

Date: October 1, 1992
To: Linda Talbot, WR/2
From: Jim Kreitlow, NCD *JK*

Subject: Sediment Sampling on Military Creek

On September 28, 1992, Tom Blake and I collected sediment samples from Military Creek. We collected four samples (see attached map). The sites include:

1. G-1-92 - Collected upstream from the pole drying yard (reference site or nonimpact site).
2. G-2-92 - Collected downstream from the pole drying yard just below foot bridge above Highway "E" (impact sample).
3. G-3-92 - Collected below Highway "E" downstream from the pole drying area (impact sample).
4. G-4-92 - Collected 100 feet above confluence with North Twin Lake.

Three composite sediment samples were collected at each sampling site. These composite samples were mixed and two subsamples of sediment were collected for particle size analysis and contaminant analysis. After each sampling site, the Eckman dredge and sampling utensils were washed with alkanox, rinsed with tap water, then triple rinsed with distilled water. These four samples will be analyzed for PCP, total organic carbon and particle size.

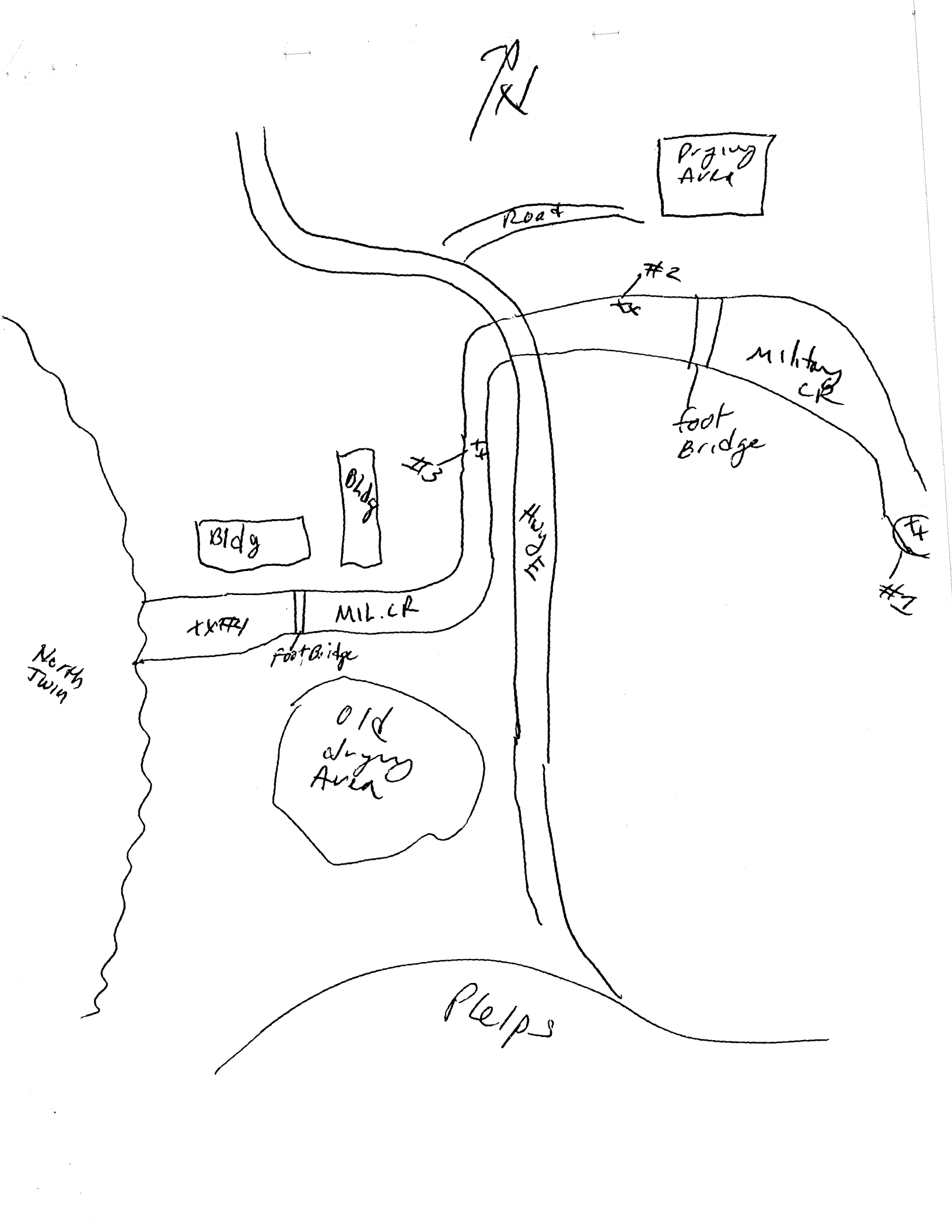
We originally planned to collect five samples. We did not collect any samples out of North Twin Lake because of lack of organic sediments. Therefore, only four samples were collected (all from Military Creek). We will reserve sampling the lake until we find out what the results are for the stream samples.

If you have any questions concerning the sampling, please contact me in Rhinelander (715-369-8947).

JK:da

Attach.

cc: Larry Maltbey, Rhinelander
Duane Schuettpelez, WR/2
Duke Andrews, Rhinelander
Bill Jaeger, Rhinelander



Military Creek Sediment Sampling
1992

Introduction

Sediment sampling was conducted on Military on September 28, 1992, as part of North Central District's special project sediment monitoring program. Parameters to be analyzed for included pentachlorophenol (PCP), total organic carbon (TOC), and particle size.

Purpose

This impact assessment monitoring was conducted in response to suspected off-site migration of contaminants from the now closed Christensen Wood Treating Pole Yard facility in Phelps, Wisconsin. This data will help both Water Resources Management and the Bureau of Solid Waste assess the threat to the environment and the need for cleanup at this site.

Sampling Locations

The following sediment sampling locations are shown on the attached map.

1. Field G-1-92, Storet #643406 - Upgradient of pole yard drying area (reference site)
2. Field G-2-92, Storet #643405 - Downstream of foot bridge below pole yard drying area (impact site)
3. Field G-3-92, Storet #643404 - Downstream of Highway E below pole yard drying area (impact site)
4. Field G-4-92, Storet #643403 - 100 feet above confluence with North Twin Lake (impact site) - Note: A sample was proposed but was not collected from North Twin Lake.

Methods

Three composite sediment grab samples were collected at each sampling site using a brass Ekman dredge. These composite samples were mixed and two subsamples of the sediment were collected for particle size analysis and contaminant analysis. After each sampling site, the Ekman dredge and sampling utensils were washed with alkanox, rinsed with tap water and triple-rinsed with distilled water. The reference site was sampled first and then subsequent samples followed preceding downstream.

Results: Note: ppb = ug/Kg
mg of PCP/KG of carbon is a correction factor for the amount of total organic carbon.

PCP

1. Field G-1-92 - Less than 20 parts per billion PCP (below detection level)
2. Field G-2-92 - 50 parts per billion PCP/4.38 mg of PCP/Kg of carbon
3. Field G-3-92 - 640 parts per billion PCP/5.08 mg of PCP/Kg of carbon
4. Field G-4-92 - 30 parts per billion PCP/2.19 mg of PCP/Kg of carbon

Total Organic Carbon

1. Field G-1-92 - 224,000 parts per million TOC
2. Field G-2-92 - 11,400 parts per million TOC
3. Field G-3-92 - 126,000 parts per million TOC
4. Field G-4-92 - 13,700 parts per million TOC

Particle Size

1. Site G-1-92 - 22% sand, 51% silt, 27% clay, classified as clay loam soil
2. Site G-2-92 - 93% sand, 3% silt, 4% clay, classified as sandy soil
3. Site G-3-92 - 37% sand, 51% silt, 12% clay, classified as silt loam soil
4. Site G-4-92 - 94% sand, 4% silt, 2% clay, classified as sandy soil

Discussion and Recommendations

Pentachlorophenol was found at all three of the impact sites ranging from 30 parts per billion (Site G-4-92) to 640 parts per billion (G-3-92). The upgradient reference site was clean at a detection limit of 20 parts per billion.

At a level of 640 ppb, there is some potential to adversely impact benthic organisms exposed to PCP's in pore water (Tom Janish, personal communication). Assuming a worse case of partitioning and little dilution and mixing, PCP may adversely impact water column organism depending on pH (Tom Janish, personal communication).

Upon discussing the site with Bob Young (Water Resources Biologist) and Duke Andrews (District Fisheries Management Supervisor), aquatic macroinvertebrate and fish (including trout) numbers in the stretch of creek are lower than you would expect to find. Is this due to PCP toxicity? This stream is classified as trout water. The above information is based on a field investigations.

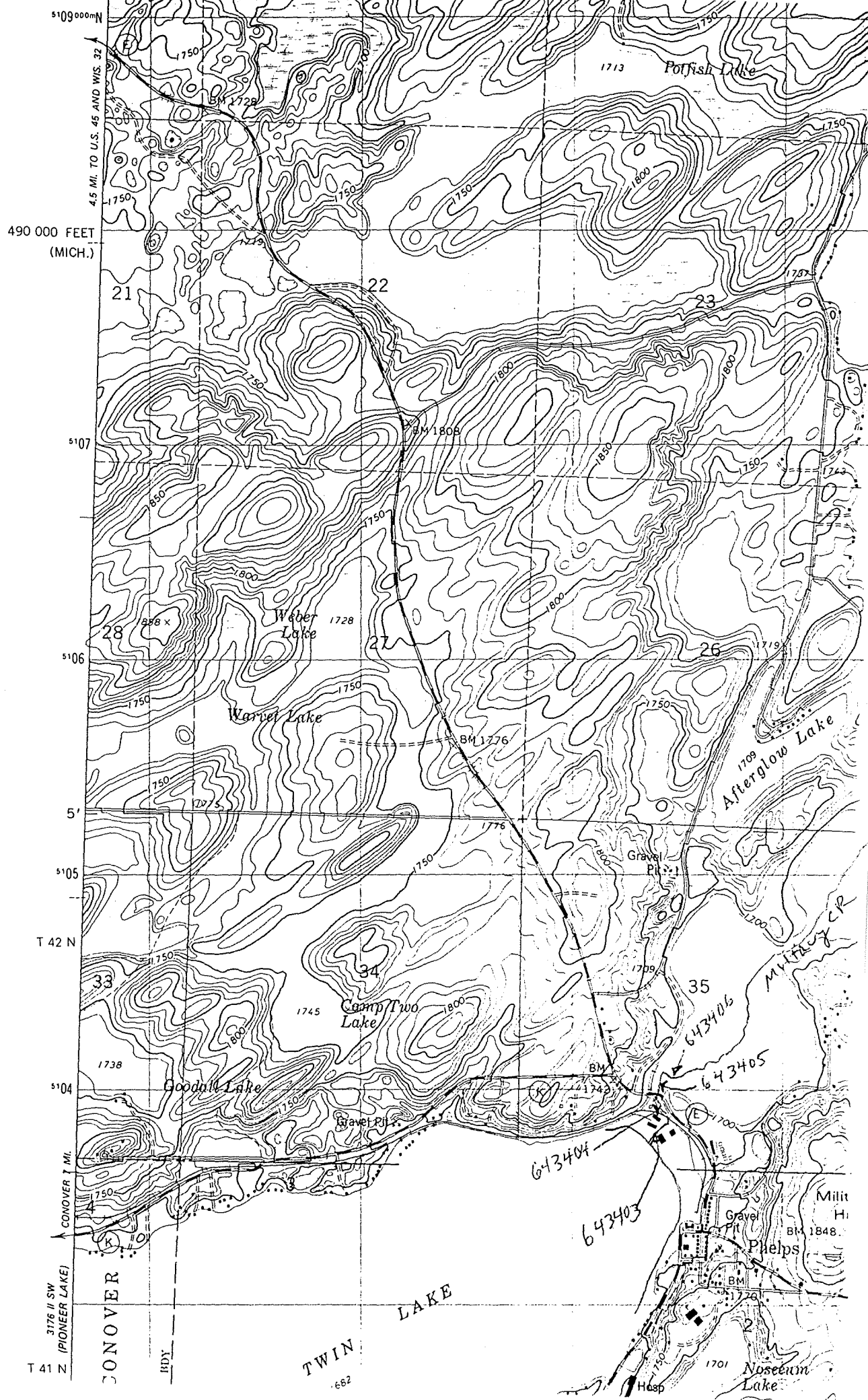
Fish from Military Creek were analyzed for PCP (collected in 1986). A small perch and burbot each contained 250 ppb PCP. This shows that PCP is bioavailable and moving into the food chain.

North Central District will conduct further sampling of the sediments in Military Creek and North Twin Lake for other compounds such as copper, chromium, arsenic, PAH,s, diesel range organics and PCP. We will try to coordinate sampling with the Bureau of Solid Waste so proper chain of command and QA/QC procedures are followed. Sediment samples could also be archived for future dioxin analysis (solid waste would fund if monies are available). A core sampling device will be used to sample deeper depths (higher contaminant levels?) and to identify possible stratification of sediment deposits.

Perhaps this site would also be a good candidate for sediment toxicity testing. Sediment samples could be collected for laboratory testing or equipment could be set up in the field.

JK:da

cc: Joe Ball, WR/2
Linda Talbot, WR/2
Lee Liebenstein, WR/2
Larry Maltbey, Rhinelander
Duke Andrews, Rhinelander
Tom Janish, WR/2
Bill Jaeger, Rhinelander
Bob Masnado, WR/2
Connie Antonuk, Rhinelander
Jim Hosch, Wausau
Randy Falstad, Wausau



T 41 N
3176 II SW
(PIONEER LAKE)

CONOVER

INDY

TWIN LAKE

100 ft above N. Twin Lake Confluence G-4-92	30 ug/kg	1.37			
Highway E Below G-3-92	640 ug/kg	12.6%			
Foot bridge Below Pale Yard Drying Area G-2-92	50 ug/kg	1.14%			
Upgradient G-1-92	< 20 ug/kg	22.4%			
Pentachloro-phenol					
TOC					

Comments:

What is pH of water and sediments of the system?

PCP can be relatively persistent, therefore it may not be surprising that PCP is still being found 10 years after plant closure.

The three soil and groundwater contamination at the site?

Do higher levels of PCP exist at lower depths in the sediments?

In water column, PCP has a half-life of 0.15 - 15 days. When adsorbed to sediments has been found to persist for periods of 12 mo. to 15 yrs depending on conditions.

Enhanced persistence of PCP under anaerobic environments.

Any water column samples for PCP?

At the level of 640 ug/kg, some potential to adversely impact benthic organisms exposed to PCPs in pore water.

Assuming a worse case of partitioning and little dilution and mixing, PCP may adversely impact water column organisms, depending on pH.

- Biol the company have a history of using other waste treatment / preservation chemicals eg arsenic, copper, zinc oil preservative
- Pentachlorophenol may be ubiquitous in the aquatic environment, sources unclear. Significant bioaccumulation levels in sediment may be from 1-5 ug/kg and possibly 10-20 ug/kg depending on the site.

Pentachlorophenol (Miscellaneous)

10

(10% decomposition within 5 weeks to almost no degradation (WHO, 1987). Of concern are the degradation projects 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

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 in 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.

Table Phe-6. MPCA (1979) System-wide Sampling of the St. Louis River Bay and Tributaries for Pentachlorophenol (PCP) in the Sediments

Latitude/Longitude Locator	Area Description	Sample Identifier	(ug/kg) PCP
46 41 45 92 00 27	Allouez Bay	SL126	5.00
46 44 39 92 04 43	Superior Bay	SL123	15.00
46 43 42 92 04 04	Superior Bay at Superior, WI	SL124	120.00
46 43 48 92 03 30	Superior Bay .5 mi NE of WI	SL125	17.00
46 45 23 92 06 53	St. Louis Bay .8 mi SE of Duluth	SL121	48.00
46 45 27 92 07 07	St. Louis Bay .5 mi SE of Duluth	SL120	130.00
46 44 17 92 07 50	St. Louis Bay 1.5 mi E of Duluth	SL119	53.00
46 43 06 92 08 45	St. Louis Bay 1 mi SE of Duluth	SL118	22.00
46 43 17 92 10 28	St. Louis Bay .5 mi S of Duluth	SL117	10.00
46 43 21 92 10 22	St. Louis Bay .5 mi S of Duluth	SL127	
46 42 40 92 10 42	St. Louis Bay 1 mi S of Duluth	SL116	24.00
46 41 24 92 10 03	Pokegama Bay 2.8 S of Duluth	SL115	22.00
46 62 13 92 12 03	St. Louis Bay 2 mi SW of Duluth	SL114	43.00
46 41 32 92 11 50	St. Louis Bay 2 mi NE of Gary	SL113	8.00
46 40 50 92 11 41	St. Louis 2 mi NE of Gary	SL112	18.00
46 44 09 92 04 36	Superior Bay at Superior, WI	SL122	17.00
46 40 27 92 11 13	Pokegama Bay 2 mi E of Gary	SL111	10.00
46 39 44 92 12 29	St. Louis at Mud Lake	SL110	33.00
46 38 54 92 14 36	St. Louis 1.5 mi SW of Gary	SL109	31.00
46 38 46 92 16 30	St. Louis 2.5 mi SW of Gary	SL108	14.00
46 44 34 92 29 00	St. Louis at Cloquet	SL24	
46 39 59 92 18 09	Jay Cooke State Park	SL107	6.00
46 38 30 92 21 22	Silver Ck at Jay Cooke State Park	SL102	29.00
46 42 37 92 25 08	St. Louis .5 mi E of Scanlon, at Dam	SL106	37.00
46 63 33 92 26 58	St. Louis at Knife Falls	SL105	29.00
47 28 51 92 02 20	St. Louis 5.5 mi SE of Hoyt Lakes	SL104	3.00
47 15 00 92 48 33	Swan River 5.5 mi N of Tiovola	SL103	
47 31 38 92 07 21	Partridge River 1.5 NE of Hoyt Lakes	SL101	5.00

(ppb)

Table Phe-7. Sediment Quality Assessment Values (SQAVs) For Pentachlorophenals Developed Through Use of the Equilibrium Partitioning Approach and Water Quality Criteria as Contained in NR 105 Wis. Admin. Code.

Percent Total Organic Carbon in Sediment Samples	SQAV for PCP Needed to Protect Benthic Aquatic Organisms. Based on Water column Chronic Toxicity Criteria in NR 105 Wis. Admin. Code (ug/kg)	SQAV for PCP Needed to Protect Human Health Based on Human Threshold Criteria in NR 105 Wis. Admin. Code (ug/kg)
0.5	71.0	6919.8
1.0	142.40	13839.6
2.0	284.80	27679.2
3.0	427.21	42349.2
4.0	569.61	56465.6
5.0	712.01	70581.9
6.0	854.41	
7.0	996.82	
8.0	1139.22	
9.0	1281.60	
10.0	1424.00	

Log Kow for Pentachlorophenol = 3.32
 Organic Carbon Partition Coefficient (Koc) = 1821 liters/Kg OC
 pH of Sediment - Water Column = 7.2

Sediment Quality Criteria (ug PCP/Kg OC) = Water Quality Criteria (ug/L) X KOC X Organic Carbon Content of sediments expressed as a decimal

Water Quality Criteria - NR 105

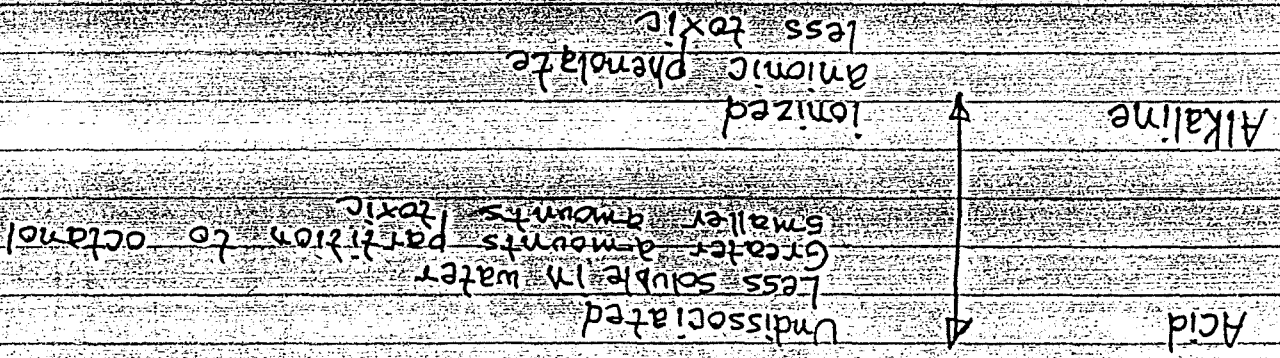
Aquatic Organisms - Chronic Toxicity Criteria 7.82 ug/L
 Human Health Concern - 760 ug/L

Pentachlorophenol
(Miscellaneous)

Washington Sediment Management Standards

Pentachlorophenol
360 ug/Kg
Sediment Quality Standards

Sediment Impact Zone
Maximum Chemical Criteria 690 ug/Kg



- Water column = undergoes degradation by photochemical and microbial action
- May not be readily degradable when associated with particulate matter and sediments.
- Toxic impurities and degradation products (e.g., tri- and tetrachlorophenol congeners chlorinated guaiacols, pyrogallol, guaiacol, pyroxyphenol, pyroxyphenol ether, dibenzofuran and dioxin)

PCP persisting in fish

methoxy ether of PCP
pentachlorocyclohexane (PCH)
2,3,4,5- and 2,3,4,6- and 2,3,5,6-tetrachlorophenol (TCP) congeners and the amino (TCH) of each

Background concentrations		Sediment From Spill	
PCP	3.0 ± 0.4 ug/Kg	PCP	77%
PCA	< 1 ug/Kg	TCP	16%
TCP	1.0 ± 0.2 ug/Kg	PCA	2%
TCA	< 0.1 ug/Kg	TCA	2%

Deposition of TCP → TCA
 10% or less of the PCP was converted to PCA
 unless either aerobic or anaerobic conditions

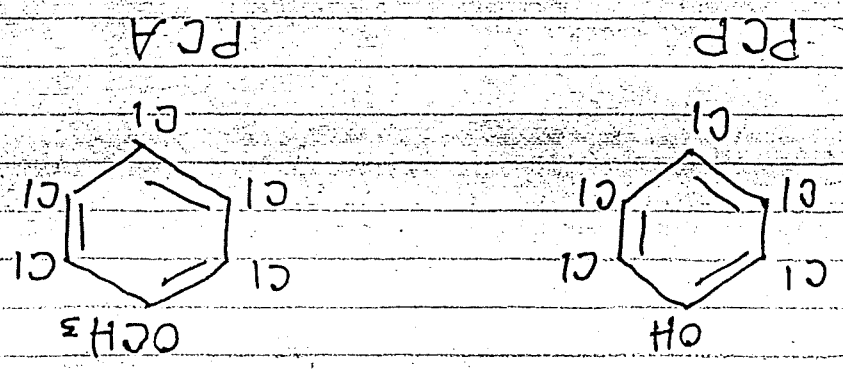
PCP → TCP → TCA
 anaerobic lake sediment

↳ Chronic input of PCP from the contaminated waterbodies and their conversion to PCP to the various degradation products.

↳ PCP not rapidly converted to PCA
 ↳ Suggested reduction observations of PCP to TCP and the conversion of TCP within the lake
 ↳ Major conversion product of TCP was TCA
 ↳ Evidence of production of PCA and TCA within the aquatic environment
 ↳ Conversion of chlorinated phenols to amino acids in aquatic systems

↳ Their enhanced hydrophobic nature would suggest a greater bioaccumulation factor for animals over plants, as well as longer persistence in organisms and sediment in aquatic systems.

✓ Major TCP conversion product was TCA
 ✓ Ambient persistence of PCP under atmospheric environments
 ✓ High concentrations (100 - 10,000 ug/Kg of PCP have been detected in river sediments and lake sediments while the same lakes water have a level of only 10 - 30 ug/L)



CORRESPONDENCE/MEMORANDUM

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.

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Attachments

cc: Bill Jaeger - NCD

Comments on Approach Taken to
Derive Sediment Quality Criteria
for Pentachlorophenols

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:

Octanol-Water Partition
Coefficient (K_{ow})

pH

4.84	1.2
3.56	6.5
3.32	7.2
3.86	13.5

In calculating sediment quality criteria on the attached pages, a K_{ow} value of 3.32 was used as it relates to a pH (7.2) that is comparable to the pH in the overlying water column (7.0). It is assumed that the surface water - sediment - groundwater compartments all have comparable near-neutral pH chemistries.

To identify that the partitioning approach establishes adequate cleanup levels and relevant sediment criteria for PCP, we recommend that the criteria be supplemented with bioassays, studies of the benthic infaunal community, and sediment chemistry.

Remediation of PCP-contaminated river bank sediments should be preceded 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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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)

$$CTC = e^{(V(pH) + \ln CCl)}$$

pH Wisconsin River at Merrill - 7.0

$$CTC = e^{(1.005 \times 7.0 - 4.9779)}$$

$$* CTC = 7.82 \text{ ug/L}$$

* 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):

$$\text{Log}_{10} Koc = 0.00028 + 0.983 \text{ Log}_{10} Kow$$

$$= 0.00028 + (0.983) (3.32)$$

$$= 0.00028 + 3.26$$

$$= 3.26028$$

$$Koc = 1821 \text{ liters/Kg OC}$$

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

Sediment Quality

$$\begin{array}{l} \text{Criteria} \\ (\text{ug PCP/Kg OC}) \end{array} = \begin{array}{l} \text{WQS} \\ (\text{ug/L}) \end{array} \times \begin{array}{l} \text{Koc} \\ \text{L/Kg OC} \end{array}$$

$$\text{Sediment Quality} = 7.82 \text{ ug/L} \times 1821 \text{ L/Kg OC}$$

$$\text{Criteria} = 14,240 \text{ ug PCP/Kg OC}$$

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

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:

$$10,000 \text{ ppm TOC} = 10,000 \text{ mg TOC/Kg sediment} =$$

$$1\% \text{ of sediments due to particle organic carbon weight fraction} = \\ 0.01 \text{ kg OC/Kg sediments} = \text{foc}$$

5. Applying the formula

$$\text{Sediment Quality Criteria} = 7.82 \text{ ug/L} \times .1821 \text{ L/Kg} \times \text{foc (Kg OC/Kg sediments)}$$

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:

<u>Percent Total Organic Carbon In Sediment Samples</u>	<u>Site Specific Sediment Quality Criteria (ug PCP/Kg Sediment - dry weight)</u>
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.

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.

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

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

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

This report contains the collective views of an international group of experts and does not necessarily represent the decisions or the stated policy of the United Nations Environment Programme, the International Labour Organisation, or the World Health Organization.

Environmental Health Criteria 71

PENTACHLOROPHENOL

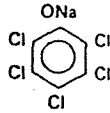
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and the World Health Organization



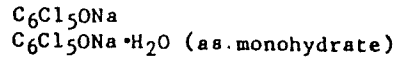
World Health Organization
Geneva, 1987

2.1.2 Sodium pentachlorophenate (Na-PCP)

Chemical structure:



Molecular formula:



Common synonyms:

penta-ate; pentachlorophenate sodium; pentachlorophenol, sodium salt; pentachlorophenoxy sodium; pentaphenate; phenol, pentachloro-, sodium derivative monohydrate; sodium PCP; sodium pentachlorophenate; sodium pentachlorophenolate; sodium pentachlorophenoxide

Common trade names:

Albapin; Cryptogil Na; Dow Dormant Fungicide; Dovicide G-St; Dovicide G; Napclor-G; Santobrite; Weed-beads; Xylophene Na; Witophen N

CAS registry number:

131-52-2 (Na-PCP);
 27735-64-4 (Na-PCP monohydrate)

2.1.3 Pentachlorophenyl laurate

The molecular formula of pentachlorophenyl laurate is C_6Cl_5OCOR ; R is the fatty acid moiety, which consists of a mixture of fatty acids ranging in carbon chain length from C_6 to C_{20} , the predominant fatty acid being lauric acid (C_{12}) (Cirelli, 1978b).

2.2 Impurities in Pentachlorophenol

Technical PCP has been shown to contain a large number of impurities, depending on the manufacturing method (section 3.2.1). These consist of other chlorophenols, particularly isomeric tetrachlorophenols, and several microcontaminants, mainly polychlorodibenzodioxins (PCDDs), polychlorodibenzofurans (PCDFs), polychlorodiphenyl ethers, polychlorophenoxyphenols, chlorinated cyclohexenones and cyclohexadienones, hexachlorobenzene, and polychlorinated biphenyls (PCBs). Table 1 presents analyses of PCP formulations taken from several publications. According to Crosby et al. (1981), the quality of PCP is depends on the source and date of manufacture. Furthermore, analytical results may be extremely

Table 1. Impurities (mg/kg PCP) in different technical PCP products

Component	Specification, producer, PCP content (%)			
	Technical ^a Monsanto (84.6%)	Technical ^b Dow (88.4%)	Technical ^c Dow (90.4%)	Technical ^d Dyn. Nobel - Rhône-Poulenc (86%)
Phenols				
Tetrachloro-	30 000	44 000	10 4000	70 000
Trichloro-	ns	<1000	<1000	ns
Higher chlorinated phenoxyphenols	ns	62 000	ns	70 000
Dibenzo-p-dioxins				
Tetrachloro-	<0.1	<0.05	<0.05	<0.01
Pentachloro-	<0.1	ns	ns	ns
Hexachloro-	8	4	1	5
Heptachloro-	520	125	6.5	130
Octachloro-	1380	2500	15	600
Dibenzofurans				
Tetrachloro-	<4	ns	ns	ns
Pentachloro-	40	ns	ns	ns
Hexachloro-	90	30	3.4	10
Heptachloro-	400	80	1.8	60
Octachloro-	260	80	<1.0	150
Hexachlorobenzene	ns	ns	400	ns

^a From: Goldstein et al. (1977).
^b From: Schwetz et al. (1974).
^c From: Schwetz et al. (1978).
^d From: Buser (1975).
 From: Umweltbundesamt (1985).
 From: Anon (1983b).
 Purified.
 Dovicide EC-7.
 Dovicide 7.
 ns = not specified.
 < = below detection limit.

variable, particularly with regard to earlier results, which should be considered with caution. Jensen & Renberg (1972) detected chlorinated 2-hydroxydiphenyl ethers, which obviously may transform to dioxins during gas chromatography, thus giving a false indication of a higher level of PCDDs. Unlike these "predioxins", other isomers are not direct precursors of dioxins, and are labelled "isopredioxins".

In Fig. 1, the structures and numbering system for the polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) are illustrated.

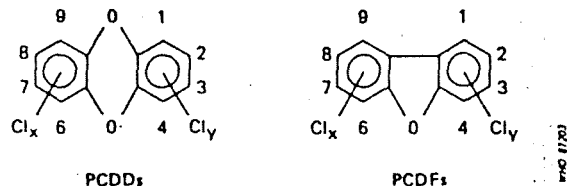


Fig. 1. Structures and numbering systems for the polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs). From: Rappe et al. (1979).

Since the toxicity of PCDDs and PCDFs depends not only on the number but also on the position of chlorine substituents, a precise characterisation of PCP impurities is essential. The presence of highly toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-T₄CDD) has only been confirmed once in commercial PCP samples. In the course of a collaborative survey, one out of five laboratories detected 2,3,7,8-T₄CDD in technical PCP and Na-PCP samples at concentrations of 250 - 260 and 890 - 1100 ng/kg, respectively (Umweltbundesamt, 1985). Buser & Bosshardt (1976) found detectable amounts of T₄CDD (0.05 - 0.23 mg/kg) in some samples of different technical PCP products, but on re-analysis were unable to confirm the compound's identity. In other cases, T₄CDD has not been identified at detection limits of 0.2 - 0.001 mg/kg (Table 1).

The higher polychlorinated dibenzodioxins and dibenzofurans are more characteristic of PCP formulations (Table 1). Hexachlorodibenzo-p-dioxin (H₆CDD), which is also considered highly toxic and carcinogenic (section 8), was found at levels of 0.03 - 35 mg/kg (Firestone et al., 1972), 9 - 27 mg/kg (Johnson et al., 1973), and < 0.03 - 10 mg/kg (Buser & Bosshardt, 1976). According to Fielder et al. (1982), the 1,2,3,6,7,9-, 1,2,3,6,8,9-, 1,2,3,6,7,8-, and 1,2,3,7,8,9-isomers of H₆CDD have been detected in technical PCP. The 1,2,3,6,7,8 and 1,2,3,7,8,9-H₆CDDs predominated in commercial samples of technical PCP (Dowicide 7) and Na-PCP. Octachlorodibenzo-p-dioxin (OCDD) is present in relatively high amounts in unpurified technical PCP (Table 1).

Recently, the identification of 2-bromo-3,4,5,6-tetrachlorophenol as a major contaminant in three commercial PCP samples (ca. 0.1%) has been reported. This manufacturing by-product has probably not been detected in other analyses because it is not resolved from the PCP peak by traditional chromatographic methods (Timmons et al., 1984).

2.2.1 Formation of PCDDs and PCDFs during thermal decomposition

The thermal decomposition of PCP or Na-PCP yields significant amounts of PCDDs and PCDFs, depending on the thermolytic conditions. For pure PCP, dimerization of PCP has been suggested as an underlying reaction process; in technical PCP, additional reactions, i.e., dechlorination of higher chlorinated PCDDs and cyclization of predioxins are involved in forming various and different PCDD isomers (Rappe et al., 1978b).

Pyrolysis of alkali metal salts of PCP at temperatures above 300 °C results in the condensation of two molecules to produce OCDD. PCP itself forms traces of OCDD only on prolonged heating in bulk and at temperatures above 200 °C (Sandermann et al., 1957; Langer et al., 1973; Stehl et al., 1973).

Although present in original technical PCP products, a number of PCDDs, other than OCDD, are generated during thermal decomposition (290 - 310 °C) in the absence of oxygen (Table 2) (Buser, 1982).

Table 2. PCDDs (mg/kg PCP) in the pyrolysate of technical PCP and Na-PCP^a

	PCP	Na-PCP
2,3,7,8-T ₄ CDD	- ^b	- ^c
1,2,3,7,8,9-H ₆ CDD	53	2.1
1,2,3,6,7,8-H ₆ CDD	66	0.95
Total H ₆ CDD	455	10.5
H ₇ CDD	5200	65
OCDD	15 000	200

^a From: Buser (1982).

^b Detection limit (1 mg/kg).

^c Detection limit (0.25 mg/kg).

The thermal conversion of organochlorine compounds, e.g., polyvinylchloride and polyvinylidene chloride, can be a source of atmospheric chlorophenols including PCP (Ahlborg et al., 1986; Dougherty, 1986^a).

Other common methods of waste disposal such as deep-sea or deep-well disposal, landfill sites, or open pits should not be considered as a means for disposing of PCP-containing wastes, because of the mobility of PCP (Powers, 1976; Crosby et al., 1981).

^a Personal communication to the Task Group on Pentachlorophenol.

5. ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

5.1 Environmental Levels

5.1.1 Air

While PCP concentrations in the air at industrial sites and in rooms contaminated with PCP have been reported (section 5.2), there is apparently little information on PCP levels in the ambient air.

Cautreels et al. (1977) sampled airborne particulate matter near La Paz, Bolivia, at an altitude of 5200 m and in a residential city area of Antwerp, Belgium. At a detection limit of 0.02 ng/m³, the atmosphere of the Bolivian mountain rural area contained 0.25 - 0.93 ng/m³ and that of the Antwerp urban area 5.7 - 7.8 ng/m³ air, respectively. More recent analytical results (Bundesamt für Umweltschutz, 1983) showed PCP air concentrations ranging between 0.9 and 5.1 ng/m³ in Switzerland.

The ubiquitous occurrence of PCP in ambient air can also be shown from rain water and snow analyses. Rain water collected in Canada (Jones, 1981), Hawaii (Bevenue et al., 1972) and West Berlin (Roskamp, 1982) contained between 0.002 and 0.3 µg PCP/litre. Water melted from snow in southern Finland revealed PCP concentrations of 0.15 and 0.98 µg/litre, respectively. PCP fallout as calculated from Finnish snow samples ranged from 1.49 to 136.0 µg/m² (Paasivirta et al., 1985).

5.1.2 Water and sediments

Levels of industrial and municipal discharges in different countries are shown in Table 13 (section 4.4.2). Municipal sewage discharges contain PCP concentrations at levels comparable with those in surface waters. However, wood-treating factories may contribute substantially to the PCP load in surface waters, which ranges from non detectable to 10 500 µg PCP/litre (Table 14), depending on the extent of pollution by different sources.

The majority of the water samples analysed for PCP contained less than 10 µg/litre, most contained less than 1 µg PCP/litre. The extreme PCP levels of up to 10 500 µg/litre reported by Fountaine et al. (1976) were found in a highly polluted stream near an industrial area in the vicinity of Philadelphia, USA.

Ernst & Weber (1978b) calculated the PCP input into the German Bight via the river Weser to be of the order of 1000 kg per year, assuming an average PCP level of 0.1 µg PCP/litre and a water flow of 300 m³/second. Taking an average

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Table 14. PCP concentrations in surface waters of different countries

Country	Surface water and location	PCP (µg/litre) (range, mean)	Reference
Canada	Fresh-water sites in British Columbia (BC)	trace - 0.30	Environment, Canada (1979)
	Marine sites in BC	ND ^a - 7.3	
Germany, Federal Republic of	Weser river and estuary	0.05 - 0.5	Ernst & Weber (1978b)
	German Bight	< 0.002 - 0.026	
	Ruhr river	< 0.1 - 0.2 (0.1)	Dietz & Traud (1978b)
	Rhine river, Cologne	0.1	Fischer & Slemrova (1978)
Japan	Tama river, Tokyo	0.1 - 0.9 0.01 - 0.09	Matsumoto et al. (1977)
	Sumida river, Tokyo	1 - 9	
	River water, Tokyo area	0.18 ± 0.14	Matsumoto (1982)
Netherlands	Rhine river 1976	Max. ^b 2.4 (0.7)	Wegman & Hofstee (1979)
	Rhine river 1977	Max. 11.0 (1.1)	
	River Meuse 1976	Max. 1.4 (0.3)	
	River Meuse 1977	Max. 10.0 (0.8)	
South Africa	124 sampling points	ND - 0.85	Van Rensburg (1981)
Sweden	River water downstream from pulp mill	9	Rudling (1970)
	Lake receiving discharges	3	
USA	Willamette river	0.1 - 0.7	Buhler et al. (1973)
	Highly polluted stream near Philadelphia - factory location - downstream	4500 - 10 500 49 - 240	Fontaine et al. (1976)
	Estuary in the Galveston Bay, Texas	ND - 0.01	Murray et al. (1981)
	Pond in Mississippi contaminated by waste from pole-treatment plant	< 1 - 82	Pierce et al. (1977)

^a ND = not detectable.
^b Max. = maximum values.

concentration of 0.5 µg PCP/litre in the surface waters of the Federal Republic of Germany (Foquet & Theisen, 1981), the total load in all surface waters of the Federal Republic of Germany was estimated by Fischer (1983) to be in the range of 60 tonnes per year, of which 30 - 40 tonnes are transported by the Rhine river.

Wong & Crosby (1981) reported PCP concentrations ranging from 1 to 800 µg/litre (average, 227 µg/litre) in the surface pond water near a local wood-treatment factory and of about 20 µg PCP/litre in agricultural drainage. Elevated PCP concentrations were also found in groundwater (3.03 - 23.3 µg/litre) and surface water samples (0.07 - 31.9 µg/litre) within saw-mill areas. Around these sites, PCP levels ranged between not detectable and 0.6 µg/litre in groundwater and between 0.01 and 0.07 µg/litre in the water of a nearby lake (Valo et al., 1984). PCP in the µg/litre range was detected in the water seeping from a landfill (Kotzias et al., 1975). A level as high as 3.35 mg/litre was found in groundwater from a monitoring well near a wood-preservation factory (Thompson et al., 1978).

A PCP-monitoring study in water was performed by Rahde & Della Rosa (1984, 1986) in a region of the Amazon jungle (Tucuruí, Brazil). The construction of a dammed reservoir affected a large area (2430 km²) with sawmills and PCP-treated wood. Water samples collected from the main river and its affluents before the flooding in 1984 contained between 5 and 14 µg PCP/litre. In 1984-85, after the flooding, the area had been covered with about 46 billions m³ of water, PCP was not detectable at a detection limit of 4 µg/litre.

In general, the sediments of a water body contain much higher levels of PCP than the overlying waters. At several fresh-water and marine sites in British Columbia, Canada, receiving effluents from the wood-treatment industry, average PCP levels in the sediments ranged from not detectable to 590 µg/kg, while the corresponding range in the overlying waters was from not detectable to 7.3 µg/litre (Table 14). During a 1978 survey of toxic substances in the Great Lakes of Canada, sediment samples from the Thunder Bay, Marathon, and Michipicoten areas of Lake Superior contained averages of 16 900, 7300, and 2300 µg PCP/kg dry sediment, respectively. In another study of contamination from a wood preservation facility on the Bay of Quinte, Lake Ontario, Fox & Joshi (1984) analysed water and sediment samples for PCP. At a site distant from the plant discharge, sediment PCP levels ranged from 1 to 61 µg/kg dry weight, while surface waters contained only 0.015 µg/litre. Sediments from the Mississippi lake monitored by Pierce & Victor (1978) averaged 364 µg/kg dry sediment, compared with levels in the lake water of only 0.1 µg/litre. A similar distribution was

observed in surface waters in the Netherlands (Wegman & van den Broek, 1983); sediment samples from Lake Ketelmeer, a deposition area for Rhine river sediments, contained a median PCP concentration of 8.4 µg/kg dry weight, while the overlying water contained 0.41 µg/litre. PCP concentrations in sediment samples collected in the vicinity of a paper mill discharge pipe in a North Sea bight, two years after going out of use (Butte et al., 1985) and in Finnish lakes contaminated by wood preservatives (Paasivirta et al., 1980) were of the same order of magnitude.

These examples indicate that PCP and Na-PCP adsorb on sediments, which concurs with findings from experimental work. Strufe (1968) reported a study in which 65% of added Na-PCP adsorbed on river mud within 20 h.

5.1.3 Soil

Soil samples, taken at 4 sites in the vicinity of a Swiss PCP-producing facility (Dynamit Nobel), contained between 25 and 140 µg per kg (dry weight) at a depth of 0 - 10 cm and between 33 and 184 µg/kg at 20 - 30 cm. These levels are higher than the PCP concentrations of 35 µg/kg (0 - 10 cm) and 26 µg/kg (20 - 30 cm) determined in soil samples from a "reference site". The simultaneous presence of some PCDDs and PCDFs (maximum values: H₇CDD, 0.6 µg/kg; OCDD, 7.68 µg/kg; P₅CDF, 1 µg/kg at 0 - 10 cm) in sample sites near the chemical factory compared to only one positive sample (H₇CDF, 0.51 µg/kg) at the remote site confirmed the contamination (Bundesamt für Umweltschutz, 1983).

The soil surrounding Finnish sawmills was found to be heavily contaminated with up to 45.6 mg/kg (0 - 5 cm) or 1 mg PCP/kg fresh weight (80 - 100 cm) near the treatment basin, up to 0.14 mg/kg in the storage area for preserved wood and 0.012 mg/kg outside the storage area. The vertical distribution of chlorophenols including PCP explains the ground-water contamination observed (Valo et al., 1984).

In Canada, soil samples from the former site of a pesticide plant contained less than 50 µg PCP/kg (Garrett, 1980). The PCP levels in the leachate and in soil in the vicinity of 3 waste-disposal sites were also in the µg/kg range (Kotzias et al., 1975). Samples of agriculturally used soils in Bavaria (Federal Republic of Germany) contained about 100 µg PCP/kg (Gebefuegi, 1981).

PCP concentrations in soil samples taken at a distance of 2.5, 30.5, and 152.5 cm from poles treated with PCP were 658, 3.4, and 0.26 mg/kg, respectively. Arsenault (1976) considered the last value as a "natural background level", which he derived from the blank of 0.2 - 0.4 ppm found in unexposed soil samples. However, such a level seems very high for a

substance that does not appear to occur naturally. This high level could be the result of the contamination of the soil or of the reagents used for analysis.

5.1.4 Aquatic and terrestrial organisms

5.1.4.1 Aquatic organisms

Levels of PCP in aquatic organisms from various collection sites are listed in Table 15. No data are available on the background levels of PCP in biota. All sampling sites in Table 15 were more or less contaminated with industrial effluents. Relatively low contamination is reflected by residues of PCP in aquatic invertebrate and vertebrate fauna in the low µg/kg-range. For example, Zitko et al. (1974) found a range of < 0.5 - 4 µg PCP/kg wet weight in the muscle tissue of different fish species (Table 15). Higher levels were detected in organisms collected in surface waters that were thought to be contaminated with wood preservatives: up to 2100 µg PCP/kg wet weight were found in marine fish in British Columbia, Canada (Environment Canada, 1979) and up to 6400 µg/kg in fresh-water fish from Finnish lakes (Paasivirta et al., 1981) (Table 15). Some sediment-dwelling organisms showed the highest residues: polychaetes from the Weser estuary contained between 103 - 339 µg PCP/kg wet weight (Ernst & Weber, 1978a). Even higher levels (266 - 133 000 µg/kg) were found in clams from a North Sea bight, near the end of a waste-water pipe from which about 26 tonnes of PCP were discharged into the mud flats until 1978 (Butte et al., 1985).

Residues of PCP in biota associated with toxic PCP water concentrations are in the mg/kg range. Following extensive application of Na-PCP as a molluscicide in rice fields in Surinam, Vermeer et al. (1974) found 8.1 mg PCP/kg wet weight in dead frogs (*Pseudis paradoxa*) and between 31.2 and 59.4 mg/kg in three species of fish, which were also found dead. Composite samples of snails (*Pomacea glauca*) contained, on average, 36.8 mg PCP/kg wet weight.

Whole samples of small fish collected from a river in British Columbia, Canada, during an accidental fish kill resulting from the spraying of hydropoles, had levels of 16.3 mg PCP/kg; two large cutthroat trout (*Salmo clarki*) contained 10.3 mg/kg (Jones, 1981).

5.1.4.2 Terrestrial organisms

As with aquatic plants, almost no data are available on residues of PCP in terrestrial plants. Grass samples taken in the vicinity of a PCP producer at Rheinfelden, Switzerland, contained between 67 - 87 µg PCP/kg dry weight, comparable

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Sorption of Chlorinated Phenols by Natural Sediments and Aquifer Materials

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■ Laboratory experiments have been conducted to study the sorption of chlorinated phenols by sediments and aquifer materials. It is shown that sorption not only of the nondissociated phenols but also of their conjugate bases (phenolates) can occur. At typical ambient concentrations, sorption equilibrium can be described by the equation $S = DC$, where S = concentration in the solid phase, D = overall distribution ratio, and C = concentration in the liquid phase. In natural waters of low ionic strength (i.e., $I \leq \sim 10^{-3}$ M) and of pH not exceeding the pK_a of the phenol by more than one log unit, phenolate sorption can be neglected and the overall distribution coefficient may be expressed by $D = K_p Q$, where K_p = partition coefficient of the nonionized phenol and Q = degree of protonation. K_p may be estimated from the octanol/water partition coefficient of the compound and from the organic carbon content of the sorbent. In the case of tetra- and pentachlorophenol, phenolate sorption usually has to be considered. It is strongly influenced by the organic carbon content of the sorbent and by the ionic strength of the aqueous medium.

Assessing the transport, fate, and the potential biological effects of xenobiotic chemicals in the aquatic environment requires knowledge of the sorption behavior of the chemicals, i.e., of their distribution between the solid and aqueous phases. Recently, much effort has been directed toward understanding the sorption of a variety of hydrophobic organic pollutants by sediments, soils, and aquifer materials (1-5). The vast majority of the chemicals investigated were compounds exhibiting no ionizable functional group(s). For such neutral compounds, including polycyclic aromatic hydrocarbons (2, 3), halogenated hydrocarbons (1, 5), and certain pesticides (4), approximately linear sorption isotherms have been found at concentrations typically encountered in natural waters:

$$S = K_p C \quad (1)$$

S is the concentration of the compound in the solid phase, C is the concentration in the liquid phase, and K_p is the equilibrium partition coefficient of the compound between the sorbent and water. The partition coefficient K_p has been shown to be primarily dependent on the lipophilicity of the compound, as expressed by its octanol/water partition coefficient K_{ow} and on the organic carbon content f_{oc} of the sorbent (1-5). Mathematical relationships between K_p , f_{oc} , and K_{ow} have been derived for various sets of compounds and natural sorbents (2-5):

$$K_p = f_{oc} K_{oc} = f_{oc} b (K_{ow})^a \quad (2)$$

where K_{oc} is the partition coefficient of the compound between water and a hypothetical natural sorbent of 100% organic carbon representing the organic material present in the sorbents investigated and a and b are constants. Values reported for a and b include $a = 1.00$ and $b = 0.48$ for polycyclic aromatic hydrocarbons, $a = 0.52$ and $b = 4.4$ for a certain group of pesticides (4), and $a = 0.72$ and $b = 3.2$ for alkylated and chlorinated benzenes (5). From the presently available data, it can be concluded that the values of a and b are primarily determined by the type of compounds (i.e., compound class(es), range of lipophilicity) on which the relationship is established, and only to a smaller degree by the type of natural sorbents used. Thus, the reported relationships are very useful for predicting partition coefficients of neutral hydrophobic organic compounds between water and natural sorbents of very different origins. It should be noted that eq 2 is valid only for sorbents containing more than about 0.1% organic carbon ($f_{oc} \geq 0.001$). For organic-poor sorbents, interactions of the chemical with the inorganic matrix of the sorbent may become important (5, 6).

The simple model used to describe the sorption of neutral hydrophobic organic chemicals by natural sorbents (eq 1 and 2) is applicable only to a limited degree to compounds which are fully or partially ionized at natural pH values. Such compounds include amines, carboxylic acids, and phenols. The sorption of benzidine, e.g., was found to be largely controlled by the pH of the aqueous phase, and nonlinear sorption isotherms were obtained which were interpreted to be the result of the superposition of several different sorption processes (7). Also, a significant enhancement of the sorption above that expected based on simple partitioning, i.e., predicted from eq 2 (derived for polycyclic aromatic hydrocarbons), was observed for two polycyclic aromatic amines (8). For anthracene-9-carboxylic acid which is predominantly present as anion at the pH of natural waters, the same authors found no significant differences between predicted (eq 2) and experimentally determined "partition coefficients". In any case, when dealing with the sorption of hydrophobic compounds containing functional groups which may ionize or which may strongly interact with the various organic and inorganic constituents of natural sorbents, processes such as ion exchange, ligand exchange (9), formation of ion pairs or ion complexes (that may be transferred into the organic phase), etc., have to be considered in addition to simple partitioning.

In the laboratory study reported here, the sorption of a series of chlorinated phenols by natural sediments and aquifer materials has been investigated. Chlorinated phenols are of growing concern as environmental pollutants (10-12). They have been widely found in surface waters

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in wastewaters, in particular, in pulp mill effluents (13-16). At typical ambient pH values, especially, the highly chlorinated phenols are present in the water predominantly as phenolate anions. The goal of this study was to establish quantitative relationships for describing the overall sorption of chlorinated phenols by sediments and aquifer materials, and to evaluate the contribution of the processes responsible for the sorption of the phenolate species (referred to as "phenolate sorption") to the overall sorptive process.

Experimental Section

Chemicals. The chlorinated phenols used in this study (the names are given in Table II) were purchased from Fluka AG, Buchs, Switzerland, or Chem Service, West Chester, PA, and used without further purification. The water for high-performance liquid chromatography (HPLC) mobile phases was doubly distilled in quartz, and the methanol was of spectral quality (SpectrAR, Mallinckrodt, S. Louis, MO). All other chemicals, acids, and salts were of the highest available purity (Fluka, purissimum and purum, or Merck p.a.).

Acidity Constants. Acidity constants were determined by titration of 5×10^{-6} – 5×10^{-4} M solutions of the chlorinated phenols in 10^{-2} M NaNO₃ solution using 10^{-2} M NaOH in thermostated vessels (20 ± 0.5 °C) under a nitrogen atmosphere. Proton activity was determined with a glass pH electrode (Metrohm AG, Herisau, Switzerland) which was calibrated before each titration. Dissociation constants were calculated with eq 3 on the basis of at least

$$pK_a = -\log \frac{[H^+]_w([H^+]_w + C_B - K_w/[H^+]_w)}{A_t - ([H^+]_w + C_B - K_w/[H^+]_w)} \quad (3)$$

six measurements at protonation degrees in the range of 0.2–0.8. $[H^+]_w$ = proton concentration; $\log [H^+]_w = (E - E_0)/k$ (Nernst equation), C_B = amount of added base per total volume solution ($V_0 + V_C$), $K_w = 10^{-14}$ mol² L⁻², and A_t = initial concentration of chlorinated phenol.

In a second approach, $(2-5) \times 10^{-4}$ M solutions of five chlorinated phenols in 5×10^{-2} M phosphate buffers were prepared, and the concentration ratio of deprotonated to neutral phenols $[A^-]/[AH]$ at different pH was determined by UV spectroscopy. Absorbances were measured at 11 wavelengths between 280 and 340 nm, and a nonlinear least-squares calibration and data reduction technique was used to allow determination of concentrations of both neutral and anionic species (which exhibit absorption maxima at different wavelengths). The dissociation constant K_a was then determined with a linear regression by using eq 4:

$$\log ([A^-]_w/[AH]_w) = \text{pH} - pK_a \quad (4)$$

Octanol/Water Partition Coefficients. Octanol/water partition coefficients were determined according to OECD guidelines (17). Since it was found that the presence of more than one chlorinated phenol did not influence the distribution of the individual compounds, the di- and trichlorophenols and, as a second group, the tetrachlorophenols and pentachlorophenol were investigated simultaneously. All extraction experiments were carried out in at least four replicates. The two phases, 1-octanol and 0.01 M aqueous HCl, were saturated with each other before use; 45, 40, and 35 mL of the aqueous phase containing the phenols were added to 5, 10, and 15 mL, respectively, of 1-octanol in a 100-mL ground-glass-stoppered bottle. The initial concentration of each phenol in the organic phase was ca. 10^{-4} M for the di- and trichlorophenols and ca. 10^{-3} M for the tetrachlorophenols and pentachlorophenol. The

Table I. Characterization of the Sorbents Investigated

sorbent		specific surface area (BET), m ² g ⁻¹ ^a	organic carbon content (f_{oc}), % g _{oc} g _s ⁻¹ ^a
no.	description		
1	lake sediment ^b	3.8	0.094
2	river sediment ^c	4.8	0.026
3	aquifer material ^c	6.4	0.0084
4	aquifer material ^c	5.7	0.0003
5	γ -Al ₂ O ₃	120	<0.0001

^a g_s = grams of solid; g_{oc} = grams of organic carbon. ^b Surface sediment (air-dried) from Greifensee, Switzerland. ^c Sample from field site in the lower Glatt Valley, Switzerland (see ref 5); prepared by dry sieving; size fraction $\phi < 63$ μ m.

two phases were equilibrated in a thermostated room at 20 ± 0.5 °C by vigorous mechanical mixing for 24 h. After centrifugation (3000 rpm, 15 min), the aqueous phase was separated from the octanol phase with a pipet. The chlorinated phenols in the aqueous phase were then quantified by the HPLC method described below.

Water. For the sorption experiments it was desirable to use water with pH and major ion composition similar to that of a typical Swiss groundwater, and as free of organic compounds as possible. This water was prepared by stirring doubly distilled water (dissolved organic carbon content 0.2 mg/L) with an excess of granulated marble while bubbling with a CO₂/N₂ mixture until solution composition change was negligible (~24 h). The desired pH was obtained by adjusting the CO₂/N₂ ratio. After equilibration, the CaCO₃/CO₂ buffered water was spiked with an aqueous solution of chlorinated phenols.

Sorbents. The sorbents used are summarized in Table I. The samples were prepared by dry sieving the air-dried material. The size fraction $\phi < 63$ μ m was chosen for the experiments since in earlier work (2, 5) it was found that sorption takes place predominantly on the silt and clay fraction. Sorbent 1 was a surface sediment from a highly eutrophic lake. The river sediment and the aquifer materials were collected at a field site described earlier (5). Some sorption experiments were carried out with γ -Al₂O₃ (Aluminium Oxyd C, Degussa, Frankfurt, GFR) used as received without further treatment.

BET surface areas were determined on a Carlo Erba Model 1800 sorptomatic using nitrogen as adsorbing gas (for more details see ref 5). The organic carbon (OC) content of the sorbents was determined by the method of Baccini et al. (18). The detection limit of the method for sediment samples is 0.1 mg of OC/g_s.

Batch Experiments. The batch experiments were carried out in 12-mL, ground-glass-stoppered test tubes (10 cm \times 1.2 cm i.d.). Whenever possible, the amount of sorbent was chosen to obtain at least 50% overall sorption of the compounds. After the sorbent (0.5–4 g dry weight) was introduced, the test tubes were filled with spiked CaCO₃/CO₂ water and closed with the stopper, leaving a minimum headspace to avoid pH and ion composition changes due to loss or uptake of CO₂. The amounts of sorbent and aqueous phase were determined by weight. It was found that the presence of several chlorinated phenols in the same batch did not noticeably influence the extraction behavior of the individual compounds. Therefore, similar to the determination of the octanol/water partition coefficients, the di- and trichlorophenols, as well as the tetrachlorophenols and pentachlorophenol, were investigated simultaneously. The initial total concentration of each phenol was typically 150–200 μ g/L (ca. 10^{-6} M).

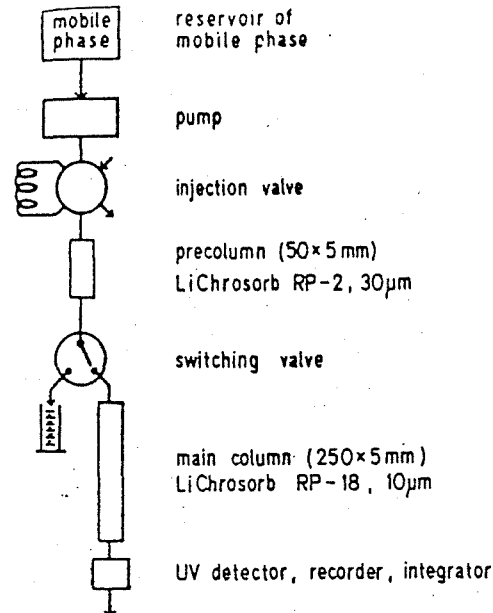


Figure 1. Scheme of the chromatographic apparatus used to determine the chlorinated phenols.

The samples were equilibrated in a thermostated room at 20 ± 0.5 °C for 15–20 h on an apparatus that inverted the sample tubes automatically every 2 min. Kinetic experiments showed that equilibrium was essentially reached after approximately 8 h. The aqueous phase was then separated from the solids by centrifugation, and the pH was measured immediately. The calibration of the pH meter (Metrohm E 532, Metrohm AG, CH-9100 Herisau, Switzerland) was checked daily. Then, the sample was weighed and acidified with ~5 drops of concentrated HCl, and, after addition of the internal standard, the phenols in the aqueous phase were quantified by the analytical procedure described below.

Quantitative Determination of Chlorinated Phenols by HPLC. A schematic representation of the chromatographic apparatus is shown in Figure 1. The acidified sample was injected onto the short precolumn (50×5 mm, LiChrosorb RP-2, $30\text{-}\mu\text{m}$ particle size) by means of a six-port valve fitted with a 10-mL loop. After 10 mL of eluent had passed the precolumn, its outlet was connected to the main column (250×5 mm, LiChrosorb RP-18, $10\text{-}\mu\text{m}$ particle size) with a switching valve.

For the di- and trichlorophenols, the methanol/water ratio of the eluent was 1/1 (v/v). 2,3,6-TCP was used as internal standard. For the tetrachlorophenols and PCP, the methanol/water ratio was increased to 3/2 (v/v), and 2,3,5,6-tetrachloronitrobenzene was used as internal standard.

The use of a precolumn allows preconcentration of the chlorinated phenols, separating them from water and from part of the early eluting compounds extracted from the sorbent. In addition, the main column is protected from contamination by irreversible sorption of complex organic substances and very fine particulate matter still suspended in the sample. Since the precolumn is packed with a short-chain reversed-phase support, the chlorinated phenols move faster in the precolumn than in the analytical column packed with a C18-derivatized silica gel. The resulting band sharpening effect greatly reduces the need to minimize dead volumes in the precolumn, the switching valve, and the connections.

The detector wavelength was set at 205 nm for di- and trichlorophenols and at 211 nm for tetrachlorophenols and pentachlorophenol. The detection limit was in the range

of 50 ng for a 0.01-L sample ($5\text{ }\mu\text{g/L}$). In most of the samples from the batch experiments, no interferences by compounds extracted from the soil were observed. However, if the method should be applied to analyze samples containing higher concentrations of nonpolar UV-absorbing organic substances, e.g., wastewater or river water, it is expected that some pretreatment of the samples or a more specific detection using, for example, an electrochemical detector will be necessary.

Determination of Relative Retentions on C18 Reversed-Phase Columns. Relative retentions k' (capacity factors) of protonated and deprotonated chlorinated phenols were measured on C18 reversed-phase columns (LiChrosorb RP-18, $10\text{ }\mu\text{m}$, Merck). A Waters M6000 pump (Waters Associates Inc., Milford, MA) was used together with a Water U6K injector and a Perkin-Elmer LC55 variable wavelength UV/vis detector (Perkin-Elmer AG, Küssnacht, Switzerland). For the protonated chlorinated phenols, the mobile phase was methanol/water, 1/1 v/v, acidified with concentrated phosphoric acid to an apparent pH of ~2. The column was stainless steel, 250×5 mm (Dr. H. Knauer KG, Oberursel, GFR). For the chromatography of the phenolates, a hand-packed 30×5 mm stainless steel column with Swagelok fittings was used. Under the extreme conditions used ($\text{pH} > 11$), the columns remained stable for 1–2 days, then the retention characteristics began to change, and the column had to be repacked. The mobile phases were prepared as follows: Doubly distilled water was thoroughly degassed by stirring rigorously under vacuum for at least 15 min. Then, methanol was added to make a mixture of water/methanol, 9/1 v/v, and the mixture was again degassed for a few minutes. The desired concentration of K^+ or Li^+ was obtained by adding known amounts of a 1 M solution of KOH or LiOH. The solutions and the solvent reservoirs were always kept under nitrogen. For the mobile phases containing Ca^{2+} as counterion, saturated $\text{Ca}(\text{OH})_2$ solution was added under nitrogen to the degassed water/methanol mixture until pH 11.5 was reached. The desired Ca^{2+} concentration was then approximated by adding CaCl_2 . The exact concentration was determined by flame atomic absorption analysis. Retention times were measured with an Autolab Minigrator integrator (Spectra Physics, Santa Clara, CA). Nitrate was used to determine the elution volume of a nonretained solute for the calculation of relative retentions.

Results and Discussion

Determination of Overall Distribution Ratios. Linearity of Isotherms. The compounds which were investigated are listed in Table II with their acidity constants, octanol/water partition coefficients, and relative retentions in reversed-phase liquid chromatography. All values in this table were experimentally determined since only limited literature data were available. From the pK_a values given in Table II it can be seen that large differences in acidic strength exist between the various chlorinated phenols (including isomeric compounds) and, therefore, in the degree of ionization in a given natural water.

For all the chlorinated phenols included in Table II, the overall equilibrium distribution ratios, i.e., the ratio of total phenol concentration in the solid phase to total phenol concentration in the aqueous phase, were determined in batch experiments at different pH values with the sorbents listed in Table I. Since calcite was a substantial constituent of the natural sorbents investigated, and since dissolution and/or decomposition of the organic matter contained in these sorbents was observed at pH values above 8.5, the accessible pH range for experiments was

Figure IV. Linear Free Energy Relationships: Correlations between the Partition Coefficients of the Nonionized Phenols and the Corresponding Octanol/Water Partition Coefficients and Relative Retentions*

sor-bent	correlations					
	$\log K_p = a \log K_{ow} + b^*$			$\log K_p = a' \log k' + b'$		
	a	b^*	R^2 ($n = 6$) ^b	a'	b'	R^2 ($n = 6$) ^b
1	0.98	-1.77	0.99	1.93	-0.16	0.97
2	0.81	-1.44	0.99	1.59	-0.10	0.96
3	0.72	-1.63	0.98	1.40	-0.40	0.91

*The sorbents are characterized in Table I, and the partition coefficients K_p are listed in Table III. ^bCorrelation made by using the compounds in Table II, except 2,3,4,6-TeCP and PCP.

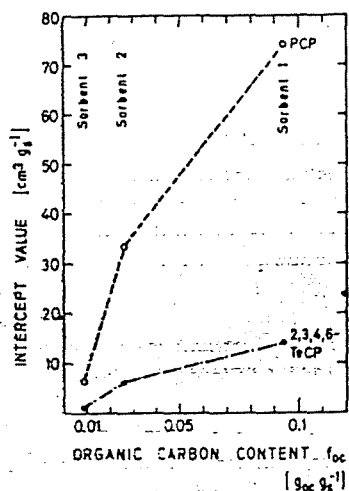


Figure 3. Intercepts obtained from the linear regression of D vs. Q (see text) for different sorbents (averaged values, with standard deviations of $\pm 10\%$). The numbers of the sorbents refer to those in Table II.

their low pK_a values, these two compounds are almost fully deprotonated in the experimentally accessible pH range. Since a linear extrapolation of the D values determined at very small degrees of protonation leads to large errors in the calculated K_p values, the K_p values for 2,3,4,6-TeCP and PCP were derived from the excellent linear relationship found between the $\log K_p$ values of the remaining phenols and the logarithms of their corresponding relative retention k' in reversed-phase liquid chromatography (see Table IV).

For sorbents 1-3 a strong dependency of K_p on the organic carbon content f_{oc} was found, and highly significant linear correlations were obtained between $\log K_p$ and $\log K_{ow}$ (Table IV). However, in contrast to the findings with nonpolar substances such as the substituted benzenes (see ref 5), much larger differences in the slopes a of the correlation lines were found between the different sorbents which may be due to specific interactions of the phenolic group with the solid matrix. For the organic-poor sorbents (sorbents 4 and 5) no correlation lines could be obtained because the measured overall partition coefficients were generally very small and K_p values could not be determined with sufficient accuracy.

From the results of the experiments conducted so far, there is clear evidence that, in certain cases, the sorption of the phenolate species cannot be neglected. The, due to the experimental conditions in most cases, small, but significantly positive intercepts always found when the experimental data are analyzed with a linear regression according to eq 9 (see example given in Figure 3) is an indication that phenolate sorption takes place. These data

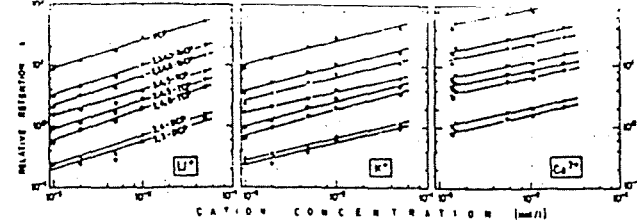


Figure 4. Relative retentions as a function of cation concentration of a series of chlorinated phenols at an apparent pH of about 11.5 on a C18 reversed-phase column. Note that, in the mobile phase at pH 11.5, the phenols are present predominantly as phenolate anions.

also suggest that the degree of phenolate sorption is, similarly to the nonionized species, strongly dependent on the organic carbon content of the sorbent. This is reflected by the increasing intercepts with increasing carbon content of the sorbent (Figure 3).

Furthermore, as qualitatively demonstrated in Figure 4, the relative retentions in reversed-phase HPLC of the phenolate anions are influenced by the cation concentration in the liquid phase. A similar behavior is observed in the partitioning of phenolate anions between water and octanol (19) and is also evident from our data with respect to sorption by natural sorbents. A comparison of Figure 4 with the relative retentions listed in Table II also show that at pH 11.5, where the chlorinated phenols are more or less fully ionized in the mobile phase, they are retained in the same sequence as the corresponding nonionized phenols, i.e., increasing retention with increasing octanol/water partition coefficient of the nonionized compound. The mechanism of the partitioning of chlorinated phenolate anions between water and a model organic phase (1-octanol) is presently under investigation. The first results of this study have been summarized in a different paper (19).

In the experimental system used in this study, a quantification of phenolate sorption by the natural sorbents investigated is difficult, since, due to the $\text{CaCO}_3/\text{CO}_2$ buffer, the calcium concentration in the aqueous phase is strongly pH dependent; i.e., it decreases significantly with increasing pH. Consequently, the effect of the higher degree of deprotonation was compensated by the decrease in cation concentration, thus rendering the system too insensitive to allow a proper quantification of the sorption of the phenolate anion. Further experiments in which, e.g., the cation concentration in the aqueous phase is kept constant over the whole pH range will be necessary to quantitatively evaluate the significance of phenolate sorption. However, on the basis of our present data, it can be concluded that, in waters exhibiting low ionic strength ($I \leq \sim 10^{-3}$ M), eq 9 can be used to estimate overall distribution coefficients of chlorinated phenols if the pH of the aqueous solution is not more than one unit above the pK_a of the compound (see example given in Figure 5 (top)). On the other hand, at typical ambient pH values, the overall distribution coefficients of the highly chlorinated phenols such as 2,3,4,6-TeCP and PCP are always significantly influenced by phenolate sorption, and predictions of D values using the simple model expressed by eq 9 are, therefore, in error for these compounds (see example given in Figure 5 (bottom)).

Prediction of Partition Coefficients K_p and of Overall Distribution Ratios D . The variations in K_{oc} values obtained for the different sorbents (Table III) are quite large compared to those found for the chlorinated and alkylated benzenes (see ref 5). However, for order of magnitude predictions of K_p , it still seems feasible to derive for the nonionized phenols a relationship similar to eq 2.

Table II. Acidity Constants, Octanol/Water Partition Coefficients, and Relative Retentions of Some Chlorinated Phenols^a

compd	abbreviation	pK _a ^b (n ≥ 6) ^c	log K _{ow} ^d (n = 4) ^e	log k' ^f (n = 3) ^g
2,3-dichlorophenol	2,3-DCP	7.61 (±0.01)	3.15 (±0.02)	0.70 (±0.03)
2,4-dichlorophenol	2,4-DCP	7.85 (±0.01)/7.80 ^h	3.23 (±0.02)	0.82 (±0.03)
2,4,6-trichlorophenol	2,4,6-TCP	6.15 (±0.01)/6.10 ^h	3.72 (±0.03)	1.16 (±0.03)
2,4,5-trichlorophenol	2,4,5-TCP	6.94 (±0.02)/6.94 ^h	4.19 (±0.04)	1.23 (±0.04)
2,3,4-trichlorophenol	2,3,4-TCP	7.18 (±0.02)	ND ⁱ	ND
3,4,5-trichlorophenol	3,4,5-TCP	7.73 (±0.02)	4.41 (±0.06)	1.34 (±0.05)
2,3,4,6-tetrachlorophenol	2,3,4,6-TeCP	5.40 (±0.02)	4.42 (±0.05)	1.51 (±0.05)
2,3,4,5-tetrachlorophenol	2,3,4,5-TeCP	6.35 (±0.02)	4.87 (±0.08)	1.63 (±0.05)
pentachlorophenol	PCP	5.25 (±0.03)/4.75 ^h	5.24 (±0.14)	1.93 (±0.05)

^aAll values were determined at 20 °C. ^bDetermined by titration; I = 10⁻² M. ^cNumber of measurements. ^dLiChrosorb RP-18, MeOH/H₂O, 1/1 (v/v); phosphoric acid to an apparent pH of ~2; nitrate was used to determine the elution volume of a nonretained solute. ^eDetermined by UV. ^fValues used for the calculations. ^gND, not determined.

Table III. Experimentally Determined Partition Coefficients K_p and K_{oc} of Nonionized Chlorinated Phenols for Different Natural Sorbents

compd	K _p , cm ³ g _s ⁻¹ , for sorbent ^b				K _{oc} , cm ³ g _{oc} ⁻¹ , for sorbent ^b			
	1	2	3	4	1	2	3	av value
2,3-DCP	21 (±7)	12 (±4)	5 (±4)	<1	223	461	595	426
2,4-DCP	25 (±6)	17 (±3)	6 (±3)	<1	266	654	715	545
2,4,6-TCP	78 (±3)	34 (±2)	9 (±1)	<1	830	1310	1070	1070
2,4,5-TCP	165 (±15)	74 (±7)	20 (±2)	<1	1760	2850	2380	2330
3,4,5-TCP	276 (±36)	115 (±26)	31 (±5)	<1	2940	4420	3690	3680
2,3,4,6-TeCP	568 ^c	200 ^c	52 ^c	<3	6040 ^c	7690 ^c	6190 ^c	6640
2,3,4,5-TeCP	1237 (±52)	362 (±61)	105 (±11)	7	13200	13900	12500	13200
PCP	3670 ^c	930 ^c	200 ^c	<13	39000 ^c	35800 ^c	23800 ^c	32900

^aK_{oc} = K_p/f_{oc} ^bSee Table II. ^cCalculated from chromatographic data (see text).

limited to values between about 6.5 and 8.5.

The sorption isotherms determined for various chlorinated phenols at different pH values showed within the error of the method of quantification a reasonable linearity over the whole range of concentration used. As an example, the isotherms obtained at different pH values for 2,3,4,5-TeCP with sorbent 2 are shown in Figure 2.

Partition Coefficients K_p of the Nonionized Phenols: Significance of Anion Sorption. Under the experimental conditions (pH 6.5–8.5), both nonionized and ionized chlorinated phenols are present simultaneously in the aqueous phase (see pK_a values in Table II). Therefore, the extraction constants for the two species cannot be determined separately. However, the marked increase of the overall distribution coefficients with decreasing pH (see example given in Figure 2) suggests that, under the conditions used (CaCO₃/CO₂ buffer, decreasing ionic strength with increasing pH, dissolved organic carbon <0.5 mg/L), the contribution of the sorption of the deprotonated species is generally small except for those cases where the difference between pH and pK_a is large (e.g., for compounds such as 2,3,4,6-TeCP and PCP). Thus, as a first approximation, the experimental data were analyzed by using a simple partitioning model neglecting phenolate sorption as well as a possible dissociation of the phenol in the organic phase:

$$AH_w = AH_s \quad K = [AH]_s/[AH]_w \quad (5)$$

$$AH_w = A_w^- + H_w^+ \quad K_a = [A^-]_w[H^+]_w/[AH]_w \quad (6)$$

$$A_t = [A^-]_w + [AH]_w + (M_s/V_w)[AH]_s \quad (7)$$

$$A_w^* = [A^-]_w + [AH]_w \quad (8)$$

where A_t = total initial concentration of the phenol in the aqueous phase (before sorbent is added), A_w^{*} = total equilibrium concentration in the aqueous phase (after

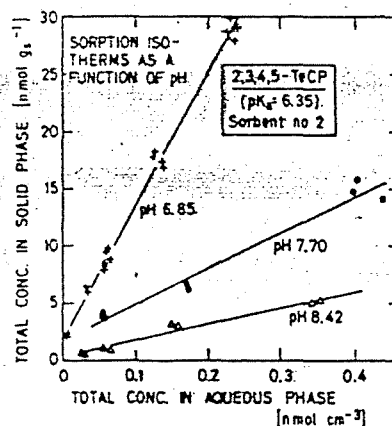


Figure 2. Sorption isotherms for 2,3,4,5-tetrachlorophenol at different pH values. Solid phase: sorbent 2 (see Table II).

equilibration with sorbent), V_w = volume of aqueous phase, and M_s = mass of sorbent phase. Combination of eq 5–8 yields the relation

$$D = K_p Q \quad (9)$$

where D is the experimentally determined overall distribution ratio:

$$D = \frac{A_t - A_w^* V_w}{A_w^* M_s} \quad (10)$$

and Q is the degree of protonation:

$$Q = \frac{1}{1 + K_a/[H^+]_w} \quad (11)$$

The partition coefficients K_p obtained from linear regressions of D vs. Q (eq 9) for the four natural sorbents are given in Table III. A good fit was obtained for all compounds except for 2,3,4,6-TeCP and PCP. Because of

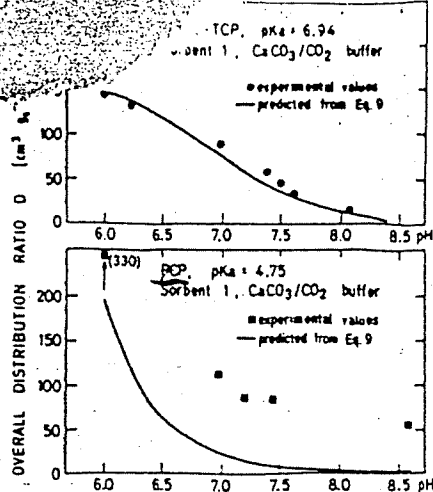


Figure 5. Predicted (eq 9) vs. experimentally determined overall distribution ratios for 2,4,5-trichlorophenol (top) and pentachlorophenol (bottom) for sorbent 1. The experimental points are averaged values with relative standard deviations on the order of $\pm 10\%$. Note that the Ca^{2+} concentration decreases with increasing pH.

The linear regression correlating the logarithms of the average K_{oc} values (Table III) with $\log K_{ow}$ yields

$$\log K_{oc} = 0.82 \log K_{ow} + 0.02 \quad (R^2 = 0.98) \quad (12)$$

Thus, the values of a and b in eq 2 are $a = 0.82$ and $b = 1.05$. In those cases in which phenolate sorption can be neglected, the overall distribution ratio can then be calculated by

$$D = f_{oc}(1.05)(K_{ow})^{0.82} [1/(1 + K_a/[H^+]_w)] \quad (13)$$

For estimating K_a and K_{ow} values of chlorinated phenols, quantitative structure-activity relationships can be used (20).

Conclusions

With this laboratory study, some important insights have been gained into the sorption behavior of chlorinated phenols. The chlorinated phenols are hydrophobic weak acids exhibiting octanol/water partition coefficients between $\sim 10^2$ and 10^6 and pK_a values in the range 5-9. The following are the most important conclusions of this work.

(1) In natural waters of low ionic strength (i.e., $I \leq \sim 10^{-4}$ M), the overall sorption of chlorinated phenols by natural sorbents is in general dominated by the partitioning of the nondissociated species between the aqueous phase and the organic phase contained in the sorbent. If the pH of the water is not more than one unit above the pK_a of the compound (i.e., $\text{pH} - pK_a \leq 1$), the contribution of phenolate sorption may be neglected and the distribution ratio of a given chlorinated phenol may be estimated from its octanol/water partition coefficient and from the organic carbon content of the sorbent. Quantitative structure-activity relationships can be derived to calculate octanol/water partition coefficients and acidity constants of chlorinated phenols.

For natural sorbents exhibiting very low organic carbon contents ($f_{oc} < 0.001$) and for pure oxides (e.g., $\gamma\text{-Al}_2\text{O}_3$), very small overall distribution ratios have been found for all chlorinated phenols investigated.

(2) For some important chlorinated phenols, i.e., for tetra- and pentachlorophenol, phenolate sorption can usually not be neglected, since, at ambient pH values, these compounds are present predominantly in the ionized form.

Thus, for these highly chlorinated phenols, predictions of overall distribution ratios based on simple partitioning of the nondissociated species are generally in error.

(3) There is strong evidence that the sorption of phenolate species is predominantly a partitioning process between the aqueous phase and the organic phase present in a natural sorbent. The degree of phenolate sorption is dependent on the ionic strength in the aqueous phase. Further work is in progress to arrive to a quantitative description of the sorption of chlorinated phenolate anions by natural sorbents.

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Registry No. 2,3-DCP, 576-24-9; 2,4-DCP, 120-83-2; 2,4,6-TCP, 88-06-2; 2,4,5-TCP, 95-95-4; 2,3,4-TCP, 15950-66-0; 3,4,5-TCP, 609-19-8; 2,3,4,6-TeCp, 58-90-2; 2,3,4,5-TeCp, 4901-51-3; PCP, 87-86-5; Al_2O_3 , 1344-28-1.

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