Health Consultation

Dioxin and Polycyclic Aromatic
Hydrocarbon chemical signatures
(fingerprints) in sediments

ST. LOUIS RIVER SEDIMENTS: US STEEL SITE

DULUTH, ST. LOUIS COUNTY, MINNESOTA

EPA FACILITY ID: MND039045430

SEPTEMBER 30, 2006

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Agency for Toxic Substances and Disease Registry
Division of Health Assessment and Consultation
Atlanta, Georgia 30333

Health Consultation: A Note of Explanation

An ATSDR health consultation is a verbal or written response from ATSDR to a specific request for information about health risks related to a specific site, a chemical release, or the presence of hazardous material. In order to prevent or mitigate exposures, a consultation may lead to specific actions, such as restricting use of or replacing water supplies; intensifying environmental sampling; restricting site access; or removing the contaminated material.

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Prepared by:

The Minnesota Department of Health
Environmental Health Division
under Cooperative Agreement with the
Agency for Toxic Substances and Disease Registry
U.S. Department of Health and Human Services

FOREWORD

This document summarizes chemical signatures, or fingerprints, in sediments associated with the US Steel site in the St. Louis River Estuary, St. Louis County, Minnesota. It is based on a formal evaluation prepared by the Minnesota Department of Health (MDH). This is a technical health consultation that addresses only a portion of the issues involved in a site-related health assessment. Therefore, not all of the steps below, that are typically part of an MDH health assessment, apply to this document. Additional assessment of this site has been conducted by MDH and has been reported in other documents.

- *Evaluating exposure:* MDH scientists begin by reviewing available information about environmental conditions at the site. The first task is to find out how much contamination is present, where it is found on the site, and how people might be exposed to it. Usually, MDH does not collect its own environmental sampling data. Rather, MDH relies on information provided by the Minnesota Pollution Control Agency (MPCA), the US Environmental Protection Agency (EPA), and other government agencies, private businesses, and the general public.
- *Evaluating health effects:* If there is evidence that people are being exposed—or could be exposed—to hazardous substances, MDH scientists will take steps to determine whether that exposure could be harmful to human health. MDH's report focuses on public health— that is, the health impact on the community as a whole. The report is based on existing scientific information.
- *Developing recommendations:* In the evaluation report, MDH outlines its conclusions regarding any potential health threat posed by a site and offers recommendations for reducing or eliminating human exposure to pollutants. The role of MDH is primarily advisory. For that reason, the evaluation report will typically recommend actions to be taken by other agencies—including EPA and MPCA. If, however, an immediate health threat exists, MDH will issue a public health advisory to warn people of the danger and will work to resolve the problem.
- *Soliciting community input*: The evaluation process is interactive. MDH starts by soliciting and evaluating information from various government agencies, the individuals or organizations responsible for the site, and community members living near the site. Any conclusions about the site are shared with the individuals, groups, and organizations that provided the information. Once an evaluation report has been prepared, MDH seeks feedback from the public. *If you have questions or comments about this report, we encourage you to contact us.*

Please write to:	Community Relations Coordinator Site Assessment and Consultation Unit Minnesota Department of Health 625 North Robert Street PO Box 64975 St. Paul, MN 55164-0975
OR call us at:	(651) 201-4897 *or* 1-800-657-3908 (toll free call - press "4" on your touch tone phone)
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Summary

"Fingerprinting" involves determination of the proportions of individual chemicals within groups of similar chemicals to the total, and comparing these proportions across individual samples. Chemical fingerprints may be used to determine the likely source(s) or operation(s) that are responsible for the contamination, or to estimate missing data in incompletely characterized environmental samples.

Forty-one sediment samples (excluding duplicates) were taken from the US Steel site in the St. Louis River Estuary in 2003. This document is a technical Health Consultation that develops fingerprints for dioxins and PAHs for US Steel sediments in the St. Louis River Estuary.

Generally consistent fingerprints were found for both PAHs and dioxins in all areas sampled in 2003 sediment samples. These results suggest thorough mixing of sediments in the river and/or a consistent source of both PAHs and dioxins across the site, and consistent weathering of both PAHs and dioxins over the years. Two volatile PAHs naphthalene and 2-methylnaphthalene are exceptions, as they were not found in similar proportions to total PAHs between sample locations. Good correlations for proportions of individual polycyclic aromatic hydrocarbons (PAHs), and polychlorinated dibenzo-p-dioxins and dibenzofurans (dioxins) between individual samples, allow the data to be used for fingerprinting these 2 chemical groups.

Results showed 1,2,3,7,8-pentachlorodibenzo-p-dioxin and 1,2,3,4,6,7,8-heptachlorodibenzofuran as the largest contributors to the 2,3,7,8-tetrachlordibenzo-p-dioxin toxic equivalence (TCDD-TEQ).

Characterization of the benzo[a]pyrene potency equivalence (B[a]P-PEQ; a measure of potential aggregate cancer potency of certain individual PAHs, described in the text) requires more laboratory analysis than does characterization of 14 commonly measured PAHs. Therefore, there is particular interest in determining a method for predicting B[a]P-PEQ from the total concentration of the 14 PAHs. Unfortunately, the ratio between these 2 measures of total PAH concentrations appears to vary, making estimates inaccurate.

This analysis of sediment data will facilitate risk estimates from samples analyzed for smaller sets of chemicals. In addition, analysis of the data suggests that upriver paper mills are not the likely source of dioxin contamination in this portion of the St. Louis River.

Background and Introduction

In the last hundred years, there have been many anthropogenic sources of pollution to the St. Louis River. These include paper mills, steel mills, coking ovens, shipbuilding and repair, cargo-loading docks, petroleum refining, treated and untreated municipal wastes, and storm sewer runoff. Wastes include nutrients for bacteria and phytoplankton, inert particulates, inorganic acids and bases, metals, other inorganic compounds, and organic

compounds. Most of these chemicals have been diluted or chemically degraded over time such that they do not represent a significant human health hazard. However some chemicals, or related long-lived degradation products are persistent and remain in the aquatic environment for extremely long times. Persistent chemicals are typically metals or groups of similar long-lived organic chemicals (e.g. polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dioxins and dibenzofurans (PCDD/Fs)). Sediments often act as repositories for these persistent chemicals, and high concentrations of contaminants can be found in some areas. These sediments act not only as a repository or a sink for the chemicals, but can also be a reservoir, or source of these chemicals in a dynamic environment, and a source of exposure for aquatic organisms, wildlife and people.

The US Steel site located in the Morgan Park area of Duluth, Minnesota began operation in 1915. The facilities on-site included coke ovens, a coke by-products plant, open-hearth and blast furnaces, a blooming mill, a billet mill, and a merchant mill. Also, a continuous rod mill, wire mill, nail mill, pot annealing equipment, staple and woven fence machines, nail cleaning, bluing and coating facilities, rod and wire cleaning facilities, and galvanizing facilities operated onsite at different times. In addition, from about 1918 until 1929 benzene and toluene were produced on-site. Operation of the steel mill continued until 1975 when open hearth and blast furnaces were shut down. The coking plant ceased operations in 1979 (MPCA 1989). Attachment 1 shows the location of the US Steel Site on the St. Louis River. Attachment 2 is an aerial photo of the US Steel facility in 1951 (from Tweed Museum Exhibition, 1992). Attachment 3 shows surface water and material flowing from the site into the St. Louis River in 1967 (Federal Water Pollution Control Administration 1967-8).

In 1983, the US Steel Site and the St. Louis River Interlake/Duluth Tar Site (SLRIDT) were added to the National Priorities List (NPL) under a single Comprehensive Environmental Response, Compensation, and Liability Information System (CERCLIS; Superfund) number (MND039045430). In 1984, MPCA placed both sites on the Minnesota Permanent List of Priorities (PLP) as separate sites. Remediation of the US Steel site has occurred since the Record of Decision (ROD) was signed in 1989. Sediments were not specifically addressed in the ROD.

Sampling Data

Sediment analytical data are available from a sampling event in 2003. Problems with the chemical analyses of these samples are discussed in detail in a previous Health Consultation (MDH 2006). Data irregularities suggested that there were likely errors related to the scaling of the quantitative data for each sample and each analysis (e.g. moisture content, organic carbon content). Therefore, while the ratios of concentrations of related compounds in individual samples analyzed simultaneously are likely accurate, the absolute concentration of individual compounds may be wrong. This means that it is not possible to determine with any certainty the potential hazard that the contaminants may pose to people exposed to them. On the other hand, since contaminant ratios were accurately characterized for each sample (i.e. the error was the same for all of the individual chemical analytes), it may be possible to determine the chemical fingerprint of

different chemical groups. These data may therefore be used to determine likely sources of the contaminant groups, or to estimate the likely proportions of other compounds in a chemical group when data are only available for a few representative compounds.

Five different groups of chemicals were analyzed in 2003 US Steel sediment data: metals, volatile organic compounds (VOCs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs), and polycyclic aromatic hydrocarbons (PAHs). Metals (analytical Method 6020) are of some interest at this site, but fingerprint analysis was not performed for metals because data suggest that they are only a minor concern in sediments. Note that mercury (analytical Method 7471A) is analyzed differently than most other metals and, given the problems with absolute quantification of sediment data (MDH 2006) mercury could not be included in a metals fingerprint. Isotopic analysis of mercury hasn't been shown to be effective in determining sources of mercury in the environment. Therefore, mercury isotopic analysis of 2003 sediment samples was not requested or preformed. VOCs (analytical Method 8260B) are not a concern in sediments at this site and VOC fingerprints were not developed. PCB data acquired in the 2003 sampling were homologue data (analytical Method 1668A HA). Homologues are groups of PCB congeners with the same number of chlorine atoms. The database on PCB homologues is sparse, and it is not likely that a homologue fingerprint would be useful. Therefore, no PCB fingerprint was developed.

PCDD/F analyses (Method 1613B) are usually reported as either individual dioxin-like congener concentrations, or as toxic equivalents of these same congeners (see below). Development of a PCDD/F fingerprint may be used to estimate total concentrations or toxic equivalencies (TEQs) from data on a limited set of congeners. For instance, data collected by EPA and MPCA in 1993 from the St. Louis River are limited to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) (EPA and MPCA 1997). Using the PCDD/F fingerprint from the site, total TCDD-TEQs (see below) for samples of US Steel sediments collected in the 1993 study can be estimated. In addition, a PCDD/F fingerprint can be used to determine likely sources of the PCDD/F contamination, or to rule out potential sources. PAH fingerprints can be used in a similar manner. PAHs are often characterized as "EPA PAHs" or, in Minnesota a subset of carcinogenic PAHs (cPAHs) are characterized as benzo[a]pyrene potency equivalents (B[a]P-PEQs; see below). PAHs in each of these groups are identified in Table 7. Both of these groups of PAHs were analyzed in 2003 US Steel samples using Method 8270C SIM (Selected Ion Monitoring). This allowed a fingerprint to be developed that can be used in the future when site-sediments may be analyzed exclusively for EPA PAHs or cPAHs. The development of PCDD/F and PAH fingerprints are described in this document.

Chemical Fingerprinting

Fingerprints of environmental contaminants are ratios of chemical analytes that are consistent when measured at different sample locations or at different times. An EPA report on fingerprinting as a forensic tool (EPA 2004) provides a good summary of fingerprinting methods. The EPA draft dioxin reassessment (EPA 2003a) shows fingerprints of dioxin-like compounds in emissions, environmental media, food and biological samples from a wide variety of sources. In addition, a recent review of dioxins

by Schecter et al. (2006) shows unique fingerprints from dioxin-like chemicals found in populations of people exposed to different sources. Polycyclic aromatic hydrocarbons have also been fingerprinted to help identify sources (e.g. Yang et al. 2002; Li et al. 2003; Christensen et al. 1997).

Consistent chemical signatures (fingerprints) in sediments result from the deposition and accumulation of chemicals in sediments emitted or released from the operation of a pollution source with either large emissions, or smaller sources with chemically similar emissions over a long period of time. Fingerprints can be affected by the decomposition of released chemicals either by chemical or biotic processes; dissolution of chemicals into surface and/or ground water, and the movement of solutes offsite; the erosion and subsequent transport of chemicals bound to particulates offsite; or the evaporation of volatile chemicals. Fingerprints are usually established for groups of chemicals that behave similarly in the environment.

Fingerprint analyses can be important when trying to determine the source of contaminants, or when a complete set of data is not available for all analytes at all sample locations for a site. Even at individual sites, the sources, and therefore the fingerprints at various locations may be different. When conducting a fingerprint analysis of a site with many sources, differences in signatures of different sources may need to be determined.

Contaminants in the St. Louis River adjacent to the US Steel site may come from many sources. Four sources are presumed to dominate: effluent from the Wire Mill Pond and Steel Creek outfalls, atmospheric deposition and associated watershed runoff, and upstream sources. Atmospheric deposition runoff and impacts from a significant upstream pollution source would likely result in similar fingerprints in different areas of the river near the site, while contamination from Wire Mill Pond and Steel Creek may have resulted in different contaminant signatures adjacent to these outfalls. Even though it is likely that there was some mixing of contaminants in the river, differences in chemical composition of sediments north and south of the spit of land between Wire Mill Pond and Steel Creek may signify differences in effluent from these 2 surface water sources. In addition, surface sediments and sediments at depth may be different, reflecting changes in source contributions over time or differences in the weathering of exposed sediments and sediments that are presently buried.

The most significant upstream sources of contaminants to the river were likely paper mills. Effluent from these facilities may have included some polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and mercury. US Steel is also a likely source of PCDDs, PCDFs, PCBs and mercury, as well as polycyclic aromatic hydrocarbons (PAHs).

Paper mills on the St. Louis River were at least 20 miles upstream from the US Steel plant. As a result the extent of their contribution to contaminated sediments adjacent to US Steel may have been limited. One way to evaluate the upstream contribution is to compare the fingerprint of PCDDs, PCDFs and PCBs associated with paper mills with the fingerprints of these chemicals in sediments near US Steel. Unfortunately, PCDD/F

congener data from upstream areas are not available, as most historic dioxin sample analysis from the St. Louis River are limited to TCDD. This document develops fingerprints for PCDD and PCDF from US Steel sediment sampling, and compares the PCDD/F fingerprints to typical PCDD/F signatures from paper and pulp manufacturing facilities (EPA 2003a). Only 4 samples were analyzed for PCB congeners; MPCA split samples. This document contains a brief discussion of these data, but they are not included in the fingerprint analyses. In addition, PAH fingerprints are developed from the 2003 samples.

Chemical Fingerprints for US Steel Sediments

Dioxin-like compounds (PCDDs, PCDFs and PCBs) in the environment

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) are persistent non-polar organic compounds. PCDDs and PCDFs are groups of 75 and 135 similar chemicals, respectively, that are not intentionally produced. Instead, they are either inadvertent byproducts of production (e.g., 2,4,5-trichlorophenoxy acetic acid), or byproducts formed from flue gases during the burning of organic compounds (e.g., plastics, coal). Natural processes, such as fires and volcanoes can also produce PCDDS and PCDFs. PCBs are a group of 209 chlorinated organics that were produced for use in high temperature oils and as insulating coolants in electric transformers. In addition, some PCBs can be accidental products of industrial processes that form PCDDs and PCDFs. Some carcinogenic PCB (cPCB) congeners behave toxicologically like dioxins and have been identified by the World Health Organization's (WHO) as dioxin-like (Van den Berg et al. 1998: see Table 1).

The MDH and the U.S. EPA have classified the complex mixtures of PCBs, PCDDs and PCDFs to which people are exposed as "likely human carcinogen(s)". Subsets of the PCBs, PCDDs and PCDFs in mixtures are also likely to be carcinogenic to humans (see Table 1). While these congeners have different potencies, it is believed that they act through the same mechanism. MDH recommends utilization of the WHO 1998 toxic equivalency factor (TEF_{WHO98}) scheme (Van den Berg et al. 1998) to weight each compound's relative cancer risk. Potency is scaled relative to the toxicity of 2,3,7,8-TCDD, which is the most studied and, apparently, the most toxic chemical in this group. Total 2,3,7,8-TCDD Toxic Equivalency (TCDD-TEQ) concentration is equal to:

$$\text{TCDD-TEQ} = \sum C_i * TEF_i \quad \text{for i = each chemical with a } TEF_{WHO98} \qquad \textit{Equation 1.}$$

Where:

C_i = the concentration for a dioxin or dioxin-like compound (mg/kg)
TEF_i = the TEF_{WHO98} for a dioxin or dioxin-like compound

(For additional information on the toxicity of dioxin and dioxin-like compounds please see MDH 2003a; 2003b).

The TEF_{WHO98} values are listed in Table 1 below.

Table 1: TCDD $TEFs_{WHO98}$

Compound	$TCDD\text{-}TEF_{WHO98}$*
Polychlorinated Dibenzo-p-dioxins (PCDDs)	
2,3,7,8-TetraCDD	1
1,2,3,7,8-PentaCDD	1
1,2,3,4,7,8-HexaCDD	0.1
1,2,3,6,7,8-HexaCDD	0.1
1,2,3,7,8,9-HexaCDD	0.1
1,2,3,4,6,7,8-HeptaCDD	0.01
1,2,3,4,6,7,8,9-OctaCDD	0.0001
Polychlorinated Dibenzofurans (PCDFs)	
2,3,7,8-TetraCDF	0.1
1,2,3,7,8-PentaCDF	0.05
2,3,4,7,8-PentaCDF	0.5
1,2,3,4,7,8-HexaCDF	0.1
1,2,3,6,7,8-HexaCDF	0.1
2,3,4,6,7,8-HexaCDF	0.1
1,2,3,7,8,9-HexaCDF	0.1
1,2,3,4,6,7,8-HeptaCDF	0.01
1,2,3,4,7,8,9-HeptaCDF	0.01
1,2,3,4,6,7,8,9-OctaCDF	0.0001
Polychlorinated Biphenyls (cPCBs)	
3,3'4,4'-TetraCB (PCB 77)	0.0001
3,4,4',5-TetraCB (PCB 81)	0.0001
2,3,3',4,4'-PentaCB (PCB 105)	0.0001
2,3,4,4',5-PentaCB (PCB 114)	0.0005
2,3',4,4',5-PentaCB (PCB 118)	0.0001
2',3,4,4',5-PentaCB (PCB 123)	0.0001
3,3',4,4',5-PentaCB (PCB 126)	0.1
2,3,3',4,4',5-HexaCB (PCB 156)	0.0005
2,3,3',4,4',5'-HexaCB (PCB 157)	0.0005
2,3',4,4',5,5'-HexaCB (PCB 167)	0.00001
3,3',4,4',5,5'-HexaCB (PCB 169)	0.01
2,3,3',4,4',5,5'-HeptaCB (PCB 189)	0.0001

* (Van den Berg et al. 1998)

Dioxin-like compound fingerprint analyses

Carcinogenic PCDD/F (cPCDD/F) congener composition may be characterized using ratios of 2 different measures: ratios of the concentration of individual congeners to the total dioxin-like PCDD/F concentration; or, ratios of the TCDD-TEQ of individual congeners to the total sample TCDD-TEQ. Samples with detection of fewer than 11 cPCDD/Fs are not included in the PCDD/F or TCDD-TEQ fingerprint analyses. Dioxin-like PCBs are not included in the analyses.

Data from all cPCDD/Fs analyzed are shown in Attachment 4. These congener data are normalized to the total cPCDD/F per sample in Attachment 5. Therefore, Attachment 5 shows the fractions of each cPCDD/F congener in each sample (i.e. the PCDD/F fingerprint for each sample). Data used in the site sediment cPCDD/F fingerprint are in bold type in Attachment 5. Similarly, Attachment 6 contains the TCDD-TEQs for each sample, and Attachment 7 contains the ratio of the TCDD-TEQ for each congener to the total TCDD-TEQ for each sample. Bolded data in Attachment 7 were used to develop the site TCDD-TEQ fingerprint. Sediment sample locations are shown in Attachment 1.

Congener fractions are calculated for each congener in a sample by normalizing the data to the total PCDD/F concentration using the following equation:

$$f_i = C_i / C_{total} \qquad \textit{Equation 2.}$$

where: C_i = concentration of a single dioxin-like congener in a sediment sample
C_{total} = total PCDD/F in a single sediment sample

The means (M_{fi}) of these normalized data for each congener fraction across samples in an area are then calculated to determine a congener fraction to be used in a fingerprint for a certain area or areas of the site using the following equation:

$$M_{fi} = \sum(f_i) \ / \ n \qquad \textit{Equation 3.}$$

where: n = number of samples in the defined area for each congener fraction

A similar procedure is used to calculate the fraction of the total TCDD-TEQs represented by each congener in a sample. The mean proportion of total TCDD-TEQs is then determined for each congener. The fingerprint is the set of means of congener fractions (normalized sample data) for all congeners of interest (i.e. dioxin-like PCDD/Fs or TCDD-TEQs) in a defined area.

Dioxin-like PCDD/F fingerprint analysis

Table 2 shows the composite PCDD/F fingerprint of St. Louis River sediment samples from the entire 2003 sampling event calculated as the mean of samples PCDD/F congener fractions with 11 or more detected cPCDD/Fs. Fingerprints were also calculated for the 4 different general sample locations: north and south of the spit (Steel Creek (SC) and Wire Mill Pond (WMP), respectively), at the surface and at depth.

Correlation coefficients (r) within sample location groups (e.g. correlation of the fractions of individual PCDD/F congeners of single surficial Wire Mill Pond samples to the mean surficial WMP PCDD/F fractions) range between 0.99 and 1.0, as shown in Table 3. These data show that the sediments in each area and at surface or depth have homogenized mixtures of dioxin-like PCDD/Fs, suggesting similar sources in each area or well-mixed sediments. The means of the PCDD/F congener fractions of all samples for each area are thus a good representation of the area fingerprint.

Table 3 also shows that the correlation coefficients of the mean congener fractions across groups are from 0.95 to 1.0. For example: the correlation coefficient (r) of mean fractions of individual congeners in surficial WMP samples (Table 2 mean congener fraction data for samples labeled WMP surficial) to the mean congener fractions for WMP samples at depth (Table 2 mean congener data for samples labeled WMP depth) is 0.98, as shown (shaded) in Table 3. Similarly, the correlation coefficients between individual groups and a composite fingerprint from the mean of all samples with 11 or more congener detections, are also very good (r from 0.98 to 1.0). These comparisons suggest a single type of source (e.g. coal burning) and/or well-mixed sediments over all areas sampled.

Table 2: Dioxin-like PCDD/F Fingerprint

Dioxin-like PCDD/F Concentration Fingerprint (means of congener fractions for all samples with >= 11 congeners detected)																			Total Dioxin-like PCDD/F
Congeners		n =	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF	1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF	1,2,3,7,8,9-HxCDF	2,3,4,6,7,8-HxCDF	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	OCDF	
All samples		17	0.00082	0.0030	0.0022	0.012	0.0072	0.12	0.61	0.0010	0.00044	0.0011	0.0024	0.0024	0.00046	0.00083	0.15	0.0016	0.083	1
WMP	Surficial	9	0.00088	0.0027	0.0023	0.013	0.0082	0.15	0.67	0.0013			0.0017	0.0014	0.00046	0.00069	0.094	0.0013	0.059	1
WMP	Depth	2	0.00064	0.0026	0.0022	0.012	0.0081	0.13	0.56	0.00060			0.0028	0.0024			0.19	0.0020	0.093	1
SC	Surficial	3	0.00080	0.0049	0.0021	0.010	0.0057	0.093	0.55	0.00084	0.00051	0.00080	0.0028	0.0036		0.0010	0.21	0.0017	0.12	1
SC	Depth	3	0.00079	0.0023	0.0016	0.010	0.0052	0.077	0.55	0.00042	0.00038	0.0013	0.0038	0.0040		0.00091	0.23	0.0021	0.11	1

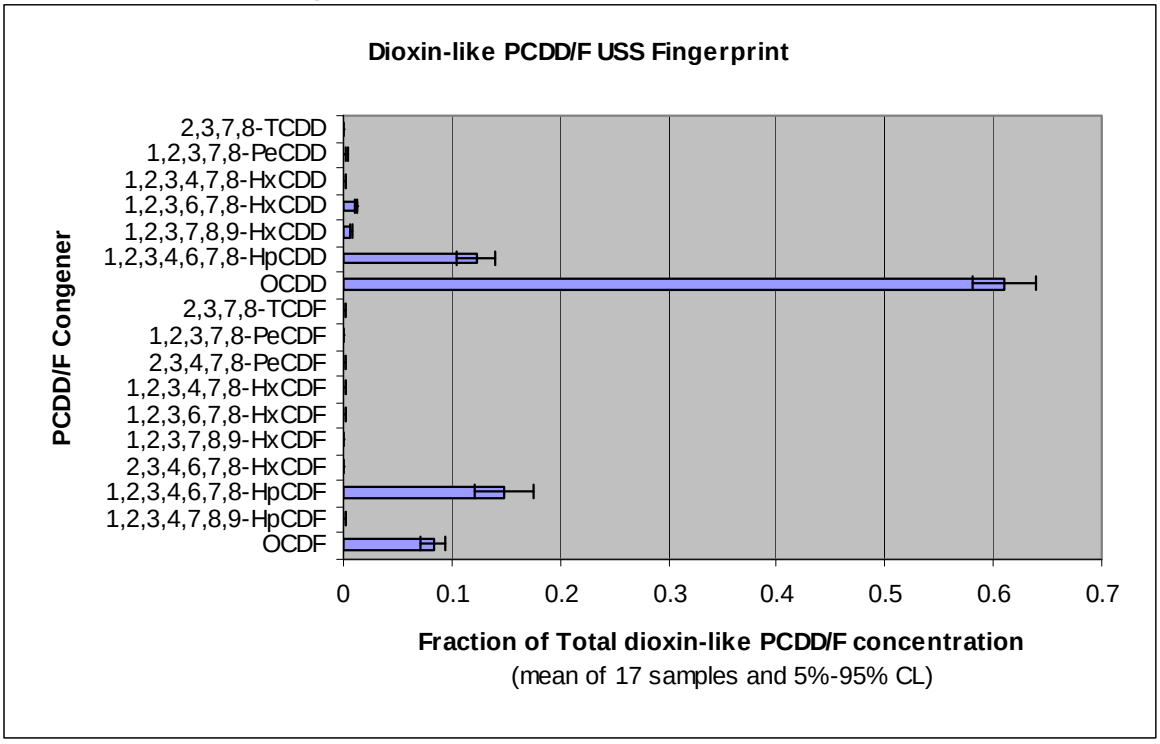
Table 3: Dioxin-like PCDD/F Fingerprint Correlations

Dioxin-like PCDD/F Fingerprint Correlations								
			Correlation Coefficients (r)					
			Range within location groups (mean vs individual sample fractions)		**Across location groups** (between means)			
		n =	Maximum	Minimum	All Samples	WMP Surficial	WMP Depth	SC Surficial
All samples		17	1.00	0.96				
WMP	Surficial	9	1.00	0.99	0.99			
WMP	Depth	2	1.00	1.00	1.00	0.98		
SC	Surficial	3	1.00	1.00	0.99	0.96	1.00	
SC	Depth	3	1.00	1.00	0.98	0.95	0.99	1.00

WMP – Wire Mill Pond
SC – Steel Creek

Figure 1 is a graphic representation of the congener fractional contribution to the total dioxin-like PCDD/F signature (fingerprint), not including PCBs and non-dioxin-like PCDD/Fs. Not that octachlorodibenzo-p-dioxin is present in the highest concentration in sediments, and that heptachlorodibenzo-p-dioxin and 1,2,3,4,6,7,8-heptachlorodibenzofuran are also major constituents in the total dioxin-like PCDD/F mixture.

Figure 1: Dioxin-like PCDD/F Fingerprint



TCDD-TEQ Fingerprint analysis

Table 4 is similar to Table 2 except that it shows the fractional contributions (fingerprint) of the different PCDD/Fs to the total TCDD-TEQ for different groupings of sediment samples.

Correlation coefficients (r) between individual congener TCDD-TEQ fractions and mean TCDD-TEQ fractions within each sample group and for the entire data set range from 0.84 and 0.99, as shown in Table 5.

Table 5 also shows the correlation coefficients (r) across location groups and the entire sample, using the mean TCDD-TEQ fractions for each location group and the entire sample (range: 0.84 to 0.96 and 0.93 to 0.99, respectively). An example of the correlation coefficient between the mean WMP surficial and mean WMP depth fingerprints is shown in the shaded boxes in Table 5 (r=0.95).

Table 4: TCDD-TEQ Fingerprint

2,3,7,8-TCDD TEQ Fingerprint (means of congener fractions for all samples with >= 11 congeners detected)																			Total 2,3,7,8-TCDD TEQ
Congeners		n =	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF	1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF	1,2,3,7,8,9-HxCDF	2,3,4,6,7,8-HxCDF	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	OCDF	
All samples		17	0.081	0.26	0.020	0.11	0.069	0.12	0.063	0.011	0.0016	0.047	0.023	0.024	0.0064	0.0075	0.15	0.0016	0.00082	1
WMP	Surficial	9	0.093	0.27	0.023	0.13	0.083	0.15	0.076	0.015			0.018	0.016	0.0067	0.0071	0.11	0.0013	0.00065	1
WMP	Depth	2	0.065	0.27	0.023	0.13	0.082	0.13	0.058	0.0066			0.029	0.024			0.19	0.0020	0.00096	1
SC	Surficial	3	0.073	0.34	0.015	0.092	0.050	0.084	0.052	0.0089	0.0013	0.021	0.021	0.034		0.0078	0.20	0.0016	0.0011	1
SC	Depth	3	0.080	0.23	0.016	0.10	0.052	0.079	0.055	0.0043	0.0020	0.062	0.038	0.039		0.0096	0.23	0.0021	0.0012	1

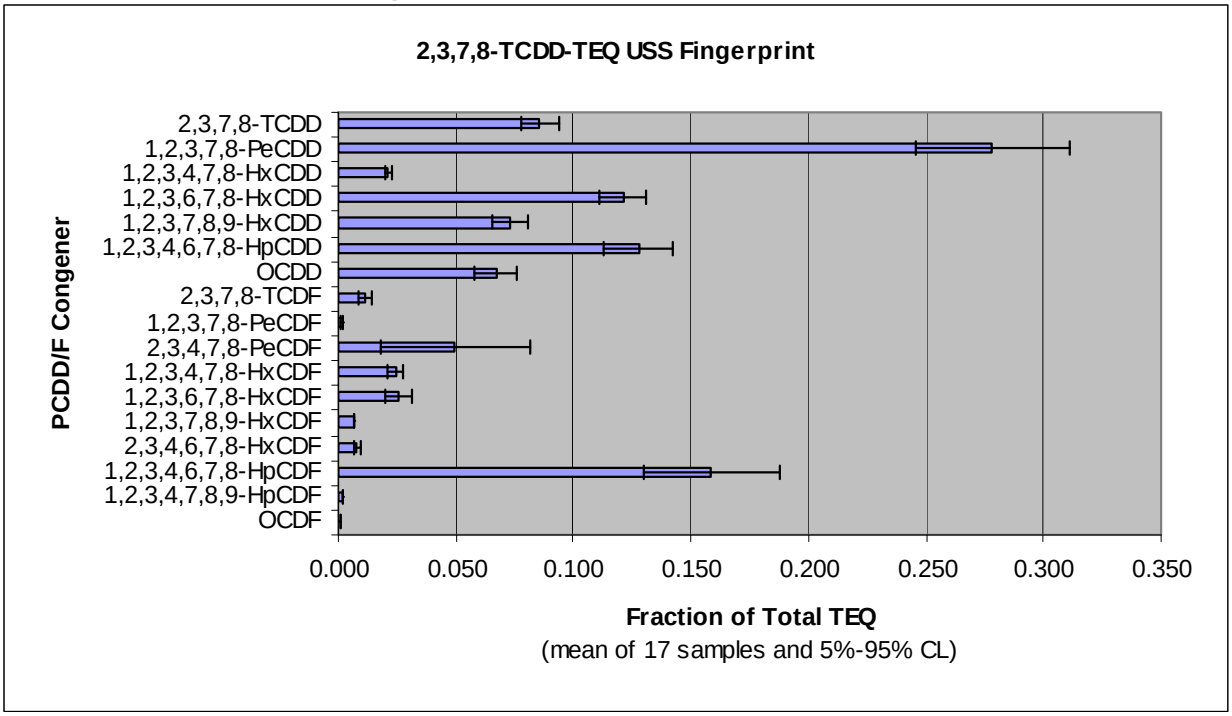
Table 5: TCDD-TEQ Fingerprint Correlations

2,3,7,8-TCDD TEQ - Fingerprint Correlations								
			Correlation Coefficients (r)					
			Range within location groups (mean vs individual sample fractions)		**Across location groups** (between means)			
		n =	Maximum	Minimum	All Samples	WMP Surficial	WMP Depth	SC Surficial
All samples		17	0.99	0.85				
WMP	Surficial	9	0.98	0.84	0.98			
WMP	Depth	2	0.99	0.96	0.99	0.95		
SC	Surficial	3	0.97	0.87	0.97	0.90	0.96	
SC	Depth	3	0.99	0.99	0.93	0.84	0.95	0.94

WMP – Wire Mill Pond
SC – Steel Creek

Figure 2 is a graphic representation of the fractional contribution of the dioxin-like PCDD/F congener TEQs to the TCDD-TEQ (i.e. the TCDD-TEQ fingerprint). Note the broad spectrum of congeners contributing to the TCDD-TEQ, with the 2,3,4,7,8-pentachlorodibenzo-p-dioxin and 1,2,3,4,6,7,8-heptachlorodibenzofuran making the largest contributions.

Figure 2: TCDD-TEQ Fingerprint



Dioxin-like PCDD/F fingerprint discussion and conclusions

Fingerprints are the proportions of different constituents of an environmental sample, or samples, that are likely to be representative of other samples with the same or similar source characteristics. Therefore, fingerprints can often be used to differentiate between sources of contamination when the source of contamination is not known, or they can be used to fill in an incomplete dataset when the source of contamination is the same.

As noted above, US Steel analytical data did not include PCB congener data. PCB congener data were only available for 4 split samples that the MPCA analyzed. Data from these samples did not vary consistently when compared to US Steel tPCB data, or MPCA or US Steel dioxin/dibenzofuran data for the same sample locations. Table 6 shows the US Steel and MPCA total PCDD/F TCDD-TEQs for these four split samples, along with the PCB TCDD-TEQ and (US Steel) tPCB. Correlation coefficients between tPCB (US Steel homologue data) and PCB TCDD-TEQs is low ($r = 0.69$) for the 4 data points. Correlations between the PCB TCDD-TEQ data and PCDD/F TCDD-TEQs were not apparent ($r = -0.27$ and $r = 0.05$ for correlations between PCB congener TCDD-TEQs, and USS TCDD-TEQ or MPCA TCDD-TEQ, respectively). In addition note that the ratio of carcinogenic PCB TCDD-TEQ to PCDD/F TCDD-TEQ for these samples ranges from about 1 to about 0.002. As noted above and discussed in a previous Health

Consultation (MDH 2006), problems with chemical analyses preclude comparison of data between samples because of apparent errors in determining the denominator, or the mass (dry) of sediment (or the amount organic carbon) from which analytes were extracted.

Table 6: TCDD-TEQ and Total PCB Data from 4 Split Samples

TCDD TEQ and tPCB Data from 4 split samples				
Sample (depth)	TCDD TEQ (ng/kg)			tPCB (ng/kg) (homologue data)
	PCDD/F		PCB (from congener data)	
	USS	MPCA	MPCA	USS
L08 (2.0'-3.0')	139	180	0.309	26000
F42 (0-0.5')	1.36	2.40	1.27	278500
G14 (0-0.5')	0.225	0.748	0	715
K42 (0-0.5')	15.0	75.6	8.66	286,000

Because only four samples were analyzed for PCB congeners and because the correlations with other measures of similar groups of chemicals were poor, PCB congener data was not used when the TCDD-TEQs were calculated.

The lack of agreement between PCB data analyzed using 2 different methods and the lack of agreement between dioxin data and all of the PCB data was anticipated. Analyses of dioxins and PCBs were conducted using different methods, and, therefore, individual samples were not simultaneously analyzed. In addition, as noted above, problems with the laboratory analyses of these samples make comparison of data derived from different analytical methods problematic. Therefore, PCB data could not be incorporated into the TCDD-TEQs. As a result, use of these fingerprint data in calculating TCDD-TEQs from a limited set of dioxin data is likely to result in a lower estimate of risk than would have resulted if PCB data were included. Additional PCB congener and dioxin data would be useful once the laboratory problems noted above and described in an earlier document (MDH 2006) are corrected.

The PCDD/F and TCDD-TEQ fingerprints for the site are consistent in all location groups (WMP, SC, surficial and depth) of US Steel site sediments sampled in 2003. This suggests a similar source for PCDD/Fs and/or well-mixed sediments. PCDD/F fingerprints may sometimes be useful for determining the possible sources of contamination, whereas TCDD-TEQ fingerprints may be used for determining possible sources, but are primarily used for evaluating potential toxicity with data on a limited number of congeners. US Steel sediment PCDD/F fingerprint (Figure1) appears to most closely resemble the fingerprints of technical-grade pentachlorophenol (PCP) and sewage sludge (see Attachment 12 for 10 PCDD/F and TCDD-TEQ profiles from the EPA Dioxin Reassessment (2003b)). However, these profiles show low fractions of 1,2,3,4,6,7,8-heptachlorodibenzofuran when compared with US Steel sediments. Note that the PCDD/F and TCDD-TEQ fingerprints from US Steel 2003 sediment samples (Figures 1 and 2) are not similar to the paper/pulp fingerprint (see the first 6 figures in Attachment 12), especially in their fractions of 2,3,7,8-tetrachlorodibenzo-p-dioxin and 2,3,7,8-tetrachlorodibenzofuran. Both TCDD-TEQ fingerprint and PCDD/F fingerprint

comparisons suggest that the upstream paper mills are not a likely source of PCDD/F in the US Steel St. Louis River sediment samples. The location of PCDD/F sources might be identified with additional sampling nearer to likely sources.

Polycyclic Aromatic Hydrocarbons in the environment

PAHs are a group of hundreds of organic chemicals with similar structures. Generally, PAHs are products of fossil fuel or organic combustion (pyrogenic). They may also be found in non-combusted fossil fuels (petrogenic). PAHs are always found in the environment as complex mixtures. While the actual toxicity of individual PAHs to humans has been quantified for only a few of these compounds, PAHs are generally considered to affect the liver (Sipes and Gandolfi 1991). Additionally, PAH mixtures can cause acute dermal irritation after photoactivation if they are exposed to light while on a person's skin (Johnson and Ferguson 1990).

Historically, the MPCA recommended that samples from sites with PAH contamination should be analyzed for 18 PAHs (called "EPA PAHs": see Table 7 for list). It was believed that this representative set of PAHs could provide the best picture of the hazards associated with PAH contamination. Since the time the list was compiled (apparently some time in the 1980's), knowledge about the toxicity of different PAHs has grown. A number of additional PAHs have been identified as probable human carcinogens (cPAHs) by the EPA (EPA 2003c), the International Agency for Research on Cancer (IARC 2005), the National Toxicology Program (NTP 2001), and the California EPA Office of Environmental Health Hazard Assessment (CA OEHHA 2002). These cPAHs are listed in Table 7 (PAHs with B[a]P-Potency Equivalents). Other PAHs have been shown to be carcinogenic to animals (e.g. napthalene; NTP 2000) or to be mutagens (e.g. 3-nitrobenzanthrone; Enya et al. 1997). Therefore, cancer slope factors for additional PAHs may be developed in the future as better human or animal data become available.

In 2002, an EPA peer-consultation workshop (EPA 2002) recommended the use of mixture surrogate (use of toxicity data from similar mixtures), mixture comparative potency (use of comparative toxicity data from a group of site samples and reference samples) or individual compound potency equivalence (component evaluation) for evaluating the toxicity of PAH mixtures. The recommendations of the workshop were to use surrogate mixtures and comparative potency if possible, as these models are preferable to using potency equivalents when evaluating sites. Application of a comparative potency approach is most relevant when evaluating ecological impacts. The human relevance of comparative potency studies with site sediments would need to be demonstrated. However, the fingerprints developed in this document from 2003 sediment PAH data may be used to determine the availability of a surrogate mixture, from published PAH mixture toxicity studies, for evaluating the PAH carcinogenicity of the site sediments. For a screening evaluation, a potency equivalence approach for cPAHs as outlined in the MDH memo of May 2001 (MDH 2001a) and the October 2005 MDH memo to the US Steel Site File (MDH 2005) is appropriate.

MDH has a draft multimedia Health Risk Value of 0.001 µg/(kg·day) for benzo[a]pyrene (B[a]P) that is based on a cancer slope factor of 7.3 $(mg/(kg \cdot day))^{-1}$ (MDH 2002). This slope factor is the geometric mean of the B[a]P slope factor range used by the EPA (2003c). A cancer Health Risk Value is determined by the MDH to be a lifetime exposure level that is expected to result in no more than 1 additional cancer in 100,000 exposed individuals.

MDH recommends that analyzed PAHs include cPAHs in Table 7 (MDH 2001a). The B[a]P-PEFs in Table 7 are based on individual cPAH cancer slope factors, or California Potency Equivalency Factors (PEF: CA OEHHA 2002). (Note: TCDD-TEQs are used to evaluate both cancer risk and chronic health hazard for dioxin-like compounds, as they are believed to be mediated by binding to a single receptor. B[a]P-PEF can only be used to evaluate cancer risk, as the mechanisms by which PAHs initiate cancer and chronic diseases may be different.) B[a]P, with a B[a]P-PEF of 1, is the index compound. Total B[a]P-PEQs can be calculated using an algorithm similar to Equation 1 (above) for dioxin and dioxin-like TEQs. If the cancer risk for some individual cPAHs is a risk driver, further review of potency slopes may be needed. An MDH sediment screening value (SSV) of 0.071 µg/kg B[a]P-PEQ has been used for screening sediments at this site (MDH 2005; US Steel 2003; 2005)

The primary health endpoints for non-carcinogenic PAHs (nPAHs) vary, but most have multiple toxicity endpoints that are similar. Therefore, given the general similarity between the non-cancer effects of PAHs, MDH has recommended that the hazard quotients for nPAHs for which there are health-based toxicity criteria be added in risk assessments for sites including the US Steel site (MDH 2001b).

It is not within the scope of this document to review the potential hazards associated with the sediments at the US Steel site. Analytical problems, discussed in a previous health consultation (MDH 2006) and briefly above, preclude more than a screening analysis and fingerprinting.

Table 7 shows the list of PAHs analyzed in the 2003 US Steel sediment samples.

Table 7: PAHs Analyzed, 2003 Sediment Samples

2003 Sediment sample PAHs analyzed B[a]P Cancer Potency Equivalence Factors and EPA PAHs					
PAH	B[a]P PEF	EPA PAH List	**PAH**	B[a]P PEF	EPA PAH List
Acenaphthene		X	7,12-Dimethylbenzanthracene	**30**	
Acenaphthylene		X	1,6-Dinitropyrene	**10**	
Anthracene		X	1,8-Dinitropyrene	**1**	
Benzo(a)anthracene	**0.1**	X	Fluoranthene		X
Benzo(b,j,k)fluoranthene †	**0.1**	X	Fluorene		X
Benzo(g,h,i)perylene		X	Ideno(1,2,3-c,d)pyrene	**0.1**	X
Benzo(a)pyrene	**1**	X	3-Methylcholanthrene	**3**	
Benzo(e)pyrene			5-Methylchrysene	**1**	
Carbazole			2-Methylnaphthalene		X
Chrysene	**0.01**	X	Naphthalene		X
Dibenzo(a,h)anthracene	**0.6**	X	5-Nitroacenaphthene	**0.02**	
Dibenz[a,h]acridine	**0.1**		6-Nitrochrysene	**10**	
Dibenz[a,j]acridine	**0.1**		2-Nitrofluorene	**0.01**	
7H-Dibenzo[c,g]carbazole	**1**		1-Nitropyrene	**0.1**	
Dibenzo[a,e]pyrene	**1**		4-Nitropyrene	**0.1**	
Dibenzo[a,h]pyrene	**10**		Perylene		
Dibenzo[a,i]pyrene	**10**		Phenanthrene		X
Dibenzo[a,l]pyrene	**10**		Pyrene		X

† Benzo(b)fluoranthene, benzo(j)fluoranthene and benzo(k)fluoranthene analysis unresolved and abbreviated as benzo(b,j,k)fluoranthene

Polycyclic Aromatic Hydrocarbon fingerprint analyses

Total PAH concentrations can be reported as tPAHs (total concentration of all PAHs analyzed), EPA tPAHs (total concentration of 18 PAHs on the MPCA "EPA list") and B[a]P-PEQ (sum of cancer potency equivalents for all cPAHs in each sample). Note, in Table 7, that there are 23 cPAFs with cancer potency equivalency factors (B[a]P PEF) and that only 6 of these are on the EPA list. US Steel 2003 sediment samples were analyzed for a total of 36 PAHs, including the 16 EPA PAHs (counting the 3 unresolved benzo(b,j,k)fluoranthenes as one chemical), 23 carcinogenic PAHs (including benzo(b,j,k)fluoranthene and 5 other EPA PAHs), carbazole, benzo(e)pyrene, and perylene. These data are shown in Attachment 8. Sediment sample locations are shown in Attachment 1. MDH is primarily interested in the B[a]P-PEQ that is calculated using the method described in the previous section.

As noted above, the accuracy of data from the 2003 sediment samples is questionable due to analytical problems discussed in a previous health consultation (MDH 2006). However, the relative concentration of chemicals analyzed in a single analysis is likely to be accurate. The fingerprints from different samples can be compared to develop a fingerprint for areas of the site.

Fingerprints should be developed with accurate data on the concentrations of as many PAHs as possible, in as many samples as possible. However, it may not be possible to detect some chemicals present at very low concentrations. Conversely at high concentrations, some compounds analyzed by GC-MS may be obscured by broad peaks of the major constituents in a sample. As the number of analytes found at concentrations above detection limits varies, ratios between measured concentrations of individual PAHs may vary even when the mixtures are identical. Therefore, not all samples should be used to develop PAH fingerprints. For this document, only samples with detections for greater than 10 carcinogenic PAHs and with B[a]P-PEQs greater or equal to the MDH Sediment Screening Value for the US Steel site (71 μg/kg) were used (MDH 2005). Statistical information on the number of PAHs detected in these samples and the omitted samples are shown in Table 8.

Table 8: Statistics for PAHs in samples used in PAH Fingerprint Analyses

		Number of PAHs detected in individual samples used in fingerprint analyses (e.g. samples with B[a]P PEQ > 0.070 mg/kg; n=24)	Number of PAHs detected in individual samples not used in fingerprint analyses (e.g. samples with B[a]P PEQ < 0.071 mg/kg; n=17)
Total # of PAHs detected	Mean	25.04	18.82
	Max	28	23
	Min	22	9
# cPAHs detected	Mean	12.67	7.82
	Max	15	10
	Min	11	2
# EPA PAHs detected	Mean	15.92	14.12
	Max	16	16
	Min	15	9

All PAH data are attached in Attachment 8. Ratios of individual PAHs to the total EPA PAHs in each sample are shown in Attachment 9. Data that are used in the EPA PAH fingerprints are in bold type in Attachment 9. Similarly, Attachment 10 contains B[a]P-PEQs for each sample and each PAH detected, and Attachment 11 contains the ratios of individual B[a]P-PEQs to the total B[a]P-PEQ for each sample. Data that were used to calculate the B[a]P-PEQ fingerprints are in bold type in Attachment 11. Equations 2 and 3 (above) were used to determine the fractions individual PAHs in the 2 PAH groups (EPA PAHs and B[a]P-PEQs), means of PAH fractions and PAH fingerprints for areas of the site.

Composite fingerprints are not useful if they are non-representative means of dissimilar samples. Therefore, it is important that composite fingerprints correlate well with the concentrations of the individual samples taken from a specific area. As noted above, 2003 sediment samples can be broken up into 4 different groupings: samples adjacent to the Wire Mill Pond outfall and adjacent to the Steel Creek outfall, both surficial samples and samples taken at depth.

If samples have the same source and/or they are well mixed, correlations between the means of ratios (fingerprint) from one area should be similar to the ratios found in individual samples from other areas. Table 9A shows the mean of the correlation coefficients (5 - 95% confidence limits of the mean) between the site area EPA PAH (16 chemicals) fingerprints (rows) and individual sample EPA PAH (16 chemicals) ratios from all areas of the site (columns). Note that the weakest correlations are between the SC depth samples and the other site locations. This may suggest a slightly different source, or it may suggest a difference in the weathering of PAHs in this location.

Naphthalene and 2-methylnaphthalene are both volatile PAHs that may volatilize when discharged into an aquatic environment. If naphthalene and 2-methylnaphthalene are excluded from the EPA PAHs (Table 9B) the correlations between fingerprints for each area and ratios of each PAH : total PAHs (14 chemicals) for individual samples improves greatly. This suggests that either naphthalene and 2-methylnaphthalene aged differently in different areas of the site, or that there are independent sources of these 2 PAHs in some areas of the site. A quick look at the locations of the highest naphthalene fractions (G-14, H-52 shown in Attachment 1) suggests that it is unlikely that these locations were impacted by an additional, exclusive naphthalene, methylnaphthalene source.

When naphthalene and 2-methylnaphthalene are excluded, correlation coefficients improve as shown in Table 9B. These data suggest that a consistent EPA PAH fingerprint requires the exclusion of naphthalene and 2-methylnaphthalene, i.e. the use of 14 EPA PAHs.

Unlike the EPA PAHs (16 chemicals), the B[a]P-PEQ for cancer does not include a contribution from naphthalene, 2-methylnaphthalene or other volatile PAHs. Table 10 shows the means and 5, 95% confidence limits (CLs) for correlations between individual sample B[a]P-PEQ ratios, by area, with area B[a]P-PEQ fingerprints. Note that the correlations between B[a]P-PEQ ratios over the entire site sediments are good. These data also suggest that B[a]P-PEQ fingerprints are likely consistent over the four site sampling areas. Therefore, all cPAH data were included in the B[a]P-PEQ fingerprint (with the exception of duplicate samples, samples with fewer than 11 cPAHs detected and samples with B[a]P-PEQ less than the MDH Sediment Screening Value of 71 μg/kg).

Table 9: EPA PAH Fingerprint Correlations

Mean of correlation coefficients (5,95% CLs) between ratios of EPA PAHs in individual samples (by area), and EPA PAH area fingerprints									
		A. All EPA PAHs (16 chemicals)				B. EPA PAHs (14 chemicals) naphthalene and 2-methylnaphthalene excluded			
		Individual samples from area:				Individual samples from area:			
Fingerprint from area:		WMP Surficial (n=10)	WMP Depth (n=6)	SC Surficial (n=5)	SC Depth (n=3)	WMP Surficial (n=10)	WMP Depth (n=6)	SC Surficial (n=5)	SC Depth (n=3)
WMP	surficial	0.797 (±0.13)	0.737 (±0.20)	0.774 (±0.19)	0.672 (±0.086)	0.913 (±0.032)	0.858 (±0.065)	0.901 (±0.040)	0.908 (±0.033)
WMP	depth	0.874 (±0.019)	0.980 (±0.0091)	0.936 (±0.017)	0.609 (±0.040)	0.926 (±0.016)	0.977 (±0.010)	0.932 (±0.017)	0.903 (±0.027)
SC	surficial	0.896 (±0.040)	0.911 (±0.0073)	0.951 (±0.023)	0.680 (±0.069)	0.935 (±0.032)	0.902 (±0.0035)	0.947 (±0.027)	0.924 (±0.050)
SC	depth	0.817 (±0.14)	0.604 (±0.20)	0.678 (±0.21)	0.944 (±0.043)	0.979 (±0.0062)	0.921 (±0.040)	0.966 (±0.014)	0.988 (±0.0020)

Table 10: Mean correlations between individual sample B[a]P-PEQs and area B[a]P-PEQs

Mean of correlation coefficients (5,95% CLs) between ratios of B[a]P PEQs in individual samples and B[a]P PEQ fingerprint (ratio means) from site areas					
		Individual samples from area:			
Fingerprint from area:		WMP Surficial (n=9)	WMP Depth (n=6)	SC Surficial (n=5)	SC Depth (n=3)
WMP	Surficial	0.920 (±0.047)	0.897 (±0.059)	0.911 (±0.065)	0.859 (±0.069)
WMP	Depth	0.982 (±0.0060)	0.994 (±0.0052)	0.979 (±0.0076)	0.917 (±0.021)
SC	Surficial	0.965 (±0.021)	0.962 (±0.036)	0.978 (±0.015)	0.942 (±0.026)
SC	Depth	0.920 (±0.055)	0.890 (±0.080)	0.943 (±0.048)	0.980 (±0.011)

Site-wide fingerprint fractions for both EPA PAHs (14 chemicals) and B[a]P-PEQs are shown in Table 13. EPA PAH (14 chemicals) fingerprint excludes naphthalene and 2-methylnaphthalene.

Table 11: B[a]P-PEQ and EPA PAH (14 chemicals) fingerprint fractions

B[a]P PEQ fingerprint fractions and EPA PAH fingerprint fractions					
PAH	**B[a]P PEQ : total B[a]P PEQs**	**[EPA PAH]: total [EPA PAHs]**	**PAH**	**B[a]P PEQ : total B[a]P PEQs**	**[EPA PAH]: total [EPA PAHs]**
Acenaphthene		**0.0127**	7,12-Dimethylbenzanthracene	**0.116**	
Acenaphthylene		**0.0157**	1,6-Dinitropyrene	§	
Anthracene		**0.0415**	1,8-Dinitropyrene	§	
Benzo(a)anthracene	**0.0196**	**0.0953**	Fluoranthene		**0.173**
Benzo(b,j,k)fluoranthene †	**0.0311**	**0.156**	Fluorene		**0.0276**
Benzo(g,h,i)perylene		**0.0361**	Ideno(1,2,3-c,d)pyrene	**0.0064**	**0.0340**
Benzo(a)pyrene	**0.172**	**0.0894**	3-Methylcholanthrene	§	
Benzo(e)pyrene			5-Methylchrysene	**0.0694**	
Carbazole			2-Methylnaphthalene		¶
Chrysene	**0.0018**	**0.0880**	Naphthalene		¶
Dibenzo(a,h)anthracene	**0.0116**	**0.0110**	5-Nitroacenaphthene	**6E-05**	
Dibenz[a,h]acridine	**0.0006**		6-Nitrochrysene	§	
Dibenz[a,j]acridine	**0.0003**		2-Nitrofluorene	§	
7H-Dibenzo[c,g]carbazole	**0.0045**		1-Nitropyrene	**0.0131**	
Dibenzo[a,e]pyrene	**0.0128**		4-Nitropyrene	§	
Dibenzo[a,h]pyrene	**0.0661**		Perylene		
Dibenzo[a,i]pyrene	**0.114**		Phenanthrene		**0.0899**
Dibenzo[a,l]pyrene	**0.360**		Pyrene		**0.130**

† Benzo(b)fluoranthene, Benzo(j)fluoranthene and Benzo(k)fluoranthene analysis unresolved and abbreviated as Benzo(b,j,k)fluoranthene

§ Not detected: 1,6-Dinitropyrene, mean detection limit (mDL) 30 µg/kg (0.2 µg/kg recommended DL (MDH 2005)); 1,8-Dinitropyrene, mDL 34 (2)µg/kg; 3-Methylcholanthrene, mDL 13 (0.8)µg/kg; 6-Nitrochrysene, mDL 103 (0.2)µg/kg; 2-Nitrofluorene, mDL 14 (200)µg/kg; 4-Nitropyrene, mDL 12 (20)µg/kg

¶ Excluded from EPA PAH (14 chemicals) fingerprint (see text)

The PAH fingerprint of 2003 US Steel sediment samples for EPA PAHs(14 chemicals) is shown in Figure 3. The B[a]P-PEQ fingerprint, calculated from cPAH concentrations and B[a]P PEFs, is shown in Figure 4

.

Figure 3: EPA PAH (14 chemicals) Fingerprint

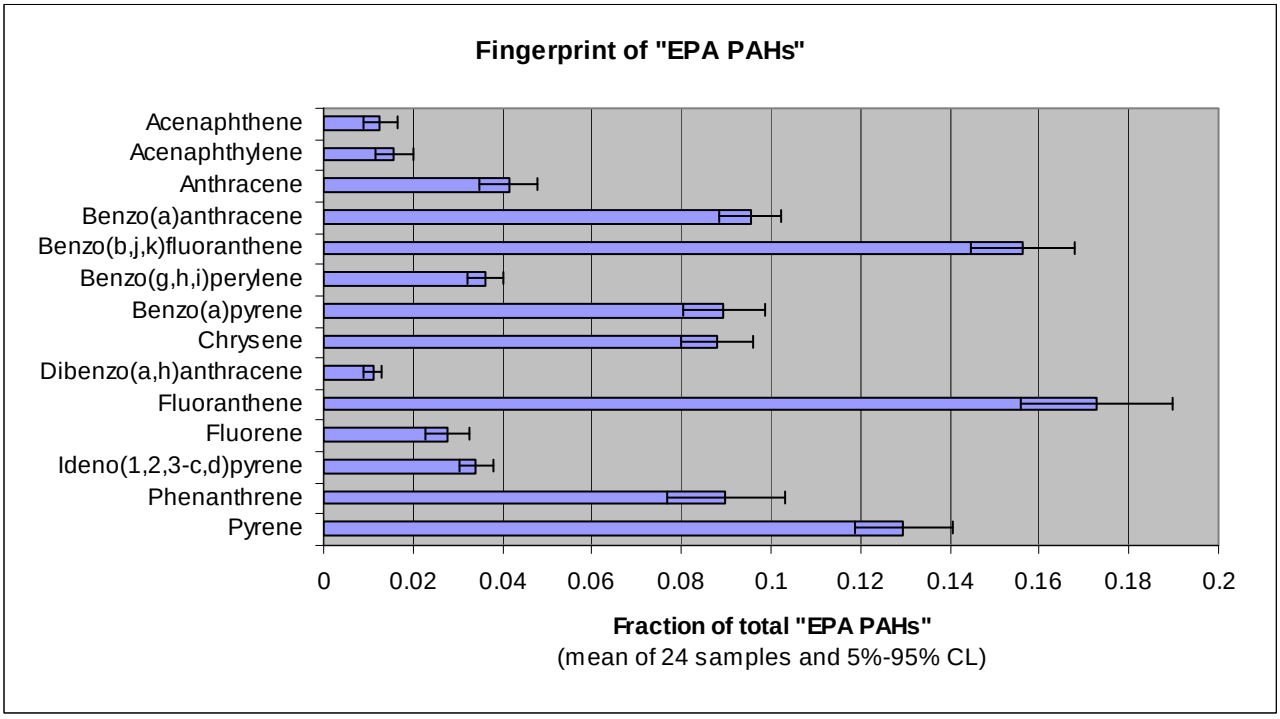
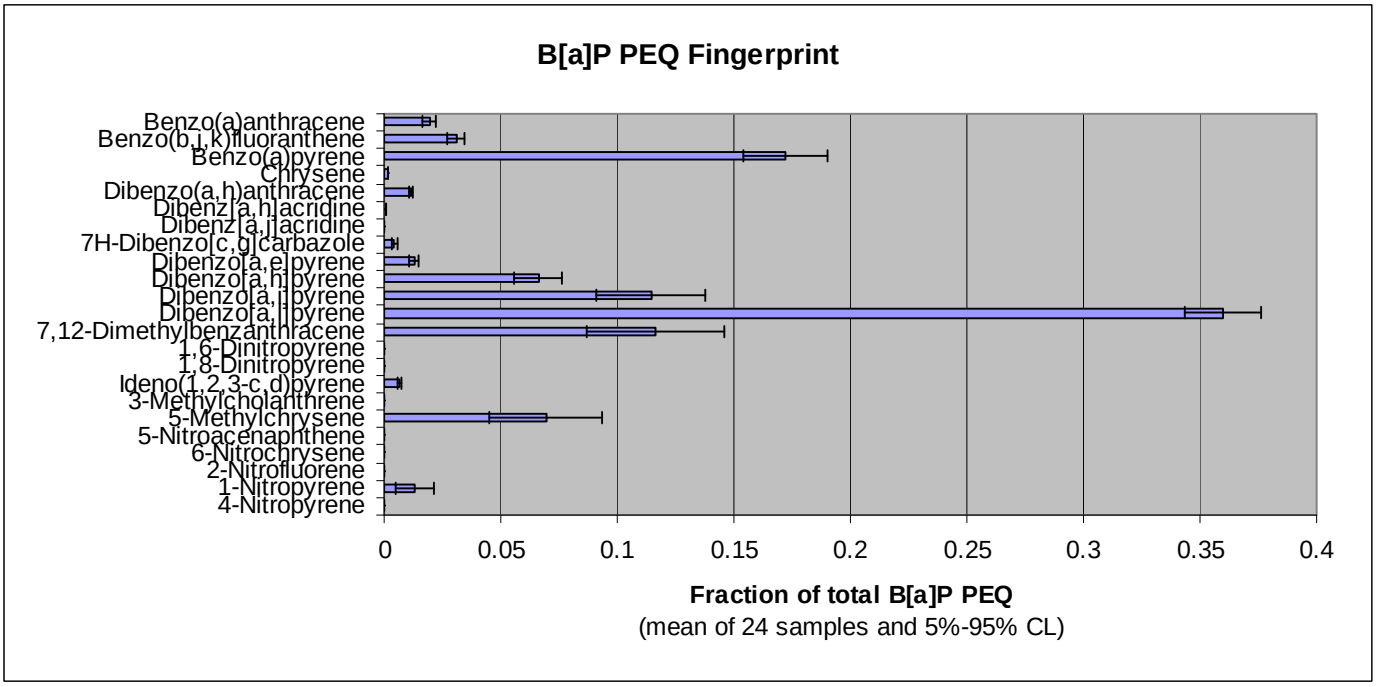


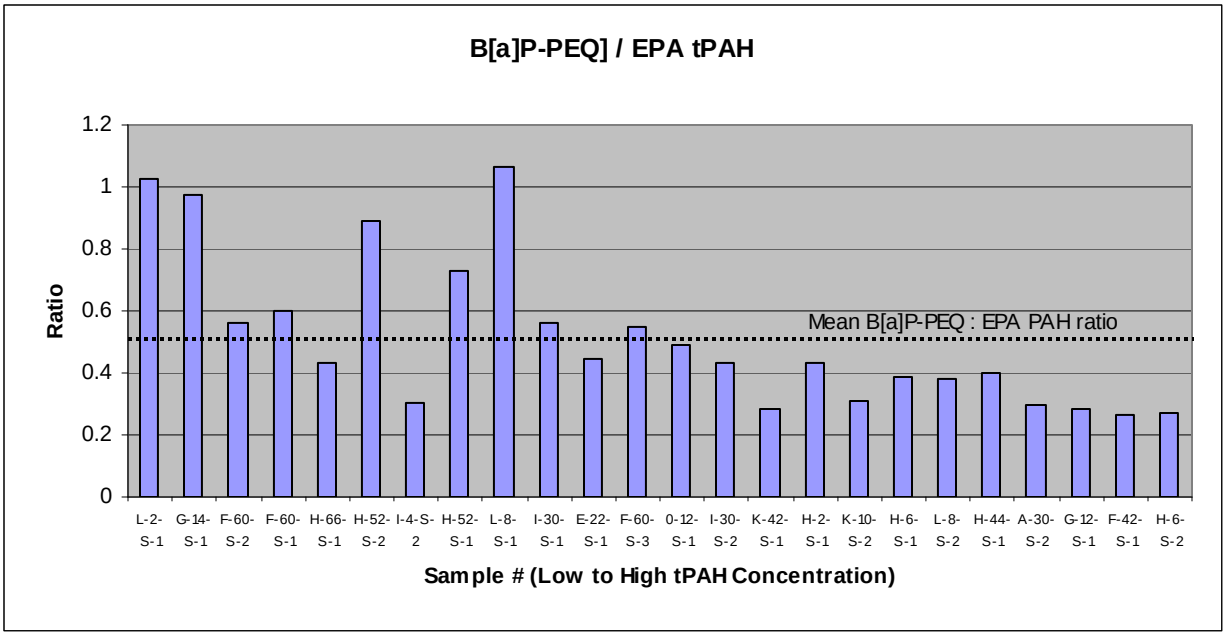
Figure 4: B[a]P-PEQ Fingerprint



Estimating B[a]P-PEQ from EPA PAHs (14 chemicals)

One of the purposes of conducting a fingerprint analysis is to be able to estimate contaminant concentrations when data are not available for all chemicals of interest. At this site, there may be interest in estimating B[a]P-PEQ in a sample for which only EPA PAHs (14 chemicals) are available. This is only possible if ratios between total concentrations are consistent and there is a good correlation between the two data groups over a number of samples. Figure 5 shows the ratios of the total B[a]P-PEQ to the total EPA PAH (14 chemicals) concentration for each 2003 US Steel sediment sample (not including duplicate samples, samples with fewer than 11 cPAHs detected and samples with B[a]P-PEQ less than the SSV of 71 µg/kg).

Figure 5: 2003 Sample Ratios - B[a]P-PEQ : EPA tPAH (14 chemicals)



Note the ratios vary from about 0.25 to greater than 1. The mean ratio is 0.51 (95% CL of the mean is 0.60). Therefore, ratios in individual samples are within a factor of 2 of the mean ratio. Ratios appear to decrease as the PAH concentration increases (subject to discussion of the accuracy of the 2003 sediment data; MDH 2006). This suggests a dependence of the B[a]P-PEQ : EPA tPAH (14 chemicals) ratio on the concentration of PAHs. As a result, there is not a unique ratio between these 2 measures of total PAHs. This difference between 2 measures of PAHs may be anticipated given the different chemical characteristics of these 2 groups of chemicals.

Naphthalene and 2-methylnaphthalene (2-ring PAHs) have been excluded from fingerprints because their relative concentrations in sediment may vary greatly over the site. They were the only 2 analyzed PAHs that are volatile and their volatility would be likely to lead to extreme differences in rates of loss from sediments depending on environmental conditions. Table 12 shows the proportion of 3 to 6-ring PAHs found in the 2 types of fingerprints for US Steel sediments. Note that 3-ring PAHs contributed almost nothing to the total B[a]P-PEQ, while 3-ring PAHs contributed about 19% of the

total EPA PAH (14 chemical) fingerprint. Conversely, the 6-ring PAHs contributed 7% of the total EPA PAHs (14 chemicals) and 56% of the B[a]P-PEQ. The biodegradation of PAHs with more than 3 rings is considerably slower than biodegradation of PAHs with 3 or fewer rings; with half-lives 5 times or greater (ATSDR 1995). As a result, as biodegradation occurs in sediments, the ratio of B[a]P-PEQ to EPA PAHs would be expected to increase. In addition, PAHs with more rings are typically more hydrophobic than PAHs with fewer rings. For example: 3-ring PAHs anthracene and phenanthrene have log K_{ow}s 4.55 and 4.6, respectively; 4-ring PAHs fluoranthene and pyrene have log K_{ow}s 5.12 and 5.11, respectively; 5-ring PAHs benzo[a]pyrene and the benzo(b,j,k)pyrenes have log K_{ow}s ranging from 5.78 to 6.13; and the dibenzo(-,-)pyrenes, 6-ring PAHs, have log K_{ow}s from 7.28 to 7.71 (Michigan DEQ 2002). As a result, PAHs with fewer rings may dissolve more readily in water than PAHs with more rings, allowing them to be washed away more quickly. Over time this will result in greater dispersion and dilution of the aggregate EPA PAHs and greater relative retention of carcinogenic PAHs. In addition, the effects of this weathering are likely to be restricted to the surface of nuggets of contamination because water cannot easily penetrate mixtures that are mainly composed of hydrophobic chemicals. As a result, maximal weathering, and therefore the highest B[a]P-PEQ : EPA PAH ratios, would be expected to occur in areas with the lowest PAH concentrations. This could explain the concentration dependence of the B[a]P-PEQ : EPA PAH (14 chemicals) ratio seen in the site data.

Table 12: Proportions of PAHs with 3-6 rings in PAH fingerprints

	3 Ring PAHs	4 Ring PAHs	5 Ring PAHs	6 Ring PAHs	Total
EPA PAHs (14 chemicals) †	0.187	0.486	0.257	0.070	1.0
B[a]P-PEQ §	6.5E-05	0.220	0.220	0.559	1.0

† Proportion of PAHs by weight

§ Proportion of total cancer potency

The MDH Health Consultation: Technical review of discrepancies in 2002 Laser Induced Fluorescence data, and 2003 and 2004 analytical data (2006) shows that proportions of PAHs are similar between 4 split samples among 2 laboratories (n = 17 – 21 individual PAHs per sample). However, when the results of PAH analyses of single samples from the 2 laboratories were plotted against each other, the slope of the regression lines for individual PAHs were between 2.1 and 17.7. Thus, the absolute value or quantitation of the PAHs in the laboratories was different. Because the proportion of PAHs in individual split samples were in agreement, yet the regression coefficient (slope) between lab results was not 1 and this coefficient varied between samples; data from these split samples suggested a systematic error in analysis. The previous Health Consultation also found that the quantitation errors were not confined to PAH analyses, but extended to metals and dioxin data. As a result it was concluded that: "it is likely that at least 1 laboratory had significant problems in determining the denominator when conducting chemical analysis of these sediment samples. There are likely problems with moisture determinations in at least 1 laboratory; and TOC data from US Steel are suspect. ...these data are likely sufficient for fingerprinting chemical signatures of separate chemical groups on the site. However, information derived from these data are not sufficient to describe the extent and magnitude of any specific chemical contamination at this site."

Therefore, while it is possible to determine both B[a]P-PEQ and EPA PAH (14 chemicals) fingerprints for the site, it is not possible to determine how the ratio of B[a]P-PEQ : EPA PAH (14 chemicals) varies with PAH concentration in sediment using available data.

Further, even if variation of B[a]P-PEQ : EPA PAH (14 chemicals) ratio varies predictably with concentration, if estimation of B[a]P-PEQ from EPA PAHs (14 chemicals) occurs after sediments are disturbed, mixing and dilution of sediments with cleaner sediments would result in changes in the concentration dependence.

PAH Fingerprint Conclusions

PAH fingerprints were developed for EPA PAHs (14 chemicals) and B[a]P-PEQs. These fingerprints, independently, were reasonably consistent over a large range of PAHs. Some differences in each of these fingerprints are expected between samples because of differences in susceptibility of individual PAHs in these groups to weathering. These differences can cause changes in ratios between individual PAHs in different sample locations, as well as changes in the ratios between PAH groups.

Chlorinated dioxin and chlorinated dibenzofuran fingerprints and polycyclic aromatic hydrocarbon fingerprints for sediments associated with the US Steel site reasonably describe the US Steel sediment chemical signature. Due to problems in the chemical analysis of the 2003 sediment samples, comparing the dioxin concentrations with the PAH concentrations is not possible. Similarly, because the EPA PAHs (14 chemicals) and B[a]P-PEQs vary as a function of concentration, likely as a result of different weathering rates, quantization of this comparison would not be reliable. In addition, if the sediments are disturbed, for instance during remediation, any concentration dependence of this ratio would be destroyed.

Non-EPA cPAHs make up about 76% of the PEQ fingerprint from 2003 sediment samples. Therefore, it is important to characterize the complete list of cPAHs in some sediment samples when PAHs are a concern.

Recommendations

The fingerprints developed in this health consultation may be used for:

- determining chemicals in sediments that could not have originated at this site and
- predicting likely concentrations of chemicals from partial analytical results within similar chemical groups – e.g. within the list of PCDD/F congeners, within the EPA PAH list and within the cPAH list.

Because of the absence of PCB congener data, determining an accurate TCDD-TEQ at any site location will require additional, coupled PCDD/F and PCB congener data.

Because of the importance of estimating the cancer potency of PAH mixtures and the differences in compound ring structures that can result in different rates of weathering, MDH recommends analyzing the complete list of cPAHs at sites where PAHs are of concern.

Public Health Action Plan

The Minnesota Department of Health will continue to assist the MPCA in their assessment of the US Steel site.

This consultation was prepared by:

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CERTIFICATION

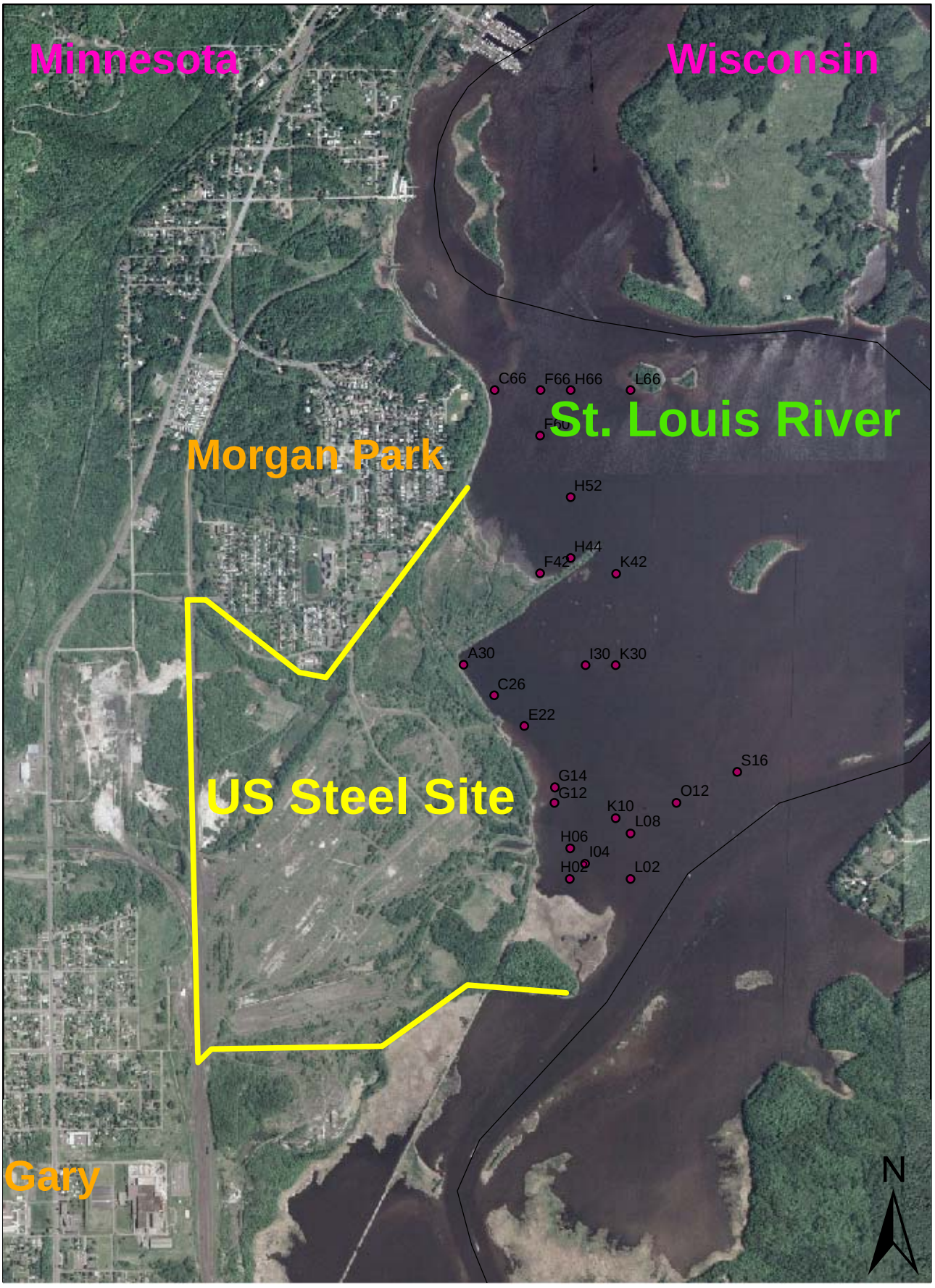
This St. Louis River, US Steel Health Consultation was prepared by the Minnesota Department of Health under a cooperative agreement with the Agency for Toxic Substances and Disease Registry (ATSDR). It is in accordance with approved methodology and procedures existing at the time the health consultation was begun. Editorial review was completed by the Cooperative Agreement partner.

Alan Parham
Technical Project Officer, SPS, SSAB, DHAC, ATSDR

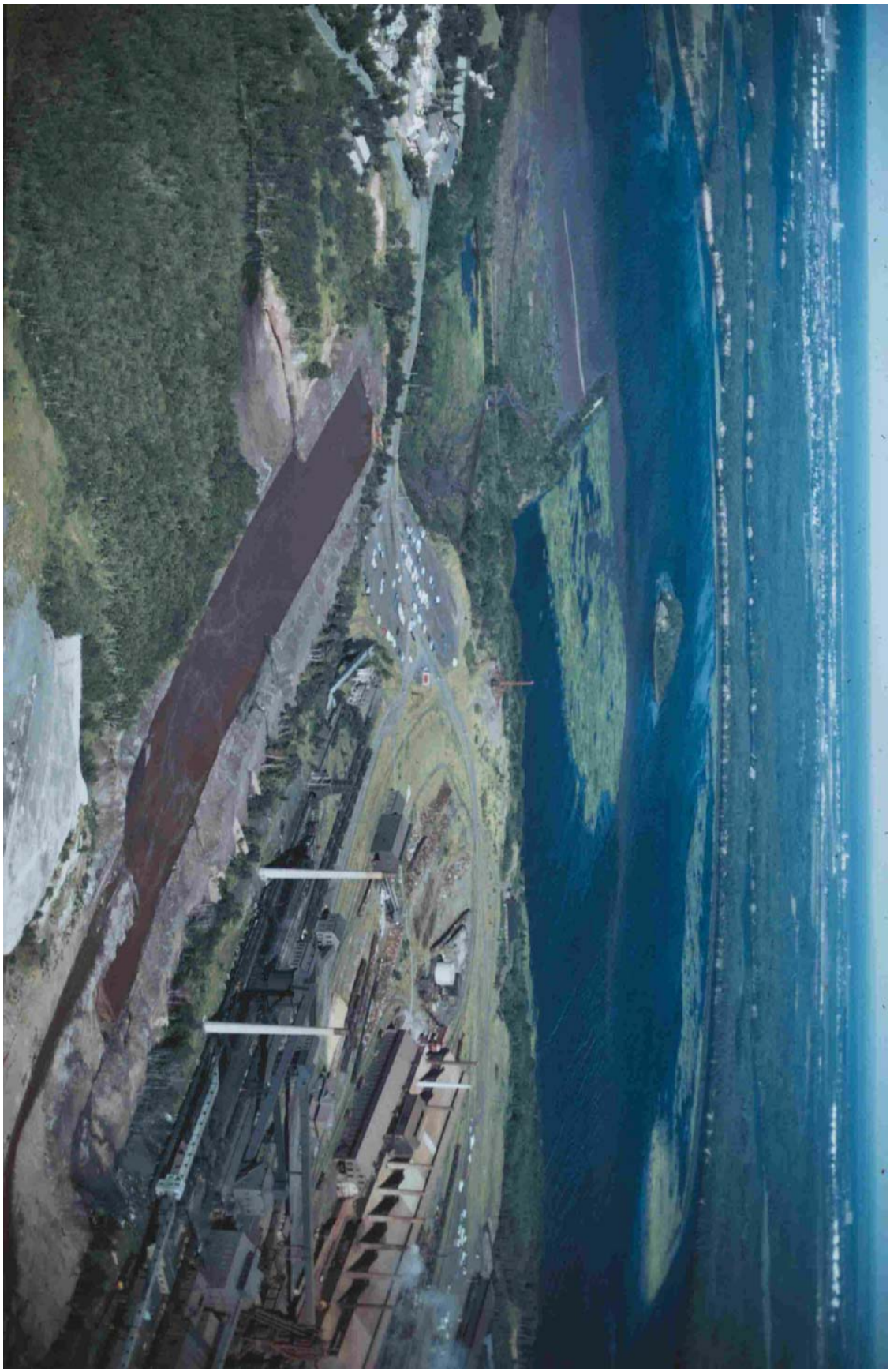
The Division of Health Assessment and Consultation, ATSDR, has reviewed this public health consultation and concurs with the findings.

Alan Yarbrough
Chief, State Program Section, SSAB, DHAC, ATSDR

Attachment 1



Attachment 2: US Steel - 1967



Federal Water Pollution Control Administration, 1967-8

Attachment 3: St. Louis River off US Steel site - 1967

Federal Water Pollution Control Administration, 1967-8

Attachment 4

Carcinogenic polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (ng/kg) in 2003 sediment samples *

Sample Location	Sample Depth	Sample Number	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF	1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF	1,2,3,7,8,9-HxCDF	2,3,4,6,7,8-HxCDF	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	OCDF
WMP	Surficial	K-30-S-1	4.8	14	13	75.5	43	1020	7000	8.3			15.5	19	4.9	5.8	1750	10.45	655
WMP	Surficial	I-4-S-1	11	46	33	180	150	2300	6000	9.2			16	7		7.6	770	11	520
WMP	Surficial	A-30-S-1	14	27	24	120	67	1500	10000	19			20	24			1100	14	800
WMP	Surficial	E-22-S-1	4.1	12	8.8	55	31	480	1800	5.4			8.6	6.2			430	5.1	260
WMP	Surficial	G-12-S-1	6.5	19	17	110	63	1100	5000	9.6			12	5.3			480	7.3	490
WMP	Surficial	H-6-S-1	3.9	14	12	73	43	880	3200				10	5.1		3.8	350	6.8	250
WMP	Surficial	I-30-S-1	3.8	10	8.8	50	34	630	3500	6.7			9.3	11			640	9	330
WMP	Surficial	H-2-S-1	2.5	10.2	8	53	33.5	520	1900	5			4.5				101.5		130
WMP	Surficial	K-42-S-1	2.6	4.4		24	16	370	2800	5.5			4.3	4.3			360		170
WMP	Surficial	0-12-S-1	1.9			15	7.9	160	1200	3.3				5.8			250		140
WMP	Surficial	C-26-S-1				4.7	3.3	75	740	0.89							120		67
WMP	Surficial	S-16-S-1	1.3					63.5	725	1.74							38		36
WMP	Surficial	K-10-S-1						59	410	0.99							69		36
WMP	Surficial	G-14-S-1						21	150								40		18
WMP	Surficial	L-2-S-1						9.9	65								13		10
WMP	Surficial	L-8-S-1						14	120								15		8.8
WMP	Depth	L-8-S-2	13	52	42	270	150	2600	13000	13			60	42			3300	46	2200
WMP	Depth	I-30-S-2	7.9	33	30	140	110	1600	6100				34	33			2600	21	1000
WMP	Depth	H-6-S-3	1.9	7.1	5.2	34	25	400	960								95		61
WMP	Depth	A-30-S-2				9.3	5.6	120	740	1.7							85		42
WMP	Depth	K-10-S-2				4		42	140								53		23
WMP	Depth	I-4-S-2						77	170								25		18
WMP	Depth	H-6-S-2						74	180								26		
WMP	Depth	L-8-S-3						4.5	23								4.5		
WMP	Depth	A-30-S-3																	
WMP	Depth	I-30-S-3																	
WMP	Depth	K-10-S-3																	
SC	Surficial	F-60-S-1	17	200	44	240	130	1900	9900	9.4	9.6	15	60	68		20	3900	38	2200
SC	Surficial	F-66-S-1	10	39	28	170	100	1600	8500	5.9			39	34		15	3200	23	1800
SC	Surficial	H-66-S-1	3.3	6.4		30	15	290	2200	6.3				19			830	6.7	440
SC	Surficial	H-44-S-1					4.2	75	580	1.7							13		13
SC	Surficial	F-42-S-1						164	1150	1.4							6.1		6.5
SC	Surficial	H-52-S-1						75	530	5.5							76		53
SC	Surficial	C-66-S-1						66	600								50		37
SC	Surficial	L-66-S-1						19.5	195								51.5		22
SC	Depth	F-60-S-3	21	66	51	300	160	2500	18000	13	12	22	98	100		29	7300	51	3100
SC	Depth	F-60-S-2	2.5	7.6		32	16	220	1600	1.1		6	15	19			820	8.7	410
SC	Depth	H-52-S-2	4.7	12	7.7	56	28	430	2900	2.6			18	14			1000	10	600
SC	Depth	F-66-S-3						3.6	18				3.5	6.3			10	6.9	9.5
SC	Depth	F-66-S-2						5.9	28								12		14
SC	Depth	H-52-S-3																	

***** Data to be used only for fingerprint analysis due to analytical problems discussed in text and in MDH 2006

Attachment 5

Ratios of carcinogenic polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in 2003 sediment samples *
(Congener Concentration / Total PCDD/F Concentration)

Sample Location	Sample Depth	Sample Number	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF	1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF	1,2,3,7,8,9-HxCDF	2,3,4,6,7,8-HxCDF	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	OCDF	Total # of cPCDD/F analytes in sample
WMP	**Surficial**	**K-30-S-1**	**0.000451**	**0.00132**	**0.00122**	**0.0071**	**0.00404**	**0.0959**	**0.658**	**0.00078**			**0.00146**	**0.00179**	**0.000461**	**0.000545**	**0.164**	**0.000982**	**0.0616**	**15**
WMP	**Surficial**	**I-4-S-1**	**0.00109**	**0.00457**	**0.00328**	**0.0179**	**0.0149**	**0.229**	**0.596**	**0.000914**			**0.00159**	**0.000696**		**0.000755**	**0.0765**	**0.00109**	**0.0517**	**14**
WMP	**Surficial**	**A-30-S-1**	**0.00102**	**0.00197**	**0.00175**	**0.00874**	**0.00488**	**0.109**	**0.728**	**0.00138**			**0.00146**	**0.00175**			**0.0801**	**0.00102**	**0.0583**	**13**
WMP	**Surficial**	**E-22-S-1**	**0.00132**	**0.00386**	**0.00283**	**0.0177**	**0.00998**	**0.155**	**0.579**	**0.00174**			**0.00277**	**0.002**			**0.138**	**0.00164**	**0.0837**	**13**
WMP	**Surficial**	**G-12-S-1**	**0.000888**	**0.0026**	**0.00232**	**0.015**	**0.00861**	**0.15**	**0.683**	**0.00131**			**0.00164**	**0.000724**			**0.0656**	**0.000997**	**0.0669**	**13**
WMP	**Surficial**	**H-6-S-1**	**0.000804**	**0.00289**	**0.00247**	**0.015**	**0.00886**	**0.181**	**0.66**				**0.00206**	**0.00105**		**0.000783**	**0.0721**	**0.0014**	**0.0515**	**13**
WMP	**Surficial**	**I-30-S-1**	**0.000725**	**0.00191**	**0.00168**	**0.00954**	**0.00649**	**0.12**	**0.668**	**0.00128**			**0.00177**	**0.0021**			**0.122**	**0.00172**	**0.0629**	**13**
WMP	**Surficial**	**H-2-S-1**	**0.000903**	**0.00368**	**0.00289**	**0.0191**	**0.0121**	**0.188**	**0.686**	**0.00181**			**0.00163**				**0.0367**		**0.047**	**11**
WMP	**Surficial**	**K-42-S-1**	**0.000691**	**0.00117**		**0.00638**	**0.00425**	**0.0984**	**0.744**	**0.00146**			**0.00114**	**0.00114**			**0.0957**		**0.0452**	**11**
WMP	Surficial	0-12-S-1	0.00107			0.00841	0.00443	0.0897	0.673	0.00185				0.00325			0.14		0.0785	9
WMP	Surficial	C-26-S-1				0.00465	0.00326	0.0742	0.732	0.00088							0.119		0.0663	7
WMP	Surficial	S-16-S-1	0.0015					0.0734	0.838	0.00201							0.0439		0.0416	6
WMP	Surficial	K-10-S-1						0.103	0.713	0.00172							0.12		0.0626	5
WMP	Surficial	G-14-S-1						0.0917	0.655								0.175		0.0786	4
WMP	Surficial	L-2-S-1						0.101	0.664								0.133		0.102	4
WMP	Surficial	L-8-S-1						0.0887	0.76								0.0951		0.0558	4
WMP	**Depth**	**L-8-S-2**	**0.000597**	**0.00239**	**0.00193**	**0.0124**	**0.00688**	**0.119**	**0.597**	**0.000597**			**0.00275**	**0.00193**			**0.151**	**0.00211**	**0.101**	**13**
WMP	**Depth**	**I-30-S-2**	**0.000675**	**0.00282**	**0.00256**	**0.012**	**0.00939**	**0.137**	**0.521**				**0.0029**	**0.00282**			**0.222**	**0.00179**	**0.0854**	**12**
WMP	Depth	H-6-S-3	0.0012	0.00447	0.00327	0.0214	0.0157	0.252	0.604								0.0598		0.0384	9
WMP	Depth	A-30-S-2				0.00927	0.00558	0.12	0.737	0.00169							0.0847		0.0418	7
WMP	Depth	K-10-S-2				0.0153		0.16	0.534								0.202		0.0878	5
WMP	Depth	I-4-S-2						0.266	0.586								0.0862		0.0621	4
WMP	Depth	H-6-S-2						0.264	0.643								0.0929			3
WMP	Depth	L-8-S-3						0.141	0.719								0.141			3
WMP	Depth	A-30-S-3																		0
WMP	Depth	I-30-S-3																		0
WMP	Depth	K-10-S-3																		0
SC	**Surficial**	**F-60-S-1**	**0.000907**	**0.0107**	**0.00235**	**0.0128**	**0.00693**	**0.101**	**0.528**	**0.000501**	**0.000512**	**0.0008**	**0.0032**	**0.00363**		**0.00107**	**0.208**	**0.00203**	**0.117**	**16**
SC	**Surficial**	**F-66-S-1**	**0.000643**	**0.00251**	**0.0018**	**0.0109**	**0.00643**	**0.103**	**0.546**	**0.000379**			**0.00251**	**0.00218**		**0.000964**	**0.206**	**0.00148**	**0.116**	**14**
SC	**Surficial**	**H-66-S-1**	**0.000858**	**0.00166**		**0.0078**	**0.0039**	**0.0754**	**0.572**	**0.00164**				**0.00494**			**0.216**	**0.00174**	**0.114**	**11**
SC	Surficial	H-44-S-1					0.00611	0.109	0.844	0.00247							0.0189		0.0189	6
SC	Surficial	F-42-S-1						0.123	0.866	0.00105							0.00459		0.00489	5
SC	Surficial	H-52-S-1						0.101	0.717	0.00744							0.103		0.0717	5
SC	Surficial	C-66-S-1						0.0876	0.797								0.0664		0.0491	4
SC	Surficial	L-66-S-1						0.0677	0.677								0.179		0.0764	4
SC	**Depth**	**F-60-S-3**	**0.00066**	**0.00207**	**0.0016**	**0.00943**	**0.00503**	**0.0786**	**0.566**	**0.000409**	**0.000377**	**0.000691**	**0.00308**	**0.00314**		**0.000911**	**0.229**	**0.0016**	**0.0974**	**16**
SC	**Depth**	**F-60-S-2**	**0.000792**	**0.00241**		**0.0101**	**0.00507**	**0.0697**	**0.507**	**0.000348**		**0.0019**	**0.00475**	**0.00602**			**0.26**	**0.00275**	**0.13**	**13**
SC	**Depth**	**H-52-S-2**	**0.000925**	**0.00236**	**0.00151**	**0.011**	**0.00551**	**0.0846**	**0.571**	**0.000512**			**0.00354**	**0.00275**			**0.197**	**0.00197**	**0.118**	**13**
SC	Depth	F-66-S-3						0.0623	0.311				0.0606	0.109			0.173	0.119	0.164	7
SC	Depth	F-66-S-2						0.0985	0.467								0.2		0.234	4
SC	Depth	H-52-S-3																		0

***** Bolded data used in fingerprint analyses

Attachment 6

2,3,7,8-Tetrachlorodibenzo-p-dioxin Toxic Equivalents (ng TEQ/kg) in 2003 sediment samples (w/o cPCBs) *

Sample Location	Sample Depth	Sample Number	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF	1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF	1,2,3,7,8,9-HxCDF	2,3,4,6,7,8-HxCDF	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	OCDF
WMP	Surficial	K-30-S-1	4.8	14	1.3	7.55	4.3	10.2	7	0.83			1.55	1.9	0.49	0.58	17.5	0.1045	0.0655
WMP	Surficial	I-4-S-1	11	46	3.3	18	15	23	6	0.92			1.6	0.7		0.76	7.7	0.11	0.052
WMP	Surficial	A-30-S-1	14	27	2.4	12	6.7	15	10	1.9			2	2.4			11	0.14	0.08
WMP	Surficial	E-22-S-1	4.1	12	0.88	5.5	3.1	4.8	1.8	0.54			0.86	0.62			4.3	0.051	0.026
WMP	Surficial	G-12-S-1	6.5	19	1.7	11	6.3	11	5	0.96			1.2	0.53			4.8	0.073	0.049
WMP	Surficial	H-6-S-1	3.9	14	1.2	7.3	4.3	8.8	3.2				1	0.51		0.38	3.5	0.068	0.025
WMP	Surficial	I-30-S-1	3.8	10	0.88	5	3.4	6.3	3.5	0.67			0.93	1.1			6.4	0.09	0.033
WMP	Surficial	H-2-S-1	2.5	10.2	0.8	5.3	3.35	5.2	1.9	0.5			0.45				1.015		0.013
WMP	Surficial	K-42-S-1	2.6	4.4		2.4	1.6	3.7	2.8	0.55			0.43	0.43			3.6		0.017
WMP	Surficial	0-12-S-1	1.9			1.5	0.79	1.6	1.2	0.33				0.58			2.5		0.014
WMP	Surficial	C-26-S-1				0.47	0.33	0.75	0.74	0.089							1.2		0.0067
WMP	Surficial	S-16-S-1	1.3					0.635	0.725	0.174							0.38		0.0036
WMP	Surficial	K-10-S-1						0.59	0.41	0.099							0.69		0.0036
WMP	Surficial	G-14-S-1						0.21	0.15								0.4		0.0018
WMP	Surficial	L-2-S-1						0.099	0.065								0.13		0.001
WMP	Surficial	L-8-S-1						0.14	0.12								0.15		0.00088
WMP	Depth	L-8-S-2	13	52	4.2	27	15	26	13	1.3			6	4.2			33	0.46	0.22
WMP	Depth	I-30-S-2	7.9	33	3	14	11	16	6.1				3.4	3.3			26	0.21	0.1
WMP	Depth	H-6-S-3	1.9	7.1	0.52	3.4	2.5	4	0.96								0.95		0.0061
WMP	Depth	A-30-S-2				0.93	0.56	1.2	0.74	0.17							0.85		0.0042
WMP	Depth	K-10-S-2				0.4		0.42	0.14								0.53		0.0023
WMP	Depth	I-4-S-2						0.77	0.17								0.25		0.0018
WMP	Depth	H-6-S-2						0.74	0.18								0.26		
WMP	Depth	L-8-S-3						0.045	0.023								0.045		
WMP	Depth	A-30-S-3																	
WMP	Depth	I-30-S-3																	
WMP	Depth	K-10-S-3																	
SC	Surficial	F-60-S-1	17	200	4.4	24	13	19	9.9	0.94	0.48	7.5	6	6.8		2	39	0.38	0.22
SC	Surficial	F-66-S-1	10	39	2.8	17	10	16	8.5	0.59			3.9	3.4		1.5	32	0.23	0.18
SC	Surficial	H-66-S-1	3.3	6.4		3	1.5	2.9	2.2	0.63				1.9			8.3	0.067	0.044
SC	Surficial	H-44-S-1					0.42	0.75	0.58	0.17							0.13		0.0013
SC	Surficial	F-42-S-1						1.64	1.15	0.14							0.061		0.00065
SC	Surficial	H-52-S-1						0.75	0.53	0.55							0.76		0.0053
SC	Surficial	C-66-S-1						0.66	0.6								0.5		0.0037
SC	Surficial	L-66-S-1						0.195	0.195								0.515		0.0022
SC	Depth	F-60-S-3	21	66	5.1	30	16	25	18	1.3	0.6	11	9.8	10		2.9	73	0.51	0.31
SC	Depth	F-60-S-2	2.5	7.6		3.2	1.6	2.2	1.6	0.11		3	1.5	1.9			8.2	0.087	0.041
SC	Depth	H-52-S-2	4.7	12	0.77	5.6	2.8	4.3	2.9	0.26			1.8	1.4			10	0.1	0.06
SC	Depth	F-66-S-3						0.036	0.018				0.35	0.63			0.1	0.069	0.00095
SC	Depth	F-66-S-2						0.059	0.028								0.12		0.0014
SC	Depth	H-52-S-3																	

***** Data to be used only for fingerprint analysis due to analytical problems discussed in text and in MDH 2006

Attachment 7

Ratios of 2,3,7,8-Tetrachlorodibenzo-p-dioxin Toxic Equivalents (w/o cPCBs) in 2003 sediment samples *
(Congener TEQ / Total TCDD TEQ)

Sample Location	Sample Depth	Sample Number	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF	1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF	1,2,3,7,8,9-HxCDF	2,3,4,6,7,8-HxCDF	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	OCDF	Σ TCDD-TEQ Ratios
WMP	**Surficial**	**K-30-S-1**	**0.0665**	**0.194**	**0.018**	**0.105**	**0.0596**	**0.141**	**0.097**	**0.0115**			**0.0215**	**0.0263**	**0.00679**	**0.00804**	**0.242**	**0.00145**	**0.000908**	**1.0**
WMP	**Surficial**	**I-4-S-1**	**0.082**	**0.343**	**0.0246**	**0.134**	**0.112**	**0.171**	**0.0447**	**0.00686**			**0.0119**	**0.00522**		**0.00567**	**0.0574**	**0.00082**	**0.000388**	**1.0**
WMP	**Surficial**	**A-30-S-1**	**0.134**	**0.258**	**0.0229**	**0.115**	**0.064**	**0.143**	**0.0956**	**0.0182**			**0.0191**	**0.0229**			**0.105**	**0.00134**	**0.000765**	**1.0**
WMP	**Surficial**	**E-22-S-1**	**0.106**	**0.311**	**0.0228**	**0.143**	**0.0804**	**0.124**	**0.0467**	**0.014**			**0.0223**	**0.0161**			**0.111**	**0.00132**	**0.000674**	**1.0**
WMP	**Surficial**	**G-12-S-1**	**0.0954**	**0.279**	**0.025**	**0.161**	**0.0925**	**0.161**	**0.0734**	**0.0141**			**0.0176**	**0.00778**			**0.0705**	**0.00107**	**0.000719**	**1.0**
WMP	**Surficial**	**H-6-S-1**	**0.0809**	**0.291**	**0.0249**	**0.152**	**0.0892**	**0.183**	**0.0664**				**0.0208**	**0.0106**		**0.00789**	**0.0726**	**0.00141**	**0.000519**	**1.0**
WMP	**Surficial**	**I-30-S-1**	**0.0903**	**0.238**	**0.0209**	**0.119**	**0.0808**	**0.15**	**0.0831**	**0.0159**			**0.0221**	**0.0261**			**0.152**	**0.00214**	**0.000784**	**1.0**
WMP	**Surficial**	**H-2-S-1**	**0.0801**	**0.327**	**0.0256**	**0.17**	**0.107**	**0.167**	**0.0608**	**0.016**			**0.0144**				**0.0325**		**0.000416**	**1.0**
WMP	**Surficial**	**K-42-S-1**	**0.115**	**0.195**		**0.107**	**0.071**	**0.164**	**0.124**	**0.0244**			**0.0191**	**0.0191**			**0.16**		**0.000755**	**1.0**
WMP	Surficial	0-12-S-1	0.182			0.144	0.0759	0.154	0.115	0.0317				0.0557			0.24		0.00134	**1.0**
WMP	Surficial	C-26-S-1				0.131	0.092	0.209	0.206	0.0248							0.335		0.00187	**1.0**
WMP	Surficial	S-16-S-1	0.404					0.197	0.225	0.0541							0.118		0.00112	**1.0**
WMP	Surficial	K-10-S-1						0.329	0.229	0.0552							0.385		0.00201	**1.0**
WMP	Surficial	G-14-S-1						0.276	0.197								0.525		0.00236	**1.0**
WMP	Surficial	L-2-S-1						0.336	0.22								0.441		0.00339	**1.0**
WMP	Surficial	L-8-S-1						0.341	0.292								0.365		0.00214	**1.0**
WMP	**Depth**	**L-8-S-2**	**0.0665**	**0.266**	**0.0215**	**0.138**	**0.0768**	**0.133**	**0.0665**	**0.00665**			**0.0307**	**0.0215**			**0.169**	**0.00235**	**0.00113**	**1.0**
WMP	**Depth**	**I-30-S-2**	**0.0637**	**0.266**	**0.0242**	**0.113**	**0.0887**	**0.129**	**0.0492**				**0.0274**	**0.0266**			**0.21**	**0.00169**	**0.000806**	**1.0**
WMP	Depth	H-6-S-3	0.0891	0.333	0.0244	0.159	0.117	0.187	0.045								0.0445		0.000286	**1.0**
WMP	Depth	A-30-S-2				0.209	0.126	0.269	0.166	0.0382							0.191		0.000943	**1.0**
WMP	Depth	K-10-S-2				0.268		0.281	0.0938								0.355		0.00154	**1.0**
WMP	Depth	I-4-S-2						0.646	0.143								0.21		0.00151	**1.0**
WMP	Depth	H-6-S-2						0.627	0.153								0.22			**1.0**
WMP	Depth	L-8-S-3						0.398	0.204								0.398			**1.0**
WMP	Depth	A-30-S-3																		**0.0**
WMP	Depth	I-30-S-3																		**0.0**
WMP	Depth	K-10-S-3																		**0.0**
SC	**Surficial**	**F-60-S-1**	**0.0485**	**0.57**	**0.0125**	**0.0685**	**0.0371**	**0.0542**	**0.0282**	**0.00268**	**0.00137**	**0.0214**	**0.0171**	**0.0194**		**0.0057**	**0.111**	**0.00108**	**0.000627**	**1.0**
SC	**Surficial**	**F-66-S-1**	**0.0689**	**0.269**	**0.0193**	**0.117**	**0.0689**	**0.11**	**0.0586**	**0.00407**			**0.0269**	**0.0234**		**0.0103**	**0.221**	**0.00159**	**0.00124**	**1.0**
SC	**Surficial**	**H-66-S-1**	**0.109**	**0.212**		**0.0992**	**0.0496**	**0.0959**	**0.0727**	**0.0208**				**0.0628**			**0.274**	**0.00222**	**0.00145**	**1.0**
SC	Surficial	H-44-S-1					0.205	0.366	0.283	0.0829							0.0634		0.000634	**1.0**
SC	Surficial	F-42-S-1						0.548	0.384	0.0468							0.0204		0.000217	**1.0**
SC	Surficial	H-52-S-1						0.289	0.204	0.212							0.293		0.00204	**1.0**
SC	Surficial	C-66-S-1						0.374	0.34								0.283		0.0021	**1.0**
SC	Surficial	L-66-S-1						0.215	0.215								0.568		0.00243	**1.0**
SC	**Depth**	**F-60-S-3**	**0.0723**	**0.227**	**0.0176**	**0.103**	**0.0551**	**0.0861**	**0.062**	**0.00447**	**0.00207**	**0.0379**	**0.0337**	**0.0344**		**0.00998**	**0.251**	**0.00176**	**0.00107**	**1.0**
SC	**Depth**	**F-60-S-2**	**0.0745**	**0.227**		**0.0954**	**0.0477**	**0.0656**	**0.0477**	**0.00328**		**0.0895**	**0.0447**	**0.0567**			**0.244**	**0.00259**	**0.00122**	**1.0**
SC	**Depth**	**H-52-S-2**	**0.101**	**0.257**	**0.0165**	**0.12**	**0.06**	**0.0921**	**0.0621**	**0.00557**			**0.0386**	**0.03**			**0.214**	**0.00214**	**0.00129**	**1.0**
SC	Depth	F-66-S-3						0.0299	0.015				0.291	0.523			0.0831	0.0573	0.000789	**1.0**
SC	Depth	F-66-S-2						0.283	0.134								0.576		0.00672	**1.0**
SC	Depth	H-52-S-3																		**0.0**

***** Bolded data used in fingerprint analyses

Attachment 8

Polycyclic aromatic hydrocarbons (µg/kg) in 2003 sediment samples *

Sample Location	Sample Depth	Sample Number	Acenaphthene	Acenaphthylene	Anthracene	Benzo(a)anthracene	Benzo(b,j,k)fluoranthene	Benzo(g,h,i)perylene	Benzo(a)pyrene	Benzo(e)pyrene	Carbazole	Chrysene	Dibenzo(a,h)anthracene	Dibenz[a,h]acridine	Dibenz[a,j]acridine	7H-Dibenzo[c,g]carbazole	Dibenzo[a,e]pyrene	Dibenzo[a,h]pyrene	Dibenzo[a,i]pyrene	Dibenzo[a,l]pyrene	7,12-Dimethylbenzanthracene	1,6-Dinitropyrene
WMP	Surficial	G-12-S-1	2,500	260	6,500	10,000	16,000	3,000	8,400	3,400		7,500	340	120		58	220	110	130	1,300	110	
WMP	Surficial	G-14-S-1	0.56	1.6	3.0	7.8	20	9.8	12	9.6		6.7	1.8	0.55	0.36	0.37	1.6	1.3	1.3	4.3	0.4	
WMP	Surficial	H-2-S-1	260	340	410	820	1,400	350	690	420	170	790	100	36		19	80	28	36	190		
WMP	Surficial	K-42-S-1	20	74	100	790	1,200	120	690	440	19	760	40	11	6.7	6.0	29	6.9	14	63		
WMP	Surficial	0-12-S-1	51	16	170	320	820	140	440	210		380	37	14		14	40	15	15	80		
WMP	Surficial	S-16-S-1	0.56	0.89	1.1	4.8	6.8	2.6	5.2	4.2		5.0				2.6				0.63		
WMP	Surficial	E-22-S-1	15	28	110	390	650	120	340	190		350	35	15			32	11	11	64		
WMP	Surficial	L-2-S-1	1.4	8.8	6.6	14	24	8.6	16	8.9		13	3.1				0.98	1.9	4.6	5.9		
WMP	Surficial	H-6-S-1	980	230	1,500	2,100	2,600	520	1,400	660		1,600	150					64	130	270	45	
WMP	Surficial	I-30-S-1	35	35	120	300	340	130	220	220		420	32				26	12	11	57		
WMP	Surficial	K-30-S-1	41	35	100	280	420	110	240	180		320					34	14		54		
WMP	Surficial	L-8-S-1	40	21	100	190	530	200	490	330	58	220	72				57	13	57	100	23	
WMP	Surficial	C-26-S-1	1.4	4.4	4.9	18	32	7.6	18	11	2.6	16	2.2				1.5		0.96	3.5		
WMP	Surficial	A-30-S-1	14	27	31	140	240	66	130	91		150	20				16	8.5		31		
WMP	Surficial	I-4-S-1	770	220	3,000	4,800	7,200		3,800	1,700		3,700	330				200			620		
WMP	Surficial	K-10-S-1	51	3.1	51	65	100	24	53	26		51	6.1							12		
WMP	Depth	A-30-S-2	140	860	2,400	6,300	9,400	1,900	4,800	3,100	490	7,500	760	140	39	61	500	120	180	1,000		
WMP	Depth	L-8-S-2	240	80	1,400	2,500	3,900	740	2,100	910		1,900	180	59		31	160	66	80	420	27	
WMP	Depth	H-6-S-2	10,000	1,200	20,000	31,000	42,000	7,700	22,000	9,100		21,000	2,100		300	210			700	3,800		
WMP	Depth	I-4-S-2	47	8.7	120	160	210	44	110	51		110	9.7				7	9.6		23		
WMP	Depth	I-30-S-2	21	61	140	780	1,200	260	630	330		640	69			22		22	21	130		
WMP	Depth	K-10-S-2	330	34	1,100	1,400	2,100	430	1,100	480		1,000	100				70	45	43	210		
WMP	Depth	L-8-S-3	3.0	0.44	11	15	19	3.3	9.7	4.3		11	0.92				0.58	0.42	0.29	1.6		
WMP	Depth	A-30-S-3	1.3	1.6	4.5	13	21	4.5	11	6.6		15	1.9				1.1	0.64		2.4		
WMP	Depth	H-6-S-3	370	60	780	1,300	1,800	360	990	430		980					100	67		200		
WMP	Depth	I-30-S-3	0.25		0.27	0.52						0.48										
WMP	Depth	K-10-S-3	0.28	0.18	0.34	0.35						0.35										
SC	Surficial	F-42-S-1	480	5,500	16,000	26,000	34,000	6,300	19,000	10,000	980	21,000	2,000	560	210	260	1,500	460	640	3,200		
SC	Surficial	H-52-S-1	13	75	57	220	400	84	210	140	20	220	50	11	5.2	16	13	11	25	83		
SC	Surficial	F-60-S-1	3.8	18	21	130	180	38	130	64	3.1	130	15	3.2	1.8	6.0	4.0		19	26		
SC	Surficial	H-44-S-1	100	1,300	1,900	4,300	6,500	1,300	3,800	2,200	310	3,700	440	120		56	380	110	180	800		
SC	Surficial	H-66-S-1	3.3	22	27	130	220	42	120	72	5.2	120	13	3.8		1.7	10	2.1	5.1	21		
SC	Surficial	F-66-S-1	8.0	15	28	88	150	32	80	53	5.6	87	10				3.2	3.0	9.6	28		
SC	Surficial	L-66-S-1	2.6	1.6	3.8	5.6	6.9	3.4	5.1	3.5		5.2					0.73		0.74	0.54		
SC	Surficial	C-66-S-1		18	47	140	200	39	100	64		120					9.6			22		
SC	Depth	F-60-S-3	19	51	57	260	520	170	270	170	31	250	31	7.6	4.9	14	8.8	16	42	59		
SC	Depth	H-52-S-2	26	38	56	88	160	56	84	54	17	95	21	4.6	2.4	8.0	5.7	5.0	28	36	3.6	
SC	Depth	F-60-S-2	3.8	11	15	49	92	19	49	28		46	5.9	1.8	1.1			2.4	4.1	13		
SC	Depth	H-52-S-3	0.31	0.87	2.4	5.6	9.7	2.0	5.2	3.3		6.0	0.66					0.40	0.48	1.4		
SC	Depth	F-66-S-3	0.51	0.78	1	3.0	5.4	1.3	2.8	2.0		3.1							0.25	0.8		
SC	Depth	F-66-S-2	0.81	0.42	0.84	1.8	3.2					1.9	0.6							4.3		

* Data to be used only for fingerprint analysis due to analytical problems discussed in text and in MDH 2006

Attachment 8 (cont'd)

Polycyclic aromatic hydrocarbons (µg/kg) in 2003 sediment samples *

Sample Location	Sample Depth	Sample Number	*1,8-Dinitropyrene*	**Fluoranthene**	**Fluorene**	***Ideno(1,2,3-c,d)pyrene***	*3-Methylcholanthrene*	*5-Methylchrysene*	**2-Methylnaphthalene**	**Naphthalene**	*5-Nitroacenaphthene*	*6-Nitrochrysene*	*2-Nitrofluorene*	*1-Nitropyrene*	*4-Nitropyrene*	Perylene	**Phenanthrene**	**Pyrene**	*tPEQ*	**tEPA-PAH**	tPAH (includes all PAHs analyzed)
WMP	Surficial	G-12-S-1		22,000	4,100	3,400		590	150	310						410	12,000	14,000	**31199**	**110460**	**116908**
WMP	Surficial	G-14-S-1		12	2.2	9.0			88	110						6.8	5.2	11	**100**	**301**	**327**
WMP	Surficial	H-2-S-1		1,400	450	330		460	100	670						130	1,000	1,200	**4116**	**10310**	**11879**
WMP	Surficial	K-42-S-1		1,400	66	120		110	120	510						60	420	940	**1918**	**7370**	**8136**
WMP	Surficial	0-12-S-1		590	76	150		160	6.8	17						100	310	420	**1910**	**3944**	**4592**
WMP	Surficial	S-16-S-1		9.5	1.1	1.5			0.98	2.1	1.3			4.5		11	3.4	8.1	**16**	**54**	**78**
WMP	Surficial	E-22-S-1		520	46	120		150	14	51						120	180	540	**1524**	**3509**	**4102**
WMP	Surficial	L-2-S-1		16	5.0	8.0		3.2	6.4	26				32		41	14	12	**154**	**183**	**281**
WMP	Surficial	H-6-S-1		4,500	1,100	560		790	270	1,200						190	2,600	2,900	**8812**	**24210**	**26359**
WMP	Surficial	I-30-S-1		430	110	79		700	21	68						58	450	570	**1841**	**3360**	**4444**
WMP	Surficial	K-30-S-1		470	64	95		280	41	87						59	270	460	**1317**	**3033**	**3654**
WMP	Surficial	L-8-S-1		280	59	150			12	16						72	250	280	**3069**	**2910**	**3620**
WMP	Surficial	C-26-S-1		21	4.1	7.2		5.3	300	390						4.3	12	15	**77**	**854**	**883**
WMP	Surficial	A-30-S-1		200	25	60			11	82						34	62	160	**599**	**1418**	**1599**
WMP	Surficial	I-4-S-1		11,000	1,500	1,400										540	4,100	8,100	**11775**	**49920**	**52980**
WMP	Surficial	K-10-S-1		150	48	25		18		9.7						25	94	98	**214**	**829**	**910**
WMP	Depth	A-30-S-2		15,000	1,100	2,000			130	660						990	7,400	10,000	**20680**	**70350**	**76970**
WMP	Depth	L-8-S-2		5,500	500	840			16	51						230	1,600	3,900	**9618**	**25447**	**27430**
WMP	Depth	H-6-S-2		66,000	13,000	140		7,600	1,800	4,300						2,900	32,000	44,000	**83624**	**318240**	**342850**
WMP	Depth	I-4-S-2		370	89	48		42		8.2				50		32	200	250	**539**	**1785**	**1999**
WMP	Depth	I-30-S-2		1,500	94	260		340	25	69						110	220	1,100	**2994**	**7069**	**8044**
WMP	Depth	K-10-S-2		3,200	550	470		270		30						270	1,700	2,200	**4887**	**15744**	**17132**
WMP	Depth	L-8-S-3		36	5.1	3.6				0.92						68	14	25	**38**	**158**	**233**
WMP	Depth	A-30-S-3		20	3.2	4.8			3.1	7.2						28	12	13	**48**	**137**	**176**
WMP	Depth	H-6-S-3		2,600	490	410		390	94	380						230	1,200	1,700	**4511**	**13514**	**14931**
WMP	Depth	I-30-S-3		1.1					0.40	0.73						20	0.70	0.78	**0.06**	**5.23**	**25.23**
WMP	Depth	K-10-S-3		0.94						0.42							0.71	0.68	**0.04**	**4.25**	**4.25**
SC	Surficial	F-42-S-1		57,000	12,000	6,200		4,600	710	1,200						2,600	49,000	35,000	**76467**	**291390**	**316400**
SC	Surficial	H-52-S-1		350	61	83		83	12	67						58	150	250	**1616**	**2302**	**2767**
SC	Surficial	F-60-S-1		200	9.9	38		26	2.4	33						18	42	150	**662**	**1141**	**1312**
SC	Surficial	H-44-S-1		7,300	1,500	1,300		790	230	720						560	6,100	3,800	**17449**	**44290**	**49796**
SC	Surficial	H-66-S-1		190	12	42		31	4.0	54						24	59	140	**493**	**1198**	**1374**
SC	Surficial	F-66-S-1		80	16	32			7.7	51						55	53	58	**523**	**796**	**953**
SC	Surficial	L-66-S-1		14	4.3				2.2	3.3						2.4	9.2	6.2	**20**	**73**	**81**
SC	Surficial	C-66-S-1		240		40				21				78		28	100	150	**377**	**1215**	**1417**
SC	Depth	F-60-S-3		510	42	170		63	16	660	6.1					44	260	380	**1643**	**3666**	**4132**
SC	Depth	H-52-S-2		160	45	54		43	20	300						32	89	130	**983**	**1422**	**1661**
SC	Depth	F-60-S-2		63	11	20		13	4.0	48						20	38	70	**277**	**545**	**628**
SC	Depth	H-52-S-3		10	0.98	2.0		1.1	0.42	2.2						5.7	5.1	6.9	**31**	**60**	**73**
SC	Depth	F-66-S-3		5.1	0.92	1.2			0.74	6.3						4.4	2.2	3.8	**14**	**38**	**46**
SC	Depth	F-66-S-2		3.5	0.9				0.9	4.7				6.0		45	3.0	2.4	**44**	**25**	**80**

* Data to be used only for fingerprint analysis due to analytical problems discussed in text and in MDH 2006

Attachment 9

Ratios of polycyclic aromatic hydrocarbons in 2003 sediment sample data *

(Individual PAHs / Total EPA PAHs)

Sample Location	Sample Depth	Sample Number	Sample Date	Total # of PAH analytes in sample	# of "EPA PAHs" in sample	# of cPAHs in sample	Acenaphthene	Acenaphthylene	Anthracene	Benzo(a)anthracene	Benzo(b,j,k)fluoranthene	Benzo(g,h,i)perylene	Benzo(a)pyrene	Benzo(e)pyrene	Carbazole	Chrysene	Dibenzo(a,h)anthracene	Dibenz[a,h]acridine	Dibenz[a,j]acridine	7H-Dibenzo[c,g]carbazole	Dibenzo[a,e]pyrene	Dibenzo[a,h]pyrene	Dibenzo[a,i]pyrene
WMP	**Surficial**	**G-12-S-1**	**9/20/2003**	**26**	**16**	**14**	**0.0226**	**0.00235**	**0.0588**	**0.0905**	**0.145**	**0.0272**	**0.076**	**0.0308**		**0.0679**	**0.00308**	**0.00109**		**0.000525**	**0.00199**	**0.000996**	**0.00118**
WMP	**Surficial**	**G-14-S-1**	**9/23/2003**	**26**	**16**	**14**	**0.00186**	**0.00532**	**0.00998**	**0.0259**	**0.0665**	**0.0326**	**0.0399**	**0.0319**		**0.0223**	**0.00599**	**0.00183**	**0.0012**	**0.00123**	**0.00532**	**0.00432**	**0.00432**
WMP	**Surficial**	**H-2-S-1**	**9/20/2003**	**27**	**16**	**14**	**0.0257**	**0.0352**	**0.0438**	**0.0804**	**0.133**	**0.039**	**0.069**	**0.0428**	**0.0162**	**0.0781**	**0.0114**	**0.00343**		**0.00205**	**0.00952**	**0.00271**	**0.00885**
WMP	**Surficial**	**K-42-S-1**	**9/23/2003**	**27**	**16**	**14**	**0.00271**	**0.01**	**0.0136**	**0.107**	**0.163**	**0.0163**	**0.0936**	**0.0597**	**0.00258**	**0.103**	**0.00543**	**0.00149**	**0.000909**	**0.000814**	**0.00393**	**0.000936**	**0.0019**
WMP	**Surficial**	**0-12-S-1**	**9/22/2003**	**25**	**16**	**13**	**0.0129**	**0.00406**	**0.0431**	**0.0811**	**0.208**	**0.0355**	**0.112**	**0.0532**		**0.0964**	**0.00938**	**0.00355**		**0.00355**	**0.0101**	**0.0038**	**0.0038**
WMP	**Surficial**	**S-16-S-1**	**9/22/2003**	**25**	**16**	**13**	**0.00911**	**0.0172**	**0.0211**	**0.0911**	**0.141**	**0.0489**	**0.102**	**0.0828**		**0.1**	**0.0166**			**0.0391**			**0.0286**
WMP	**Surficial**	**E-22-S-1**	**9/22/2003**	**24**	**16**	**12**	**0.00427**	**0.00798**	**0.0313**	**0.111**	**0.185**	**0.0342**	**0.0969**	**0.0541**		**0.0997**	**0.00997**	**0.00427**			**0.00912**	**0.00313**	**0.00313**
WMP	**Surficial**	**L-2-S-1**	**9/20/2003**	**24**	**16**	**12**	**0.00765**	**0.0481**	**0.0361**	**0.0765**	**0.131**	**0.047**	**0.0875**	**0.0487**		**0.0711**	**0.0169**				**0.00536**	**0.0104**	**0.0252**
WMP	**Surficial**	**H-6-S-1**	**9/16/2003**	**23**	**16**	**11**	**0.0405**	**0.0095**	**0.062**	**0.0867**	**0.107**	**0.0215**	**0.0578**	**0.0273**		**0.0661**	**0.0062**					**0.00264**	**0.00537**
WMP	**Surficial**	**I-30-S-1**	**9/17/2003**	**23**	**16**	**11**	**0.0104**	**0.0104**	**0.0357**	**0.0893**	**0.101**	**0.0387**	**0.0655**	**0.0655**		**0.125**	**0.00952**				**0.00774**	**0.00357**	**0.00327**
WMP	**Surficial**	**K-30-S-1**	**9/22/2003**	**23**	**16**	**11**	**0.0116**	**0.0113**	**0.0307**	**0.0906**	**0.145**	**0.0349**	**0.0823**	**0.0614**		**0.106**	**0.0112**				**0.00906**	**0.00418**	
WMP	**Surficial**	**L-8-S-1**	**9/18/2003**	**24**	**16**	**11**	**0.0137**	**0.00722**	**0.0344**	**0.0653**	**0.182**	**0.0687**	**0.168**	**0.113**	**0.0199**	**0.0756**	**0.0247**				**0.0196**	**0.00447**	**0.0196**
WMP	Surficial	C-26-S-1	9/22/2003	23	16	10	0.00164	0.00515	0.00574	0.0211	0.0375	0.0089	0.0211	0.0129	0.00305	0.0187	0.00258				0.00176		0.00112
WMP	Surficial	A-30-S-1	9/17/2003	21	16	9	0.00987	0.019	0.0219	0.0987	0.169	0.0465	0.0917	0.0642		0.106	0.0141				0.0113	0.00599	
WMP	Surficial	I-4-S-1	9/19/2003	17	13	8	0.0154	0.00441	0.0601	0.0962	0.144		0.0761	0.0341		0.0741	0.00661				0.00401		
WMP	Surficial	K-10-S-1	9/17/2003	19	15	8	0.0615	0.00374	0.0615	0.0784	0.121	0.029	0.0639	0.0314		0.0615	0.00736						
WMP	**Depth**	**A-30-S-2**	**9/17/2003**	**26**	**16**	**13**	**0.00199**	**0.0122**	**0.0341**	**0.0896**	**0.134**	**0.027**	**0.0682**	**0.0441**	**0.00697**	**0.107**	**0.0108**	**0.00199**	**0.000554**	**0.000867**	**0.00711**	**0.00171**	**0.00256**
WMP	**Depth**	**L-8-S-2**	**9/18/2003**	**25**	**16**	**13**	**0.00943**	**0.00314**	**0.055**	**0.0982**	**0.153**	**0.0291**	**0.0825**	**0.0358**		**0.0747**	**0.00707**	**0.00232**		**0.00122**	**0.00629**	**0.00259**	**0.00314**
WMP	**Depth**	**H-6-S-2**	**9/16/2003**	**23**	**16**	**11**	**0.0314**	**0.00377**	**0.0628**	**0.0974**	**0.132**	**0.0242**	**0.0691**	**0.0286**		**0.066**	**0.0066**		**0.000943**	**0.00066**			**0.0022**
WMP	**Depth**	**I-4-S-2**	**9/19/2003**	**22**	**15**	**11**	**0.0263**	**0.00488**	**0.0672**	**0.0897**	**0.118**	**0.0247**	**0.0616**	**0.0286**		**0.0616**	**0.00544**				**0.00392**	**0.00538**	
WMP	**Depth**	**I-30-S-2**	**9/17/2003**	**23**	**16**	**11**	**0.00297**	**0.00863**	**0.0198**	**0.11**	**0.17**	**0.0368**	**0.0891**	**0.0467**		**0.0905**	**0.00976**			**0.00311**		**0.00311**	**0.00297**
WMP	**Depth**	**K-10-S-2**	**9/17/2003**	**22**	**15**	**11**	**0.021**	**0.00216**	**0.0699**	**0.0889**	**0.133**	**0.0273**	**0.0699**	**0.0305**		**0.0635**	**0.00635**				**0.00445**	**0.00286**	**0.00273**
WMP	Depth	L-8-S-3	9/18/2003	21	15	10	0.019	0.00279	0.0696	0.0949	0.12	0.0209	0.0614	0.0272		0.0696	0.00582				0.00367	0.00266	0.00184
WMP	Depth	A-30-S-3	9/17/2003	21	16	9	0.00948	0.0117	0.0328	0.0948	0.153	0.0328	0.0802	0.0481		0.109	0.0139				0.00802	0.00467	
WMP	Depth	H-6-S-3	9/16/2003	21	15	9	0.0274	0.00444	0.0577	0.0962	0.133	0.0266	0.0733	0.0318		0.0725					0.0074	0.00496	
WMP	Depth	I-30-S-3	9/17/2003	10	9	2	0.0478		0.0516	0.0994						0.0918							
WMP	Depth	K-10-S-3	9/17/2003	9	9	2	0.0659	0.0424	0.08	0.0824						0.0824							
SC	**Surficial**	**F-42-S-1**	**9/23/2003**	**28**	**16**	**15**	**0.0014**	**0.0154**	**0.0464**	**0.0739**	**0.0952**	**0.0182**	**0.0539**	**0.0301**	**0.00311**	**0.0589**	**0.00551**	**0.00154**	**0.000551**	**0.000526**	**0.00413**	**0.00099**	**0.00123**
SC	**Surficial**	**H-52-S-1**	**9/19/2003**	**27**	**16**	**14**	**0.00565**	**0.0326**	**0.0248**	**0.0956**	**0.174**	**0.0365**	**0.0912**	**0.0608**	**0.00869**	**0.0956**	**0.0217**	**0.00478**	**0.00226**	**0.00695**	**0.00565**	**0.00478**	**0.0109**
SC	**Surficial**	**F-60-S-1**	**9/19/2003**	**26**	**16**	**13**	**0.00333**	**0.0158**	**0.0184**	**0.114**	**0.158**	**0.0333**	**0.114**	**0.0561**	**0.00272**	**0.114**	**0.0131**	**0.0028**	**0.00158**	**0.00526**	**0.00351**		**0.0167**
SC	**Surficial**	**H-44-S-1**	**9/24/2003**	**26**	**16**	**13**	**0.00226**	**0.0294**	**0.0429**	**0.0971**	**0.147**	**0.0294**	**0.0858**	**0.0497**	**0.007**	**0.0835**	**0.00993**	**0.00271**		**0.00126**	**0.00858**	**0.00248**	**0.00406**
SC	**Surficial**	**H-66-S-1**	**9/24/2003**	**26**	**16**	**13**	**0.00275**	**0.0184**	**0.0225**	**0.108**	**0.184**	**0.035**	**0.1**	**0.0601**	**0.00434**	**0.1**	**0.0108**	**0.00317**		**0.00142**	**0.00835**	**0.00175**	**0.00426**
SC	Surficial	F-66-S-1	9/22/2003	23	16	10	0.0101	0.0189	0.0352	0.111	0.189	0.0402	0.101	0.0666	0.00704	0.109	0.0126				0.00402	0.00377	0.0121
SC	Surficial	L-66-S-1	9/23/2003	22	16	10	0.0231	0.0176	0.0396	0.0848	0.133	0.0459	0.084	0.0547		0.0792	0.00982				0.0101		0.00792
SC	Surficial	C-66-S-1	9/24/2003	17	12	8		0.0148	0.0387	0.115	0.165	0.0321	0.0823	0.0527		0.0988					0.0079		
SC	**Depth**	**F-60-S-3**	**9/19/2003**	**28**	**16**	**15**	**0.00518**	**0.0139**	**0.0155**	**0.0709**	**0.142**	**0.0464**	**0.0736**	**0.0464**	**0.00846**	**0.0682**	**0.00846**	**0.00207**	**0.00134**	**0.00382**	**0.0024**	**0.00436**	**0.0115**
SC	**Depth**	**H-52-S-2**	**9/19/2003**	**28**	**16**	**15**	**0.0183**	**0.0267**	**0.0394**	**0.0619**	**0.113**	**0.0394**	**0.0591**	**0.038**	**0.012**	**0.0668**	**0.0148**	**0.00323**	**0.00169**	**0.00563**	**0.00401**	**0.00352**	**0.0197**
SC	**Depth**	**F-60-S-2**	**9/19/2003**	**24**	**16**	**12**	**0.00698**	**0.0202**	**0.0275**	**0.09**	**0.169**	**0.0349**	**0.09**	**0.0514**		**0.0845**	**0.0108**	**0.0033**	**0.00202**			**0.00441**	**0.00753**
SC	Depth	H-52-S-3	9/19/2003	22	16	10	0.00514	0.0144	0.0398	0.0928	0.161	0.0331	0.0862	0.0547		0.0994	0.0109					0.00663	0.00795
SC	Depth	F-66-S-3	9/22/2003	19	15	7	0.0134	0.0204	0.0262	0.0786	0.142	0.0341	0.0734	0.0524		0.0813							0.00655
SC	Depth	F-66-S-2	9/22/2003	16	13	6	0.0324	0.0168	0.0336	0.0721	0.128					0.0761	0.024						

***** Bolded data used in fingerprint analyses

Ratios of polycyclic aromatic hydrocarbons in 2003 sediment sample data * (Individual PAHs / Total EPA PAHs)

Sample Location	Sample Depth	Sample Number	*Dibenzo[a,l]pyrene*	*7,12-Dimethylbenzanthracene*	*1,6-Dinitropyrene*	*1,8-Dinitropyrene*	**Fluoranthene**	**Fluorene**	***Ideno(1,2,3-c,d)pyrene***	*3-Methylcholanthrene*	*5-Methylchrysene*	**2-Methylnaphthalene**	**Naphthalene**	*5-Nitroacenaphthene*	*6-Nitrochrysene*	*2-Nitrofluorene*	*1-Nitropyrene*	*4-Nitropyrene*	Perylene	**Phenanthrene**	**Pyrene**	**Σ EPA PAH Ratios**	Σ all PAH Ratios	*Σ cPAH Ratios*
WMP	**Surficial**	**G-12-S-1**	**0.0118**	**0.000996**			**0.199**	**0.0371**	**0.0308**		**0.00534**	**0.00136**	**0.00281**						**0.00371**	**0.109**	**0.127**	**1.0**	1.06	*0.437*
WMP	**Surficial**	**G-14-S-1**	**0.0143**	**0.00133**			**0.0399**	**0.00732**	**0.0299**			**0.293**	**0.366**						**0.0226**	**0.0173**	**0.0366**	**1.0**	**1.09**	***0.224***
WMP	**Surficial**	**H-2-S-1**	**0.0224**	**0.00771**			**0.133**	**0.0395**	**0.0362**		**0.0438**	**0.01**	**0.0652**						**0.0138**	**0.0857**	**0.114**	**1.0**	1.17	*0.509*
WMP	**Surficial**	**K-42-S-1**	**0.00855**				**0.19**	**0.00896**	**0.0163**		**0.0149**	**0.0163**	**0.0692**						**0.00814**	**0.057**	**0.128**	**1.0**	1.1	*0.522*
WMP	**Surficial**	**0-12-S-1**	**0.0203**				**0.15**	**0.0193**	**0.038**		**0.0406**	**0.00172**	**0.00431**						**0.0254**	**0.0786**	**0.106**	**1.0**	1.16	*0.63*
WMP	**Surficial**	**S-16-S-1**	**0.00948**				**0.154**	**0.0188**	**0.0301**		**0.114**	**0.0172**	**0.0331**	**0.0196**			**0.0677**	**0.0256**	**0.271**	**0.0625**	**0.136**	**1.0**	1.66	*0.786*
WMP	**Surficial**	**E-22-S-1**	**0.0182**				**0.148**	**0.0131**	**0.0342**		**0.0427**	**0.00399**	**0.0145**						**0.0342**	**0.0513**	**0.154**	**1.0**	1.17	*0.618*
WMP	**Surficial**	**L-2-S-1**	**0.0323**				**0.0875**	**0.0273**	**0.0437**		**0.0175**	**0.035**	**0.142**				**0.175**		**0.224**	**0.0765**	**0.0656**	**1.0**	1.54	*0.693*
WMP	**Surficial**	**H-6-S-1**	**0.0112**	**0.00186**			**0.186**	**0.0454**	**0.0231**		**0.0326**	**0.0112**	**0.0496**						**0.00785**	**0.107**	**0.12**	**1.0**	1.09	*0.401*
WMP	**Surficial**	**I-30-S-1**	**0.017**				**0.128**	**0.0327**	**0.0235**		**0.208**	**0.00625**	**0.0202**						**0.0173**	**0.134**	**0.17**	**1.0**	1.32	*0.654*
WMP	**Surficial**	**K-30-S-1**	**0.0185**	**0.0173**			**0.149**	**0.0211**	**0.0328**		**0.0879**	**0.0117**	**0.0289**						**0.0184**	**0.0837**	**0.149**	**1.0**	1.22	*0.605*
WMP	**Surficial**	**L-8-S-1**	**0.0344**	**0.0079**			**0.0962**	**0.0203**	**0.0515**			**0.00412**	**0.0055**						**0.0247**	**0.0859**	**0.0962**	**1.0**	1.24	*0.654*
WMP	Surficial	C-26-S-1	0.0041				0.0246	0.0048	0.00843		0.00621	0.351	0.457						0.00504	0.0141	0.0176	**1.0**	1.03	*0.123*
WMP	Surficial	A-30-S-1	0.0219				0.141	0.0176	0.0423			0.00776	0.0578						0.024	0.0437	0.113	**1.0**	1.13	*0.561*
WMP	Surficial	I-4-S-1	0.0124				0.22	0.03	0.028										0.0108	0.0821	0.162	**1.0**	1.06	*0.442*
WMP	Surficial	K-10-S-1	0.0145				0.181	0.0579	0.0302		0.0217		0.0117						0.0302	0.113	0.118	**1.0**	1.1	*0.398*
WMP	**Depth**	**A-30-S-2**	**0.0142**				**0.213**	**0.0156**	**0.0284**			**0.00185**	**0.00938**						**0.0141**	**0.105**	**0.142**	**1.0**	1.09	*0.466*
WMP	**Depth**	**L-8-S-2**	**0.0165**	**0.00106**			**0.216**	**0.0196**	**0.033**			**0.000629**	**0.002**						**0.00904**	**0.0629**	**0.153**	**1.0**	1.08	*0.482*
WMP	**Depth**	**H-6-S-2**	**0.0119**				**0.207**	**0.0408**	**0.00044**		**0.0239**	**0.00566**	**0.0135**						**0.00911**	**0.101**	**0.138**	**1.0**	1.08	*0.411*
WMP	**Depth**	**I-4-S-2**	**0.0129**				**0.207**	**0.0499**	**0.0269**		**0.0235**		**0.00459**				**0.028**		**0.0179**	**0.112**	**0.14**	**1.0**	1.12	*0.437*
WMP	**Depth**	**I-30-S-2**	**0.0184**				**0.212**	**0.0133**	**0.0368**		**0.0481**	**0.00354**	**0.00976**						**0.0156**	**0.0311**	**0.156**	**1.0**	1.14	*0.582*
WMP	**Depth**	**K-10-S-2**	**0.0133**				**0.203**	**0.0349**	**0.0299**		**0.0171**		**0.00191**						**0.0171**	**0.108**	**0.14**	**1.0**	1.09	*0.432*
WMP	Depth	L-8-S-3	0.0101				0.228	0.0323	0.0228				0.00582						0.43	0.0886	0.158	**1.0**	1.48	*0.393*
WMP	Depth	A-30-S-3	0.0175				0.146	0.0233	0.035			0.0226	0.0525						0.204	0.0875	0.0948	**1.0**	1.28	*0.517*
WMP	Depth	H-6-S-3	0.0148				0.192	0.0363	0.0303		0.0289	0.00696	0.0281						0.017	0.0888	0.126	**1.0**	1.1	*0.462*
WMP	Depth	I-30-S-3					0.21					0.0765	0.14						3.82	0.134	0.149	**1.0**	4.82	*0.191*
WMP	Depth	K-10-S-3					0.221						0.0988							0.167	0.16	**1.0**	1	*0.165*
SC	**Surficial**	**F-42-S-1**	**0.00889**				**0.247**	**0.0351**	**0.0182**		**0.0115**	**0.00227**	**0.00451**	**0.000276**					**0.00739**	**0.224**	**0.1**	**1.0**	1.07	*0.335*
SC	**Surficial**	**H-52-S-1**	**0.0361**				**0.152**	**0.0265**	**0.0361**		**0.0361**	**0.00521**	**0.0291**						**0.0252**	**0.0652**	**0.109**	**1.0**	1.2	*0.621*
SC	**Surficial**	**F-60-S-1**	**0.0228**				**0.175**	**0.00868**	**0.0333**		**0.0228**	**0.0021**	**0.0289**						**0.0158**	**0.0368**	**0.131**	**1.0**	1.15	*0.621*
SC	**Surficial**	**H-44-S-1**	**0.0181**				**0.165**	**0.0339**	**0.0294**		**0.0178**	**0.00519**	**0.0163**						**0.0126**	**0.138**	**0.0858**	**1.0**	1.12	*0.507*
SC	**Surficial**	**H-66-S-1**	**0.0175**				**0.159**	**0.01**	**0.035**		**0.0259**	**0.00334**	**0.0451**						**0.02**	**0.0492**	**0.117**	**1.0**	1.15	*0.601*
SC	Surficial	F-66-S-1	0.0352				0.101	0.0201	0.0402			0.00968	0.0641						0.0691	0.0666	0.0729	**1.0**	1.2	*0.617*
SC	Surficial	L-66-S-1	0.013				0.165	0.0395	0.0364		0.00887	0.0349	0.0315						0.0293	0.0871	0.0887	**1.0**	1.12	*0.467*
SC	Surficial	C-66-S-1	0.0181				0.198		0.0329				0.0173				0.0642		0.023	0.0823	0.123	**1.0**	1.17	*0.584*
SC	**Depth**	**F-60-S-3**	**0.0161**				**0.139**	**0.0115**	**0.0464**		**0.0172**	**0.00436**	**0.18**	**0.00166**					**0.012**	**0.0709**	**0.104**	**1.0**	1.13	*0.47*
SC	**Depth**	**H-52-S-2**	**0.0253**	**0.00253**			**0.113**	**0.0316**	**0.038**		**0.0302**	**0.0141**	**0.211**						**0.0225**	**0.0626**	**0.0914**	**1.0**	1.17	*0.449*
SC	**Depth**	**F-60-S-2**	**0.0239**				**0.116**	**0.0202**	**0.0367**		**0.0239**	**0.00734**	**0.0881**						**0.0367**	**0.0698**	**0.129**	**1.0**	1.15	*0.546*
SC	Depth	H-52-S-3	0.0232				0.166	0.0162	0.0331		0.0182	0.00696	0.0365						0.0945	0.0845	0.114	**1.0**	1.21	*0.539*
SC	Depth	F-66-S-3	0.021				0.134	0.0241	0.0315			0.0194	0.165						0.115	0.0577	0.0996	**1.0**	1.2	*0.434*
SC	Depth	F-66-S-2	0.172				0.14	0.036				0.036	0.188				0.24		1.8	0.12	0.0961	**1.0**	3.21	*0.713*

***** Bolded data used in fingerprint analyses

Attachment 10

Benzo[a]pyrene Potency Equivalents (µg/kg) in 2003 sediment samples *

Sample Location	Sample Depth	Sample Number	*Benzo(a)anthracene*	*Benzo(b,j,k)fluoranthene*	*Benzo(a)pyrene*	*Chrysene*	*Dibenzo(a,h)anthracene*	*Dibenz[a,h]acridine*	*Dibenz[a,j]acridine*	*7H-Dibenzo[c,g]carbazole*	*Dibenzo[a,e]pyrene*	*Dibenzo[a,h]pyrene*	*Dibenzo[a,i]pyrene*	*Dibenzo[a,l]pyrene*	*7,12-Dimethylbenzanthracene*	*1,6-Dinitropyrene*	*1,8-Dinitropyrene*	*Ideno(1,2,3-c,d)pyrene*	*3-Methylcholanthrene*	*5-Methylchrysene*	*5-Nitroacenaphthene*	*6-Nitrochrysene*	*2-Nitrofluorene*	*1-Nitropyrene*	*4-Nitropyrene*	*tPEQ*
WMP	Surficial	G-12-S-1	1000	1600	8400	75	204	12		58	220	1100	1300	13000	3300			340		590						31199
WMP	Surficial	G-14-S-1	0.78	2	12	0.067	1.08	0.055	0.036	0.37	1.6	13	13	43	12			0.9								99.888
WMP	Surficial	H-2-S-1	82	140	690	7.9	60	3.6		19	80	280	360	1900				33		460						4115.5
WMP	Surficial	K-42-S-1	79	120	690	7.6	24	1.1	0.67	6	29	69	140	630				12		110						1918.37
WMP	Surficial	0-12-S-1	32	82	440	3.8	22.2	1.4		14	40	150	150	800				15		160						1910.4
WMP	Surficial	S-16-S-1	0.48	0.68	5.2	0.05				2.6				6.3				0.15			0.026			0.45		15.936
WMP	Surficial	E-22-S-1	39	65	340	3.5	21	1.5			32	110	110	640				12		150						1524
WMP	Surficial	L-2-S-1	1.4	2.4	16	0.13	1.86				0.98	19	46	59				0.8		3.2				3.2		153.97
WMP	Surficial	H-6-S-1	210	260	1400	16	90					640	1300	2700	1350			56		790						8812
WMP	Surficial	I-30-S-1	30	34	220	4.2	19.2				26	120	110	570				7.9		700						1841.3
WMP	Surficial	K-30-S-1	28	42	240	3.2					34	140		540				9.5		280						1316.7
WMP	Surficial	L-8-S-1	19	53	490	2.2	43.2				57	130	570	1000	690			15								3069.4
WMP	Surficial	C-26-S-1	1.8	3.2	18	0.16	1.32				1.5		9.6	35				0.72		5.3						76.6
WMP	Surficial	A-30-S-1	14	24	130	1.5	12				16	85		310				6								598.5
WMP	Surficial	I-4-S-1	480	720	3800	37	198				200			6200				140								11775
WMP	Surficial	K-10-S-1	6.5	10	53	0.51	3.66							120				2.5		18						214.17
WMP	Depth	A-30-S-2	630	940	4800	75	456	14	3.9	61	500	1200	1800	10000				200								20679.9
WMP	Depth	L-8-S-2	250	390	2100	19	108	5.9		31	160	660	800	4200	810			84								9617.9
WMP	Depth	H-6-S-2	3100	4200	22000	210	1260		30	210			7000	38000				14		7600						83624
WMP	Depth	I-4-S-2	16	21	110	1.1	5.82				7	96		230				4.8		42				5		538.72
WMP	Depth	I-30-S-2	78	120	630	6.4	41.4			22		220	210	1300				26		340						2993.8
WMP	Depth	K-10-S-2	140	210	1100	10	60				70	450	430	2100				47		270						4887
WMP	Depth	L-8-S-3	1.5	1.9	9.7	0.11	0.552				0.58	4.2	2.9	16				0.36								37.802
WMP	Depth	A-30-S-3	1.3	2.1	11	0.15	1.14				1.1	6.4		24				0.48								47.67
WMP	Depth	H-6-S-3	130	180	990	9.8					100	670		2000				41		390						4510.8
WMP	Depth	I-30-S-3	0.052			0.0048																				0.0568
WMP	Depth	K-10-S-3	0.035			0.0035																				0.0385
SC	Surficial	F-42-S-1	2600	3400	19000	210	1200	56	21	260	1500	4600	6400	32000				620		4600						76467
SC	Surficial	H-52-S-1	22	40	210	2.2	30	1.1	0.52	16	13	110	250	830				8.3		83						1616.12
SC	Surficial	F-60-S-1	13	18	130	1.3	9	0.32	0.18	6	4		190	260				3.8		26						661.6
SC	Surficial	H-44-S-1	430	650	3800	37	264	12		56	380	1100	1800	8000				130		790						17449
SC	Surficial	H-66-S-1	13	22	120	1.2	7.8	0.38		1.7	10	21	51	210				4.2		31						493.28
SC	Surficial	F-66-S-1	8.8	15	80	0.87	6				3.2	30	96	280				3.2								523.07
SC	Surficial	L-66-S-1	0.56	0.69	5.1	0.052					0.73		7.4	5.4												19.932
SC	Surficial	C-66-S-1	14	20	100	1.2					9.6			220				4						7.8		376.6
SC	Depth	F-60-S-3	26	52	270	2.5	18.6	0.76	0.49	14	8.8	160	420	590				17		63	0.122					1643.272
SC	Depth	H-52-S-2	8.8	16	84	0.95	12.6	0.46	0.24	8	5.7	50	280	360	108			5.4		43						983.15
SC	Depth	F-60-S-2	4.9	9.2	49	0.46	3.54	0.18	0.11			24	41	130				2		13						277.39
SC	Depth	H-52-S-3	0.56	0.97	5.2	0.06	0.396					4	4.8	14				0.2		1.1						31.286
SC	Depth	F-66-S-3	0.3	0.54	2.8	0.031							2.5	8				0.12								14.291
SC	Depth	F-66-S-2	0.18	0.32		0.019	0.36							43										0.6		44.479

* Data to be used only for fingerprint analysis due to analytical problems discussed in text and in MDH 2006

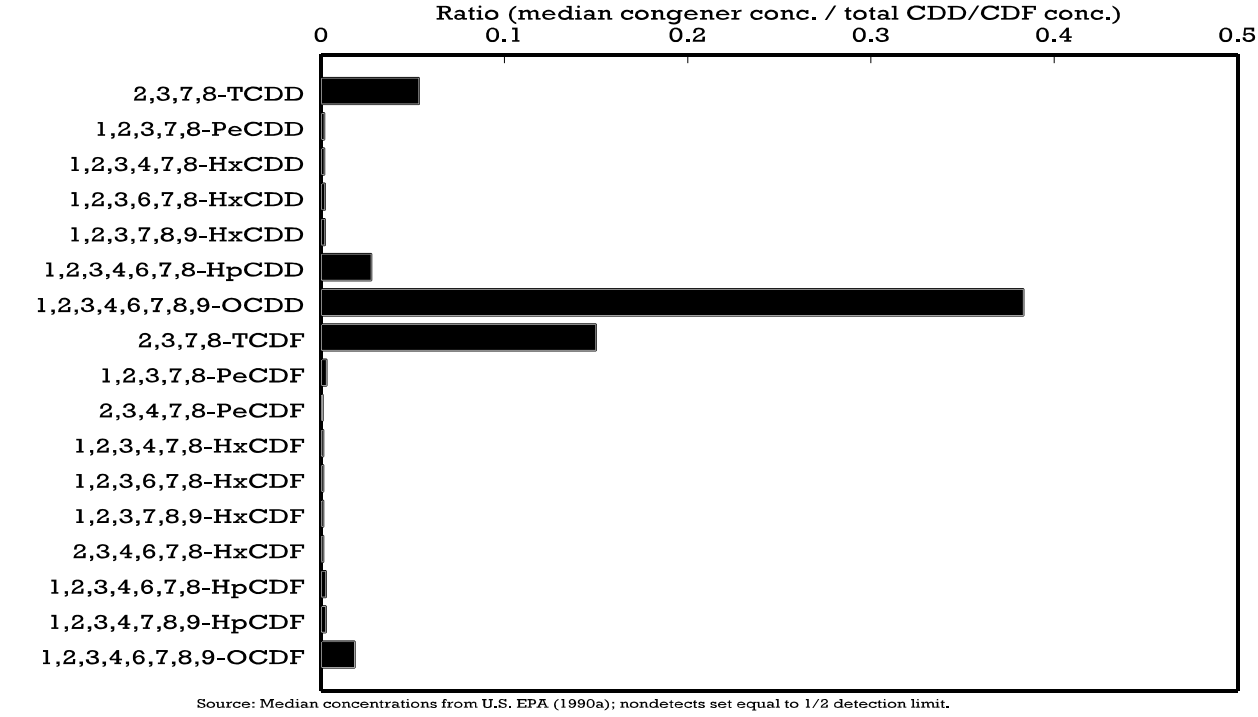
Attachment 11

Ratios of Benzo[a]pyrene Potency Equivalents (B[a]P-PEQ ratios) in 2003 sediment sample data *

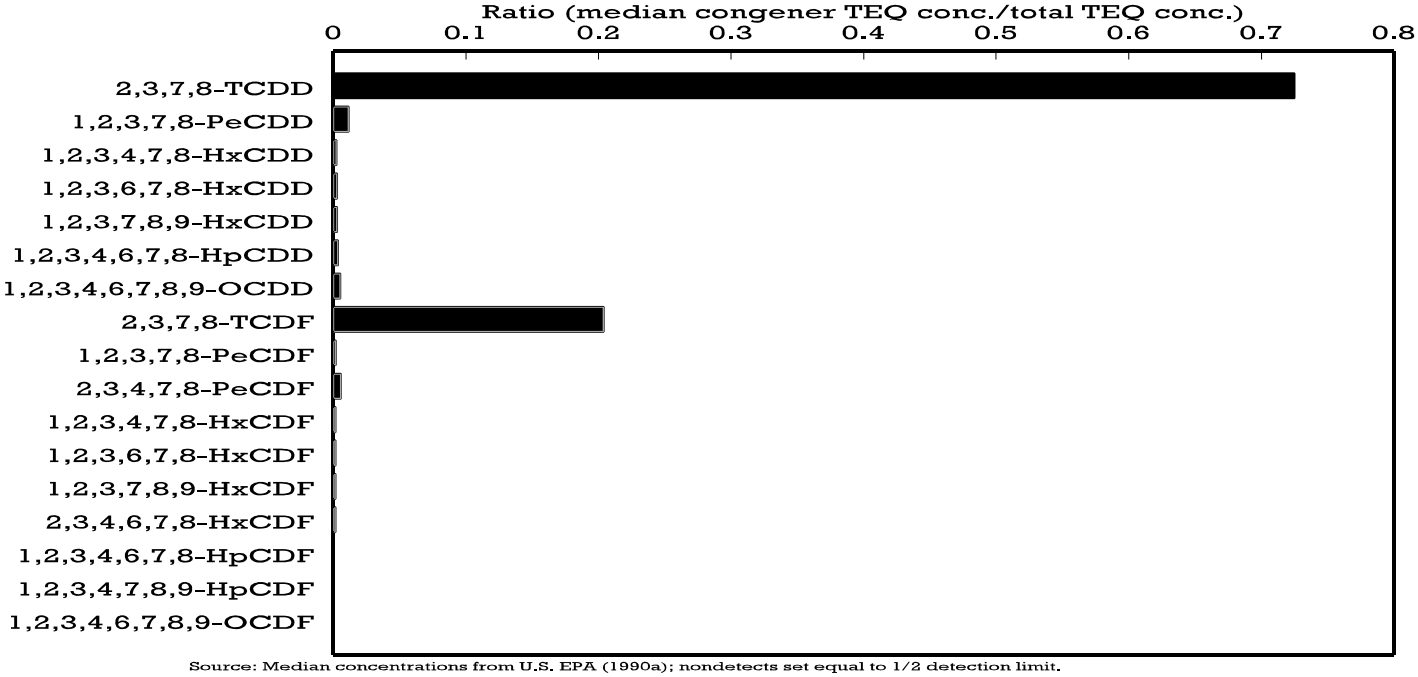
Sample Location	Sample Depth	Sample Number	(Individual cPAH PEQ / Total PEQ)																					Σ PEQ
			Benzo(a)anthracene	*Benzo(b,j,k)fluoranthene*	*Benzo(e)pyrene*	*Chrysene*	*Dibenzo(a,h)anthracene*	*Dibenz[a,h]acridine*	*Dibenz[a,j]acridine*	*7H-Dibenzo[c,g]carbazole*	*Dibenzo[a,e]pyrene*	*Dibenzo[a,h]pyrene*	*Dibenzo[a,i]pyrene*	*Dibenzo[a,l]pyrene*	*7,12-Dimethylbenzanthracene*	*1,6-Dinitropyrene*	*1,8-Dinitropyrene*	*Indeno(1,2,3-c,d)pyrene*	*3-Methylcholanthrene*	*5-Methylchrysene*	*5-Nitroacenaphthene*	*6-Nitrochrysene*	*2-Nitrofluorene*	*1-Nitropyrene*	*4-Nitropyrene*	
WMP	**Surficial**	**G-12-S-1**	**0.0321**	**0.0513**	**0.269**	**0.0024**	**0.00654**	**0.000385**		**0.00186**	**0.00705**	**0.0353**	**0.0417**	**0.417**	**0.106**			**0.0109**		**0.0189**						**1.0**
WMP	**Surficial**	**G-14-S-1**	**0.00781**	**0.02**	**0.12**	**0.000671**	**0.0108**	**0.000551**	**0.00036**	**0.0037**	**0.016**	**0.13**	**0.13**	**0.43**	**0.12**			**0.00901**								**1.0**
WMP	**Surficial**	**H-2-S-1**	**0.0199**	**0.034**	**0.168**	**0.00192**	**0.0146**	**0.000875**		**0.00462**	**0.0194**	**0.068**	**0.0875**	**0.462**				**0.00802**		**0.112**						**1.0**
WMP	**Surficial**	**K-42-S-1**	**0.0412**	**0.0626**	**0.36**	**0.00396**	**0.0125**	**0.000573**	**0.000349**	**0.00313**	**0.0151**	**0.036**	**0.073**	**0.328**				**0.00626**		**0.0573**						**1.0**
WMP	**Surficial**	**0-12-S-1**	**0.0168**	**0.0429**	**0.23**	**0.00199**	**0.0116**	**0.000733**		**0.00733**	**0.0209**	**0.0785**	**0.0785**	**0.419**				**0.00785**		**0.0838**						**1.0**
WMP	**Surficial**	**S-16-S-1**	**0.0301**	**0.0427**	**0.326**	**0.00314**				**0.163**				**0.395**				**0.00941**			**0.00163**			**0.0282**		**1.0**
WMP	**Surficial**	**E-22-S-1**	**0.0256**	**0.0427**	**0.223**	**0.0023**	**0.0138**	**0.000984**			**0.021**	**0.0722**	**0.0722**	**0.42**				**0.00787**		**0.0984**						**1.0**
WMP	**Surficial**	**L-2-S-1**	**0.00909**	**0.0156**	**0.104**	**0.000844**	**0.0121**				**0.00636**	**0.123**	**0.299**	**0.383**				**0.0052**		**0.0208**				**0.0208**		**1.0**
WMP	**Surficial**	**H-6-S-1**	**0.0238**	**0.0295**	**0.159**	**0.00182**	**0.0102**					**0.0726**	**0.148**	**0.306**	**0.153**			**0.00635**		**0.0897**						**1.0**
WMP	**Surficial**	**I-30-S-1**	**0.0163**	**0.0185**	**0.119**	**0.00228**	**0.0104**				**0.0141**	**0.0652**	**0.0597**	**0.31**				**0.00429**		**0.38**						**1.0**
WMP	**Surficial**	**K-30-S-1**	**0.0213**	**0.0319**	**0.182**	**0.00243**					**0.0258**	**0.106**		**0.41**				**0.00722**		**0.213**						**1.0**
WMP	**Surficial**	**L-8-S-1**	**0.00619**	**0.0173**	**0.16**	**0.000717**	**0.0141**				**0.0186**	**0.0424**	**0.186**	**0.326**	**0.225**			**0.00489**								**1.0**
WMP	Surficial	C-26-S-1	0.0235	0.0418	0.235	0.00209	0.0172				0.0196		0.125	0.457				0.0094		0.0692						**1.0**
WMP	Surficial	A-30-S-1	0.0234	0.0401	0.217	0.00251	0.0201				0.0267	0.142		0.518				0.01								**1.0**
WMP	Surficial	I-4-S-1	0.0408	0.0611	0.323	0.00314	0.0168				0.017			0.527				0.0119								**1.0**
WMP	Surficial	K-10-S-1	0.0303	0.0467	0.247	0.00238	0.0171							0.56				0.0117		0.084						**1.0**
WMP	**Depth**	**A-30-S-2**	**0.0305**	**0.0455**	**0.232**	**0.00363**	**0.0221**	**0.000677**	**0.000189**	**0.00295**	**0.0242**	**0.058**	**0.087**	**0.484**				**0.00967**								**1.0**
WMP	**Depth**	**L-8-S-2**	**0.026**	**0.0405**	**0.218**	**0.00198**	**0.0112**	**0.000613**		**0.00322**	**0.0166**	**0.0686**	**0.0832**	**0.437**	**0.0842**			**0.00873**								**1.0**
WMP	**Depth**	**H-6-S-2**	**0.0371**	**0.0502**	**0.263**	**0.00251**	**0.0151**		**0.000359**	**0.00251**			**0.0837**	**0.454**				**0.000167**		**0.0909**						**1.0**
WMP	**Depth**	**I-4-S-2**	**0.0297**	**0.039**	**0.204**	**0.00204**	**0.0108**				**0.013**	**0.178**		**0.427**				**0.00891**		**0.078**				**0.00928**		**1.0**
WMP	**Depth**	**I-30-S-2**	**0.0261**	**0.0401**	**0.21**	**0.00214**	**0.0138**			**0.00735**		**0.0735**	**0.0701**	**0.434**				**0.00868**		**0.114**						**1.0**
WMP	**Depth**	**K-10-S-2**	**0.0286**	**0.043**	**0.225**	**0.00205**	**0.0123**				**0.0143**	**0.0921**	**0.088**	**0.43**				**0.00962**		**0.0552**						**1.0**
WMP	Depth	L-8-S-3	0.0397	0.0503	0.257	0.00291	0.0146				0.0153	0.111	0.0767	0.423				0.00952								**1.0**
WMP	Depth	A-30-S-3	0.0273	0.0441	0.231	0.00315	0.0239				0.0231	0.134		0.503				0.0101								**1.0**
WMP	Depth	H-6-S-3	0.0288	0.0399	0.219	0.00217					0.0222	0.149		0.443				0.00909		0.0865						**1.0**
WMP	Depth	I-30-S-3	0.915			0.0845																				**1.0**
WMP	Depth	K-10-S-3	0.909			0.0909																				**1.0**
SC	**Surficial**	**F-42-S-1**	**0.034**	**0.0445**	**0.248**	**0.00275**	**0.0157**	**0.000732**	**0.000275**	**0.0034**	**0.0196**	**0.0602**	**0.0837**	**0.418**				**0.00811**		**0.0602**						**1.0**
SC	**Surficial**	**H-52-S-1**	**0.0136**	**0.0248**	**0.13**	**0.00136**	**0.0186**	**0.000681**	**0.000322**	**0.0099**	**0.00804**	**0.0681**	**0.155**	**0.514**				**0.00514**		**0.0514**						**1.0**
SC	**Surficial**	**F-60-S-1**	**0.0196**	**0.0272**	**0.196**	**0.00196**	**0.0136**	**0.000484**	**0.000272**	**0.00907**	**0.00605**		**0.287**	**0.393**				**0.00574**		**0.0393**						**1.0**
SC	**Surficial**	**H-44-S-1**	**0.0246**	**0.0373**	**0.218**	**0.00212**	**0.0151**	**0.000688**		**0.00321**	**0.0218**	**0.063**	**0.103**	**0.458**				**0.00745**		**0.0453**						**1.0**
SC	**Surficial**	**H-66-S-1**	**0.0264**	**0.0446**	**0.243**	**0.00243**	**0.0158**	**0.00077**		**0.00345**	**0.0203**	**0.0426**	**0.103**	**0.426**				**0.00851**		**0.0628**						**1.0**
SC	Surficial	F-66-S-1	0.0168	0.0287	0.153	0.00166	0.0115				0.00612	0.0574	0.184	0.535				0.00612								**1.0**
SC	Surficial	L-66-S-1	0.0281	0.0346	0.256	0.00261					0.0366		0.371	0.271												**1.0**
SC	Surficial	C-66-S-1	0.0372	0.0531	0.266	0.00319					0.0255			0.584				0.0106						0.0207		**1.0**
SC	**Depth**	**F-60-S-3**	**0.0158**	**0.0316**	**0.164**	**0.00152**	**0.0113**	**0.000462**	**0.000298**	**0.00852**	**0.00536**	**0.0974**	**0.256**	**0.359**				**0.0103**		**0.0383**	**7.42E-05**					**1.0**
SC	**Depth**	**H-52-S-2**	**0.00895**	**0.0163**	**0.0854**	**0.000966**	**0.0128**	**0.000468**	**0.000244**	**0.00814**	**0.0058**	**0.0509**	**0.285**	**0.366**	**0.11**			**0.00549**		**0.0437**						**1.0**
SC	**Depth**	**F-60-S-2**	**0.0177**	**0.0332**	**0.177**	**0.00166**	**0.0128**	**0.000649**	**0.000397**			**0.0865**	**0.148**	**0.469**				**0.00721**		**0.0469**						**1.0**
SC	Depth	H-52-S-3	0.0179	0.031	0.166	0.00192	0.0127					0.128	0.153	0.447				0.00639		0.0352						**1.0**
SC	Depth	F-66-S-3	0.021	0.0378	0.196	0.00217							0.175	0.56				0.0084								**1.0**
SC	Depth	F-66-S-2	0.00405	0.00719		0.000427	0.00809							0.967										0.0135		**1.0**

***** Bolded data used in fingerprint analyses

Attachment 12



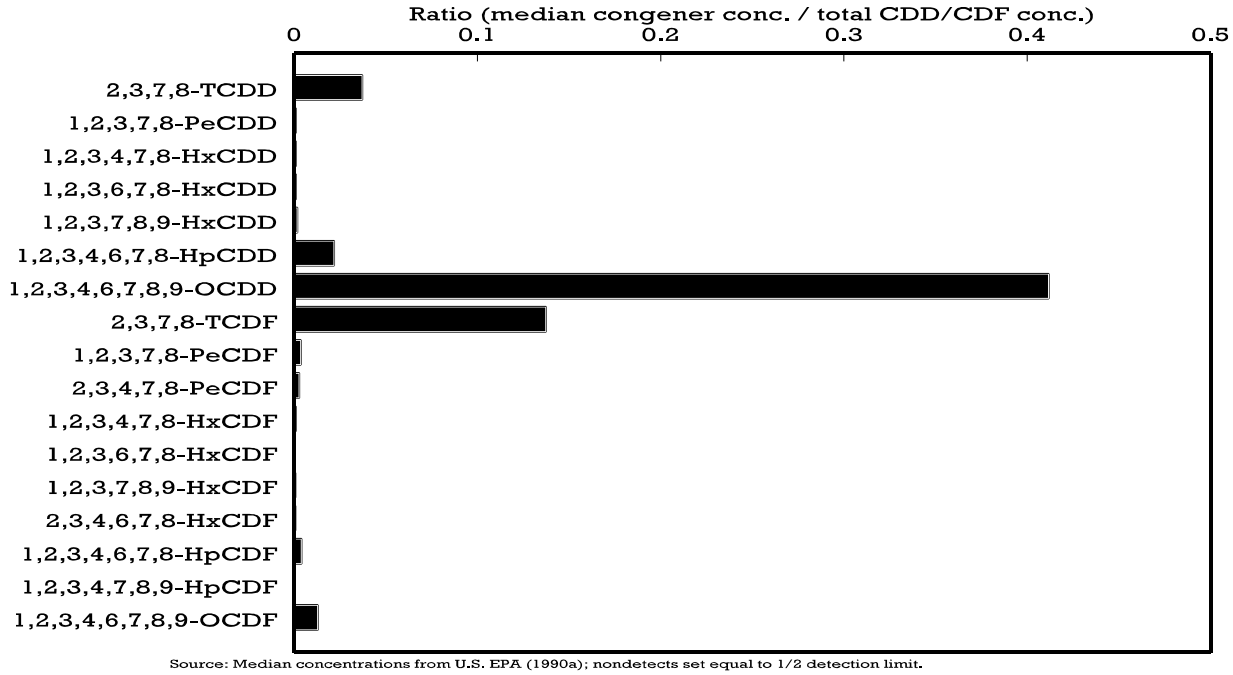
Source: Median concentrations from U.S. EPA (1990a); nondetects set equal to 1/2 detection limit.



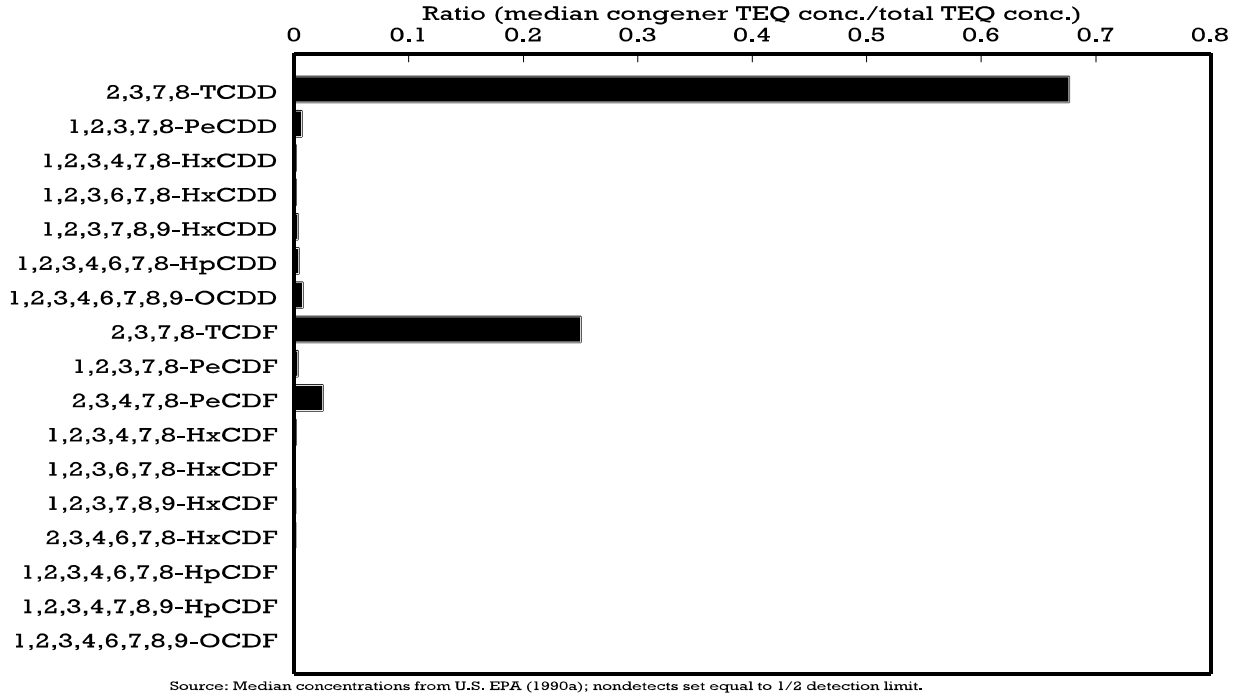
Source: Median concentrations from U.S. EPA (1990a); nondetects set equal to 1/2 detection limit.

Figure 8-1. 104 Mill Study Full Congener Analysis Results for Pulp

From EPA 2003b



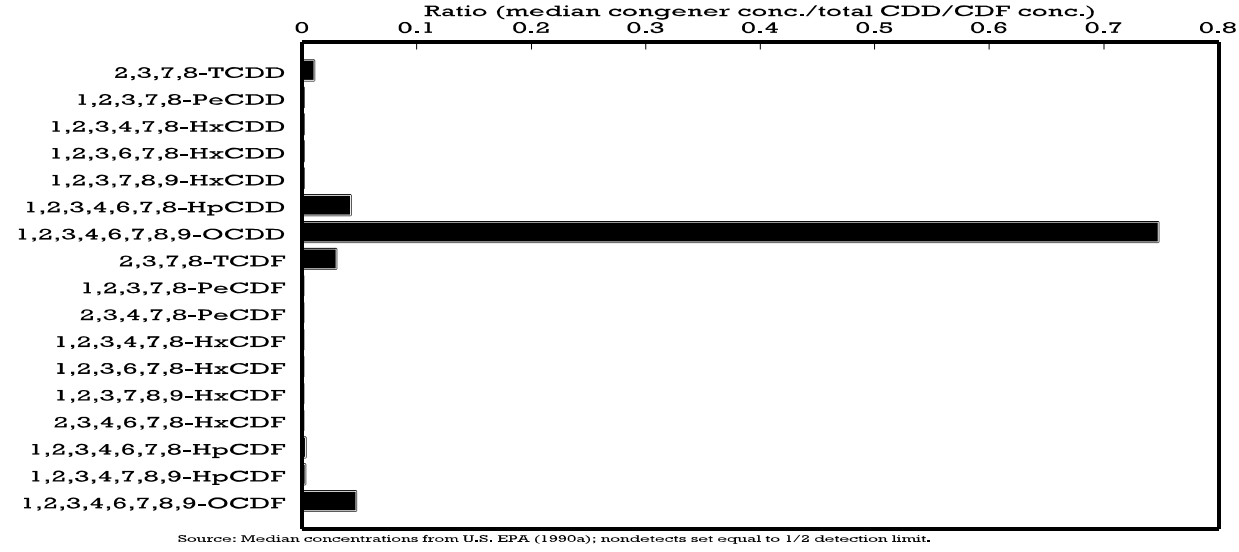
Source: Median concentrations from U.S. EPA (1990a); nondetects set equal to 1/2 detection limit.



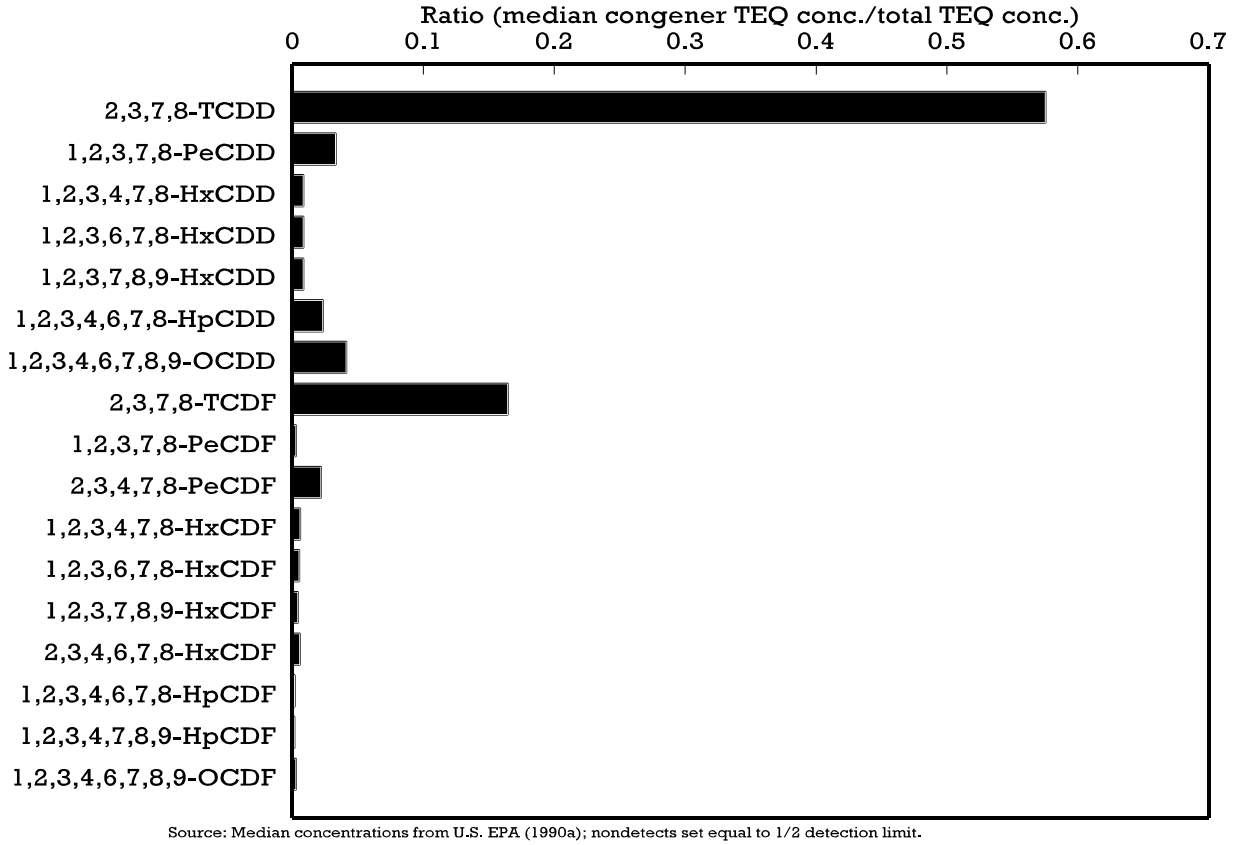
Source: Median concentrations from U.S. EPA (1990a); nondetects set equal to 1/2 detection limit.

Figure 8-2. 104 Mill Study Full Congener Analysis Results for Sludge

From EPA 2003b



Source: Median concentrations from U.S. EPA (1990a); nondetects set equal to 1/2 detection limit.



Source: Median concentrations from U.S. EPA (1990a); nondetects set equal to 1/2 detection limit.

Figure 8-3. 104 Mill Study Full Congener Analysis Results for Effluent

From EPA 2003b

Attachment 12 (Continued)

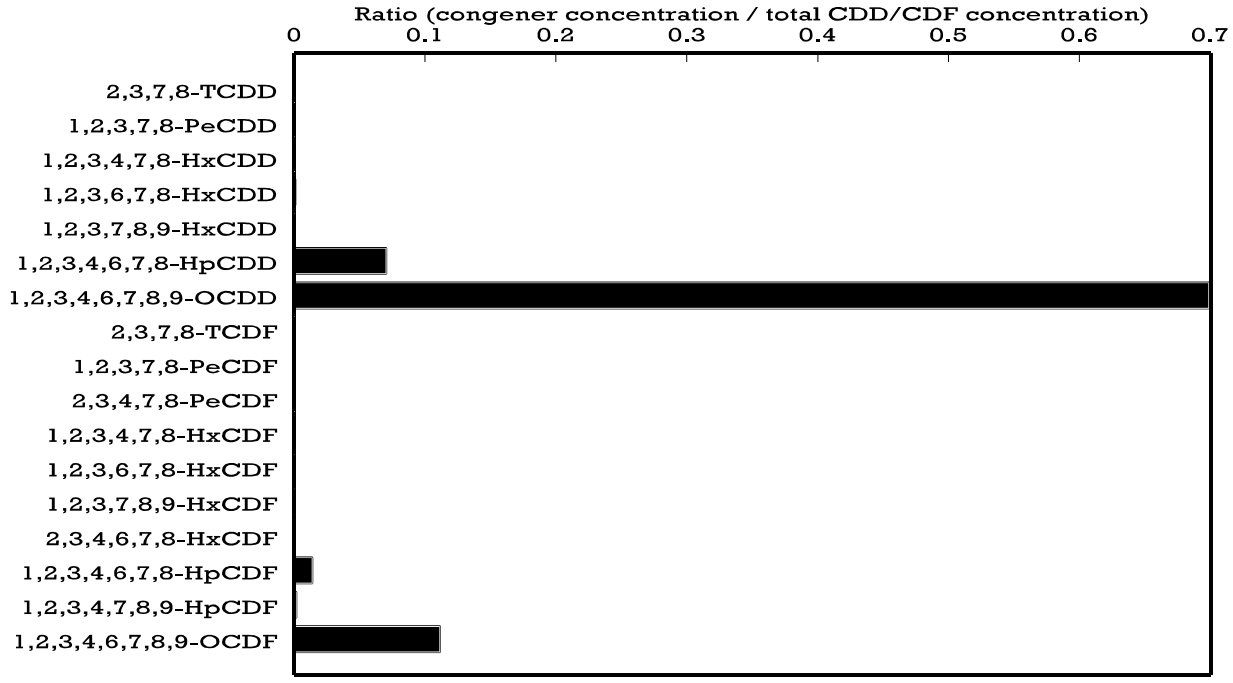
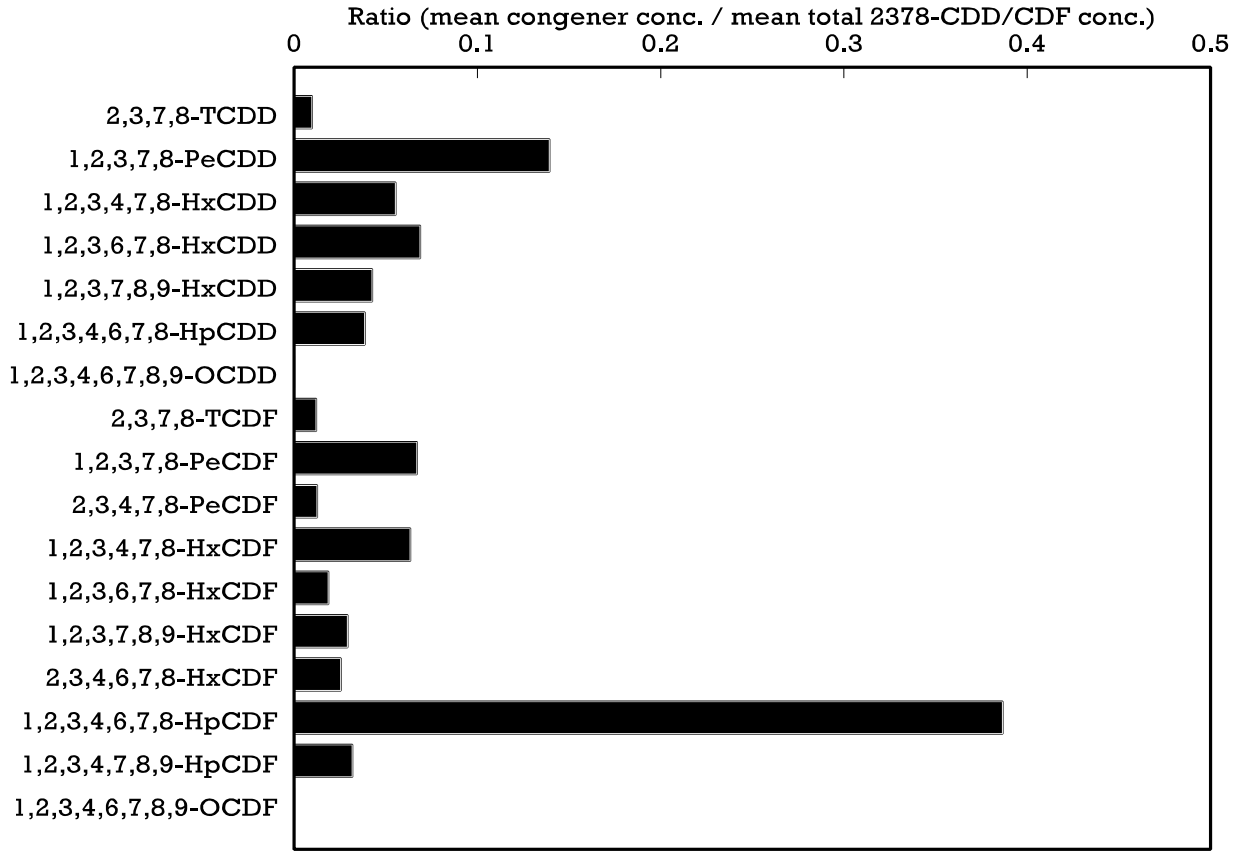


Figure 8-4. Congener Profiles for Technical PCP

From EPA 2003b

Attachment 12 (Continued)

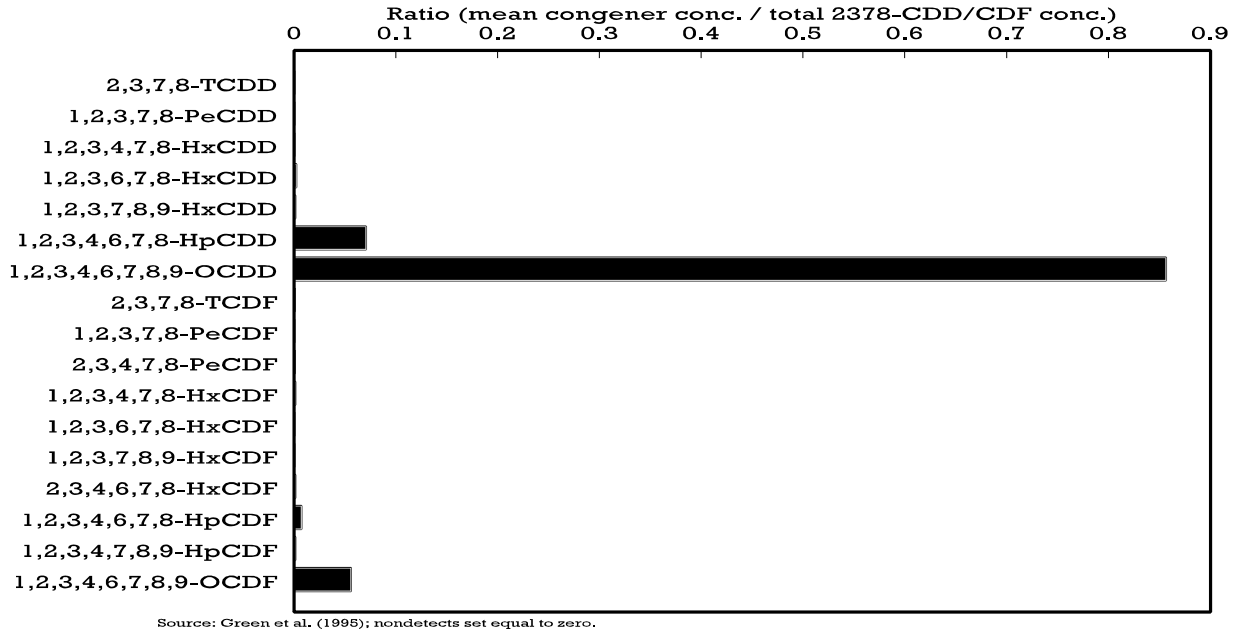


Source: Based on mean concentrations reported in Table 8-24; nondetects set equal to zero.

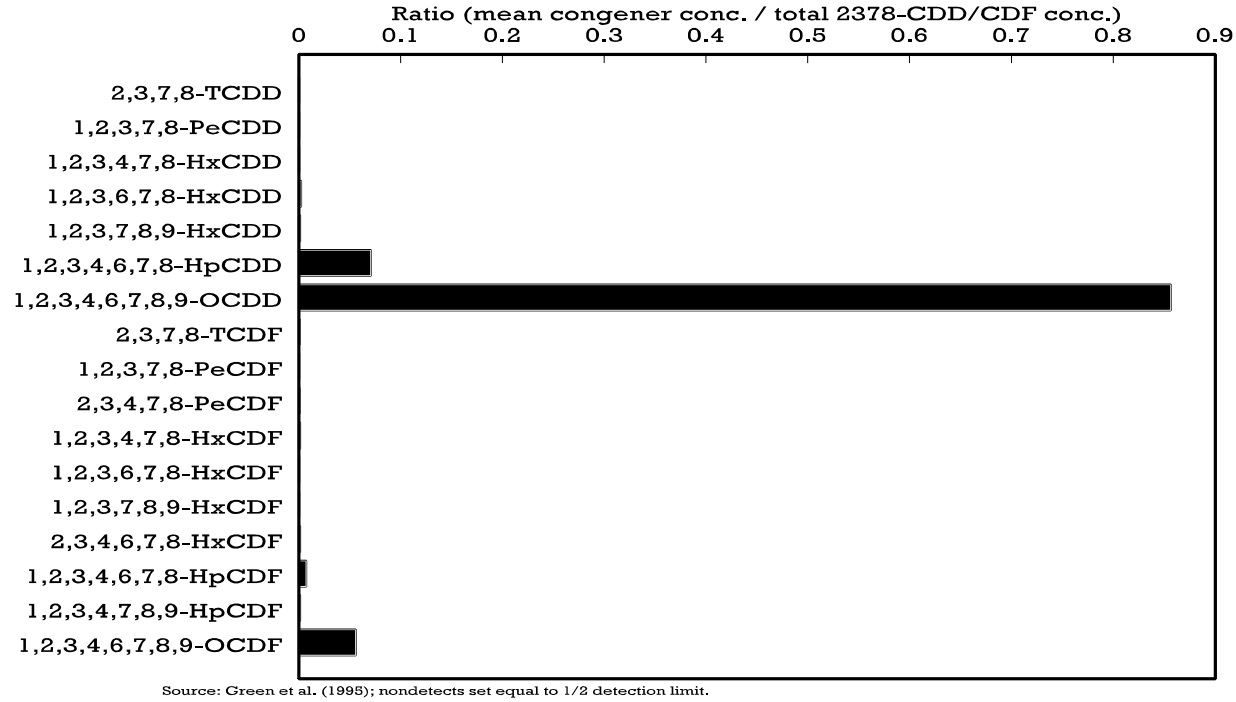
Figure 8-5. Congener Profile for 2,4-D (salts and esters)

From EPA 2003b

Attachment 12 (Continued)



Source: Green et al. (1995); nondetects set equal to zero.



Source: Green et al. (1995); nondetects set equal to 1/2 detection limit.

Figure 8-6. Congener Profiles for Sewage Sludge

From EPA 2003b