

DEPARTMENT OF NATURAL RESOURCES  
NORTH CENTRAL DISTRICT

FROM: Jim Kreitlow

DATE: 6/19/95

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S. Ironside, Friendship  
 J. Zimmermann, WI Rapids

B. Baker-WR/2                     T. Bainbridge-SD  
 J. Bode-WR/2                     D. Weisensell-LMD  
 E. Boebel-WR/2                 A. Bernhardt-WCD  
 L. Kosmond, WR/2               S. Fix-SD  
 C. Ledin-WR/2                  Planner-NWD  
 L. Liebenstein-WR/2             M. Jones-SED  
 B. Wallace-WR/2                T. Smith-NWD  
 T. Janisch-WR/2                C. Koperski-WD  
 D. Schuettpelz-WR/2          S. Gayan, SED  
 D. Valvassori-WR/2           C. Bougie, LMD  
 T. Lohr, WR/2                  L. Talbot, WR/2  
 M. Turville-Heitz, WR/2      G. Hill, WR/2  
 J. Amrhein-WR/2                J. Ball-WR/2  
    P. Cunningham, FM/4  
    J. Lenon, WR/2

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Confer with me  
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 What about this?  
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COMMENTS:

I've passed a message on  
to Lee Liebenstein about  
meeting at 9:00am on the 22nd.  
I'll get you know; if that's  
OK.

Jim

→ Jim Kreitlow  
NCD

Background Information And  
Proposed Sampling And  
Monitoring Plan For The  
Sediments And Water Of  
Military Creek Associated  
With The C.M. Christiansen  
Wood Treatment Facility  
(Draft For Discussion)

Contaminants And Sediment  
Unit  
June 8, 1995

## STREAM CLASSIFICATION AND CHARACTERIZATION

Military Creek is in the Upper Wisconsin River, Northern Sub-basin, Tamarack/Pioneer River Watershed (UW 45).

Military Creek is approximately five miles in length. Miles 0-1.7 are classified as CLASS I and miles 1.7-5.0 are classified as CLASS II Trout Water. Also, miles 0-1.7 are classified as an Exceptional Resource Water.

The lower 1,000 feet of Military Creek above its point of juncture at North Twin Lake is potentially impacted from discharges from the C. M. Christiansen wood treatment facility. A worst case scenario has the potential input sources as being contaminated groundwater flowing into the creek, surface water runoff from the pole yard, dip pond overflows, or direct dumping or discharge of wood treatment waste or sludges or other chemicals associated with the site. There is or was a recognizable drainageway from the pole yard to the creek.

Approximately 330 feet of the creek above and north of County Highway E and approximately 660 feet below County Highway E are potential impacted from site releases. Softer sediments may exist in the approximately 330 foot stretch below the highway and before the bend in the creek where it turns in a southwesterly direction. The creek bottom in the remainder of the stretch between the bend and the juncture with North Twin Lake has harder cobble and rubble strewn materials and little areas of soft sediments. The creek bottom at the juncture with the lake is sand dominated.

The impacted 1,000 length of the creek is approximately 10 - 15 foot wide and 2 - 4 feet in depth. Military Creek has very low flows as evidenced by the 2.5 and 3.7 CFS for the  $Q_2$  and  $Q_{10}$  respectively. Military Creek originates and flows through the Nicolet National Forest before reaching North Twin Lake north of Phelps, Wisconsin. The Wisconsin Wetland Inventory Map indicates that for its 5 mile length, the creek generally flows through a narrow valley but widens at its lower end above the juncture of North Twin Lake.

North Twin Lake has a surface area of 32 acres and a maximum and mean depth of 23 and 8 feet respectively. Musky, walleye, largemouth and smallmouth bass are present in the lake.

For its entire length, with the exception of segment below County Highway E and the lake, the creek flows through mapped wetlands. The cover type classes on the Wisconsin Wetlands Inventory Maps indicates the surrounding wetlands contain tamaracks, willows and alder shrubs, and coniferous shrubs/scrub habitat for typical spruce-tamarack lowland forest habitat. The Wetlands Inventory Map indicates there is a small amount of mapped wetlands to the west side of the segment of Military Creek above County Highway E that is on the site and potentially impacted from site discharges.

The soils in the mapped wetlands adjacent to Military Creek are classified as Seelyeville and Markey Mucks. These are typically black to dark brown mucks in the top 40 - 60 inches and are of herbaceous origin. In some areas, 1 - 4 inches of peat moss is at the surface. In places the mucks are derived from primarily from woody plants and contain wood fragments.

Soils in the upland portion of the site are Padus fine sandy loams. Permeability is moderate in the subsoil of the Padus soil and rapid or very rapid in the substratum. Poor filtering capacity can result in polluted ground water. Other soils in the watershed include champion silt loams (ChC), Padus fine sandy loams (PaC), and Rubicon sand (RoC).

#### EXISTING SEDIMENT CHEMISTRY DATA IN COMPARISON WITH SEDIMENTS QUALITY GUIDANCE AND OBJECTIVE VALUES TO PROTECT BIOTA

Data is available for sediment based on the Kreitlow samples of November 1992 and the Solid Waste Site Evaluation Units (SEU) samples of September 1993. Three impacted reach and one reference sample were taken in the Kreitlow collection. Five impacted reach (includes duplicate as individual sample) and one reference sample were taken in the SEU samples. The general location and designation for these samples from each study is given in Table 1. The analytic results from the Kreitlow sampling are in Table 2. The SEU results are in Tables 3 and 4.

The Khazae to Parkinson memo of 01/20/94 indicates a number of organic compounds were detected but qualified as estimated concentrations because of a number of QC problems. Some were related to common lab contaminants (methylene chloride and acetone). Other than the narrative, estimated and concentrations of the organics involved and the sediment sample sites where they were found is not given in the 01/20/94 memo. Background and study site results need to be compared to determine if the compounds and estimated concentrations have any significance.

#### FIELD OBSERVATIONS OF IMPACTS

Jim Kreitlow notes in a 02/01/93 memo that in his discussions with Bob Young (Water Resources Biologist) and Duke Andrews (District Fish Staff Specialist) that aquatic macroinvertebrate and trout numbers from the stretch of creek potentially impacted by the C. M. Christianson site are lower than what would be expected. In a discussion with Dave Johnson, who participated in the September 1993 SEU sediment sampling of the creek, he indicated that the stretch of creek at and below the site was largely devoid of biota. He also indicated that the cores they took were relatively homogeneous in appearance and did not contain recognizable segments or strata.

#### FERAL FISH COLLECTION FROM NORTH TWIN LAKE AND ANALYSIS FOR DIOXIN

Collection of white sucker and walleye from North Twin Lake were made in 1993 and analyzed for 2, 3, 7, 8 substituted dioxin and furan congeners. The fish picked up minimal levels of HpCDD and OCDD that translated into minimal TCDD-EQ. The levels in the fish may be representative of ubiquitous background sources or based on lab blank results may be from lab contamination and may not be attributable at all to the higher chlorinated dioxin and furan in the creek sediment.

Burbot and perch collected from Military Creek in 1986 had PCP concentrations in tissue as high as 0.250 ug/g.

#### CAGED FISH

In August of 1994, caged fish were placed at three creek locations and one in North Twin Lake out from the creek mouth. The three creek locations are the same from where Ekman dredge sediment samples were taken in 1993. A number of pesticides, trichlorophenols, pentachloroanisole and pentachlorophenols were analyzed for,

No compounds were detected in fish tissue at levels above the SLOH detection limits with the exception of the fish from the 30 day exposure from the North Twin Lake site. The 0.01 ug/g value for pentachloroanisole may not be distinguishable from the reported detection level. Based on the simple partitioning model, table 6, it is predicted that based on the sediment concentration and partitioning of PCP from the organic carbon to the pore water and overlying surface water, fish would bioconcentrate PCP levels in tissue that exceeded the state SLOH detection level of 0.02 ug/g. This simple partitioning model may be over-predicting the amount of PCP that is released from the pore water to the overlying surface water. Dilution in the stream may be occurring. The PCP may be degrading in the water or metabolized in the fish. Depending on the pH, the PCP may be disassociating in the water.

#### LITERATURE REVIEW

In modeling, a biodegradation half life of PCP in sediment of 45 days is assumed. Environmental partitioning of PCP is pH dependent and tends to be transported from soil and sediment to water, especially at pH of around 7.0 and higher. At the pH's potential involved in Military Creek, the majority of the PCP would potentially be dissolved in water in the phenolate form.

Photolysis would be involved in the degradation of PCP in the water column. Estimated half life for dissolved PCP would be about 0.15 to 15 days. Declining aqueous concentrations could be caused by photolysis and hydraulic turnover and possibly biodegradation in sediments. The lower the pH, the more PCP in the undissociated pentachlorophenol form, more uptake by fish, more toxicity directly to aquatic organisms vs. higher pH's (approximately 7.0) when in the pentachlorophenate anion form.

The higher the pH, the lower the  $K_{ow}$  (octanol-water partitioning coefficient). The  $K_{ow}$  at a pH of 4 is 4 and the  $K_{ow}$  at a pH of 8 is 0.

The bioconcentration factor for PCP is 52 at pH 9 and 607 at pH of 7.

The pH is generally lower in spring and higher in autumn; therefore, most uptake in fish is potentially in spring when more pH in the undissociated pentachlorophenol form.

The acute toxicity and bioaccumulation of PCP are a direct function of pH.

Lower pH's, lipophilic form of PCP is dominant and hydrophobic absorption of PCP to organic sediment removes PCP from the water column.

Understanding the toxicology of PCP has been confounded by the fact that commercial preparations particularly in the period up to the mid-1980's contained various amounts of toxic impurities including dioxins and furans. In studies that have compared the toxicity of pure PCP with technical or commercial grade, the toxicity has been found higher in commercial and technical grades. It has been shown to be fetotoxic (toxic to fetal life stages) and teratogenic (able to cause birth defects).

In experimental outdoor streams photolysis accounted for a 5-28% decline in initial PCP concentration compared to a 26-46% decline due to microbial degradation and loss to absorption to sediment or uptake by biota at less than 15%. PCP photochemically reduced to tri- and tetrachlorophenols and ring chlorines are replaced by hydroxyl groups. The resulting compounds are oxidized by air and subsequently dechlorinated ultimately being converted into small fragments, carbon dioxide, and hydrochloric acid.

#### INFORMATION SUMMARY

Based on existing data for the on-land and sediments for the C.M. Christianson site, the following observations are made:

1. The concentrations of PCP in site soils are approximately 1,000 times greater than the concentration in creek sediments.
2. The PAH concentrations in site soils are approximately 10 times greater than those in the creek and sediments.
3. Nineteen pesticides were detected in site soils and only three were found in the creek sediments at low-level concentrations. Pesticides in site soils are much higher in concentration for the three also found in the creek sediments. Pesticide levels in soil site S-11 are much higher than the other soil sample sites. Where was the location of the soil sample sites?
4. In the manufactured PCP product, the concentration ratio of PCP to dioxin/furans impurities is 300 to 1. In the creek sediments, the ratio is approximately 2.5 to 1, which may indicate differential transport of dioxins/furans to the creek compared to PCP or differential weathering and loss of PCP and persistence of dioxins and furans once the pentachlorophenol product reached the creek.
5. Metal levels and sediments do not appear to be elevated above upstream background levels. Jim Kreitlow indicated concerns with copper, chromium, and arsenic because of possible use in wood preservatives solutions. A better comparison of data could be made if particle size information was available for the samples. Zinc appears elevated at S-22 but this may be due to the indicated analytical interference. The

site soils do not appear to have any significant elevations above background with exception of S-14 for zinc and S-14 and S-15 for lead.

6. At the given PCP soil concentrations, it would be interesting to know what the dioxins/furans concentrations are and TCDD-EQ. The TCDD-EQ of dioxins and furans in a manufactured PCB product can range from 1,500,000 to 2,700,000 pg TCDD-EQ/g (90% PCP content assumed).

If the PCP/dioxin impurity ratio stays the same, soil sample site S-11 at 87,000 mg/kg (8.7%) would have a TCDD-EQ of approximately 190,000 pg/g. If there has been a differential loss of PCP from weathering, and the dioxins are persistent in soil, TCDD-EQ could be much higher. The action level for human health concerns based on dermal contact is 1,000 pg/g (1 ppb).

7. The Kreitlow EKMAN dredge samples results for PCP (50, 640, and 30 ug/kg) are somewhat less than the SEU deep coring results (1,300, 1,600, 1,400, and 70 ug/kg). The differences may not be great enough to indicate PCP concentrations are elevated in deeper strata.
8. Given the higher concentrations of PCP, PAHs, and pesticides on land compared to the sediments, the following may have taken place at the facility: the facility operated from 1958 to 1978. In the intervening period between 1978 and the present the contaminated sediments could have been transported downstream into the lake or buried beneath cleaner sediments. At the time of the 1986 creek fish samples enough PCP may have been present yet in the surface sediments to allow fish bioaccumulation either through food or water uptake. Given the amount of residual higher chlorinated dioxins and furans in the sediment which are from impurities in the commercial PCP product, the amount of PCP must have been substantial at one time. The level of dioxins and furans in Military Creek sediments associated as impurities in PCP at a 300 to 1 ratio would represent a PCP concentration of approximately 350-400 mg/kg vs. the approximate 1 mg/kg presently measured in the sediments.

#### WORKPLAN FOR MILITARY CREEK

1. Site reconnaissance

A site visit is to be made and reconnaissance done with Jim Kreitlow to get familiar with groundlevel relationships of site, site processing areas, runoff areas from site to creek, creek characteristics, wetlands, and North Twin Lake.

2. Prepare a health and safety plan

If WDNR WR personnel will be on-site and doing sediment sampling, prepare basic health and safety plan (HASP). Identify contaminants of potential concern (COPC), potential exposure routes to personnel while onsite, protective levels to be used, and personnel and equipment decontamination procedures.

### 3. Water quality monitoring

Design and implement a baseline water quality monitoring program prior to doing in-creek work for the sediments. Because pH plays such a key role in determining the form and subsequent toxicity and bioaccumulation of PCP, pH should be measured. Our recently purchased YSI instrument with the different probes can be used to measure water quality in the water column from surface to bottom at the upstream reference site and several sites in the creek at and downstream from the facility. Parameters which should be measured include dissolved oxygen, pH, temperature, and conductivity. Morning and late afternoon measurements should be made.

### 4. Measure creek flows and discharge volumes

Measure creek flow velocities and discharge volumes. Use newly purchased current meter to measure flows at one site above County Highway E culvert to characterize flows at time of in-creek sampling activity.

### 5. Establish creek characteristics and soft sediment at deposit locations indept.

Establish transects across the creek at approximately 100 foot intervals beginning above the site and going down stream to the point of juncture with North Twin Lake (a total of 12 transects). Measure and describe the creek in terms of width, water depth, and bank characteristics. At each transect use sounding pole to probe sediments and determine thickness of soft sediment deposits across the bottom of the creek.

### 6. Benthic Macroinvertebrate Sampling

Collect macroinvertebrate samples from upstream reference site and 3 or 4 sites at and below the study site. Collections made with the SMART corer of the top 15 centimeters of sediment and sieved through the buckets with No. 60 mesh screens. Five replicates per site or 20 to 25 samples will be taken for analysis. The sorting and identifications should be done under contract with either UW-Stevens Point or UW-Superior. Standard workup should be done to develop diversity and richness indices.

### 7. Toxicity Testing

Collections of the top 15 centimeters (6 inches) of sediment from the reference site and 3 or 4 sites potentially impacted by the facility. Sites and collection for toxicity testing should be near as possible as sites used for collection of macroinvertebrates and for collections done for sediment chemistries.



## 8. Sediment Chemistry

Attempts will be made to have analytical work done by PRP. The following group of parameters should be considered for analysis at the sediment sample sites.

Particle size  
TOC  
pH  
Diesel range organics (DRO)  
~~Oil and grease~~  
Pentachlorophenols  
Chlorophenols  
PAHs  
Pesticides

Core samples should be segmented into the following:

0 to 15 centimeters	0-6 inches
15 to 45 centimeters	6-18 inches
45 to 75 centimeters	18-30 inches
and 75 to 105 centimeters	30-42 inches

The number of segments taken will depend on the depth of soft sediments retrieved in the coring device. If visible strata are present, consideration may be given to altering the above segmentation to analyze visually different strata.

## 9. Sediment Traps

Placement of sediment traps at three locations - the reference site, one station above County Highway E and one station below County Highway E. Three jars will be mounted on a 2 inch X 2 inch stake pounded into the stream bottom at locations where sediment transport, deposition, and resuspension are likely. The sediment traps will be placed at the end of all other instream activities that will be undertaken at the site. The traps will be checked after approximately one month to see what amount of sediments have accumulated. Considerations for analysis will be made depending on amount of material collected and available funding.

Contaminant of Potential Concern (COPC)

- Pentachlorophenol
- Metabolite, dissociated, and breakdown products of Pentachlorophenol. e.g. At least 32 photolytic or biodegradation products of PCP have been identified:
  - ✓ Tetra-, tri-, and dichlorophenol isomers
  - ✓ Penta-, tetra-, tri-, and dichloroanisoles
  - ✓ Tetrachlorohydroquinone
  - ✓ Tetrachlororesorcinol
  - ✓ Hydroxy quinone
  - ✓ Phenoxyphenol
  - ✓ Diphenyl ether
  - ✓ Pentachlorophenate
- Impurities in manufactured PCP commercial and technical grade product.
  - ✓ Trichlorophenols
  - ✓ 2,3,4,6 Tetrachlorophenols
  - ✓ 2,3,4,5 Tetrachlorophenols
  - ✓ Other chlorophenols
  - ✓ Penta CDF/Ds
  - ✓ Hexa CDF/Ds
  - ✓ Hepta CDF/Ds
  - ✓ Octa CDF/Ds
  - ✓ Hexachlorobenzene
  - ✓ Phenoxyphenols
    - Heptachlorophenoxyphenols
    - Octachlorophenoxyphenols
    - Nonachlorophenoxyphenols

Some of the metabolites and impurities are potentially toxic, mutagenic, or teratogenic. Thorough biological assessment is needed of any biodegraded or photodegraded PCP product to determine if any residual toxicity/teratogenicity remains due (1) intermediate metabolites, or (2) constituents that came from the impurities of the manufactured product.

Several polychlorinated phenols including 2,4,5-TCP, 2,4,6-TCP, 2,3,4,5-Tetra CP, 2,3,4,6-Tetra CP and 2,3,5,6-Tetra CP are toxic to aquatic organisms. The toxicity of technical or commercial grade PCP has been found to be greater than purified PCP.

- Diesel fuel or other petroleum products that may have been used as a carrier for the PCP in the pits used for pole treatments.
- Polycyclic Aromatic Hydrocarbons (PAHs) the relatively high levels of total PAHs in the site soils (35, 38, 53, 63, and 2,112 mg/Kg) may potentially indicate creosote may also have been used as a wood preservative on-site at one time.



# Proposed Monitoring For Military Creek

10.

Monitoring Assessment Activity	Reference Site				Above Co. Hwy E				Below Co. Hwy E				Deep Lake Contour											
	MC-1				MC-2				MC-3				MC-4				MC-5				MC-6			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
TOC	X		X		X				X				X				X				X			
Particle Size	X		X		X	X	X	X	X		X		X	X	X	X	X		X		X		X	
pH	X		X		X		X		X				X		X		X				X		X	
DRO	X		X		X		X		X		X		X		X		X		X		X		X	
Oil & Grease	X		X		X		X		X				X		X		X				X		X	
Chloro-phenols																								
4-AAP	X		X		X	X	X	X	X		X		X	X	X	X	X		X		X			
GCMS	X				X		X						X		X						X			
PAHs							X								X									
Pesticides							X								X									
	1. 0-6"				1. 0-6"				1. 0-6"				1. 0-6"				1. 0-6"				1. 0-6"			
	2.				2. 6"-18"				2. 6"-18"				2. 6"-18"				2. 6"-18"				2. 6"-18"			
	3. 18"-30"				3. 18"-30"				3. 18"-30"				3. 18"-30"				3. 18"-30"				3.			
	4.				4. 30"-42"				4. 30"-42"				4. 30"-42"				4. 30"-42"				4.			
					• Collection of the 30"-42" segment may not be possible																			

# Propose ' Monitoring For Military Creek 11.

Monitoring Assessment Activity	Reference Site	Above Co. Hwy E		Below Co. Hwy E		Deep Lake Contour
		MC-1	MC-2	MC-3	MC-4	MC-5
Water Quality Monitoring Temp., PH D.O. Conductivity Surface Bottom YSI	X	X			X	X
Creek Flows and Discharge Volumes		X				
Bank Characterization Water Depths Location and Depth Soft Sediments	Transects at 100 foot intervals Sounding Pole to probe for soft sediment depths and locations in Creek cross section. 12 transects in 1200 ft of creek. Each quarter of cross section probed					
Sediment Traps	X	X			X	
Toxicity Testing Benthic and Water Column (Top 15cm)	X	X	X	X	X	X
Macro-invertebrate Samples (Top 15cm) Cores	X	X	X	X	X	

M. CHRISTIANSEN  
HELPS, WY  
MAPLE LOCATION

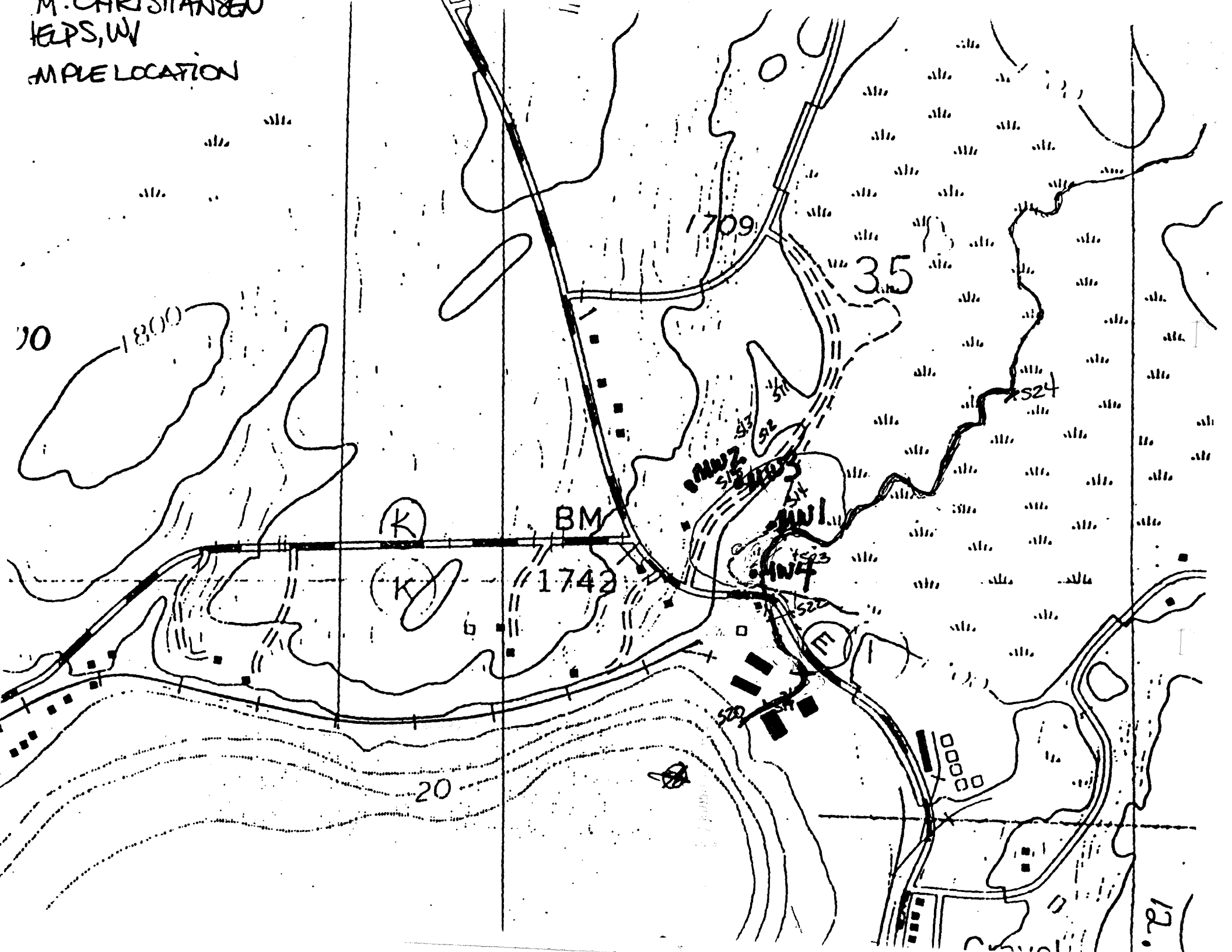


Table 1. Dates, Locations, and Method of Sampling Sediments from Two Studies on Military Creek.

<u>Kreitlow</u>	<u>Site Evaluation Unit</u>
<p>1. Reference - <b>G</b>/1/92 upgradient of pole drying area</p> <p>2. <b>G</b>/2/92 - Downstream of foot bridge below pole drying area</p> <p>3. <b>G</b>/3/92 - Downstream Co. Hwy. E</p> <p>4. <b>G</b>/4/92 - 100 ft above juncture with North Twin Lake</p>	<p>1. Reference S-20 upgradient</p> <p>2. S-22 100 ft. east of MW-3</p> <p>3. S-22 Dup</p> <p>4. S-21 30 ft. upstream of Co. Hwy E culvert</p> <p>5. S-23 Below Co. Hwy E bridge. 40 ft east of metal shed</p> <p>6. S-24 3 ft. upstream of juncture with lake</p>
<u>Samples Taken Kreitlow</u>	<u>Site Evaluation Unit</u>
<p>Ekman Dredge</p>	<p>1. S-20 2 ft. core</p> <p>2. S-22 1 ft. core</p> <p>3. S-22 Dup 1 ft. core</p> <p>4. S-21 2 ft. core</p> <p>5. S-23 1 ft. core</p> <p>6. S-24 Trowel 2-5 in.</p>

Table 2. Sediment Samples Results from Kreitlow Collection of November 1992.

	Background			
	6/1/92	6/2/92	6/3/92	6/4/92
Pentachlorophenol	< 20 ug/Kg	50 ug/Kg	640 ug/Kg	30 ug/Kg
2,4,6-TCP	< 100 ug/Kg	< 100 ug/Kg	< 100 ug/Kg	< 100 ug/Kg
2,4,5-TCP	< 100 ug/Kg	< 100 ug/Kg	< 100 ug/Kg	< 100 ug/Kg
TOC (%)	22.4	1.14	12.6	1.37
Sand (%)	22	93	37	94
Silt (%)	51	3	51	4
Clay (%)	27	4	12	2
Pentachlorophenol ug PCP/Kg OC	--	4,380	5,080	2,190



Table 3. Sediment Sample Results  
 From Site Evaluation Unit Collection of  
 September 1993.

	Background	S-20	S-22	S-22(DUP)	S-21	S-23	S-24
Total Dioxin Isomers (ug/kg)	0.630	646.01	562.66	286.49	15.97	19.60	
Total Furan Isomers (ug/kg)	0.070	148.11	110.34	66.07	3.26	5.00	
Total Furan + Dioxin Isomers (ug/kg)	0.700	794.12	673.00	352.56	19.23	24.60	
<b>TCDD-EQUIVALENCIES</b> *							
Dioxin Isomer EQ (pg TCDD-EQ/g ppt)	1.41	1611	1190	650	28.8	34	
Furan Isomer EQ (pg TCDD-EQ/g)	0.92	893	623	333	8.2	14	
Total TCDD-EQ (pg TCDD-EQ/g)	2.33	2504	1813	983	37	48	
* Because of high detection levels, other Wisconsin reference site values used.							
Pentachlorophenol (ug/kg)	ND(800)	1300	1600	1400	70	ND(800)	
Total PAHs (ug/kg)	1,630	2,500	2,250	3,610	2,340	440	
Endrin (ug/kg) ①	ND	ND	7.2	ND	ND	ND	
4,4'-DDT ①	ND	6.9	9.6	ND	ND	ND	
Endrin aldehyde ①	ND	7.8	11.0	9.3	ND	26	
pH	6.6	6.9	7.2	7.3	6.7	6.4	
① See qualifiers associated with analytical results							

Table 3 (Cont). Sediment Sample Results From Site Evaluation Unit Collection of September 1993

	Background					
	S-20	S-22	S-22(DUP)	S-21	S-23	S-24
Arsenic	4.5	1.8	1.7	3.4	2.1	1.7
Cadmium	ND (7.0)	ND (1.3)	ND (1.1)	ND (1.8)	ND (1.7)	ND (4.1)
Chromium	41.5	16.0	14.3	33.7	15.8	7.1
Copper	13.3	13.7	12.8	25.8	13.2	16.9
Lead	20.2	13.3	13.6	46.3	23.8	31.1
Mercury	ND (0.94)	ND (0.20)	ND (0.16)	ND (0.28)	ND (0.24)	ND (0.58)
Nickel	16.4	8.5	9.0	20.9	8.9	ND (7.3)
Zinc	89.6	240 *	179 *	91.4	53.9	109

\* Estimated values because of interference

Table 4. Soil Sample Results From Site Evaluation Unit Collection of September 1993. 11.

	S-11	S-12	S-13	S-14	S-15	S-18	S-19
Pentachloropheno (mg/kg) PAHs (ug/kg)	87,000	3000	1400	2300	36	11	N.D.
Acenaphthene.	N.D.	1900	1100	N.D.	N.D.	N.D.	970
Fluorene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	360
Phenanthrene	N.D.	2,100,000	N.D.	N.D.	N.D.	N.D.	690
Fluoranthene	N.D.	1200	26,000	9000	11000	N.D.	22000
Pyrene	N.D.	6900	21000	17000	19000	N.D.	16000
Benzo(a)anthracene	N.D.	770	3000	N.D.	N.D.	N.D.	2600
Chrysene	N.D.	2100	6800	5700	6000	N.D.	6000
Benzo(b)fluoranthene	N.D.	N.D.	3000	3300	2100	N.D.	2400
Benzo(k)fluoranthene	N.D.	N.D.	2500	N.D.	N.D.	N.D.	2000
Total PAHs (ug/kg)	N.D.	2,112,870	63,400	35,000	38,100	N.D.	53,020
N-nitrosodi- phenylamine (ug/kg)	N.D.	42000	29000	18000	N.D.	N.D.	19000
bis(2-ethyl- hexyl)phthalate (ug/kg)	N.D.	1500	800	14000	N.D.	N.D.	490

Table 4.(cont) Soil Sample Results From  
Site Evaluation Unit Collection of  
September. 1993.

ug/Kg

	S-11	S-12	S-13	S-14 ✓	S-15	S-18	S-19
alpha-BHC	—	7.8	—	—	—	—	—
Beta-BHC	4600	730	146	320	69	—	—
delta-BHC	4600	170	—	—	—	—	—
gamma-BHC	—	—	—	—	—	—	9.0
Heptachlor	—	—	11	—	—	—	—
Aldrin	13000	290	—	—	410	—	—
Heptachlor epoxide	—	180	400	160	680	1.4	110
Endosulfan	—	220	376	—	840	—	84
Dieldrin	1800	210	—	—	570	—	48
4,4'-DDE	—	200	58	480	—	—	—
Endrin	4900	—	—	500	340	—	—
4,4'-DDD	18000	190	—	390	—	—	—
Endo sulfan sulphate	3000	—	—	510	—	—	—
4,4'-DDT	—	220	200	—	330	—	86
Methoxychlor	—	660	58	—	—	—	—
Endrin ketone	4400	290	—	—	170	—	—
Endrin aldehyde	—	190	—	490	—	—	—
alpha-Chlordane	—	150	—	240	—	—	—
gamma-Chlordane	7800	150	—	810	1100	—	—

" — " indicates not detected.

\* See Data Sheets in Khazae memo of  
03/21/94 for qualifiers associated with

Table 5. Sediment Quality Guidelines and Objectives For Pentachlorophenol

Site Specific Sediment Quality Criteria  
(ug PCP/Kg Sediment - dry wt.)

Percent Total Organic Carbon In Sample	NR 105 Prevent Exceedance of Chronic Toxicity Criteria In Sediment Pore Water and Overlying Surface Water	State of Wash. Sediment Management Standards - Puget Sound
1	142.4	360 (Not
2	284.8	based on
3	427.2	TOC relationship
4	569.6	bulk chemistry;
5	712.0	no adverse
6	854.4	effect to
7	996.8	aquatic
8	1,139.2	organisms)
9	1,281.6	
10	1,424.0	

Table 6. Prediction of Pentachlorophenol Uptake By Fish From Sediment

$$\text{Predicted Fish Tissue Residue FTR} = \frac{C_{\text{sed}}}{(foc)(K_{oc})} (BCF)$$

$$K_{oc} = 53,000 \text{ L/kg}$$

$$BCF = 770 \text{ L/kg}$$

foc = Based on Kreitlow 1993 Samples

C<sub>sed</sub> = Based on Kreitlow 1993 Samples

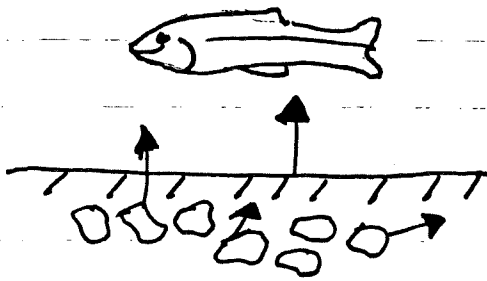
<u>Sample Site</u>	<u>foc</u>	<u>PCP ug/kg</u>	<u>FTR ug/g</u>
G-2-92	0.0114	50	0.064
G-3-92	0.126	640	0.074
G-4-92	0.0137	30	0.032

SLOH PCP detection level in tissue is 0.01 ug/g.

# Predicting Sediment Pore Water Concentrations And Comparison With Water Quality Criteria

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

$$\sum C_{pw} \times TEF$$



	Sediment Sample	Total Estimated TCDD-EQ in Sediment Pore Water pg TCDD-EQ/L
	S-21	0.649
	S-22	2.0 (Dissolved)
	S-22(DUP)	1.38
	S-23	0.01
	S-24	0.015
NR 105 Human Cancer Criteria Proposed in Great Lakes Initiative	—	0.03 (Dissolved + Particulate)
} Wildlife Protection	HNC	0.0031
	HCC	0.067
		0.0086

$$\sum C_{pw} \times TEF \times BEF$$

Differing Bioaccumulation of each Congener in Fish Considered

S-21	0.14
S-22	0.55
S-22(DUP)	0.37
S-23	0.0027
S-24	0.0043

$$\frac{\text{Pg/g Lipid}}{\text{Pg/g OC}} = \text{Bioavailability Index } \textcircled{1}$$

BI's of Kuehl used  
based on Peterwell Flowage  
Study using Carp.

	Fish at 8% Lipid Pg/g	x 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
		Total	11.48

Fish Tissue  
Levels Used Otter 0.89  
In GLI Mink 0.67

Fish Consumption 10  
Advisories For  
Human Consumption



$$\text{Fish Tissue Residue Concentration} = \left( \frac{C_{\text{sed}}}{f_{\text{oc}} \times K_{\text{oc}}} \right) (\text{BCF})$$

	Pore water Pg/L	BCF	Whole Fish Pg/g	TEF	TCDD-EQ in fish Pg TCDD-EQ/g
1,2,3,4,6,7,8 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
Total			254.6		0.30

Fish Tissue Otter 0.89  
 Levels Used Mink 0.67  
 In Great Lakes  
 Initiative To  
 Protect Mammals  
 Consuming Fish

Fish Consumption 10  
 Advisories For  
 Human Consumption

SW - 846  
 Determinative Analytical Methods For Organic  
 Compounds

Compound	Applicable Methods
4-Chloro-3-methylphenol	<u>8040</u> , 8250/8270 8275, 8410
2-Chlorophenol	<u>8040</u> , 8250/8270 8275, 8410
4-Chlorophenol	8410
2-Methylphenol o-Cresol	8250/8270, 8410
3-Methylphenol m-Cresol	8270
4-Methylphenol p-Cresol	8250/8270, 8275, 8410
Cresols (Methylphenols)	<u>8040</u>
2,4-Dichlorophenol	<u>8040</u> , 8250/8270, 8275 8410
2,6-Dichlorophenol	<u>8040</u> , 8250/8270
2,4-Dimethylphenol	<u>8040</u> , 8250/8270
Hydroquinone	8270
2-Methyl-4,6-dinitrophenol	8040
2-Nitrophenol	<u>8040</u> , 8250/8270 8410
4-Nitrophenol	<u>8040</u> , 8151, 8250/8270 8410
Pentachlorophenol	<u>8040</u> , 8151, 8250/8270 8410
Phenol	<u>8040</u> , 8250/8270, 8410
Resorcinol	8270
2,3,4,6-Tetrachlorophenol	8250/8270
Tetrachlorophenols	<u>8040</u>
2,4,5-Trichlorophenols	8250/8270 8410
2,4,6-Trichlorophenols	<u>8040</u> , 8250/8270, 8410
Trichlorophenols	<u>8040</u>

Method 8040 Overall

Applicable Methods

## Phenolic Compounds

9066

## 4-AAP

Phenolic compounds are separated from the original sample matrix by distillation under acid conditions ( $\text{pH} < 4.0$ ). Phenolic compounds in distillate are then reacted with alkaline ferricyanide and 4-amino-antipyrine (4-AAP) to form a red complex. Colorimetric

## METHOD 8040

PHENOLS1.0 Scope and Application

1.1 Method 8040 is used to determine the concentration of various phenolic compounds in groundwater, liquid, and solid matrices. Specifically, Method 8040 may be used to detect the following substances:

Phenol	4-Chloro-3-methylphenol
2-Chlorophenol	2,4-Dimethylphenol
2,4-Dichlorophenol	2-Nitrophenol
2,6-Dichlorophenol	4-Nitrophenol
Trichlorophenols	2,4-Dinitrophenol
Tetrachlorophenols	2-sec-Butyl-4,6-dinitrophenol (DNBP)
Pentachlorophenol	2-Cyclohexyl-4,6-dinitrophenol
Cresol (methyl phenols)	2-Methyl-4,6-dinitrophenol
4,6-Dinitro-o-cresol	

1.2 Method 8040 is recommended for use only by, or under the close supervision of, experienced residue analysts.

2.0 Summary of Method

2.1 Method 8040 provides chromatographic conditions for the detection of phenolic compounds. Prior to analysis, samples must be extracted using appropriate techniques. Water and groundwater samples are extracted at a pH of less than or equal to 2 with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Both neat and diluted organic liquids may be analyzed by direct injection. Solid samples are extracted at a pH of less than or equal to 2 with methylene chloride using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. A 2- to 5- $\mu$ l sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by a flame ionization detector (FID). An aliquot of each sample must be spiked with standards to determine the spike recovery and the limits of detection for that particular sample.

2.2 Method 8040 also provides for the preparation of pentafluorobenzyl-bromide (PFB) derivatives with additional cleanup procedures for electron capture gas chromatography to aid the analyst in the elimination of interferences.

2.3 The sensitivity of Method 8040 usually depends on the level of interferences rather than on instrumental limitations. The detection limits listed in Table 1 for some phenols represent sensitivities that can be achieved in wastewaters in the absence of interferences. However, in typical waste samples, detection limits would be higher. The use of derivatization cleanup, if necessary, will also increase detection limits.

## PHENOLIC COMPOUNDS

Phenols are a diverse and widely utilized group of organic chemicals characterized by a benzene ring with one or more hydroxyl groups. The more complex phenols have one or more of the hydrogen atoms replaced with chlorine, nitro, or methyl groups. Phenols were first produced by the distillation of coal tars, and after 1930 synthetic production grew more important. Phenol is now used as an intermediate in the production of other compounds such as phenolic resins, germicides, pharmaceuticals, fungicides, dyes, herbicides, plastic, explosives, and skin medications. Table Phe-1 contains some physicochemical and biological properties for selected phenolic compounds. Table Phe-1, Column 4, indicates which of the phenolic compounds are included in EPA's listing of 126 priority pollutants.

Phenolic compounds such as the anionic forms of chlorophenols, nitrophenols, and cresols, along with herbicides, represent the majority of ionic organic compounds of environmental significance (Smith et al., 1988). Examples of non-ionic organic compounds are PCBs and chlorinated insecticides. Phenolic compounds generally have high aqueous solubilities and associated reduced partitioning to sediment organic matter. Based on their relatively high solubilities, low octanol-water partition coefficients, and anionic nature, most of the phenols do not strongly sorb to sediments or bioaccumulate in aquatic organisms. Increased chlorination of the aromatic ring of the phenol molecule decreases compound solubility, and increases octanol-water partition coefficients, persistence in sediments, and toxicity. The more highly chlorinated phenols such as pentachlorophenol (PCPs) or the tetrachlorophenols can exhibit significant adsorption to sediments and bioaccumulation in organisms. The solubilities of phenolic compounds are functions of the system pH.

Sorption of phenolic compounds to sediment organic matter will depend on the organic carbon content of the sediments and the system pH. Sorption of phenolic compounds as influenced by partitioning will be reduced at higher pHs because of increased solubility and decreased undissociated (nonionized) compound being present (Schellenberg et al., 1984). Decreasing pH drives the formation of undissociated chlorinated phenol compounds that have greater sorption coefficients. These compounds will partition to organic carbon associated with the sediment, suspended particulate matter, and dissolved organic matter.

The primary environmental fate mechanisms for phenolic compounds include biodegradation and photolysis (Smith et al., 1980). Photolysis (nonmetabolic degradation requiring light energy) would be most applicable to air-water surface while biodegradation occurs at the water sediment interface if sufficient microbes are present. Moore and Ramamoorthy (1984) indicate that phenol and a number of other phenolic compounds such as cresols, methylphenol, phenylphenol, and nonylphenol are seldom detected in sediments because of their biodegradability. Smith et al. (1980) indicate sediment residues of phenols rarely exceed the micrograms-per-kilogram range. However, Moore and Ramamoorthy also indicate some of the alkylphenols have been found in sediments at high concentrations particularly near waste discharge sites. They indicate that while comparable residues probably occur in the sediments of other industrial zone rivers, the environmental implications of such levels are unknown.

The biodegradability of the chlorophenols generally decreases with increasing chlorine substitution. PCP degrading microorganisms have been isolated from waters and soils. However low oxygen conditions are generally unfavorable for the biodegradation of PCPs, allowing it to exist in water (the half-life is 80-192 days in anaerobic water) and sediments

(10% decomposition within 5 weeks to almost no degradation (WHO, 1987). Of concern are the degradation products of PCP which include such metabolites as various di-, tri-, and tetrachlorophenol isomers, anisole, quinone, hydroxy diphenyl ether. The conversion of chlorinated phenol to anisole may be of considerable environmental significance in aquatic systems (Pierce et al., 1980). The enhanced hydrophilic nature of anisoles suggests a greater bioaccumulation factor over phenol, as well as longer persistence in organisms and sediment.

Some identified contaminated sediment situations and causative phenolic compounds are listed in Table Phe-2. Because of their widespread and multiple uses, phenolic compounds are commonly found in municipal and industrial discharges. Residues are generally lower in municipal wastewater treatment plant effluents. Chlorinated phenols are commonly discharged from industries using chlorination as part of their process chemistry. High chlorinated phenol concentrations have been reported for effluents from pulp and paper mills, wood preservation plants and certain chemical industries. The chlorinated phenols have been used as microbiocides by the paper industry to keep the microbial populations in water systems at acceptable levels (Sullivan and Delfino, 1982). Pentachlorophenol and sodium pentachlorophenate are two fungicides used in paper mills and can end up in mill wastewater. U.S.D.A. (1980) indicates pentachlorophenols and pentachlorophenates are ubiquitous in the aquatic environment and in cases, sources are unclear. Chlorophenols can be produced by the chlorination of treated wastewaters and drinking waters containing phenol (Callahan et al., 1985). 2,4-dimethylphenol is found in the water runoff from asphalt surfaces. Since phenols and cresols are water soluble, they can be leached from coal piles as precipitation passes through. Phenols and cresols are also by-products from the burning of coal. The burning of one ton of coal produces eight gallons of coal tar which in turn is partially composed of 0.7% phenols and 1.1% cresol (Craig and Lesser, undated).

Of concern with commercially manufactured pentachlorophenol preparations is the finding in recent years that the PCP product is sometimes contaminated with chlorinated dibenzo-P-dioxins and chlorinated dibenzofurans (U.S.D.A., 1980). These compounds are formed as by-products of the manufacturing process. Release of PCP into the aquatic environment may also mean the concurrent release of these product impurities.

The U.S. ACOE has, in recent years, routinely analyzed for phenolic compounds in association with their dredging maintenance projects in the Superior-Duluth Harbors and St. Louis Bay and River Channels. Table Phe-1, Column 5, contains their detection limits for these specific phenolic compounds. Table Phe-3 contains the historical phenolic concentrations found in the ACOE sediment sample results for various segments of the Duluth-Superior Harbor.

The only phenolic compounds that the ACOE found above their detection limits were for the individual compound phenol and total phenols. The individual phenolic compounds are analyzed for utilizing a gas chromatography procedure. Total phenols is the result of analysis using the 4-AAP (4-aminoantipyrene) colorimetric method. The analytical procedure measures the color development of reaction products between 4-AAP and some phenols. Because many phenolic compounds do not react, "total phenols" does not represent all phenols.

The 4 AAP method does not determine those para-substituted phenols where the substitution is an alkyl, aryl, nitro, benzoyl, nitroso, or aldehyde group. Because of this, 2,4,6-trichlorophenol, 2-nitrophenol, 4 nitrophenols, 2,4-dinitrophenols and

pentachlorophenol are not detected by the 4 AAP method. It is possible to have 6 of the 11 priority pollutant phenolic compounds present in high concentrations and not be detected by the 4 AAP analytical method (U.S. EPA, 1982).

In the few samples where the compound phenol was found in the sediments, the concentrations ranged from 40-160 µg/kg (mean = 83.3; n = 3). In the samples where total phenols were detected, the concentrations ranged from 50-77,000 µg/kg (mean = 1,530; n = 68). The highest total phenol concentrations were found in a set of samples taken in the Duluth-Superior Harbor segments on 10-30-86. Analysis for 11 individual phenolic compounds by gas chromatography procedures from the 10-30-86 samples shows none were found above detection levels. If the total phenol results are valid, some untested phenolic compounds apparently were contributing to elevated concentrations that range from 1,000-77,000 µg/kg total phenols at 9 of the 24 sites. Some other sample results for total phenols in the 10-30-86 set of samples had concentrations comparable to testing performed at other dates (100-200 µg/kg range). Bahnick et al. (1981) found the total phenol concentrations in sediments at eight sampling sites within the AOC and one site in Lake Superior as listed in Table Phe-4. The Lake Superior site is six miles north of the Superior entry.

Bahnick and Markee (1985) studied certain organic microcontaminants associated with the Duluth-Superior harbor sediments and suspended particulate matter and their transport to Lake Superior. The results of an initial survey in 1980 of organic compounds associated with suspended particulate matter from a site below the Western Lake Superior Sanitary District (WLSSD) facility outfall found non-halogenated hydrocarbons, organic acids, aldehydes, ketones, amines, esters, alcohols, and nonchlorinated phenols. Bahnick and Markee indicate most of the organic compounds appeared to be naturally occurring plant decomposition products. Bahnick and Markee do not indicate the concentration levels for these compounds they detected.

Bahnick and Markee (1985) detected pentachlorophenol (PCP) in the sediments and particulates from sites above and below the WLSSD discharge point in St. Louis Bay during 1982. They screened their samples for 2,4,5-trichlorophenol (a precursor of 2,3,7,8-tetrachlorodibenzo-p-dioxin) but the results were negative at a detection level of 2 µg/kg for particulates and 0.2 µg/kg for sediments. The results of the PCP analysis is shown in Table Phe-4. Detection limits for PCP in sediments was 0.01 µg/kg and 0.1 µg/kg or less for particulates.

The results show that particulates were higher in PCP concentration than sediments by factors of 4 (site 2) and 20 (site 1). Using these values in conjunction with the particulate loading and resuspended sediments caused by shipping in the harbor, Bahnick and Markee predicted that 6.6 and 352,736 lbs/yr of PCP would reach Lake Superior from particulate transport and sediment resuspension, respectively. This projection assumes that concentration of PCP in sediments and particulates harbor-wide are at the same levels as the two sites sampled in the Bahnick and Markee study. This assumption would need further sampling to confirm.

Bahnick and Markee (1985) indicate sampling of Duluth Harbor in 1977 found levels of PCP of 1.4 to 36 µg/kg. They attribute lower levels of PCP found in their 1982 samples (Table Phe-4) to be due to the WLSSD facility coming on-line during the winter of 1978-1979. A marked improvement in harbor water quality was noted after facility start up. However, it should be noted that the 1977 sampling of eight sites in the harbor (Bahnick et

al., 1981) were not in the immediate upstream-downstream region of the WLSSD discharge point. A repeat sampling of the same eight widely separated 1977 sites, post-WLSSD start-up would be needed to confirm if levels of PCP are lower and if the decrease could be attributed to WLSSD treatment of wastewater. The Bahnick et al. (1981) study found PCP in the sediments at a control site in Lake Superior, 6 miles north of the Superior Entry, at a concentration of 1.2 ug/kg. The concentration of total phenols in sediments at a number of sites in this same study is shown in Table Phe-5.

System-wide and upriver sediment sampling performed by the MPCA (1979) at 25 sites yielded PCP values that ranged from 3.0 - 130 ug/kg (Table Phe-6). Some of the higher values for PCP were from sediment sampling sites near the discharge outfalls of the Superior Wastewater Treatment Plant (120 ug/kg) and the WLSSD plant (130 and 48 ug/kg).

Some of the lowest values were associated with sampling sites in Allouez Bay (5.0 ug/kg) and upstream or tributaries to the St. Louis River (3.0-6.0 ug/kg).

Table Phe-1 contains Wisconsin and Minnesota ambient water quality criteria for phenolic compounds related to surface water use classifications:

- a) Protection of human health based on ingestion of aquatic organisms and water.
- b) Protection of surface waters and organisms inhabiting them from having objectionable tastes and odors to human consumers, and
- c) Protection of aquatic organisms from acute and chronic concentrations of phenolic compounds in the water column.

The EqP approach to developing sediment quality values is used to describe the sorption and release of neutral hydrophobic organic chemicals by sediment organic carbon. Water quality criteria are used to derive sediment quality values. The physicochemical properties of phenolic compounds to dissociate or ionize at increasing pH with subsequent changes in its hydrophobicity make the EqP approach difficult to apply for reliably predicting pore water concentrations of the compound and toxicity to benthic organisms and potential for release to the overlying water column. The role of pH in organic molecule-sediment organic matter interactions for phenols is likely to be complex and needs detailed investigations (Issacson and Frink 1984). Issacson and Frink found that a significant fraction of phenol, 2-chlorophenol, and 2,4-dichlorophenol were irreversibly held by the sediment fraction due to hydrogen bond interactions. The bonding depends on the amount and nature of the organic matter associated with the sediments. Sorption of the phenols was greater than expected from just hydrophobic partitioning reactions.

In attempting to apply the EqP approach to developing sediment quality assessment values (SQAV) for PCP, the octanol-water partition coefficient as a function of pH has to be considered. In applying the EqP approach to developing the SQAV for PCP, the assumption has to be made that the water column-sediment compartments all have comparable near neutral - pH chemistries and that this pH remains relatively constant. In reality changes in pH in the environmental compartments would likely affect the hydrophobicity of PCP and the undissociated/dissociated forms, making the predictions of the



concentration of PCP in the sediment pore water and sediment/water column interface uncertain. The partitioning of organic anions to natural sorbents is believed to be influenced significantly by both hydrophobic and electrostatic interactions (Jafvert et al., 1990).

If the pH of the sediment-water column were to remain at near neutral pH and possible influencing interactions are not considered, Table Phe-7 shows the concentration of PCP in the sediments, depending on TOC content, that would be necessary to order to protect aquatic organisms (chronic toxicity criteria) and human health concerns. The SQAV based on the site specific TOC concentration would not allow PCP to partition from the sediments to sediment pore water and overlying water column in amounts greater than the water quality criteria in NR 105, Wis. Admin. Code. Based on Table Phe-7, the most stringent SQAV for PCP would be 71.2 ug/kg assuming the lowest TOC in sediment and the need to protect benthic and water column organisms from chronic toxicity.