

Health Consultation

ST. LOUIS RIVER/INTERLAKE/DULUTH TAR
NATIONAL PRIORITY LIST (SUPERFUND SITE)

DULUTH, ST. LOUIS COUNTY, MINNESOTA

EPA FACILITY ID: MND039045430

APRIL 4, 2003

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.

In addition, consultations may recommend additional public health actions, such as conducting health surveillance activities to evaluate exposure or trends in adverse health outcomes; conducting biological indicators of exposure studies to assess exposure; and providing health education for health care providers and community members. This concludes the health consultation process for this site, unless additional information is obtained by ATSDR which, in the Agency's opinion, indicates a need to revise or append the conclusions previously issued.

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HEALTH CONSULTATION

Sediment Operable Unit

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Prepared by:

Minnesota Department of Health
Under a Cooperative Agreement with the
Agency for Toxic Substances and Disease Registry

FOREWORD

This document summarizes public health concerns at the St. Louis River/Interlake/Duluth Tar Superfund Site (Sediment Operable Unit), Duluth, Minnesota. It is based on a formal site evaluation prepared by the Minnesota Department of Health (MDH). A number of steps are necessary for this evaluation:

- **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's found on the site, and how people might be exposed to it. Usually, MDH does not collect its own environmental sampling data. We rely on information provided by the Minnesota Pollution Control Agency (MPCA), U.S. 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. Their report focuses on public health; that is the health impact on the community as a whole—and 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 contaminants. The role of MDH in dealing with individual sites is primarily advisory. For that reason, the evaluation report will typically recommend actions to be taken by other agencies—including EPA and MPCA. However, if an immediate health threat exists, MDH will issue a public health advisory warning 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 cleaning up the site, and community 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.

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Introduction

The St. Louis River Interlake-Duluth Tar (SLRIDT) Site (the site) is a National Priorities List (Superfund) site on the St. Louis River in Duluth, Minnesota. Beginning in about 1904, pig iron, coke, and gas were produced at this site from iron ore and coal.

Over the years, different areas of the site have been open water. Currently the site contains three embayments (see Attachment #1): Stryker Bay (approximately 35 acres), Hallett Dock Company Slip #6 (Slip #6; approximately 23 acres), and Hallett Dock Company Slip #7 / Keene Creek (Slip #7; approximately 27 acres); as well as about 130 acres of land between the inlets. The site lies about four miles upstream from the St. Louis River's outlet into Lake Superior. It is bounded by residential and light industrial areas to the north; residential areas to the west; by the St. Louis River to the south; and by a shipping dock to the east.

Approximately 960 and 4200 people live within 0.5 mile and 1 mile of the site, respectively (2000 census).

Stryker Bay, the westernmost boundary of the site, extends about one-half mile north-south and about 1000 feet in the east-west direction. Typically, within 100 feet of the shoreline, the depth of the bay drops to approximately 4 feet, and the depth across most of the bay remains a fairly constant 4 - 6 feet. Stryker Bay is shallower at the northern end and forms a small wetland at the northern tip. Storm sewers and a small stream feed this wetland. Stryker Bay is not in a shipping area. Furthermore, there are no commercial docks for large lake vessels upstream of Stryker bay on the St. Louis River. There are a number of residences along the western shore of the bay. Some of these residences have private, recreational docks in the bay. The bay is intermittently used for recreation, including swimming, water-skiing, and fishing.

Slip #6 is located in the middle of the site and extends approximately one-half mile north from the St. Louis River, with a relatively uniform width of 250 feet. The Hallett Dock Company currently uses Slip #6 as a loading facility for ships traversing the Great Lakes, as well as ocean-going ships.

The western portion of the Slip #7 / Keene Creek (Slip #7) embayment is part of the site. Slip #7 has been used in the past as a loading facility. The eastern side of Slip #7 is currently used for docking barges. Keene Creek has been redirected so that it no longer flows into Slip #7. Area residents have been observed fishing in this bay.

Seiches (a tide-like fluctuation in water level), caused by wind forces shifting water in Lake Superior, can cause 7.9 hour periodic water level oscillations of 3 centimeters (cm) to 25 cm in the St. Louis Harbor area. This oscillation is considered the driving force for mass transport in the lower St. Louis Harbor (Stortz and Sydor, 1980). Near the site, seiches can cause water level fluctuations of up to 15 cm. As the water level changes, relatively strong currents can be expected in narrow areas like the mouth of Stryker Bay (MDNR, 2001). These currents will increase mixing and turbidity and affect the sedimentation process. Furthermore, large seiches can result in a reversing of St. Louis River flow. For

example, upstream flow (26.5 cm/sec) at the site of the old Arrowhead Bridge (1/2 mile downstream from the site) is calculated to be similar to flow downstream (28.2 cm/sec) when a 15 cm seiche is modeled (Stortz and Sydor, 1980). Therefore, contamination from this site can be assumed to be dispersed upstream, as well as downstream from the site.

Concerns presently being addressed at this site are related to contaminated sediments associated with historic industrial activities. The forum for addressing these concerns is a Peer Review process that was created by the Minnesota Pollution Control (MPCA) Citizens' Board in November 1999. The Peer Review Team (PRT) includes experts in groundwater, dredging, capping and pricing of remedial alternatives. Data is presented by the MPCA and the potentially responsible parties (PRPs) to the PRT for review. At the request of the MPCA, MDH is also reviewing documents presented to the PRT and attending PRT meetings. An extensive amount of study has been conducted by the PRPs to provide information about the effectiveness and cost of proposed remedies. This health consultation reviews the product of those studies: the Data Gaps Report (Service, 2002).

MDH is specifically concerned about potential human exposure to contaminants at the present time, during any cleanup activities, and in the future. Therefore, our recent questions have been on data gaps that may significantly affect estimates of human exposure to contaminants or the longterm effectiveness of remedial actions. MDH has previously raised concerns about the cleanup of these sediments: in testimony to the Minnesota Pollution Control (MPCA) Citizens' Board (Attachment #2, (MDH, 1999)); and in a health consultation (MDH, 2001b), written in cooperation with the U.S. Agency for Toxic Substances and Disease Registry (ATSDR).

One of the focuses of the Data Gaps Report (Service, 2002) is the potential public exposure to contaminants that would be emitted during dredging of contaminated sediments. This health consultation is a review of experimental data, the proposed emissions model and conclusions of the Data Gaps Report. In addition, this Health Consultation contains a brief review of chemicals of concern; identifies routes of potential exposure; reviews concerns that are dependent on the choice of remedial option, and; provides MDH recommendations.

Potential Human Health Risks

Human health may be adversely impacted when people are exposed to significant amounts of toxic chemicals. Because individual chemicals behave differently in the environment, potential routes of exposure are chemical dependent. Therefore, quantification of human health risks associated with contaminated sediments may require analysis of several routes of exposure. These include ingestion of chemicals partitioned into sediments or surface water; dermal exposure to chemicals in sediment or surface water; inhalation of volatile chemicals partitioned first into surface water and then into air, and/or; ingestion of fish or other foods contaminated by chemicals. If exposures are limited by removal of contaminants from areas where exposures may occur or by creating barriers to exposure, the probability of adverse health effects is also limited.

Chemicals of concern

Previous MDH documents have identified polycyclic aromatic hydrocarbons (PAHs) and mercury as the primary chemicals of concern for human health at the SLRIDT site. Polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), octachlorostyrene (OCS), and hexachlorobenzene (HCB) are also potential chemicals of concern at this site and most contaminated aquatic sites in the St. Louis River area. A survey for these 5 chemicals has not been conducted at SLRIDT. All 7 of the above listed chemicals and chemical groups are addressed in greater detail in the 2001 MDH Health Consultation (MDH, 2001b).

The chemical listed above are of concern not only because of potential risks associated with exposure to them at this site, but also because they may be transported offsite into the St. Louis River and then to Lake Superior. Canada and the United States have developed a Binational Toxics Strategy (BNS) "...toward the goal of virtual elimination of persistent toxic substances resulting from human activity, particularly those which bioaccumulate, from the Great Lakes Basin, so as to protect and ensure the health and integrity of the Great Lakes ecosystem" (<http://www.epa.gov/glnpo/p2/bns.html>). The chemicals of concern are all Level I substances targeted by the BNS.

Naphthalene and similar PAHs

MDH has previously reviewed polycyclic aromatic hydrocarbon contamination data at this site and discussed toxicity issues (MDH, 2001b). PAHs are a class of generally hydrophobic, non-polar organic compounds that result from the burning of organic materials. They exist in mixtures in the environment. These mixtures have been shown to have both carcinogenic and non-carcinogenic effects on humans and animals. Historically, chemical analysis has been restricted to a handful of individual carcinogenic PAHs (cPAHs) and non-carcinogenic PAHs (nPAHs) out of the hundreds of PAHs found in the environment. However, in early 2000, MDH began recommending PAH analysis include an extended list of 25 cPAHs with available California Office of Environmental Health Hazard Assessment (OEHHA) potency slopes or potency equivalency factors (PEFs) (CA OEHHA, 2002). MDH finalized recommendations in a 2001 memo to MPCA (MDH, 2001a) and cited this memo in the 2001 Health Consultation on SLRIDT sediments (MDH, 2001b). Recent samples from SLRIDT have not been analyzed for these additional cPAHs (see below).

Naphthalene is the PAH of most concern during cleanup activities because it is very volatile and prevalent in sediments. Additional PAHs, primarily methylated naphthalenes, will have similar volatilities, but they do not appear to be as prevalent in sediments at this site.

Naphthalene is currently classified as an nPAH by EPA, but the International Agency for Research on Cancer (IARC) classifies naphthalene as possibly carcinogenic to humans (Group 2B) due to the evidence of carcinogenicity in laboratory animals exposed for long periods of time, at high concentrations (IARC, 2002). Current MDH criteria have been developed from data showing naphthalene to cause nasal and respiratory effects in rats exposed to low concentrations for 2 years, or exposed to much higher amounts for 4

hours. Using standard risk assessment methods, MDH has developed a shortterm (acute) health criterion of 200 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$), and a longterm (chronic) health criterion of 9 $\mu\text{g}/\text{m}^3$ for naphthalene (Attachment #3; MDH, 2003). Exposures to air concentrations below these values are expected to be safe. A few people may be affected by naphthalene at concentrations around the odor threshold (between 200 and 440 $\mu\text{g}/\text{m}^3$). It is likely that most people will not be affected by acute naphthalene exposures well above the acute criterion of 200 $\mu\text{g}/\text{m}^3$.

Mercury

Mercury and methyl mercury are neurotoxins and exposures are of particular concern during fetal and early postnatal development. The methylated form of mercury accumulates in biota because it is readily absorbed and only slowly excreted. As a result, concentrations of methyl mercury are the highest in animals at the top of the food chain. Ingestion of fish tissue containing high levels of methyl mercury is the dominant exposure to mercury for most people. The MDH Fish Consumption Advisory has more restrictive advice for women of child-bearing age and children than for the general population. In general, women of child-bearing age and young children are advised not to eat walleyes greater than 25 inches in length, and to limit eating walleyes 15 to 20 inches from the lower St. Louis River to one meal a month or less. In addition, the advice for the general population advises limiting consumption of walleye larger than 20 inches to once a month. This advice is somewhat less stringent than fish consumption advice for the St. Louis River prior to 2001, and is based on changes in methods of calculating fish consumption advice as well as data from a limited number of fish.

Limited sediment mercury data show that mercury in sediments in Stryker Bay is elevated above current background levels (e.g. REMAP, 1995). Furthermore, as discussed in the previous Health Consultation (MDH, 2001b), industrial activities at this site were, potentially, a large source of mercury to the local area and the region.

Mercury is of concern if it is converted to methyl mercury and enters the food chain. Methyl mercury accumulates in the food chain, with high trophic level fish having much higher concentrations of methyl mercury than sediments (USGS, 2001). Methyl mercury concentrations in sediments can change over the course of hours, days, months and years, because it is produced from inorganic mercury by bacteria (Gilmour et al., 1992) and it is reconverted to inorganic mercury biotically and abiotically (Matilainen and Verta, 1995; Sellers et al., 1996; Regnell et al., 1998). Therefore, changes in methylation or demethylation rates may have a greater impact on fish tissue concentrations than the amount of inorganic mercury in sediments.

The National Oceanic and Atmospheric Administration (NOAA, 1996) has stated:

In order to select an effective remedial alternative, it may be necessary to characterize the major pathways to receptors of concern and aspects of the aquatic system that enhance methylation and influence mercury availability.

The role of [mercury] speciation in determining concentrations in, and toxicity to, biota may need to be understood prior to attempts to control the geochemical cycling of

mercury within a waterbody. Remediation attempts have been unsuccessful at sites where these factors have been ignored.

Additional chemicals of potential concern

MDH recommended in the 2001 Health Consultation (MDH, 2001b) that regular sediment analyses include an extended list of 25 carcinogenic PAHs (including 6 already analyzed and 19 additional cPAHs), and that sediments at the site be screened for a number of chlorinated organic chemicals (i.e. polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), octachlorostyrene (OCS), and hexachlorobenzene (HCB)). These additional chemicals of concern listed in Table #1, were not addressed in the Data Gaps Report.

Table #1

Recommended additions to chemical analysis list for sediments	
<i>Polycyclic Aromatic Hydrocarbons</i>	<i>Chlorinated organics</i>
Benzo[j]fluoranthene	Polychlorinated biphenyls
Dibenz[a,j]acridine	Polychlorinated dibenzodioxins
Dibenz[a,h]acridine	Polychlorinated dibenzofurans
Dibenz[a,h]anthracene	Octachlorostyrene
7H-Dibenzo[c,g]carbazole	Hexachlorobenzene
Dibenzo[a,e]pyrene	
Dibenzo[a,h]pyrene	
Dibenzo[a,i]pyrene	
Dibenzo[a,l]pyrene	
7,12-Dimethylbenz[a]anthracene	
3-Methylcholanthrene	
5-Methylchrysene	
1-Nitropyrene	
4-Nitropyrene	
1,6-Dinitropyrene	
1,8-Dinitropyrene	
5-Nitroacenaphthene	
6-Nitrochrysene	
2-Nitrofluorene	

Potential routes of exposure

Six different potential routes of exposure to chemicals from contaminated sediments in the St. Louis River and at the SLRIDT site have been identified. Based on MDH sediment screening criteria, a limited number of important (driving) pathways were identified for each chemical of potential concern. Table #2 lists the potentially significant routes of concern for those chemicals.

Table #2
Significant Exposure Pathways of Concern (based on sediment screening evaluation)

Chemical / Chemical Group	Ingestion of chemicals in sediment	Dermal exposure to chemicals in sediment	Ingestion of chemicals in fish tissue	Ingestion of chemicals in water	Dermal exposure to chemicals in water	Inhalation of chemical vapors
Polycyclic aromatic hydrocarbons (PAHs)		*	*		*	*
Polychlorinated dibenzodioxins (PCDDs)			*			
Polychlorinated dibenzofurans (PCDFs)			*			
Polychlorinated biphenyls (PCBs)			*			
Hexachlorobenzene (HCB)			*		*	*
Octachlorostyrene (OCS)			*			
Mercury / methyl mercury			*			

Remedial action-specific issues of concern

The Data Gaps Report (Service, 2002) contains reviews and reports of experimental data. Currently, two general remedial actions are being discussed for the contaminated SLRIDT sediments: dredging and removal of contaminated sediment to a contained disposal facility (CDF) - either onsite or offsite; or capping contaminated sediments in place. Dredging and capping have the potential to cause future exposures in very different ways.

Dredging

Dredging will move most of the contaminated materials to a structure (e.g., tomb) designed to isolate them from the environment. The Peer Review Team had lengthy discussion about the redeposition, or fallback, that may be expected during dredging (PRG, 2002). While there is evidence that dredging will leave contamination behind, MDH has been unable to locate any studies on the extent of “fallback” at dredging sites. The Data Gaps Report does not address this issue, and discussion of the magnitude of the problem and possible solutions is needed.

On the other hand, the movement of contaminants away from the dredging area can be somewhat controlled during dredging (e.g. by use of hydraulic dredging), and if necessary, controls can be added so that there is very little movement of these suspended materials offsite (National Research Council, 1997; pg 113-116). The biggest public

health concern during dredging operations is that volatile contaminants (e.g. naphthalene) may escape from the water/sediment slurry and be emitted into the air (National Research Council, 1997; pg 112); and people can be exposed by breathing the contaminated air.

Capping

Capping of contaminated sediments will leave 100% of the contaminants on site, under a blanket of possibly 3-4 feet of clean materials. Long-term capping of contaminants in an aquatic environment, particularly a shallow environment, can be more difficult than entombment in an upland area. Water flow around or through contaminated sediments and a cap can move contaminants or erode a cap. In addition, application of a cap and compaction of underlying layers will displace porewater, and possibly non-aqueous phase liquid (NAPL). Such displacement could potentially cause a short-term release and introduce contaminants into the new overlying materials. If, as suggested in the Data Gaps Report, emissions outside of the dredged cell are greater than emissions in the active cell, then small disturbances of the sediment may have a disproportional effect on air emissions. In any event, it is expected that there will be a pulse of contaminants into the aquatic environment when a cap is applied.

The site is in an area with a vertical groundwater gradient toward the surface, and groundwater activity below, within and above contaminated sediments is of potential concern. Groundwater can potentially transport contaminants and it can also erode the cap. Of additional concern are frost or ice penetration into the cap and the effect of plant growth, including woody plant growth, in the cap. These activities can create channels through parts of a cap, and also break up the matrix of a cap. Such activities could increase the mixing and erosion potential. Proposed capping materials include silt, which would increase the ability of the cap to grow vegetation and the effects of ice intrusion, and sand, that would decrease plant growth and matrix-disrupting effects of frost on the cap. If the contaminants remain on site, monitoring and repair of the cap will be necessary for many generations, or essentially forever.

Discussion

If sediments are moved into a CDF, the footprint of contamination can be significantly reduced and future exposures can be limited or eliminated by controlling contaminant access and interactions with groundwater, surfacewater, frost, air, plants and animals with engineering controls. If contaminants are capped in place, the contamination footprint remains at its current size, and controls are generally limited to the top of the contaminated sediments.

If contaminants are left on site, monitoring releases will be necessary while the contaminants remain. Institutional controls have often proven to be ineffective (Environmental Law Institute, 1999). MDH is concerned that a cap or CDF may not be maintained, monitored and repaired, and contaminants may become a health hazard in the future. Therefore, MDH favors a remedial action that permanently restricts exposures to levels below health concern at this site.

Hybrid remedial designs have been discussed and MDH recognizes that combinations of dredging and capping may be considered. Unless the issues inherent to both remedies are addressed in a hybrid plan, hybrid remedial actions may fail to adequately limit risks.

Data Gaps Report Review

Air emissions experiments and proposed model

Introduction

Concerns about emissions during dredging were discussed in a 2001 health consultation (MDH, 2001b). The health consultation recommended: "...monitoring of emissions should be conducted during the entire [dredging] operation and provisional plans should be prepared for further limiting emissions should emissions exceed levels of concern."

PAHs that volatilize from a slurry of sediment and water will be largely the light, sparingly soluble PAHs that have high Henry's Law Constants (H_k). These will primarily be naphthalene and methylated naphthalenes. Not only does the Henry's Law constant (an equilibrium constant) decrease for larger PAHs, but molecular diffusion of these larger molecules is slower, thereby decreasing the speed at which they traverse the boundary layers.

The Data Gaps Report Air Analysis reports on emissions experiments conducted in the laboratory and applies the resulting data to two models. The Data Gaps Report presents a model for air emissions during dredging, then uses emissions estimates from that model as inputs for the EPA ISCST3 air dispersion model. MDH has not reviewed the application of the air dispersion model to emissions data from this site. MPCA technical staff are better qualified to review air dispersion models. This review focuses on experiments and theory used in the Data Gaps Report to develop emissions estimates for dredging.

The greatest errors in modeling ambient air concentrations are usually the inputs into the dispersion model. When the source is contaminated sediments, errors can be in the estimates of sediment concentrations from which emission estimates are extrapolated, or errors in the model used to estimate emissions during dredging. Available data on PAH concentrations as model inputs for Data Gaps Report are very limited. For the purpose of modeling air emissions, Stryker Bay was divided into 15 dredging cells, each approximately 3 acres. There are no sediment data for 2 of the 15 proposed dredging cells in Stryker Bay. In addition, analytical data from a total of 38 point locations was used to characterize some 35 acres of the bay. Furthermore, data are not available on whether and where the contamination is in a non-aqueous phase liquid (NAPL). Therefore confidence in the emission estimates, even from a proven emissions model, would be limited.

Experimental data review

The Data Gaps Report contains experimental data for PAH and volatile organic compound (VOC) emissions from sediment slurries. Emission data are reported for four different slurries with targeted concentrations of 45% ($0.45 \text{ kg}_{\text{sed}}/\text{kg}_{\text{slurry}}$), 8%, 8% and 1% solids by weight (i.e. different volumes). One of the 8% slurries was stirred throughout

testing, while the remainder were stirred immediately prior to testing and allowed to settle out during the experiments. Slurries were made from a single homogenized sediment sample and diluted with St. Louis River water. The sediment used as the PAH and naphthalene source was taken from one of the most contaminated areas in Stryker Bay. The Data Gaps Report does not indicate whether the sediment used in the experiment contained NAPL.

The sediment slurry concentrations used to estimate emissions at different locations during dredging seem reasonable representations of sediment solids concentrations in dredged materials. However, the accuracy of the experimental slurry concentrations and factors which result in slurry concentration variation during dredging were not discussed in the Data Gaps Report, and MDH does not have experience with dredging operations. The 1% slurry, in particular, may be a very high estimate for suspended solid concentration in the vicinity of a dredging operation, and emissions from that slurry likely overestimate emissions in areas not being dredged. The National Research Council Report on contaminated sediments states that in most studies, suspended solids are less than 100 milligrams per liter (mg/L) except in immediate proximity to the dredging head, and, in most field studies, less than 10 mg/L has been measured 100 meters from the dredging head (National Research Council, 1997; pg 110). Therefore, while the model indicates that contribution of emissions distal to dredging is small relative to total emissions in the model, it actually exceeds emissions in the active cell (see Table #4). Basing estimates on emission rates from a 10 grams per liter (g/L) (1%) slurry in the inactive cells may overestimate suspended solids contributions from this part of the model by 2 to 3 orders of magnitude.

In addition because a very small amount of particulates are transported outside of the dredging area, naphthalene in water outside the active cell will be dissolved. Dissolved naphthalene volatilizes rapidly, so it is unlikely that significant amounts of dissolved naphthalene will remain in water far from the active cell. Therefore, the use of experimental data from a 1% slurry to describe volatilization over about 42 acres outside of a 3 acre dredge area, appears to be a large overestimation. Use of 1% slurry emissions data for cells bordering the active cell should provide a very conservative estimate of non-active emissions from those cells. Current emissions from the rest of Stryker would probably provide a reasonable emission rate estimate for the non-adjacent cells in Stryker Bay.

Experiments described in the Data Gaps Report Air Model appendix were intended to help quantify naphthalene emissions from dredging operations and a CDF. Emission rates from sediments were estimated using an experimental apparatus that allowed a steady air stream to flow over sediment / water slurries and subsequent air sample collection for analysis. In this manner it is possible to measure potential air emissions under controlled conditions.

It is critical to an experiment that the initial quantities of the chemicals of interest are known. In addition in complicated experiments where errors can occur, it is useful to measure the amount of chemical in different compartments (e.g. sorbed and dissolved) at

the beginning and end of the experiment. Minimally, the amount of chemical in the sediment slurries at the beginning of each experiment and the amount remaining at after each experiment should have been measured. In this way the mass balance of an experiment could have been checked. Monitoring mass balance is extremely important in experiments with multiple physical compartments and a potential different preparation of samples or volatile losses.

In the Data Gaps Report air emissions experiments, not only was no mass balance performed, the actual quantity of chemicals available in the slurries prepared for the experiments is uncertain. While Data Gaps Report Table (DGR Table) A1-1 shows a reasonable match between the targeted and measured solids composition of the slurries, DGR Table A2-3 shows a very poor agreement between their targeted chemical composition of the slurries and the measured chemical composition of the slurries. Because water used to make up the slurries contained very little PAHs, the sediment fraction should initially contain all the PAHs in the slurries. Furthermore, the PAH concentration in the sediment (solid) fraction should be the same for all slurries. A total of 2.1 kg of material, sediment, and water, was used in each slurry mixture tested (DGR Section A1-1.3). Dried sediment has about 1.5 times the density of water; therefore, the total amount of sediment in each experiment was approximately 980, 172, 189 and 32 grams (g) for the 45%, 8% mixed, 8% quiescent, and 1% slurries (calculated from measured solids composition (Table A1-1) and total mass of 2.1 kg). The volume of each experimental slurry was not reported.

The targeted amount of each chemical (including naphthalene) in each experiment can be calculated from the assumed concentration in source sediments and the amount of source sediments in each slurry. DGR Table A2-3 shows the results of chemistry analyses of source sediments. This table shows analytical data for two ‘solids’ samples (bulk and 45% sediment; reported in milligram chemical / kilogram sediment (mg/kg)) and three ‘liquid’ samples (micrograms per liter (µg/L)), for which no solids or moisture data are available. The Data Gaps Report implies that DGR Table A2-3 includes all of the chemical data for each experimental slurry. If this is the case, there is a large discrepancy between the measured amount of naphthalene and the targeted amount of naphthalene in the experimental slurries. Table #3 below compares the total amount of naphthalene in each slurry (calculated from DGR Table A2-3 and total experimental mass of 2.1 kg for slurries) with its targeted amount.

Table #3

Total naphthalene in slurries: Measured and Target					
Solids in Slurry	Bulk sediment	46.80% (of 2.1 kg)	8.20% (of 2.1 kg)	9.00% (of 2.1 kg)	1.50% (of 2.1 kg)
Measured naphthalene	(1300 mg/kg)	10811 mg/test	32 mg/test	173 mg/test	15 mg/test
Target naphthalene	(11000 mg/kg)	10811 mg/test	1894 mg/test	2079 mg/test	347 mg/test
Ratio- measured:target		12%	100%	1.7%	4.3%

If there are no more analytical data on the chemical mixtures in the slurries than the data described in DGR Table A2-3, comparison of emission data between experiments is problematic. In addition, the use of data from these experiments to describe emissions

during dredging becomes problematic as well. Note in Table #3 (and DGR Table A2-3 and DGR Section A2-3.2) that bulk sediment was analyzed. However, chemical analysis of the bulk sample showed about 9 times less naphthalene than the 45% sediment samples. While the Data Gaps Report explained that the bulk sample was not mixed properly, there is no way to tell if the sediment added to the other slurries was mixed. The Data Gaps Report says “for purposes of air modeling, it is assumed the source sediment is as characterized by sample ‘45-SED’.” Without offering data or corroboration, the Data Gaps Report suggests that the chemical concentrations measured in the 45% sediment sample are “more consistent with the other analytical results.” Mass balance is very important in experiments that characterize contaminant movement, and failure to accurately measure chemicals in source media makes the usefulness of these experiments to describe air emissions during dredging questionable.

There is another possible explanation for the confusing 8% and 1% slurry data in DGR Table A2-3. The laboratory report on these slurry samples says that the media were liquid, and suggests by the absence of solid and moisture data that the analysis may have characterized dissolved chemicals including naphthalene. This would suggest that the solubility of naphthalene in the slurries was up to 86 mg/L (from DGR Table A2-3). Clearly this is not possible, as the solubility of naphthalene in water is 31 mg/L. Any co-solvent effect that could elevate the amount of naphthalene in solution significantly would require considerable (maybe 1% or more) organic solvent dissolved in the aqueous mixture. The data discrepancies outlined in Table #3 suggest: non-homogeneous sediment; different pretest preparation of samples; different methods for sampling slurries for analysis, or; analytical problems. Therefore, it is difficult to draw any conclusions from the chemical data.

Emissions model description

The Data Gaps Report proposes a model for use in quantifying naphthalene emissions from sediments during dredging. This model is based on a proposed linear relationship between sediment concentration of naphthalene and the amount of emissions up to a maximum emission rate, above which any increase in naphthalene concentration in sediment will not increase emissions. The Data Gaps Report describes the sediment naphthalene concentration at which the maximum emission rate is first achieved as the “breakpoint.” Further, the Data Gaps Report says that the emissions experiments described above were conducted at naphthalene sediment concentrations above the “breakpoint.” The Data Gaps Report asserts that as the concentration of naphthalene in sediment increases, the movement of naphthalene from sediment to water becomes restricted as the naphthalene concentration in water approaches the solubility of naphthalene in water. Therefore, the “breakpoint” where maximum emissions occur can be calculated from the maximum solubility of naphthalene in water.

The following rearranged equilibrium partitioning equation was the basic equation used in the Data Gaps Report to calculate the naphthalene sediment concentration “breakpoint.”

$$\text{Solubility} \times K_{oc} \times f_{oc} = [\text{naphthalene}_{sed}] (@ \text{“breakpoint”})^1 \quad \text{-equation \#1}$$

The Data Gaps Report modified the above equilibrium partitioning equation to include an additional factor (a solubility correction factor) that represents solubility interactions between different PAHs (% naphthalene in the non-aqueous phase liquids (NAPL)). Justification for this additional factor of 0.052 is not clear. Furthermore, if a “breakpoint” is used in this model without sound justification, it should have been supported experimentally. The resulting equation used to calculate “breakpoints” for the Data Gaps Report (Section A2-3.3.3 Source Strength Adjustment) is:

$$\text{Solubility} \times \% \text{ naphthalene in NAPL} \times K_{oc} \times f_{oc} = [\text{naphthalene}_{sed}] (@ \text{“breakpoint”}) \quad \text{-equation \#2}$$

The ‘solubility’ proposed in the Data Gaps Report (7 mg/L) is a naphthalene concentration measured in a sample from the site. It is stated that this measured concentration is “the highest measured naphthalene solubility (7 mg/L) in any of the solubility related tests (DRET, SBLT)” (DGR Section A2-3.3.3). Actually, 22 mg/L naphthalene was recorded in a 0.7 µm filtered sample from the SBLT (DGR SBLT Table 4-4). See Appendix 2 of this health consultation for further discussion.

The dissolved naphthalene concentration in the air emission experimental slurries was not measured, and the assumption of a dissolved concentration less than the solubility of naphthalene is problematic. Measuring the solubility of naphthalene is difficult since the chemical is volatile. The solubility for naphthalene in water is about 31 mg/L (31.7 mg/L; ATSDR, 1995). While this solubility cannot be decreased, it can be increased above 31 mg/L if there is substantial co-solvent present. However, when a NAPL is present, the equilibrium concentration in water may be considerably less than the solubility (i.e. 5-11 mg/L: more discussion in a later section of this document).

In addition, the Data Gaps Report proposes using a site-specific K_{oc} . Determination of K_{oc} from laboratory experiments is not a simple task. MDH reviewed the K_{oc} experiments conducted for the Data Gaps Report, and concluded that they were calculated using incorrect data as well as data from experiments that contained errors in methods. Appendix 2 contains a discussion of the derivation of the Data Gaps Report “site-specific K_{oc} ,” including discussion about why K_{oc} cannot be determined from samples containing NAPL.

The Data Gaps Report emissions model assumes that the naphthalene concentration in sediment in the experimental slurries was the target or “nominal” concentration, and calculated the hypothetical emissions total during dredging for 2 different “breakpoints” (238 mg/kg_{sed} and 1000 mg/kg_{sed} naphthalene). Figure #1 shows the proposed relationship between naphthalene sediment concentrations and total naphthalene air emissions (first 2 hours) proposed by the Data Gaps Report for the 238 mg/kg_{sed} “breakpoint.” Note that the actual emissions may be different under different experimental conditions, but that the “breakpoints” in the Data Gaps Report model remain the same regardless of experimental conditions (more discussion of this below).

¹ DGR Section A2-3.3.3

Also, note that for a single experimental data point (triangles in Figure #1), the model proposes 2 lines: the maximum emission rate between 238 and 11,000 mg/kg naphthalene in sediment and; a line from the maximum emission rate to zero for sediments with 0 - 238 mg/kg naphthalene. While there are no experimental data that support this model, an analysis conducted in Appendix 1 of this Health Consultation demonstrates that experimental data demonstrates that the model is incorrect, especially in predicting emissions from slurries with low suspended solids concentrations.

For comparison, Figure #2 graphically compares 8% mixed slurry emissions modeled with “breakpoints” at 238 mg/kg_{sed}, 1000 mg/kg_{sed}, 5,000 mg/kg_{sed} and 15,000 mg/kg_{sed} naphthalene. Note that use of the Data Gaps Report model with a 15,000 mg/kg_{sed} “breakpoint” results in the same predicted emission rates as a model without a “breakpoint” for naphthalene concentrations at the site (< 15,000 mg/kg naphthalene). Note in Figure #2 that there is one experimental datapoint (triangle) from which the Data Gaps Report proposed an emissions model.

Table #4 (below) shows the effect of using different breakpoints to calculate air emissions during dredging.

Table #4

Total modeled naphthalene emissions during 1 year of Stryker Bay dredging								
DGR model "breakpoint" - minimum sediment concentration at which maximum emissions occur -	15,000 mg/kg naphthalene (same as no "breakpoint")		5000 mg/kg naphthalene		1000 mg/kg naphthalene		238 mg/kg naphthalene	
	kg/yr	%total	kg/yr	%total	kg/yr	%total	kg/yr	%total
Active emissions during dredging	947	12%	1,403	7%	1,582	5%	2,302	7%
Emissions from inactive cells	1,195	15%	1,769	9%	1,996	6%	2,904	9%
CDF active emissions	5,161	66%	15,482	77%	25,888	81%	25,888	77%
Quiescent CDF pool emissions	469	6%	1408	7%	2,354	7%	2,354	7%
Total naphthalene air emissions	7,752	100%	20,062	100%	31,821	100%	33,448	100%
Total naphthalene dredged (calc from cell avgs)	223,152		223,152		223,152		223,152	
Percent total naphthalene dredged that is emitted	3.5%		9.0%		14.3%		15.0%	

It is clear that the Data Gaps Report model is very sensitive to the choice of a “breakpoint”. In other words, a low “breakpoint” assumes a very high rate of increase in air emissions as sediment concentrations of naphthalene increase. Appendix 1 of this health consultation demonstrates that the proposed model breakpoint of 238 mg_{naphthalene}/kg_{sediment} predicts values that do not agree with the experimental data from the Data Gaps Report. If the Data Gaps Report model is correct, better experimental confirmation than presently exists is needed. In order to accept this model right now, one has to accept very implausible (and likely incorrect) assumptions that are not supported by the poor quality experimental data.

Partitioning: equilibrium versus dynamic systems

In a closed system at equilibrium, concentration ratios between all compartments are constant and all net fluxes between compartments are zero. When a closed system is disturbed and no longer exists at equilibrium, there is movement of chemicals between compartments, and ratios of chemical concentrations between compartments will change. Concentrations under non-equilibrium conditions are not determined by equilibrium ratios, but are determined largely by the chemical flux between compartments. At steady-state, as at equilibrium, concentration ratios between compartments are also constant; however there is a constant rate of movement of contaminants from one phase to another. Chemical concentration ratios between compartments at steady-state may be very different than ratios at equilibrium. And certainly, chemical ratios between compartments in a dynamic open system are not at equilibrium.

Movement of naphthalene from sediment to air requires the chemical to move between different compartments: sediment, water, and air. The speed at which a chemical can move from one compartment to the next is determined by the amount of mixing of the bulk medium (e.g. sediment, water or air), the molecular diffusivity of a chemical through the mediums, and the distance that the chemical must diffuse. Any movement through a compartment that is not aided by mixing must be accomplished by diffusion. Therefore, diffusion is usually confined to boundary layers that border the bulk media. Diffusion is also important in stagnant sediments.

Models of mass transfer across these boundary layers and into the different media describe slow diffusion across the boundary layers and rapid transfer from one layer to another to maintain equilibrium conditions across extremely small areas of adjacent boundary layer surfaces. Therefore, as boundary layers become thinner (a result of mixing) or molecular diffusivity increases (a function of temperature, typically a minor factor), flux from one compartment to another increases. This was demonstrated experimentally by the data from the 8% mixed slurry (assuming targeted naphthalene concentrations): mixing increased the emission of chemicals from 8% sediment slurries. These experimental emission rates are marked with triangles in Figure #1. (However, note in Figure #1 that the measured emissions from the 45% and 1% slurries are similar, and the emissions from the 8% quiescent slurry is about 40% less. This suggests either inconsistent preparation of samples, non-homogenous source sediments, problems with sample collection, analytical errors, or the presence of a NAPL.)

Experimental data from the Data Gaps Report suggest that emissions were not restricted by a solubility limit. Solubility remains constant over time. If, as suggested in the Data Gaps Report, solubility restricts movement of contaminants from sediment to air, experimental data should show steady emissions of naphthalene. As shown in Figures #3-#6 (chemical emission rates corrected for chemical loss and normalized to emission rates over the first 2 hours), all experiments had decreasing volatilization of naphthalene over time. Changes in emission rates must be a result of changes in the system. There are two apparent potential causes for this rate decrease: 1) Mixing during the test was insufficient to maintain the initial rate of transport of naphthalene through the water

column, and 2) there are two (or more) compartments of sediment-adsorbed naphthalene that release naphthalene at different rates.

If the lack of mixing decreases the naphthalene renewal at the water-air surface or solubility limits desorption from sediments, the emission rate reduction over time should be less for the 8% mixed slurry than from the 8% quiescent slurry. As shown in Figures #4 and #5, the reduction in emission rate for the 8% quiescent slurry may be less than the reduction for the 8% mixed slurry; however the difference is small and likely insignificant (56% and 91% for hours 2-6 and 6-24, respectively, versus 47% and 85%). Therefore, it is unlikely that the lack of mixing or solubility limitations are responsible for most of the decrease in emission rates through time.

If naphthalene is sorbed to sediment particles differently, with different affinity for different types of particles (e.g. different types of organic carbon) or with longer diffusion paths as more desorbs, then experimental data may show less of a decrease in emission rate in experiments with the 45% slurry than in other experiments. However, if the rate of transfer through the water column is sufficiently fast, and there is no solubility limitation to the desorption from sediment, the difference may be insignificant. While decreases in the naphthalene emission rate may have been the least in the 45% slurry experiment, variation between all experiments was not large (see Figures #3-#6). Because water mixing does not appear to limit emission rate decreases, by default, slowed diffusion of naphthalene from sediments over time is the suggested explanation for the emission rate decreases.

There is considerable information in the environmental chemistry literature that shows PAHs, in general, have different affinities for organic carbon of different origins. PAH partitioning into water has been shown to be decreased in areas with significant tar or pyrogenic materials (Maruya et al., 1996). In addition, research by Gustafsson et al. (1997) and others has shown that soot or black carbon in sediments does not allow PAHs to desorb as readily as natural or other organic carbon.

In summary, the Data Gaps Report experimental data suggest that there is probably not a solubility limit to naphthalene emissions under conditions similar to those encountered in these experiments. Further, if there is a solubility limit under some conditions, the solubility limit will change as experimental conditions change. The known mechanisms whereby chemicals partition between different phases or media, as well as very limited experimental data, suggest that even if there is a sediment concentration above which there will be no increase in emissions (i.e. a “breakpoint”), this sediment concentration could be very different under different experimental conditions. Therefore, the single “breakpoint” concept is of little utility when attempting to model emissions during dredging.

While experiments in the Data Gaps Report were not designed to find a possible cause of decreasing naphthalene emission rates over time, the data do suggest that emission rates may be limited by diffusion and desorption of naphthalene from the sediments.

Naphthalene partitioning model

Naphthalene partitioning from sediments can be very different if contamination exists as a NAPL, or if it is sorbed to organic particulates in the sediment. Equilibrium between naphthalene in a NAPL and water, and equilibrium between sediment organic carbon and water, are two distinctly different conditions. If there is a NAPL in the sediments, then partitioning should be calculated between the NAPL and water, as well as directly between the NAPL and air. If there is no NAPL, then the important partitioning is between the organic carbon in the sediment and water. These are important distinctions, because the presence of a NAPL can lead to very different emission rates than will be encountered when dredging sediment-sorbed naphthalene. The concentration of naphthalene in water *at equilibrium* (i.e. in a non-dynamic system) with naphthalene sorbed to sediment is:

$$\text{dissolved naphthalene (mg/L)} = [\text{naphthalene}] \text{ (mg/kg)} / K_{oc} \text{ (L/kg)} / f_{oc}$$

for dissolved ≤ 31 mg/L -equation #3

The concentration of naphthalene in water at equilibrium with naphthalene in a NAPL can be approximated by (Schwarzenbach et al., 1993):

$$\text{dissolved naphthalene (mg/L)} \approx C_w^{\text{sat}} * \text{Exp}(+) \Delta S_m / R * ((T_m / T) - 1) * f_{\text{NAPL}} * \gamma_{\text{org mix}}$$

for dissolved ≤ 31 mg/L -equation #4

Where:

C_w^{sat} (mg/L)	= water solubility (31 mg/L)
ΔS_m (J/mol/K)	= entropy of melting (~48 - 59 J/mol/K)
R (J/mol/K)	= gas constant (8.3145 J/mol/K)
T_m (K)	= melting temperature (353.75 K)
T (K)	= temperature (293.15 K)
f_{NAPL}	= fraction of naphthalene in NAPL
$\gamma_{\text{org mix}}$	= fugacity of naphthalene in the organic mixture (~1 - 1.8)

Note that the naphthalene concentration in water (e.g. 5 - 11 mg/L @ $f_{\text{NAPL}} = 5.2\%$ naphthalene) is almost totally dependent on the fraction of naphthalene in the NAPL and therefore, the dissolved concentration (at equilibrium) will remain constant as long as a similar composition NAPL is present. Experimental data from the Data Gaps Report Sequential Batch Leaching Report shows up to 22 mg/L naphthalene in water (DGR SBLT Table 4-4; see Appendix 2 for discussion). Dissolved naphthalene was not measured in the air emissions experiments, and it is possible that samples contained NAPL. As concentrations of naphthalene decrease in sediments, there is probably a point where there is no longer a NAPL. At those locations, the concentration in water is determined (again, at equilibrium) by the equilibrium partitioning equation (equation #3) above. Figure #7 shows potential dissolved naphthalene concentrations at equilibrium with sediment, with and without NAPL.

NAPL in a slurry can also emit volatile chemicals directly to the air. The potential for this type of air release was not studied in the Data Gaps Report, or by MDH during our review.

The Data Gaps Report emissions model is structured to model emissions from contaminants that are sorbed to sediments, or solid phase contaminants. The presence of a NAPL in the sediments or slurries is not discussed in the air emissions sections of the Data Gaps Report, but NAPL could have large effect on emissions calculations. When attempting to apply the Data Gaps Report experimental data to the emissions model, estimates of dissolved naphthalene could be off by a factor of 6 depending on the presence or absence of a NAPL. If there is a NAPL, there is likely a maximum naphthalene concentration in water that is below the solubility of naphthalene. This maximum is not related to the naphthalene sediment concentration, but is reached when there is a NAPL present, and is absent when there is no NAPL. Sediment-sorbed naphthalene will be associated with generally higher dissolved concentrations of naphthalene than will naphthalene from a NAPL, because naphthalene in a PAH NAPL has less fugacity than naphthalene sorbed to natural organic carbon. If there is no NAPL, the dissolved naphthalene concentration adjacent to sediment containing 11,000 mg/kg naphthalene may be about 31 mg/L.² The presence or absence of a NAPL is critical in evaluating experimental data, and it may also be needed to calculate conservative and realistic emission estimates from available physical and chemical data on naphthalene.

Additional air emission issues

1. Appendix I, attached, ('Using the Data Gaps Report air emission model to predict naphthalene emissions') compares experimental data with model calculations, and shows that the Data Gaps Report air emission model does not accurately predict emissions from sediment slurries.
2. DGR Section A2-3.3.2 (Air-side Resistance) Air speed in the thin boundary layer at the surface is considerably less than the air speed higher up. Therefore, it is incorrect to compare pseudo-laminar flow at the water surface of the experimental apparatus directly with wind speed.

Increasing windspeed will increase emissions from dredging areas and containment facilities. But increased windspeed also increases the dilution of contaminants, thereby decreasing potential exposures. Therefore, inputs to the dispersion model are potentially complex, and the results are not easily predictable. The highest acute exposures typically occur when there is an atmospheric inversion and the windspeed is low. Because emissions from water are somewhat dependent on windspeed (wind causes a thinning of the water and air-side boundary layers), emissions at low windspeed may be below those predicted by a simple emission model. Conversely, emissions at high windspeed may exceed those in the emissions model.

Analysis of the relative relationship between increasing dilution and increasing emissions as functions of windspeed should be conducted.

² Calculated with $f_{oc} = 23\%$; $K_{oc} = 933$

3. DGR Section A2-3.3.1 (Temperature Variability) Henry's Law Constant describes the equilibrium partitioning of a chemical between air and water. Henry's Law for individual chemicals varies as a function of temperature. In addition, diffusivity for a specific chemical varies as a function of temperature to the 1.75 power (T (as K°)^{1.75}). The rate of volatilization from water is a function of Henry's Law and a function of transfer velocity, which is dependent on molecular diffusivity. Therefore at equilibrium, changes in concentrations of chemical in air and in water due to temperature changes are reflected in the change in Henry's Law. But changes in the rate of transfer in disequilibrium conditions are also related to $T_1^{1.75} - T_2^{1.75}$.

Henry's Law constants at different temperatures as well as ratios of Henry's Law and ratios of molecular diffusivities at other temperatures with their values at 20° are listed in the Table #5 below (EPA, 2001).

Table #5

Temperature	H _k - naphthalene	H _k Ratio (to 20° C)	Molecular diffusivity ratio (to 20° C)
22.4° C	40.48 pa/m ³ /mol	120%	101%
20° C	33.85 pa/m ³ /mol	- -	- -
17.3° C	27.56 pa/m ³ /mol	81%	98%
8.5° C	13.63 pa/m ³ /mol	40%	93%

These data suggest that temperature-dependant changes in the rate of volatilization will be related to changes in Henry's Law, and will not be appreciably affected by changes in molecular diffusivity. However, given that Henry's Law is an equilibrium constant, the temperature dependence of the rate of volatilization is very dependent on naphthalene concentrations in the water / air boundary layers. These data suggest that emissions may be significantly decreased if the cells containing the highest quantities of naphthalene are dredged in the early spring or the late fall.

4. DGR Section A3-1.2.2 (Use of monitoring) Other sites have monitored PAHs emitted by dredging. The section quotes "highest average" PAH concentrations, but does not say what the averaging time of the samples was. However, the interview information reviewed in the Data Gaps Report suggest that air emissions at PAH dredging sites have not been problematic.
5. DGR Section A3-1.2.4 (Chemical specific Emissions) Naphthalene data cited suggest that not only are emissions during dredging low (maximum ratio 137 mg_{naph}/kg_{sed} : 1488 ng_{naph}/m_{air}³), but that post-dredging levels in the dewatering basin were about ½ of pre-dredging levels. Current naphthalene concentrations in water and air near Stryker Bay should also be measured.
6. DGR Section A4-1.4 (Objectives of dispersion modeling) MDH agrees that "Acute standards and odors (should be) modeled as one-hour concentrations. Chronic

standards (should be) modeled as the average of the seven-month construction season.”

Review of the Data Gaps Report suggests that numerous steps can be taken to decrease the potential exposure of the public to emissions during dredging. These include:

- A. Cells containing high naphthalene concentrations can be dredged in the early spring or late fall.
- B. Cells dredged during a single year can be chosen so that both highly contaminated and relatively clean cells can be dredged each year. All yearly calculations in Table #4 (above) are based on dredging cells in a single year that have maximum naphthalene concentrations that average 2,990 mg/kg. The average of all of the cell maximums for Stryker Bay is 1780 mg/kg naphthalene. Therefore, there is room to balance emissions between dredging years.
- C. CDF emissions are the largest source of naphthalene. Offsite handling of wastes and CDF design alterations, including the use of simple floating covers or geotextile tubes, could significantly reduce emissions.
- D. Ambient air should be monitored at all times during dredging. Real-time monitoring should identify hazardous conditions and trigger responses such as; use of shortterm emission control measures, temporarily shifting dredging to a less contaminated area, stopping activities until meteorological conditions change, or notification and/or shortterm evacuation of residents.

Summary of additional MDH reviews of the Data Gaps Report
Dredging Elutriate Test Report

The purpose of the Dredging Elutriate Testing (DRET) was to “measure the effects of St. Louis River/Interlake/Duluth Tar Site (SLRIDT) sediments on St. Louis River water quality when mixed together in the immediate area of the disturbance”(Service, 2002; Appendix DRET, Executive Summary). MDH did not review the DRET Report entirely, but confined review to sections and tables that characterized sediment samples. MDH has the following comments:

1. DGR Table DRET3-2 states that the moisture content of samples collected from Stryker Bay, Slip #6 and Slip #7 were 157%, 55% and 88%, respectively. This is an apparent error that is not identified or explained in the text.
2. DGR Table DRET4-3 shows analytical results of three samples (one from each of the bays). Numerous PAHs in samples from Slip #6 and Slip #7 were detected at higher concentrations in (operationally defined) dissolved phase, than in the total samples. These discrepancies were not explained, and without duplicate or additional samples, the conflicting data cannot be reconciled. In addition, the fraction total organic carbon (f_{toc}) was only determined for 1 sediment sample. Not only is it important to determine spatial variability of organic carbon measurements, but analytical variability is also important. (In addition, f_{toc} was improperly reported as 230,000 mg/L OC in DGR Table DRET4-3).

Minimally, the Data Gaps Report should have identified and addressed the uses and limitations of these data.

Ice Report

MDH reviewed the original Ice Report in December 2001. Other than the addition of observations during the winter of 2001-2002, there are no notable changes in the new report. The two winters of observation now include an “atypical winter,” 2000-2001, and “an uncharacteristically warm (winter) with minimal snow cover,” 2001-2002.

The Report includes mention that “where the ice thickness was equal to the water depth the ice was typically frozen to the bottom, eliminating the potential for ice movement.” However, there is no discussion of frozen sediments. In addition, while the Ice Report states that thermal expansion under minimal snow cover “can create significant lateral forces that produce ice movement, bottom gouge, ridge formation, and ride-up,” the report also states that “Duluth always has a snow cover.” This is not entirely true, as evidenced by conditions this winter (Attachment #4; MDH and MPCA, 2003).

The Ice Report does not address concerns raised by MDH with regard to ice intrusion into sediments or a cap, the potential formation of ice feet, or lenses, and the effect of ice on the sediment matrix. These issues were discussed in the 2001 MDH Health Consultation (MDH, 2001b).

Additional Data Gaps Report Review

MDH has reviewed most sections of the Data Gaps Report that directly apply to human exposure to contaminants during dredging and the longterm protectiveness of a remedy at the SLRIDT site. Currently we are in the process of reviewing some related sections of the Data Gaps Report, and if we have additional contributions to make to the ongoing discussions we will write an additional review. In lieu of a full review, MDH offers the following comments.

Groundwater model

MDH expects to complete a review of the groundwater sections of the Data Gaps Report soon. Initial areas of concern are:

- Groundwater flow can move contaminants through a cap or a CDF.
- Groundwater can disturb the matrix of a cap or a CDF, leading to localized failure.
- Modeling contaminant flow through a cap with a one-dimensional model can not account for heterogeneous and non-contiguous layers at the site.
- There appear to be numerous springs in the bays and slips. These springs were shown in a temperature survey of the bottom water at the site conducted in 2000, and their existence is supported by observations in Stryker Bay during an MDH site visit (Attachment #3; MDH and MPCA, 2003).

Extent of sediment contamination

The Data Gaps Report (GH 7-3.1, GH 7-3.2) states that there is a lack of association between metals data in layers and total PAH (tPAH) data in the same layers and concludes that there is no association between releases of tPAH and metals onsite. The

lack of co-location of contaminants does not exclude the probability that both metals and organics were discharged by facilities that operated at this site. Co-location of contaminants assumes that transport of these contaminants to sediments is the same, and that movement in sediments is the same. While movement of non-polar organics can be easily modeled, the partitioning and movement of metals and metallic compounds/species can be more complicated. Some metals may remain relatively insoluble as long as conditions remain reduced and there is sufficient sulfide. Groundwater and seiche flow through contaminated sediments can make the prediction of metallic species and movement in sediment even more difficult.

Information not contained in the Data Gaps Report

Mercury methylation

There are limited data on the mercury contamination in sediments at the SLRIDT site. Any sediment sampling and analysis performed at this site should include analysis of mercury.

In the MDH 2001 Health Consultation (MDH, 2001b) on sediments at the SLRIDT site, MDH discussed concerns about building a wetland over sediments contaminated with mercury. The most serious concern related to mercury at the SLRIDT site is that creating a wetland cap may increase the methylation rates of mercury from the site. Wetlands have been shown to be the major source of methyl mercury in watersheds (Rudd, 1995; Saint Louis et al., 1996). In addition, field studies have suggested that groundwater flow may increase the flow of mercury into a system (Krabbenhoft et al., 1998). Mercury in sediments can form many different sulfide complexes, including some that are soluble (Paquette and Helz, 1997; Benoit et al., 1999). While MDH does expect that mercury concentrations in surficial sediments will be lowered with remedial action, we are concerned that methylation rates may be increased. If Stryker Bay is converted into a wetland because of the construction of a cap, methylation rates are expected to rise. If methylation rates increase, it will be important to limit the amount of mercury available for methylation by maintaining low concentrations of total mercury in surficial sediments. The Data Gaps Report only addresses mercury by suggesting, with the one-dimensional groundwater model, that the movement of mercury through a cap will be minimal.

Dredging also offers some challenges for containment of mercury. Some mercury will be resuspended during dredging. However, using a conservative estimate, the total amount of mercury discharged in decanted dredged water will be at most about 35 grams (MDH, 2001b). A CDF should be designed to isolated contaminants, including mercury, from groundwater and surfacewater. Following dredging, maintenance of current water depths should not result in a long-term increase in methylation.

MDH General Comment on the Data Gaps Report

Review of the experimental studies in the Data Gaps Report generally shows inadequate laboratory procedures and incomplete explanation of methods and results in sections reviewed by MDH. A significant amount of information in the reviewed studies is imported from other sections or reports that have not been reviewed by MDH. MDH is

concerned that there is a cascading of effects that is not clearly presented in the Data Gaps Report - where errors in methods, analysis, or interpretation are carried over and impact other calculations and interpretations. This segregation of errors, and lack of full disclosure of the sources and limitations of data, can lead to improper and unjustified conclusions.

For instance, computation of the naphthalene site-specific K_{oc} used in the Data Gaps Report Air Analysis Appendix contains significant errors. Appendix 2 of this health consultation contains a review of the site-specific K_{oc} derivation. This review concludes that the data presented are not sufficiently reliable to replace a more general, published, carefully derived K_{oc} of 933 L/kg (ATSDR, 1995) with the K_{oc} (3200 L/kg) used in the Data Gaps Report.

As mentioned elsewhere in this health consultation, any partitioning study should include a mass balance component or study. Not only did the air emissions experiments not include a mass balance study, only the emissions appear to have been appropriately characterized. Furthermore, the presence or absence of a NAPL will significantly affect experimental results and air emission model predictions. The Data Gaps Report contained no discussion of the presence or absence of NAPL in sediments that may be dredged. Chemical composition data for the slurries used in the experimental studies were not reliable. This makes drawing quantitative conclusions impossible. Some inferences can be made by comparing emission rates within individual studies, as done in Figures #3-#6, and by then comparing normalized results, but any conclusions can not be stated with confidence.

Children's Health

As part of an MDH Health Consultation, issues related to children's health are addressed explicitly. Children are exposed to chemicals differently than adults. Children will splash and play in water, sometimes drinking it and any suspended particles. They also eat, drink and breathe more than adults on a body weight basis. Therefore, they may have significantly greater exposures than adults. In addition children are not fully developed, and developing organs may be more sensitive to chemical hazards.

Scenarios for exposure to chemicals in sediments or other media are evaluated by MDH using a child receptor. Activities of a child and child intake rates are used in determining potential exposures by all routes of exposure. In addition, criteria used to evaluate the toxicity of chemicals are calculated to be protective of children and other sensitive sub-populations.

Summary

The Data Gaps Report contains a large amount of information characterizing a number of issues related to cleanup of the SLRIDT site. MDH reviewed sections of the Data Gaps Report that discussed topics previously raised by MDH. These included sections on potential air emissions during dredging; ice impacts on a cap over contaminated sediments and; the effect of groundwater on remedial options.

MDH review of the air emissions experiments identified several instances for which sampling methods were poorly described or not available, targeted naphthalene concentrations in experimental samples were not achieved, and there was incomplete or missing data. Problems encountered in the experiments or in data analysis were not identified or discussed in the text of the report. In addition, the proposed Data Gaps Report air emission model contains significant errors and is inconsistent with the experimental data in the Report.

No chemical mass balance was performed in the experiments conducted for the Data Gaps Report. This is a significant weakness: there is no way to verify that the design and methods allowed analyses of intended compartments. It is not possible to resolve apparent errors in chemical analyses of the 1% slurry and both 8% slurries without additional data. The Data Gaps Report suggests that target concentrations better represent the actual concentrations of contaminants in sediment than do the analytical measurements, so it is assumed that there was an error in methods in sampling the slurries. These errors do not affect the conceptual or the comparative analysis of normalized data within samples, but they may affect between sample comparisons and the quantification of emissions by any model that uses the experimental data. If analyses were bad, the experimental data are useless for describing a functional relationship between: naphthalene in sediments, naphthalene in water, and naphthalene in air.

The Data Gaps Report proposes that there is a sediment concentration of naphthalene above which no additional naphthalene will be emitted from a slurry. A consequence of this proposal is that the modeled relationship of air emissions to sediment naphthalene has a very rapid rise at very low naphthalene concentrations. In addition, Data Gaps Report proposes that this “breakpoint” is the same under different experimental conditions. This analysis is not substantiated by experimental data, and is likely incorrect. Further, the model uses one experimental point to determine two lines (see Figure #1); therefore the experimental data neither support or refute the model, as one point is “consistent” with any model (see Figure #2). While solubility may have an effect on naphthalene emissions, this effect is very difficult to approximate in a dynamic system. Changing experimental conditions will change any solubility limit. Therefore, while the output of the model is very sensitive to a single parameter (bulk chemical solubility), the model contains no adjustment to account for: dispersion of naphthalene in the water due to mixing of the slurry, or; additional dilution by added water (i.e. the model uses a single sediment concentration, solubility limit, regardless of the amount of suspended solids in the slurry).

Furthermore, the Data Gaps Report errs by including a correction factor of 0.052 when calculating a theoretical, solubility-limited “breakpoint.” In addition, it is likely that there was NAPL present in some experiments. This is suggested by data that shows high concentrations of naphthalene in sediments, yet water concentration of naphthalene in those experiments well below the solubility of naphthalene.

Conclusions

The general conclusion of MDH analysis of the air emissions data and model is that the public can be protected from exposure to chemicals at levels of concern during dredging. However, the effort necessary to achieve protection is not well understood.

Review of the air emissions model in the Data Gaps Report suggests that:

- ❖ Even a good model of air emissions may err by a factor of 10. Given the uncertainties of air emission models; real-time monitoring of PAHs in ambient air, and contingency plans for reacting to exceedances of acceptable concentrations, should be in place during dredging.
- ❖ The Data Gaps Report proposes the use of experimental emission rates that are not well supported by data.
- ❖ The Data Gaps Report emission model is not accurate, does not reflect environmental processes. Furthermore, the model appears to overestimate emissions, especially at low solids concentrations, and provides results that do not agree with experimental data or that are irrelevant.
- ❖ Combining uncertain experimental emission rates with an incorrect model that appears to overestimate emission rates yields unusable inputs into a dispersion model.
- ❖ Emissions during dredging may approach levels of concern, but the majority of those emissions will come from a CDF that can be covered. Enclosed processing of dredged spoils, offsite transport of slurries and utilization of geotextile sediment containment tubes may also significantly decrease PAH emissions.
- ❖ The most significant data gap, that could impact emissions calculations, may be the lack of data on the magnitude of sediment contamination and the extent of NAPL in the bays.
- ❖ Mass balance should be performed when conducting experiments with volatile chemicals in different phases or media.
- ❖ 2-methyl naphthalene is emitted from sediment slurries at similar rates as naphthalene. The toxicity of 2-methyl naphthalene and other methylated naphthalenes may be similar to naphthalene. Therefore, methylated naphthalene concentrations in sediment should be added to naphthalene concentrations when determining air emissions from sediments.
- ❖ Temperature could have a significant effect on the naphthalene emissions during dredging. Therefore, cells containing the highest concentrations of naphthalene in sediments should be dredged in the early spring or late fall.

The Ice Report in the Data Gaps Report was essentially unchanged from the Ice Report previously submitted by the PRPs. It did contain new field observations from last winter. Analyses of ice intrusion into sediment, the possible formation of ice feet or lenses, and the disruption of the sediment matrix, which have been identified by MDH as processes that may impact the longterm effectiveness of a cap, are not included in the Data Gaps Report.

MDH has also begun reviewing selected areas of the Groundwater Report and expects to have full comments shortly. Concerns are generally related to the groundwater-aided

movement of contaminants through a cap or from a CDF, and the potential for groundwater to contribute to the erosion and ultimate failure of a cap or a CDF.

Discharges of contaminants from the sediments during placement of a cap have not been addressed. Furthermore, a review of fallback or the redeposition of residual contamination on sediments after dredging needs to be conducted. This would help us develop a common understanding of these problems.

Mercury issues related to this site are not discussed in the Data Gaps Report. MDH is mainly concerned about the increase in methylation that can occur in wetland areas that would be created by capping. This may be offset because mercury movement from areas under a cap will be below those currently experienced, but the mobility of mercury is not well understood and therefore cannot be accurately assessed.

Sediment samples taken for the Data Gaps Report were not analyzed for all chemicals that have been identified as potential chemicals of concern by MDH. These include an extended list of carcinogenic PAHs and chlorinated organics.

Recommendations

- ❖ Dredging at other PAH-contaminated sites should be observed, or a pilot study should be conducted on-site to gather better air emission data.
- ❖ If the air emission model is refined:
 - recognize that even a good model may only be accurate to within a factor of 10;
 - review the experimental data from the air emissions experiments to determine if there are usable data from which to calculate emissions of naphthalene;
 - gather additional sediment concentration data. These data may be 2-ring homologue data, accompanied by an estimate of chemical ratios, or more typical analytical data;
 - determine the extent of NAPL at the site and use this information in the model;
 - research and discuss direct volatilization from NAPL to air; and,
 - do not include a “breakpoint” that attempts to describe a solubility limitation of emissions.
- ❖ A better understanding of the extent of residue contamination following dredging is needed.
- ❖ Isolation of a CDF from impacts of groundwater and surfacewater needs to be addressed in a dredging feasibility study.
- ❖ Plans for air monitoring should be developed with community input early in the remedial planning phase.
 - Dissolved and ambient air concentrations of naphthalene should be determined under present conditions, as well as during dredging and capping of contaminated sediments.
- ❖ Contaminant releases that accompany application of a cap need to be itemized and quantified.
- ❖ Longterm effectiveness of a cap (and a CDF) needs to be further addressed in the Data Gaps Report

- Ice effects on the sediment and cap matrix are potentially serious and need study and clarification.
- Groundwater effects on contaminated sediments and a cap in areas where it breaks through, need study and clarification.
- Plant root penetration and potential woody growth on a cap needs to be characterized.
- ❖ The effectiveness of longterm maintenance, monitoring and repair strategies for a cap and a CDF need to be addressed, preferably prior to a Feasibility Study.
- ❖ Sediment PAH analyses should include analysis of the extended list of cPAHs.
- ❖ Chlorinated organic concentrations in sediments should be measured, especially if sediments are left in place and capped.

Public Health Action Plan

- MDH will continue to be active in the community workgroup for the SLRIDT site.
- MDH will continue to monitor progress at this site and be available for consultation.
- MDH will assist with review of further documents, as requested.

This consultation was prepared by:

Carl Herbrandson, Ph. D.
Toxicologist
Site Assessment and Consultation Unit
Environmental Surveillance and Consultation Section
Minnesota Department of Health

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CERTIFICATION

This St. Louis/Interlake/Duluth Tar Site 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.

Signed copy available on request

Alan W. Yarbrough
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.

Signed copy available on request

Roberta Erlwein
Chief, State Program Section, SSAB, DHAC, ATSDR

Figure #1
DGR model naphthalene emissions
(238 mg/kg "breakpoint")

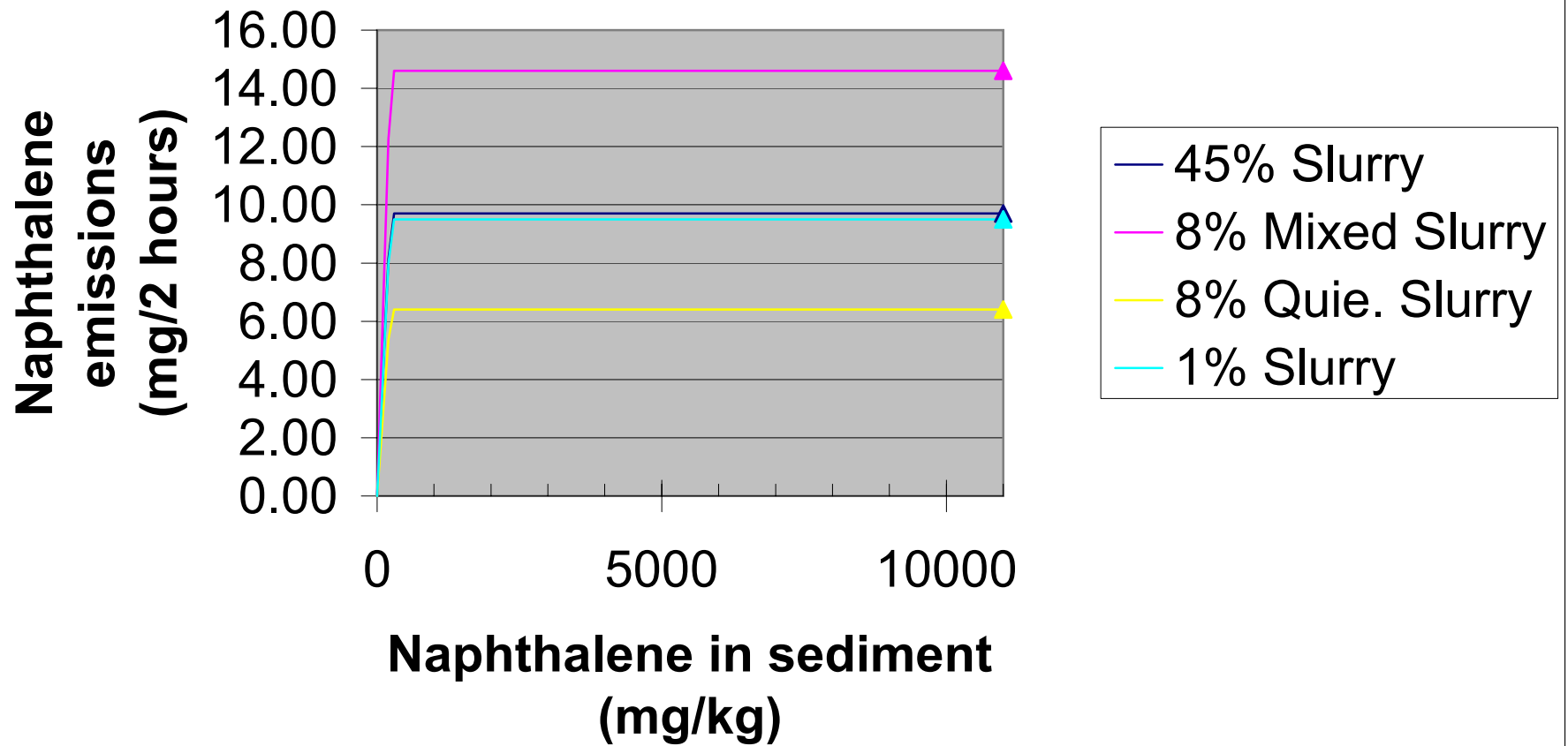


Figure #2
Model interpretation of naphthalene emissions from the 8% mixed slurry (Different "breakpoints")

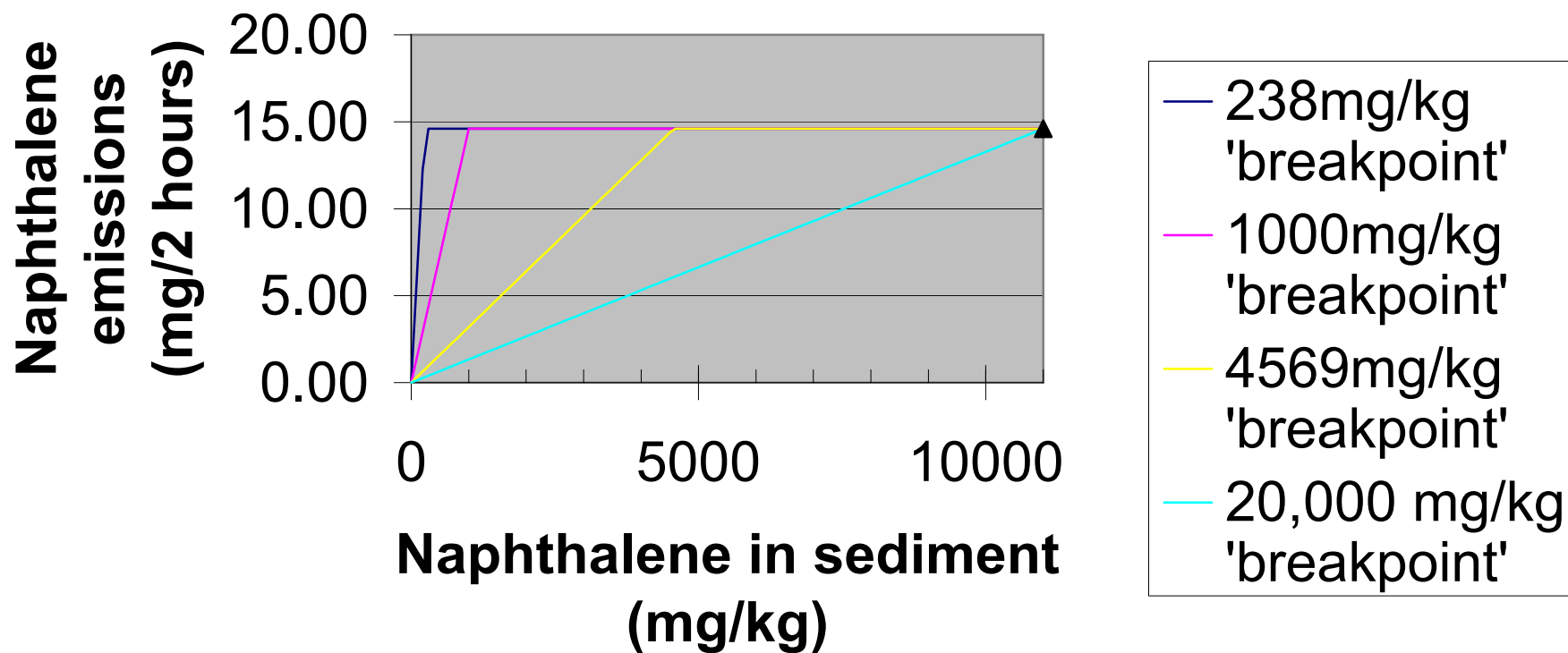


Figure #3
Corrected, normalized rate - 45%

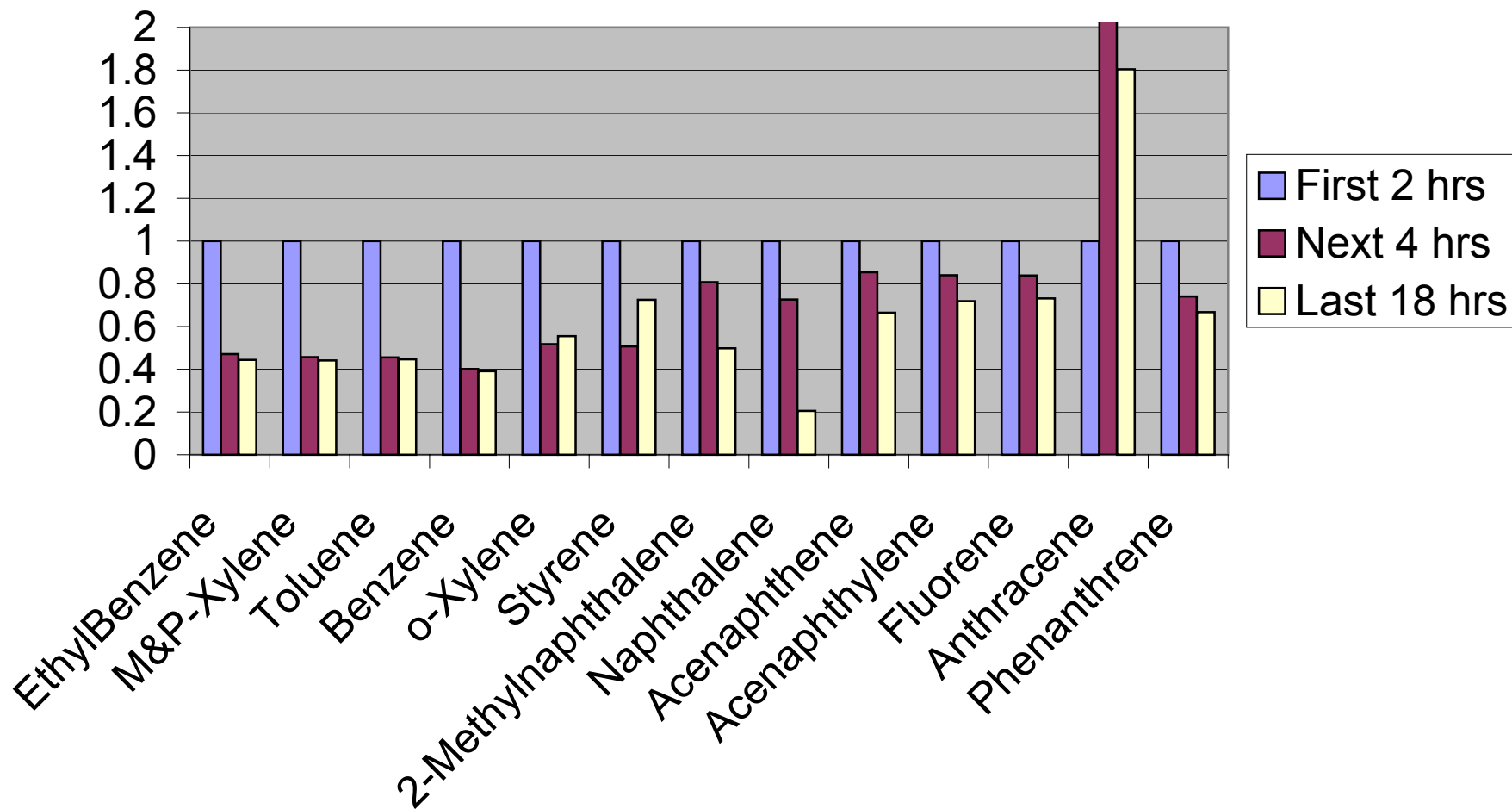


Figure #4
Corrected, normalized rate - 8% Mixed

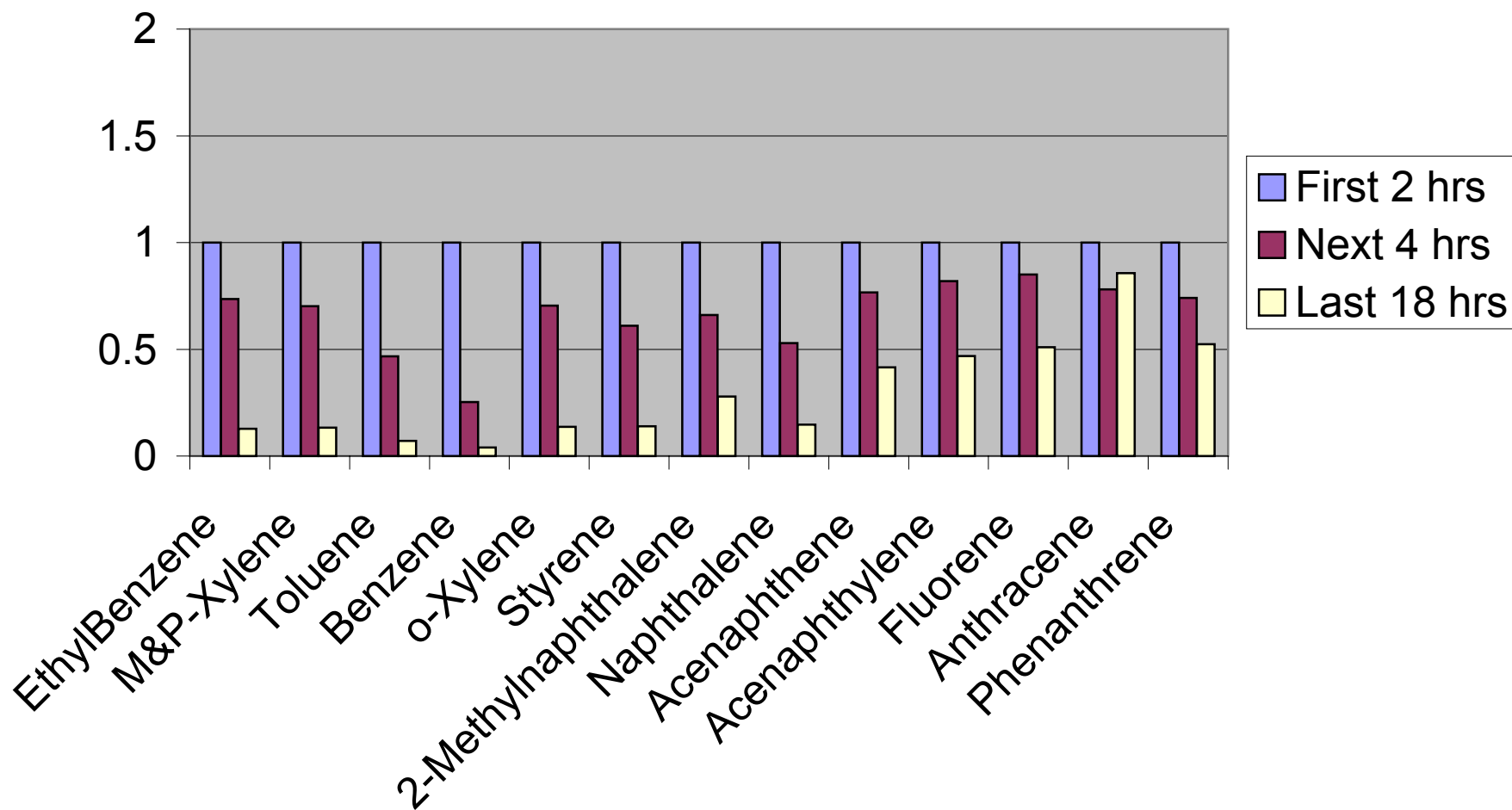


Figure #5
Corrected, normalized - 8% Quiescent

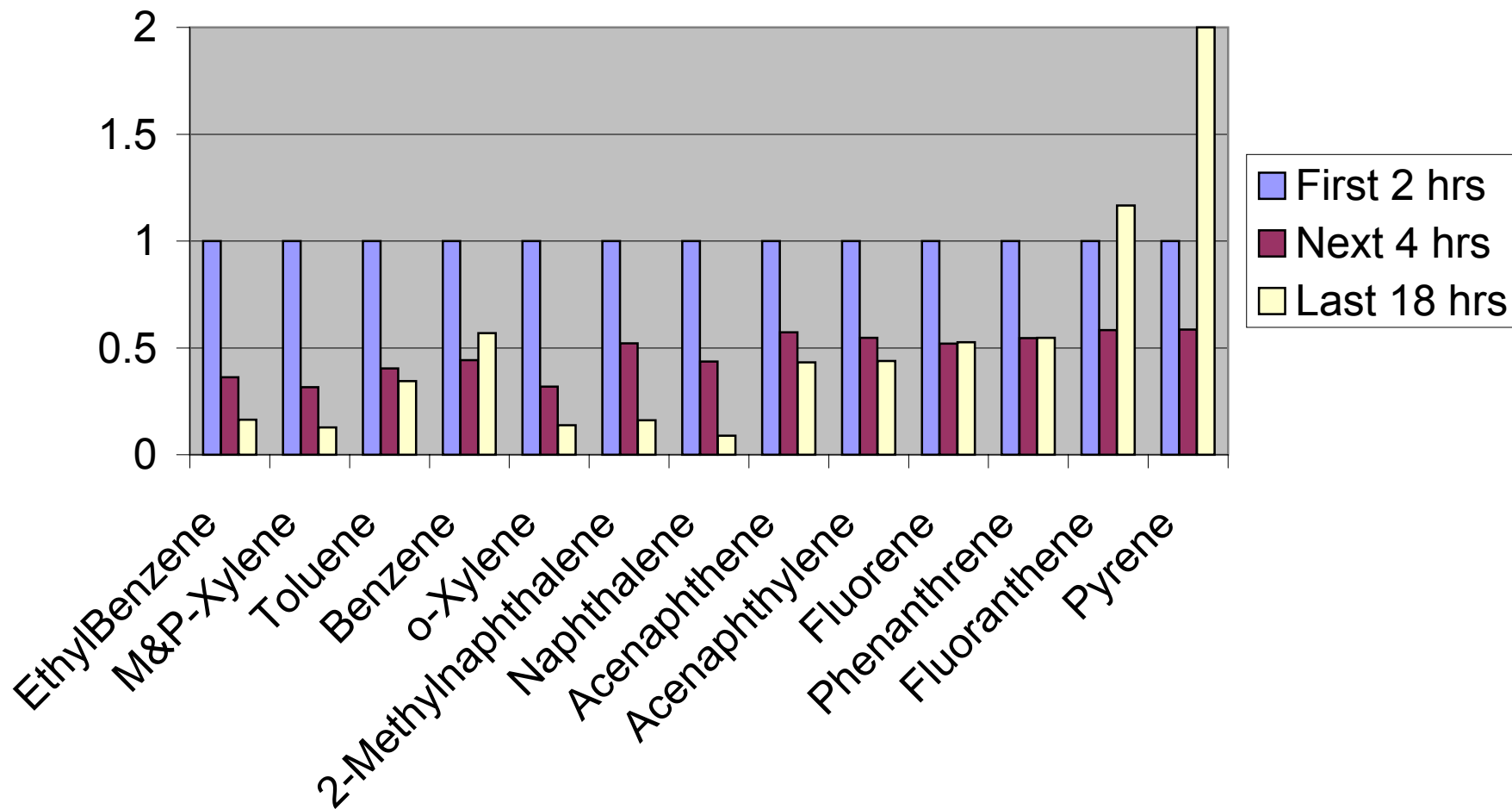


Figure #6
Corrected, normalized - 1%

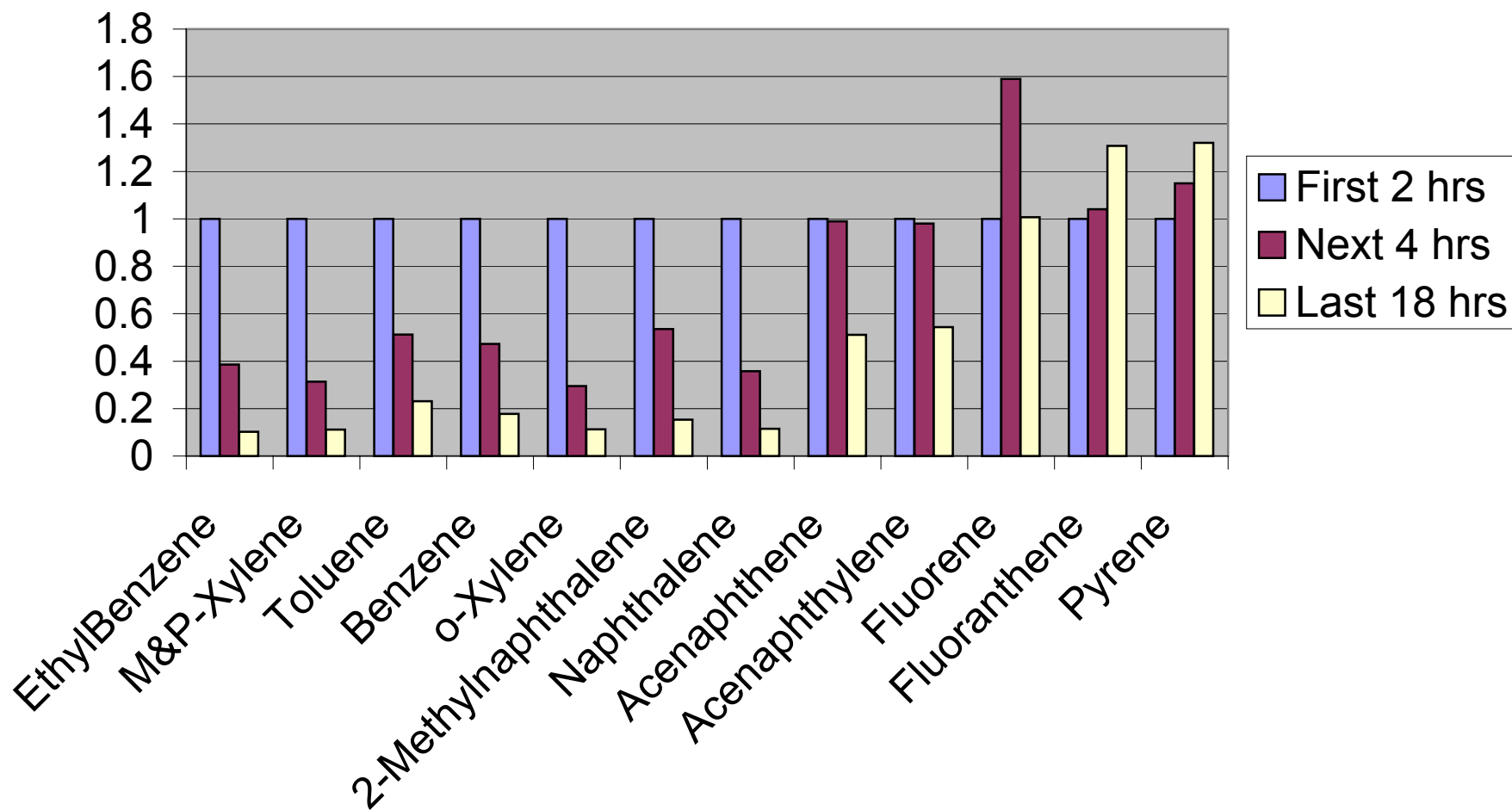
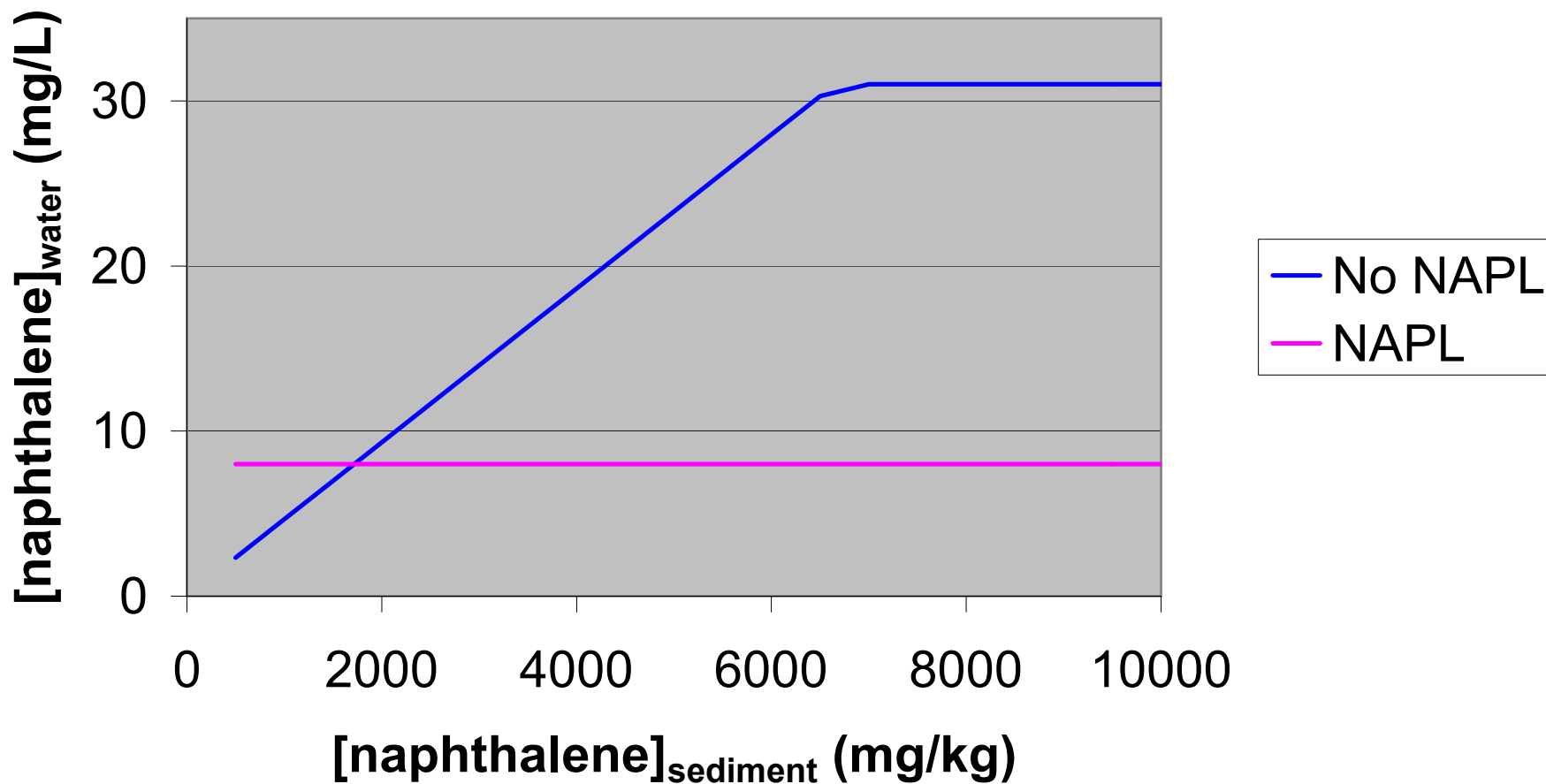


Figure #7
Dissolved naphthalene w & w/o NAPL



Appendix 1

Using the Data Gaps Report air emission model to predict naphthalene emissions

The air emission model in the Data Gaps Report proposes that as the naphthalene concentration in sediment increases, air emissions increase proportionally until naphthalene emissions reach a maximum. The naphthalene concentration in sediment at this point is considered to be the 'breakpoint' and naphthalene emissions at all sediment concentrations above this 'breakpoint' will be the same as emissions at this 'breakpoint.' According to the model, this 'breakpoint' is a result of flux from sediment to air being limited by the maximum solubility of naphthalene in water. The model also proposes that this chemical concentration limit is the same under all experimental conditions: high and low ratios of sediment:water, and with and without mixing. Theoretical problems with the model are discussed in the main body of the Health Consultation.

The Data Gaps Report proposes that the solubility limit to naphthalene emissions are achieved with sediment containing 238 mg/kg naphthalene. Application of this proposed 'breakpoint' to experimental data from the Data Gaps Report suggests that there are significant errors with the emission model proposed in the Data Gaps Report.

The Health Consultation contains an extensive discussion on the inadequacies of the analytical characterization of the experimental slurries. The lack of reliable data may impact the actual calculations in this appendix, but it does not affect a qualitative analysis and it is unlikely to affect the conclusions of this analysis. For the sake of the analyses below, it is assumed that all naphthalene in each experimental slurry came from additions of solid sediment containing 11,000 mg naphthalene per kg solids.

Data from the Data Gaps Report (Table A2-2) shows that naphthalene emissions from the experimental slurries over the first 2 hours were 9.7, 14.6, 6.4, and 9.5 mg for the 45% (46.8% measured solids - Table A1-1), 8% mixed (8.2%), 8% quiescent (9.0%), and 1% (1.5%) slurries respectively. The Data Gaps Report model says that emissions would be the same if the naphthalene concentration in sediment used to make up the slurries was 238 mg/kg. Under these conditions, the total amount of naphthalene in the experimental slurries would have been 234, 41, 45, and 7.5 mg naphthalene for the 45%, 8% mixed, 8% quiescent, and 1% slurries respectively. Comparison of the predicted emissions from the model and the total naphthalene in the 238 mg/kg sediment additions shows that the predicted emissions exceed the total naphthalene in the 1% slurry by about 27%. In addition, if the emissions are estimated from the 24-hour Data Gap Report emissions, the expected emissions will be about 2.5 times the total naphthalene in the 1% slurry. Similarly, predicted 24 hour emissions from the 8% mixed slurry of 238 mg/kg naphthalene and water will be about 1.1 times the total amount of naphthalene in an experimental slurry.

Table #1A shows the amount of naphthalene in experimental and proposed slurries, and the actual experimental results as well as the predicted results.

Table #1A

		Experimental Results:		Projected results from Data Gaps Report model:		
		Slurry made with 11,000 mg _{naphthalene} /kg _{sed}		Slurry made with 238 mg _{naphthalene} /kg _{sed}		
Experimental conditions	Initial naphthalene per experiment	Total naphthalene emitted (% initial)		Initial naphthalene per experiment	Projected total naphthalene emitted (% initial)	
	mg/sample	2 hr	24 hr		2 hr	24 hr
		mg	mg			
45% Slurry	10,811	9.7 (0.09%)	41.2 (0.38%)	234	9.7 (4%)	41.2 (18%)
8% Mixed Slurry	1,894	14.6 (0.77%)	45.6 (2.41%)	41	14.6 (36%)	45.6 (111%)
8% Quiescent Slurry	2,079	6.4 (0.31%)	16.8 (0.81%)	45	6.4 (14%)	16.8 (37%)
1% Slurry	347	9.5 (2.75%)	18.9 (5.46%)	7.5	9.5 (127%)	18.9 (252%)

Since the Data Gaps Report predicts greater naphthalene emissions than contained in the sediments it cannot be expected to accurately predict emissions during dredging.

Appendix 2

Site-specific derivation of K_{oc}

A sequential batch leaching test (SBLT) was performed for the Data Gaps Report on sediment samples from the 3 bays of the SLRIDT site, to derive site-specific partitioning coefficients. In order to derive coefficients that describe partitioning between sediment (normalized to total organic carbon (T_{oc})) and water, it is necessary for concentrations to reach equilibrium between the 2 mediums, and for the concentration in water to be below the solubility of the chemical (e.g. naphthalene). If the concentration in the sediment is too high, the dissolved concentration cannot increase to reflect the K_{oc} of the chemical, but is limited by its solubility. If, on the other hand, the dissolved concentration does not approach the solubility, K_{oc} can be determined from the relationship described in equation #1.

$$K_{oc} \text{ (L/kg)} = [\text{naphthalene}_{\text{sediment}}] \text{ (mg/kg)} / [\text{naphthalene}_{\text{dissolved}}] \text{ (mg/L)} / f_{oc} \text{ -equation \#1}$$

(for dissolved naphthalene ≤ 31 mg/L)

Where f_{oc} = the fraction of organic carbon in the sediment

In an SBLT, determination of K_{ocs} can be made from sediment and dissolved analytical data from multiple samples that are successively prepared by serial dilution of the same sediment sample. If the dissolved concentration of a specific chemical remains the same over successive iterations, then the experiment for that specific chemical is probably limited by the solubility of the chemical. Therefore, the K_{oc} cannot be determined from these data. On the other hand, if the dissolved portion decreases, K_{ocs} can be calculated from each iteration, or by combining the data from all iterations.

If calculated K_{ocs} are similar for each iteration for the same chemical, then at least the portion desorbed was adsorbed similarly to sediments. If the K_{oc} increases with successive leachings, the chemical may be adsorbed to different types of organic carbon in the sediment with different affinities. Differing affinity for different types of organic materials was briefly discussed in the Health Consultation, with references to scientific literature that describe an increased affinity (increased K_{oc}) of PAHs for aromatic and anthropogenic organic particulates.

The presence of NAPL in a sediment sample makes determination of a K_{oc} useless. Furthermore, K_{oc} is not a useful metric in a system that contains a NAPL. Partitioning between a NAPL and water is not driven by the amount of NAPL in a system, but by the fraction of the NAPL that is the chemical of interest. Therefore, while sediment concentration of the chemical may vary broadly in the presence of a NAPL, the dissolved concentration can remain constant.

Problems encountered when calculating K_{oc}

Measuring dissolved concentrations of non-polar organic chemicals, especially very hydrophobic (i.e. with $\log K_{ow}$ s > 4 or 5) and very volatile chemicals (e.g. benzene, naphthalene), can be difficult. Significant amounts of hydrophobic chemicals can be

sorbed to organic carbon in small colloids that may pass through filters used to separate phases. These sorbed chemicals may be operationally-defined as 'dissolved' which can skew a calculation of K_{oc} and bias it low. Care was taken in the SBLT report to limit this bias. On the other hand, sequential filtration of volatile chemicals can lead to increased loss of dissolved chemical, leading to K_{oc} calculations for volatile chemicals being biased high. Therefore, if additional handling of laboratory samples increases a calculated K_{oc} (as a result of decreased dissolved chemical) it may not be possible to determine if the increase is a result of removal of colloids or volatilization of chemical. To be assured that volatilization losses have not occurred in the laboratory during phase separation, it is important to conduct mass balance on chemicals, especially volatile chemicals.

Serial filtration of samples is appropriate for high K_{ow} compounds such as benz[a]anthracene ($\log K_{ow} = 5.91$), but does not appreciably improve estimates of dissolved concentrations for chemicals with low K_{ow} s such as naphthalene ($\log K_{ow} = 3.36$). In addition, naphthalene may be lost from the dissolved phase during successive handlings which could decrease the dissolved concentration. Therefore, successive filtrations with 0.7, 0.5, and 0.22 μ m filters, such as was done in the SBLT is not advised for characterizing dissolved naphthalene concentrations.

Data from the colloid study in the SBLT Report support this analysis. Naphthalene concentrations in operationally-defined dissolved samples from Stryker Bay were about 22,000 μ g/L (100%), 9400 μ g/L (42%) and 4,500 μ g/L (20%) after being filtered with 0.7 μ m, 0.5 μ m and 0.22 filters successively. Benz[a]anthracene concentrations in operationally-defined dissolved samples from Stryker Bay were about 4.1 μ g/L (100%), 4.0 μ g/L (96%) and 0.24 μ g/L (6%) after being filtered with 0.7 μ m, 0.5 μ m and 0.22 filters successively. The K_{ow} of benz[a]anthracene is 355 times greater than the K_{ow} of naphthalene, and yet the ratios of the amount lost following sequential filtration differ by only a factor of 4. This suggests that sequential filtration of sediment containing naphthalene may not only remove colloids, but may also release significant amounts of volatile naphthalene. (It is uncertain, but doubtful, that this sample contained naphthalene in a NAPL, because naphthalene in a NAPL (~ 5% naphthalene) will equilibrate with about 5 - 11 mg/L dissolved naphthalene.)

K_{oc} calculation

Stryker Bay

The Stryker Bay SBLT data in Data Gaps Report SBLT Table 4-4 show that the dissolved naphthalene concentration does not change through successive leachings of sediment. Therefore, the dissolved concentration is likely limited by the presence of naphthalene in a NAPL or by sediment concentrations that can saturate water at equilibrium. Because successive leachings result in similar dissolved concentrations between 5 and 11 mg/L (0.7 μ m filtered concentrations of 8,000, 9,500, 7,500, and 7,800 μ g/L) it is likely that the sediment used in this test contained a NAPL. In addition, because the initial sediment concentration was 3,300 mg/kg naphthalene, and the final sediment concentration was 1600 mg/kg, and yet the dissolved concentrations of naphthalene were similar (8,000 and 7,800 μ g/L), either: the sediment contained a NAPL; the system did not reach equilibrium, or; there were discrepancies between the 2 tests. It

is clear from the data that, in the case where there was no NAPL, the sediment concentration used to calculate a K_{oc} for naphthalene in Stryker Bay must be below the lowest measured sediment concentration for the Stryker Bay sample, i.e. less than 1600. Therefore, the resulting K_{oc} must be below 892 L/kg ($\text{naphthalene}_{\text{sed}} / T_{oc} / \text{naphthalene}_{\text{water}}$; $1600 / 23\% / 7.8$). The K_{oc} of these sediments is expected to be greater than the published value of 933 L/kg (ATSDR, 1995) because the sediments contain considerable anthropogenic carbon. Yet these results suggest that a K_{oc} calculated from this sample is equal to or less than the published K_{oc} . This may also suggest the presence of a NAPL in this sample.

The Data Gaps Report calculated a Stryker Bay site-specific K_{oc} from the pre-leaching SBLT sediment concentration (3,300 mg/kg), and the assumed maximum dissolved naphthalene (4.5 mg/L; see above, colloid test). The resulting K_{oc} that is cited in other sections of the Data Gaps Report is 3,200 L/kg ($3,300 / 23\% / 4.5 = 3,200$). This K_{oc} was calculated using improper data and should not be used.

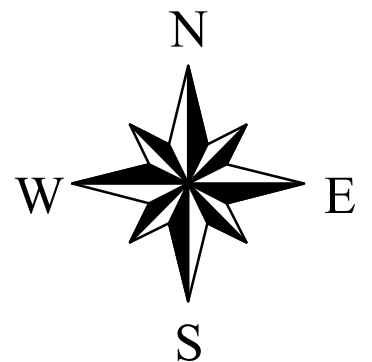
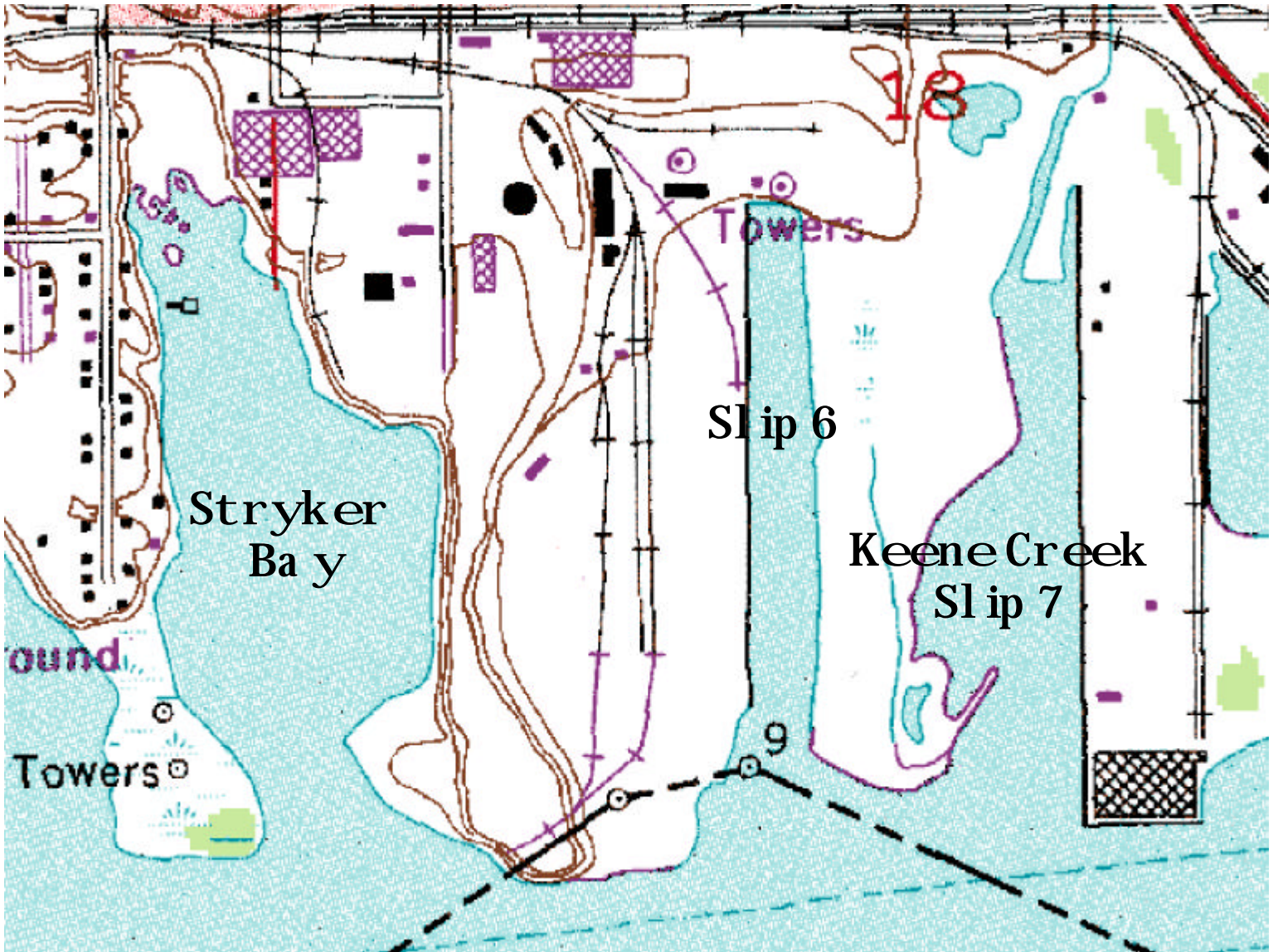
The discussion in this appendix suggests the importance of discerning if PAHs in sediment are in a NAPL, or sorbed to the sediment. In addition MDH recommends that because there are no reliable data from which to calculate a site-specific K_{oc} , published K_{oc} s be used at this site.

Reference

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Attachment 1

St. Louis River/Interlake/ Duluth Tar Superfund Site



Attachment #2

MDH Testimony Before the MPCA Citizens' Board Committee Meeting
Duluth, MN
October 25, 1999

Carl Herbrandson, Ph.D.
Environmental Toxicologist
Minnesota Department of Health

At MDH, our concern is human health - - and we focus our analysis of effects during the choice of remedy only on its implications as related to human health.

Introduction:

- I work in collaboration with MPCA toxicologists - - and since MPCA toxicologists are intimately involved in this site my involvement has been limited primarily to consultation and review.
- A couple of years ago I did work with Helen Goeden on development of health criteria for assessing potential risk to human health at this site
- I have also briefly reviewed the ROD
- Directly involved in USX Site (a site which has had less involvement by MPCA toxicologists) for the last 2 years - - spent some time looking at dredging and its effect on distribution / redistribution of persistent chemicals including mercury

While MDH has some concern about PAH contamination at this site, I believe that the MPCA has covered this concern. Mercury in the sediments of Stryker Bay has potentially broader Public Health implications, and is of concern to MDH because it may be contributing to the methyl-mercury pool in the lower St. Louis River and to levels of methyl-mercury in fish which are then caught and eaten.

- This is the only river in the state with a mercury-based DoNotEat fish consumption advisory for predator fish (25-30" walleye) in the state. While mercury in sediment and mercury in fish do not always correlate well due to issues like: variable rates of mercury methylation and fish movement throughout a watershed, the EPA has suggested that if sediment concentrations of mercury are less than 1/10th of those found in layers 101 and 102 at this site, fish consumption is probably a human health issue.
- There is a lot we do not know about mercury geo and hydro-chemistry. We know that mercury has an affinity for materials which make up sediment, so generally, it is not very mobile in sediments. We also know that for mercury to be accumulated in fish it needs to be converted to methylmercury. And we know that conversion to methylmercury is increased in anoxic sediments. Therefore, we expect the production of methylmercury to be elevated in a wetland.
- So how can mercury move in the aquatic environment??
 - We know that mercury can be transported with suspended sediments. Mercury, and (mono)methyl-mercury, movement in groundwater is very slow, but it is unknown if mercury or methyl-mercury could be co-transported with other compounds in a wetland or what other chemical species of mercury may be

manufactured in a wetland. It is also not known if or how vegetation in wetlands may affect the mobility of buried sediments. There is some information demonstrating that significant amounts of methyl-mercury can be found in macrophytes (such as cat-tails - Miles CJ; Fink, LE) , presumably taken up from sediments. Some portion of the methyl-mercury appears to be volatilized into the air. This may be just one way in which mercury can move in a wetland

- The presence of mercury contamination in Stryker Bay, at concentrations up to 2.7 ppm is of concern to MDH. If it could be covered in place and we could be assured that it would stay there, we would agree that the capping alternative is protective of human health. Given our understanding of mercury in the environment at this time, MDH believes that there may be significant uncertainty in any such assurances.
 - The sediments in Stryker Bay are spread over a large area; they have a very large surface area relative to their volume - - both on top (currently in contact with water - - and potentially in contact with a wetland in the future) - - and they are also exposed, on the bottom, to groundwater which may discharge into the bay / river.
 - MDH believes that there are significant uncertainties which may be associated with the maintenance of a barrier in Stryker Bay which is impermeable to mercury- - these include
 - the effect of groundwater movement and hydraulic pressure
 - maintaining the integrity of a cap in a wetland / river shoreline environment.
- The greatest advantage to dredging alternatives are that they provide the opportunity to control the infiltration of groundwater into sediments (or dredged wastes) through the minimization of the surface area to volume ratio, and possibly by construction of barriers, or through stabilization of the spoils. With a decreased profile to groundwater, surface water, and wetland, long-term uncertainties and the long-term potential availability of mercury from sediments can be minimized.
- While dredging may provide greater long-term security - and less long-term uncertainty, dredging is not a clean operation. Sediments can be resuspended and contaminants can be redistributed and made available to aquatic organisms, or they can volatilize into the air we breathe.
 - We are not engineers and we do not expect to be involved in the development of a detailed remedial action plan for this site, but from the studies we have reviewed involving PCB and toxaphene contaminated sediments, we believe that dredging can be done with minimal resuspension and redistribution of contaminants. It is our understanding from our reading of the literature that choice of dredging methods, appropriate use of sediment screens, and controlled dewatering facilities when properly employed by experienced contractors can control contamination and make overall dredging effects on the environment very minimal. (for example: One study conducted during a PCB cleanup showed no increase in PCBs in water (and suspended particulates) 15-70 m downstream from the dredging activity - Hafferty, Pavlou, Hom) - - hydraulic dredge - - no sediment screen.
- There are sites / conditions where we would definitely not recommend dredging (such as

in a rapidly flowing river - - or in the deep limnetic sediments). This is not one.

Volatilization of contaminants from dredged spoils does occur. However, we expect volatilization from dredging at this location to be limited because the sediment will not be dried. During dredging at this site, we would expect that very little mercury would be volatilized, and that the only compounds which may be released into the air in significant amounts would be the light - non-carcinogenic PAHs, such as naphthalene.

- Studies have shown that chemicals similar to the light - non-carcinogenic PAHs at this site volatilize at a rate related to the evaporation of water and the drying of the sediments. Therefore if drying is kept to a minimum, volatilization can be kept to a minimum.
- Most studies / concern about volatilization I have seen are specifically related to dredging operations where there is land disposal of the dredged materials. It is my understanding that at this location, the sediments will remain wet, thereby limiting the volatilization of light PAHs. It is also my understanding that previous dredging or soil excavation at this site was accompanied by drying and baking of the sediments prior to burning - - clearly activities which maximize volatilization.
- Dredging is always associated with smells - - typically swamp gases such as methane and H₂S are released. Both of these gases volatilize from water and sediment much more readily than PAHs. PAHs are ubiquitous - and it is not known how much dredging could contribute to already existing levels of PAHs in air - - - studies have shown that levels of PCBs in air may be increased by dredging PCB containing sediments, but that study also raised questions about the possibility that some of the significant levels of PCBs attributed to the dredging may have been volatilizing from open water in the bay itself. Again - - at this site, these dredged spoils will not be dried out, therefore, volatilization / odors will be minimized.

In conclusion, MDH supports this ROD and hopes that the issues we have raised and discussed will be considered during the development of the detailed Remedial Action Plan.

Attachment #3



Memo

Date: February 19, 2003

To: Shelley Burman, Supervisor
Risk Evaluation/Air Modeling Unit

From: Hillary M. Carpenter, Ph.D.
Health Risk Assessment Unit

Subject: Air Health-based Value for Naphthalene

This memo is in response to your agency's December 5 request for an air health-based value (HBV) for naphthalene to be used in a clean up of the St. Louis River Interlake Duluth Tar site. During consultation with staff familiar with the project, it was decided that two numbers were needed; consequently, the Minnesota Department of Health (MDH) has derived both an acute HBV (200 $\mu\text{g}/\text{m}^3$) and a chronic HBV (9 $\mu\text{g}/\text{m}^3$) for inhalation exposures to naphthalene. A description of the techniques, assumptions and caveats used in developing these numbers follows.

Acute. There are limited data addressing the impacts of acute exposures of experimental animals to naphthalene. However, because there are a number of anecdotal reports of naphthalene toxicity in humans (nausea, vomiting, abdominal pain, and hemolytic anemia) at concentrations above those that trigger an odor (200 – 440 $\mu\text{g}/\text{m}^3$) MDH recommends the use of an acute HBV (one hour exposure) of 200 $\mu\text{g}/\text{m}^3$ as a reasonable maximum exposure level.

This use of this number is supported by results from a study on rats that reported respiratory changes (cell swelling and sloughing) following four hours of exposure to 380 mg/m^3 of naphthalene (Buckpitt, 1982). In this study 204 mg/m^3 was a No Observed Adverse Effect Level (NOAEL). Applying an uncertainty factor of 1000 (10 for intraspecies variability, 10 for interspecies variability, and 10 for database deficiencies) gives an acute value of 200 $\mu\text{g}/\text{m}^3$ for a four-hour exposure. As an additional precaution MDH recommends that this number be applied using a 1 hour averaging time.

Chronic. Two studies chronic rodent bioassays, one in mice (NTP, 1992) and one in rats (NTP, 2000) are the basis for MDH's chronic HBV of 9 $\mu\text{g}/\text{m}^3$ naphthalene. Both of these studies involved the administration of naphthalene for 6 hours per day, five days per week for two years. Both studies produced a Lowest Observed Adverse Effect Level (LOAEL) of 10 ppm naphthalene with fairly marked respiratory and nasal impacts as adverse endpoints.

Manipulating this exposure to allow for a 24 hour/day and a seven day/week yields an adjusted LOAEL of 1.78 ppm which converts to a value of 9.3 mg naphthalene/ m^3 . Applying an uncertainty factor of 1000 (10 for intraspecies variability, 10 for interspecies variability, and 10 for the use of a LOAEL rather than a NOAEL) results in a final chronic HBV for naphthalene of 9 $\mu\text{g}/\text{m}^3$. Although, by definition MDH considers a chronic exposure to be one that occurs on a daily over a 70-year lifetime, MDH recommends that exposures that take place for more than 10 percent of an individual's lifetime be assessed using chronic values. MDH anticipates that chronic HBVs will be applied using annual emission estimates. MDH understands that the exposures associated with the remediation of this site will be occurring for a maximum of seven months each year, but feels that the potential for public health

impacts be assessed using the chronic number.

Please be advised that although MDH has a reasonable level of confidence in the chronic naphthalene number, and in fact intends to propose this value as a HRV during the next rule revision, available data do not address two additional toxic endpoints reported in humans, cataracts and the blood disorder hemolytic anemia. MDH is therefore less certain about the conservative nature of the naphthalene number for these endpoints.

MDH has less confidence in the acute value and suggests that it be considered a site-specific screening number to be used to trigger some remedial action.

If you have any questions regarding the development of these numbers please call me at (651) 215-0928.

HMC:rlk

References:

Buckpitt, A.R. (1982). Comparative biochemistry and metabolism. Part 2: Naphthalene lung toxicity. AFAMRL-TR-82-52, pg 25-30. Air Force Aerospace Medical Research Laboratory, Wright-Patterson Air Force Base, Ohio.

NTP (1992). National Toxicology Program. Toxicology and carcinogenesis studies of naphthalene (CAS No. 91-20-3) in B6C3F1 mice (inhalation studies). NTP Technical Report Series No. 410. NIH publication no. 92-3141. U.S. Department of Health and Human Services, Public Health Service, National Institutes of Health, Research Triangle Park, N.C.

NTP (2000). National Toxicology Program. Toxicology and carcinogenesis studies of naphthalene (CAS No. 91-20-3) in F344/N rats (inhalation studies). NTP Technical Report Series No. 500. NIH publication no. 01-4434. U.S. Department of Health and Human Services, Public Health Service, National Institutes of Health, Research Triangle Park, N.C.

cc: Barb Jackson, MPCA
Doug Beckwith, MPCA
Bruce Brott, MPCA
Doug Wegstein, MPCA

Attachments

Attachment #4

DEPARTMENT: Health / Pollution Control
Agency

State of Minnesota
Office Memorandum

DATE: February 7, 2003

TO: Jane Mosel and Mike Bares, Minnesota Pollution Control Agency

FROM: Carl Herbrandson, Ph.D., Toxicologist, MDH;
Steve Hennes, M.S., Toxicologist, MPCA

PHONE: 651 / 215-0925

SUBJECT: SLRIDT Site visit

On February 6 2003, from about 2:30 to 4:30 PM, Carl Herbrandson and Steve Hennes walked the ice at the SLRIDT site. It was a cloudless sunny day with a temperature of about 0° F and a N-NE wind of about 8-10 MPH. The ice looked about 3 feet thick and in most areas it was covered by about 1 inch of snow. In some areas, mainly in the river and near the mouth of the bays, the ice was uncovered and clear, but crisscrossed by cracks.

We started at the tip of Slip #7 and walked to the river. We proceeded up river to Stryker Bay, walked around the bay clockwise, and then walked back to our start point in Slip #7. We did not walk into Slip #6, but observed it from the river. See attached figure for route and location of notable observations.

Ice in the middle of Slip #7 was about 1 ½ foot below ice along parts of the western and northern sides of the bay. This phenomenon was also noted at places in Stryker bay and also along the river.

The artesian (?) well in the shed attached to the large warehouse on the eastern shoe of Slip #7 was flowing rapidly (maybe > 1 L/sec). The water heated the area enough to keep ice from building up around the well or the shed. The pool of water extended to the gravel roadway between the shed and the bay, and then disappeared into the ground.

There were numerous pressure ridges of ice in the river. While most were about 2-3 feet high, some reached about 4 feet. The largest ridge extended from the eastern tip of Slip #7 to Indian point. There were several branches from this ridge. Most went out into the river, but one went from this ridge north to the land between Slip#6 and Stryker Bay.

There was an ice fishing house in the mouth of Slip #6 (see attached figure) that appeared to have been brought from shore at Hallett Dock Co..

A small pressure ridge was apparent at the narrowest point in the mouth of Stryker Bay (see attached figure). Residents' docks, about 7-8 total, were all pulled to shore except for the Simonson's small dock, a wooden dock that sat on the edge of a wetland on wooden blocks, and a dock that was suspended above the ice from a single piling (see pictures). Snowmobiles and 4-wheelers appeared to regularly use the bay.

Four apparent groundwater springs were noted in shallow areas of Stryker Bay (see attached figure and pictures): one in the middle of the wetland at the head of the bay; a second a little south of the first, in cattails along the eastern shore; the third in the area of the former discharge pipe, along the shoreline; and the fourth about 30 feet from the eastern shore, and about 100 feet north of the mouth to the bay.

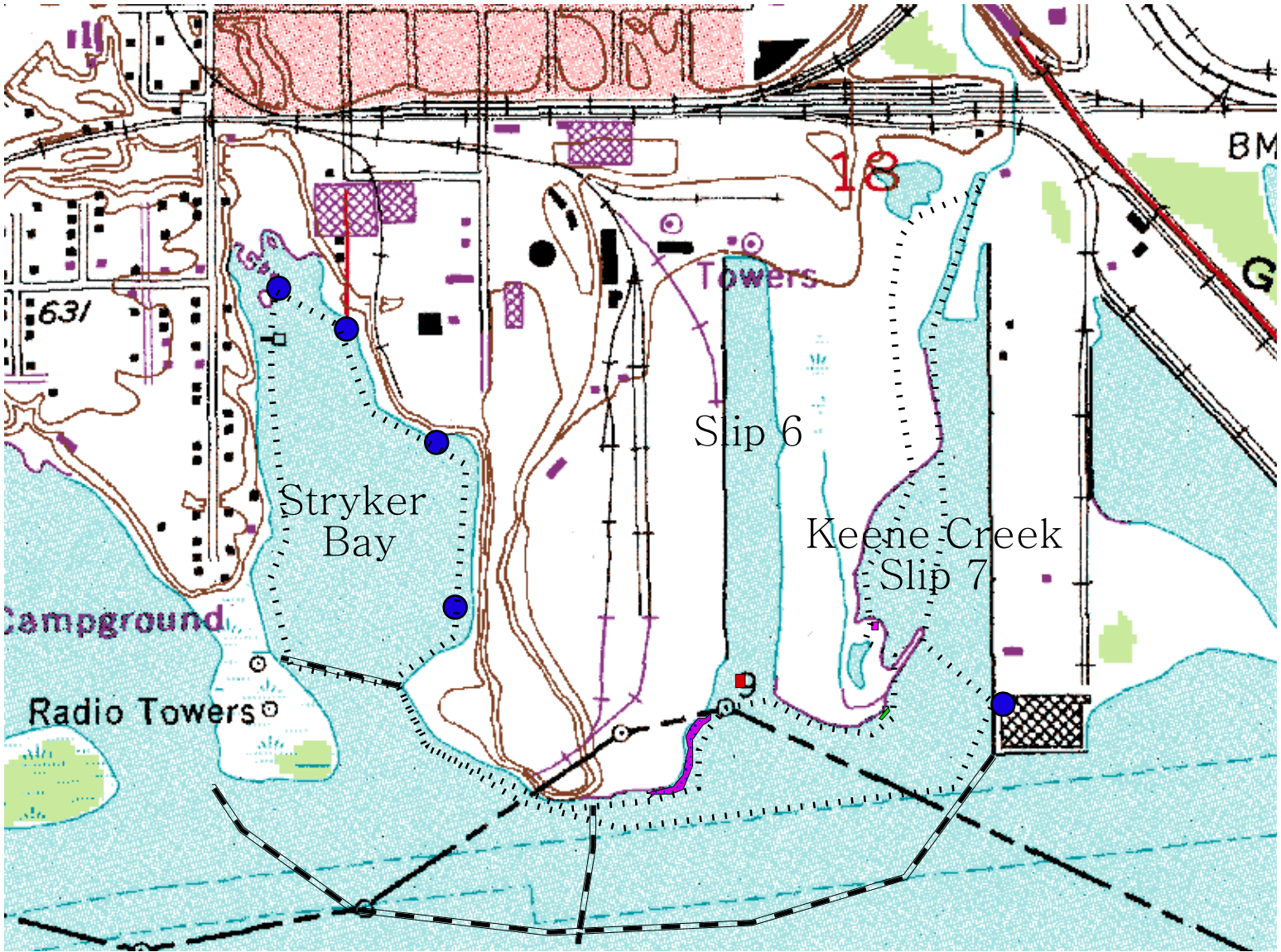
Along the western shore of the mouth of Slip #6 we observed ice (4-6 inches thick) with about 3-4 inches of sediment attached to the bottom, pushed up on shore (see attached figure and pictures).

The contaminated sediments sign at the mouth of Slip #7 had apparently been unbolted from the sign posts and turned to face the shore. In addition, the area around the sign posts had either been eroded away, or the post had been lifted or heaved about 1 foot. About 1 foot dia. of sediment/concrete remained attached to the posts, about 1 foot above the terrain (shore? sediment?)(see attached figure and pictures).

In the wetland area of Slip #7, on the vegetated sandbar, there was a large wooden box that contained 2-10x12x7 inch data logger-type metal boxes. One was identified as a multiplexer. Several cables extended out into the water (ice) of the bay. There were several sets of footprints around the box.

Site Visit 2-6-2003

St. Louis River/Interlake/ Duluth Tar Superfund Site



1000 0 1000 2000 Feet

- Walking path
- Pressure ridges
- Spring locations
- ▲ Pushed up ice
- Ice fishing house
- Electronics box
- ▲ Contaminated sediments sign

