (Broman et al. 199

Isomer Group 2,3,7,8 Substit. Isom.	Log Koc	Koc L/kg
TCDD	7.3	19,952,623
PeCDD	8.2	158,489,320
HxCDD	8.5	316,227,770
HpCDD	7.8	63,095,734
OCDD	7.9	79,432,823
TCDF	6.9	7,943,282
PeCDF	7.9	79,432,823
HxCDF	7.8	63,095,734
HpCDF	8.2	158,489,320
OCDF	7.4	25,118,864
2,3,7,8 TCDD	6.8	6,309,573
1,2,3,7,8 PeCDD	6.8	6,309,573
1,2,3,4,7,8 HxCDD	7.4	25,118,864
1,2,3,6,7,8 HxCDD	7.4	25,118,864
1,2,3,7,8,9 HxCDD	6.6	3,981,072
1,2,3,4,6,7,8 HpCDD	7.8	63,095,734
2,3,7,8 TCDF	7.5	31,622,777
1,2,3,78 PeCDF	7.6	39,810,717
2,3,4,7,8 PeCDF	7.4	25,118,864
1,2,3,4,7,8 HxCDF	7.4	25,118,864
1,2,3,6,7,8 HxCDF	7.4	25,118,864
2,3,4,6,78 HxCDF	6.8	6,309,573
1,2,3,7,8,9 HxCDF	6.6	3,981,072
1,2,3,4,6,7,8 HpCDF	7.9	79,432,823