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REGION 1
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SUBJ: Human Health Risk Screening Analysis for a Recreational Exposure to
sediments in the Woonasquatucket River, Providence, RI

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TO: Woonasquatucket Team

INTRODUCTION

The following is a human health risk screening analysis for an older child or an adult who may be directly exposed to sediments in the Woonasquatucket river during recreational activities. A risk screening analysis is similar to a risk assessment in that similar formulas and methods are used to assess risk. The major difference is that the results of a risk screening are generally more uncertain than those of a risk assessment due to a) a limited data set (resulting in an uncertain exposure dose), b) limited information about exposure, and/or c) data of lower quality than is typically used in a risk assessment. In the case of the Woonasquatucket river this assessment is defined as a risk screening because it is based on limited data, (i.e. 7 samples collected over 7 miles of river in areas that are not very representative of actual exposure), and there is limited information about exposure, (i.e. who is exposed and how often?). Thus this risk screening analysis adopts conservative but reasonable estimates of exposure and toxicity. As a result the true risk is likely to be lower than that estimated here. The results of the risk screen indicate that adverse health effects from direct contact to sediments along the river under a recreational scenario are unlikely. Previous fish sampling efforts indicated that edible fish in the Woonasquatucket River has unacceptably high levels of dioxins, PCBs, mercury and lindane. The most likely source of contamination in fish are the sediments in the river. Thus the sediments may result in an indirect risk to human health through the fish ingestion pathway. If you have any questions about this calculation, do not hesitate to call me at (617)223-5528.

BACKGROUND

In May, 1996 EPA collected sunfish and eel from the Woonasquatucket River and analyzed fillet and offal for cadmium, copper, chromium, nickel lead, zinc, mercury, PCB congeners,

hexachlorobenzene, DDE, DDD, DDT, lindane, chlordane, nonachlor and dioxin homologues¹. A risk screen was performed for a hypothetical subsistence fisherman who would harvest all the fish he ingests from the Woonasquatucket River. The results of the screen indicated that adverse cancer and noncancer health effects could occur in subsistence fishermen who ingested 70g/dy of whole eel or sunfish, (or fish similar to these), for a lifetime from the Woonasquatucket river. Estimated cancer risks in sunfish were due mainly to PCBs (1.3E-03), and 2,3,7,8-TCDD (equivalents) (2.5E-02). Noncancer risks were due mainly to mercury (HQ=1.9), PCBs (HQ=76), and lindane (HQ=1.5).

Over a year later limited sediment sampling was conducted along a seven mile stretch of the Woonasquatucket River. Samples were analyzed for metals, pesticides, total PCBs and congeners 77, 126 and 169, PAHs, and dioxins. Seven samples were collected from the top 4 inches of sediment in low flowing areas directly behind 7 dams in the river. Since there is an immediate need to assess whether exposure to river sediments should be restricted, I have conservatively assumed that the bottom sediment samples collected for this effort would have similar concentrations as the more accessible bank areas. NOTE: This is a very uncertain assumption and may result in an overestimate of the actual risk since most of the sediment samples collected are below water and in areas not likely to be accessed by recreational visitors, (i.e. middle of river instead of on banks).

HAZARD IDENTIFICATION

This screen is focussed on those chemicals which are expected to be the major contributors to excess cancer and noncancer risks. These chemicals are chosen by comparing the maximum concentrations detected in river sediments to a residential risk-based screening level. A residential risk-based screening level is a concentration in soil which is associated with a 1E-06 cancer risk or hazard quotient of 0.1 assuming a young child and adult would be exposed to these soils 350 days/yr for 30 years. These levels are considered to be protective of public health. The Woonasquatucket river is not a residential setting so screening with a risk-based concentration is conservative. The screen results in 7 contaminants of concern (COCs). These are PCBs, benzo(a)anthracene, benzo(b)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, and dioxins.

EXPOSURE ASSESSMENT

Receptor: The receptor for this analysis is an older child or adult who might use areas along the river to picnic, wade or walk. Since this is a screen I have assumed adult body weights, surface areas, and adherence factors for both the older child and adult, rather than conducting an age-specific analysis. This type of analysis is unlikely to result in a big difference in risk estimates but could result in a slight underestimate of risk.

The City of Providence is developing areas around sections of the river as a "Greenway" or an

¹ Memo from A. Burke to I. Balkissoon, "Human Health Risk Screening Analysis for a Subsistence Fisherman in the Woonasquatucket River, Providence, RI," 9/30/96.

area with grass, groomed paths and bikepaths. Since it is unknown where the Greenway will extend to and thus which parts of the river an individual might be exposed to, each dammed area along the river will be considered a discrete exposure area.

Pathway: A recreational user could be exposed to contaminated sediments in the Woonasquatucket river by coming in direct contact with sediments and by accidentally ingesting sediments which had adhered to the hands. These pathways are evaluated in this risk screen. The inhalation pathway is not expected to contribute significantly to the total risk from contaminated sediments since all of the COCs have low vapor pressures and would not be expected to volatilize to any great extent.

Frequency and Duration of Exposure: It will be assumed that the same individual will frequent a discrete exposure area consistently over the long term. This is a conservative assumption since individuals are likely to visit different areas along the river over time. It was also assumed that an individual would visit the river twice a week during the summer months (June, July, August) and once a week during May, September and October. This results in an exposure frequency of 32 days/yr. A long term duration of 24 years (for ages 7-31) was assumed.

Ingestion Rate: Upper end estimates of the amount of soil that an adult would accidentally ingest approximate 100mg/dy. This is a typical default assumption for soil ingestion in residential settings. There is no information on how much sediment an adult or young child might accidentally ingest in a recreational scenario. Since this is a risk screen I have assumed the same ingestion rate as for residential soils. This is a *very* conservative assumption and actual sediment ingestion rates are likely to be much lower.

RISK SCREENING RESULTS

The equation for deriving a protective level of a contaminant in soil or sediment is described below. To estimate risk one simply puts in the site-specific contaminant concentration and solves for TR or target risk. The default value used in this assessment for each exposure parameter is listed next its' symbol below.

$$C_s \text{ (mg/kg)} = \frac{TR \times BW \times AT_c}{F \times D \times CPF \left[\frac{RAF_s \times IR}{10^6 \text{ mg/kg}} + \frac{(SA \times AF \times RAF_d)}{10^6 \text{ mg/kg}} \right]}$$

Where:

C_s = contaminant concentration in soil = risk-based concentration (mg/kg)

TR = target excess lifetime cancer risk - 1E-06

Bwa = adult body weight (70kg)

AT_c = averaging time, carcinogen (70yrs x 365dys/yr) - 25550 days

CPF = cancer potency factor (chemical specific)

F = exposure frequency (32 dys/yr)

IR = soil ingestion rate, (100mg/dy) x FI (fraction ingested from source (1)

AF - soil adherence factor, Kissel et al (1996) - 0.23mg/cm² (reed gatherers)

RAF_o = oral relative absorption factor = amount absorbed from the oral route from the site/amt absorbed from tox study = chemical specific

RAF_{dermal} = dermal relative absorption factor = amount absorbed via the dermal route from the site/amt absorbed from tox study (chemical specific)

SA = hands, lower arms, feet, lower legs

Tables 1 through 4 report the estimated cancer and noncancer risks for each contaminant of concern in the first four areas of the river, (i.e Esmond Dam, Allendale Dam, Lymanville Dam and Manton Dam). Risks were not calculated for other areas of the river due to time constraints but the risks in these sections of the river, (i.e. Dyerville, Olneyville and Lonigan Dams), are likely to be lower than the Manton Dam since concentrations of contaminants continue to drop off with distance from the Allendale Dam.

TABLE 1
RME CANCER RISK AND HAZARD QUOTIENT FOR DIRECT CONTACT TO
SEDIMENTS IN THE WOONASQUATUCKET RIVER
FROM RECREATIONAL EXPOSURES
ESMOND DAM

CHEMICAL	EXPOSURE PT CONCENTRATION (MG/KG)	EXCESS CANCER RISK	HAZARD QUOTIENT
Total PCBs	0.21	5.1E-08	0.07
B(a)A	1.6	1.3E-07	NA
B(b)F	3.7	1.3E-07	NA
B(a)P	2.5	1.3E-06	NA
DBA	0.47	3.7E-07	NA
IP	2.2	1.8E-07	NA
TCDD TEQS	0.00003	2.7E-07	NA
TOTAL		3.3E-06	0.07

TABLE 2
RME CANCER RISK AND HAZARD QUOTIENT FOR DIRECT CONTACT TO
SEDIMENTS IN THE WOONASQUATUCKET RIV ER
FROM RECREATIONAL EXPOSURES
ALLENDALE DAM

CHEMICAL	EXPOSURE PT. CONCENTRATION (MG/KG)	EXCESS CANCER RISK	HAZARD QUOTIENT
Total PCBs	0.71	1.7e-07	0.23
B(a)A	4.5	3.8E-07	NA
B(b)F	9.4	8E-07	NA
B(a)P	5.4	4.5E-06	NA
DBA	0.7	5.5E-07	NA
IP	5.4	4.5E-07	NA
TCDD TEQS	0.004	3.6E-05	NA
TOTAL		4.1E-05	0.07

TABLE 3
RME CANCER RISK AND HAZARD QUOTIENT FOR DIRECT CONTACT TO
SEDIMENTS IN THE WOONASQUATUCKET RIV ER
FROM RECREATIONAL EXPOSURES
LYMANSVILLE DAM

CHEMICAL	EXPOSURE PT. CONCENTRATION (MG/KG)	EXCESS CANCER RISK	HAZARD QUOTIENT
Total PCBs	1.2	2.9E-07	0.4
B(a)A	2.6	2.2E-07	NA
B(b)F	6.0	5.1E-07	NA
B(a)P	3.5	2.9E-06	NA
DBA	0.56	4.7E-07	NA
IP	3.5	2.9E-07	NA
TCDD TEQS	0.006	5.4E-05	NA
TOTAL		5.7E-05	0.07

TABLE 4
RME CANCER RISK AND HAZARD QUOTIENT FOR DIRECT CONTACT TO
SEDIMENTS IN THE WOONASQUATUCKET RIVER
FROM RECREATIONAL EXPOSURES
MANTON DAM

CHEMICAL	EXPOSURE PT. CONCENTRATION (MG/KG)	EXCESS CANCER RISK	HAZARD QUOTIENT
Total PCBs	0.23	5.5E-08	0.08
B(a)A	3.8	3.2E-07	NA
B(b)F	5.1	4.3E-07	NA
B(a)P	3.5	2.9E-06	NA
DBA	0.59	4.6E-07	NA
IP	2.7	2.2E-07	NA
TCDD TEQS	0.0004	3.6E-06	NA
TOTAL		7.8E-06	0.08

At the Esmond Dam (prior to the proposed source for dioxins) it can be seen that benzo(a)pyrene is responsible for the majority of the cancer risk. As one moves downstream past the Allendale Dam TCDD becomes the major contributor to cancer risk estimates. At the Lymansville Dam (at which the highest concentrations of dioxins are measured), the majority of the cancer risk is from TCDD. After this the risks from benzo(a)pyrene and TCDD again are about equal (at the Manton Dam). All estimated cancer risks and hazard quotients are well within EPA's acceptable risk range for the Superfund program. Given the estimated cancer risk and HQ, adverse chronic effects from recreational exposures to river sediments are unlikely. Although additional dams downstream of the Manton Dam were not quantitatively evaluated, the risks are expected to be less than the Manton dam since the concentrations of PAHs and TCDD generally decrease.

UNCERTAINTIES

There are several uncertainties in this risk screening evaluation which could result in an under- or overestimate of the actual risk, although most tend to overestimate the risk. These include the following:

1. Exposure Point Concentration - Since there were no sediment samples in areas where a recreational user might be exposed, (i.e. along the banks), it was assumed that sediment samples collected at the bottom of the river behind dams was representative of what an individual might be

exposed to along the banks. This is a very conservative assumption which may overestimate the true risk since bank sediment samples may be much lower than those collected at depth in depositional areas.

2. Frequency and Duration of Exposure - Because there was limited sampling along the river, it was assumed that the area around each dam was a discrete exposure area and that an individual would visit the same spot 32 times per year. This is likely to overestimate actual exposure since it is more likely that an individual would visit different areas along the river over time. In addition, the duration assumed was 24 years when in fact the average individual doesn't live in one place more than 9 years.

3. Sediment ingestion rate - Since there is little to no information on sediment ingestion rates, it was assumed that the sediment ingestion rate would equal a residential soil ingestion rate. This is likely to overestimate the actual sediment intake since the exposure time in a recreational event is much shorter than in a residential event and the same types of activities (resulting in a higher ingestion rate), are not being performed.

4. Adult exposure parameters Because this is a screen and due to time constraints, an age-specific analysis was not conducted for the older child (ages 7-31). Instead adult parameters were adopted for the older child. Although this is not expected to result in a large difference in the estimated risk, it may result in a slight underestimate of risk.

5. Dioxins - acute exposure An acute exposure is defined as a short-term exposure to high concentrations of a chemical. A characteristic sign of acute exposures to dioxins is delayed lethality after a pronounced wasting syndrome. Dermal effects similar to chloracne are also a prominent sign of acute toxicity. The estimated dose for a recreational user exposed to dioxins in Woonasquatucket river sediments is not high enough to result in this type of acute toxicity.

6. Dioxins - Noncancer effects - Dioxins have been shown to result in a myriad of noncancer effects such as developmental toxicity, impaired reproduction, alterations in endocrine function, immunotoxicity, liver damage, etc. EPA does not currently quantitatively evaluate the health hazards for noncarcinogenic effects since some adverse effects might be occurring at or near background levels of exposure. Thus this risk screen may underestimate noncancer risks from exposures to dioxins. However, it is important to note that the estimated exposure dose for dioxin is very low even for many of the noncancer endpoints.

7. Dermal toxicity to carcinogenic PAHs Carcinogenic PAHs were present in fairly high concentrations in several stretches of the Woonasquatucket river. Although EPA quantitatively evaluates systemic effects from dermal exposure to PAHs, we are currently unable to evaluate dermal toxicity. Carcinogenic PAHs are known to cause skin cancer in laboratory animals. B(a)P is used as a positive control for skin cancer in many animal bioassays. It is likely that skin cancer effects occur at lower levels than do systemic effects. Thus the potential for skin cancer may be underestimated in this risk screen.

SUMMARY AND CONCLUSIONS

This risk screen indicates that adverse health effects from direct contact to sediments in the Woonasquatucket river during recreational exposures are unlikely for an older child or adult. There are several uncertainties in this assessment but most are likely to overestimate rather than underestimate exposure and thus risk. Perhaps the greatest uncertainty is what individuals are actually exposed to. I have taken the highest concentrations present in bottom sediments, which recreational users are not expected to be exposed to, and assumed these represent shoreline concentrations. If there are higher concentrations of contaminants in bank samples this would result in higher risks than those estimated in this screen.

In general, risks are expected to be low due to the low frequency of exposure inherent in this type of a recreational scenario. This is not the same type of exposure that would occur under a residential setting in which this type of contamination would be considered a health hazard. Very short term exposures, such as from a one day clean up of the river, are not expected to result in adverse effects. There is the potential, however, for skin irritation and it would be expected that anyone wading through the river would have protective thigh high rubber waders and rubber gloves.

This screen does not evaluate exposures to individuals who may ingest fish from the river which are contaminated with chemicals present in sediments. A prior risk assessment, based on actual fish samples from the Woonasquatucket river, evaluated the health risk to a subsistence fisherman and concluded that there was an unacceptable excess cancer risk from dioxins, PCBs, mercury, and lindane. As a result the Rhode Island Department of Public Health issued a health advisory for (part of?) the Woonasquatucket river. Additional studies should address the site-specific bioaccumulation potential of these compounds (i.e. from sediment to fish) in order to target those areas of river sediment which are contributing to the human health risk in fish.

DATA NEEDS:

- 1) In order to more accurately assess exposure to a recreational user of the Woonasquatucket river shoreline sediment samples in areas of high access are necessary. Samples should be collected in areas where the proposed "Greenway" is expected to run and should include analysis for cPAHs, dioxins, PCBs and dioxin-like congeners.
- 2) Additional information is needed about who the sensitive receptor is, (for instance is a child of 0-6yrs of age likely to regularly frequent river sediments?), and what is reasonable for frequency of exposure.
- 3) If it is decided that sediments are to be remediated, site-specific bioaccumulation studies should be conducted.
- 4) Additional studies to determine "background" concentrations of dioxins, PCBs and cPAHs in other urban rivers in New England should be conducted.

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0.033

Table VIII

Woonasquatucket Sediment Sampling
USEPA Atlantic Ecology Division

DIOXIN ANALYSIS
PG/G DRY WT. *PP*

Sample Name: Data File Name: Reg. 1 ID Sample Description:	Toxicity Equivalence Factors (TEFS)	27707A	27708A	27717A	27709A	27713A	27714A	27716A
		A8013.D	A8014.D	A8023.D	A8015.D	A8019.D	A8020.D	A8022.D
		06197	06198	06199	06200	06202	06203	06205
		Esmond Dam	Allendale Dam	Lymanville Dam	Manton Dam	Dyerville Dam	Olneyville Dam	Longan Dam
2,3,7,8-TCDD		ND	4170 +	5970 *	444	INT	302	138
2,3,7,8-TCDF		ND	17.2	ND	ND	53.6	ND	ND
2,4,6,8-TCDF		ND	ND	ND	ND	ND	ND	ND
1,2,3,7,8-PeCDD		ND	ND	ND	ND	ND	ND	ND
1,2,3,7,8-PeCDF		ND	ND	ND	ND	6.11	ND	ND
2,3,4,7,8-PeCDF		ND	ND	ND	ND	24.3	6.49	ND
1,2,3,4,7,8-HxCDD		ND	29.2	29.7	ND	ND	ND	ND
1,2,3,6,7,8-HxCDD		67.1	62.3	47.1	14.4	35.8	46.1	ND
1,2,3,7,8,9-HxCDD		66.6	65.2	ND	15.5	41	49.1	ND
1,2,3,4,7,8-HxCDF		40.4	28.1	ND	ND	46.3	ND	ND
1,2,3,6,7,8-HxCDF		39.7	24.7	ND	ND	32.9	ND	12
1,2,3,7,8,9-HxCDF		ND	16.7	9.77	ND	ND	ND	ND
2,3,4,6,7,8-HxCDF		ND	8.22	ND	ND	ND	ND	ND
1,2,3,4,6,7,8-HpCDD		840	739	917	161	416	631	373
1,2,3,4,6,7,8-HpCDF		377	387	356	127	270	192	206
1,2,3,4,7,8,9-HpCDF		ND	ND	ND	ND	ND	ND	ND
OCDD		6450	6750	11800	1630 *	1500	6260	4580
OCDF		653	615	700	203	208	421	528
CB77		697	1120	1500	766	253	330	455
CB126		ND	ND	ND	ND	ND	ND	ND
CB169		ND	ND	ND	ND	ND	ND	ND
TEF Concentrations		33.8				40.63		

INT = Interference

ND = Not Detected

+ = Exceed High Risk TCDD Concentrations

HCX = 1,2,4,5,7,8-hexachloro(9H)xanthene

Values are Estimated for HCX no Standard Run

HCX	27707A	27708A	27717A	27709A	27713A	27714A	27716A
2,3,7,8-TCDD	ND	22600	7500	2110	448	345	115
2,3,7,8-TCDD	ND	4170	5970	444	INT	302	138

02/13/98

Dioxin.wk4

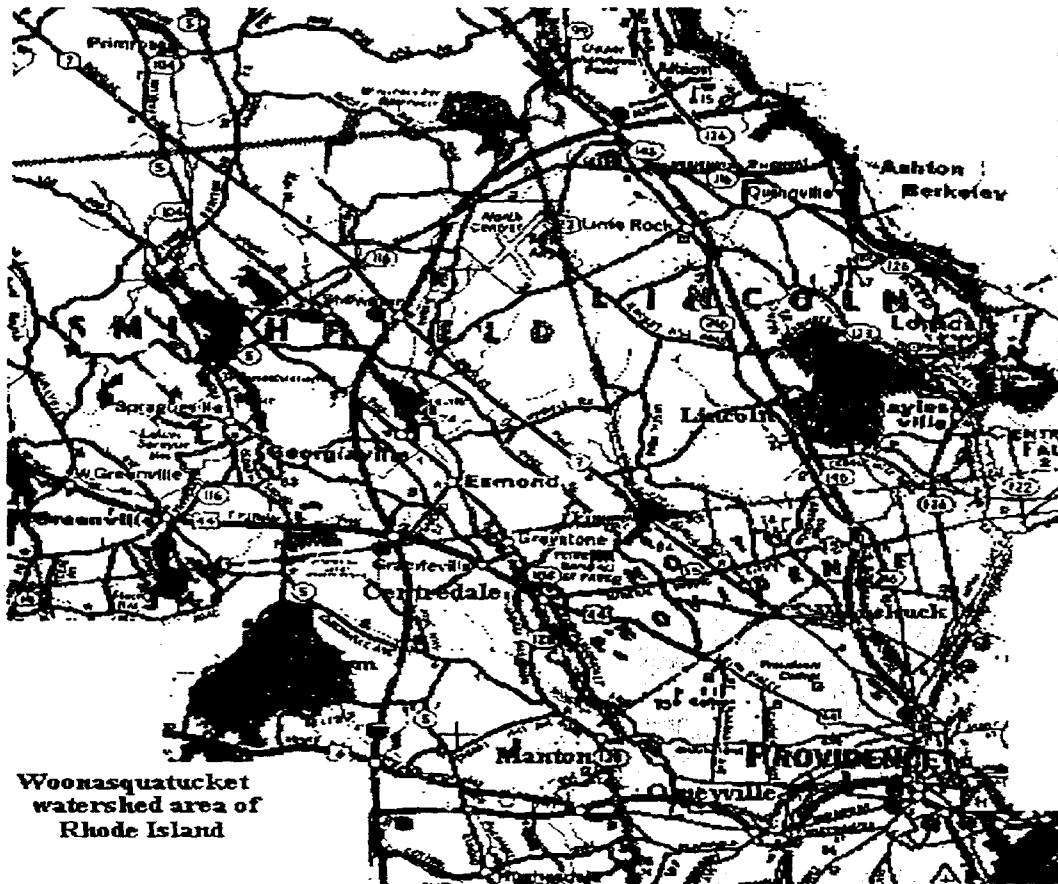
Original Includes Color Coding.

Available at the US EPA New England Superfund Records Center,
Boston, MA

Woonasquacket River
Sediment/Water Quality Analysis

Project Report

July 31, 1998



Prepared by:

U.S. Environmental Protection Agency
Region I, New England
Office of Environmental Measurement and Evaluation
Ecosystem Assessment

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SUMMARY

Background

The Woonasquatucket River, with its tributaries, is about 30 kilometers long and encompasses an area of approximately 200 square kilometers. The river begins in the hills near North Smithfield, in the north western corner of Rhode Island and flows to Narragansett Bay, an inlet to the Atlantic Ocean. The upper half of the river is zoned primarily for residential development. The lower half of the river contains some areas of good habitat but in others is heavily industrialized and urbanized with many mill complexes.

There are 6 cities and towns in the watershed including: Providence, Smithfield, Johnston, North Providence, North Smithfield and Glocester. The lower basin is highly urbanized from the Dyerville Dam in Providence to the mouth of the River in Downtown Providence.

The Woonasquatucket has been polluted and physically altered since the industrial revolution. The lower basin, once a tidal estuary, is now impounded with extensive channelization. Present conditions in the river are the result of current and historical activities. The upper basin ending at the Smithfield/Johnston town line is influenced by non-point sources and one point source, Smithfield WWTP, which discharges into the river just above the Johnston town line. In the lower basin, from Johnston to the mouth in the Providence River, point sources, storm water runoff and combined sewer overflows (CSOs) are major sources of bacteriological pollutants. The river is also littered with trash, tires, hot water heaters, refrigerators, and shopping carts which contribute to non-point sources in the lower basin. See Appendix G for a map of the basin.

Today, people use the Woonasquatucket River for a number of recreational activities such as canoeing, kayaking and boating in the lower river from the Lonigan Dam to Waterplace Park. A 9 hole golf course is planned in the area above the Olneyville Dam. A greenway is planned and being developed along the lower basin.

Purpose and Scope

The Woonasquatucket River is a priority waterbody for EPA-New England and the RI Urban Team. In June 1996, fish were collected and analyzed by EPA's Narragansett Laboratory and Providence Urban Initiative personnel. Based on elevated dioxin levels detected in fish, a fish consumption advisory was issued by Rhode Island Department of Health (RIDOH). In January 1997, the EPA, Office of Ecosystem Protection and the Rhode Island State Program, requested assistance from EPA's Office of Environmental Measurement and Evaluation(OEME). The assistance requested was to examine and evaluate ambient sediment quality in the Woonasquatucket River, and in conjunction with this, begin to identify sources that may have resulted in these elevated fish tissue concentrations.

EPA collaborated with the Providence Plan on the scope and objectives of the study. The project objectives identified in the quality assurance project plan included determining current chemical concentrations in the sediments. EPA, Rhode Island Department of Environmental Management (RIDEM) and RIDOH will use the results of this study to conduct a risk screening for human and ecological health, and target future monitoring.

Conclusions

Dioxin contamination was detected at all seven sampling sites. Two sites, Allendale Dam and Lymansville dam had levels significantly higher than the other sediment sampling locations. (Appendix A-4). Various metals were present in concentrations above the ecologically significant screening values i.e. Lower Effects Level (LEL) and Severe Effects Level (SEL) (Appendix A-1). Only one site, however, the Dyerville Dam, had a simultaneous extracted metals/acid volatile sulfide (SEM/AVS) ratio greater than one. A ratio greater than one indicates a potential for acute toxicological impacts to benthos from these metals. Numerous polynuclear aromatic hydrocarbons (PAHs), chlorinated pesticides and polychlorinated biphenyls (PCBs) were also detected at all seven sites at concentrations that may pose a chronic risk to the benthic community as well as upper food chain receptors (Appendices A-2 and A-3). In addition, because of the biomagnification potential of dioxin and, based on NYDEC sediment guidelines that take into consideration upper food chain impacts, as well as the TOC values present in the river, the possibility of acute effects to piscivores is also present (Appendix D).

The human health risk screening evaluated exposure to an older child and adult, ages 7-31, who might occasionally utilize areas along the river to picnic, wade or walk i.e. visits of 2days/wk during the summer months of June through August, and 1day/wk in May, September and October. Results of this risk screen indicate that adverse health effects from direct contact to sediments in the river during recreational exposures is unlikely for an older child or adult (Appendix B). These results would be expected due to the low frequency of exposure assumed for this type of a scenario. This analysis did not evaluate exposure to a child, (young or older), who might have more frequent exposures to the river, (for instance if a beach or home existed along the river). This is not the same type of exposure that would occur under a residential setting in which the existing level of contamination would be considered a health hazard.

In addition, as noted earlier, a conservative human health risk screening to evaluate the consumption of fish was performed in 1996. The results of this screening led to the issuance of a fish consumption advisory. The fish consumption advisory was based on tissue data of fish caught in areas with the lower dioxin concentrations. Fish tissue concentrations from areas with higher sediment concentrations of dioxin may show higher concentrations and pose a greater risk..

Both risk screening assessments raise concerns about the limited data and recommend additional sediment sampling be conducted to define the lateral and vertical extent of the contamination. Water quality measurements, biosurveys and/or toxicity tests, as well as additional fish tissue

sampling should also be considered. Lastly, additional information to define the duration and frequency of recreational exposures and other present and potential uses of the river is also needed.

SAMPLING PROGRAM

Water and sediment sampling was conducted during October 23-24, 1997, by a team of OEME personnel. Sediment samples and water column measurements were collected at seven sites in the Woonasquatucket River, from the Esmond Dam area of North Providence, just south of the Smithfield line, to the lower basin upstream from Valley Street Bridge in Providence. Sampling locations were selected based on discussions with the Urban Initiative team, Providence Plan personnel and site visits by EPA OEME and UEI personnel. See the site location map in Appendix F.

The water at each of the sites was analyzed on-site for dissolved oxygen (DO), temperature, conductivity and pH. Sediments were collected using an Eckman dredge, and analyzed for total metals, PAHs, PCBs, pesticides, AVS, SEM, dioxin and total organic carbon (TOC). Table I lists the sites and parameters analyzed at each site. EPA's New England Regional Laboratory in Lexington, MA performed the analyses for metals, AVS, SEM, PCBs, pesticides, PAHs and TOC. Analyses for Dioxins and Furans were performed by EPA's Narragansett Lab using a low resolution mass spectrometer and confirmed by EPA Region VII Laboratory in Kansas City, Kansas through high resolution mass spectrometry analysis. Data was reviewed for usability by the EPA Region I, OEME quality assurance section.

Table I: Sampling Site Summary

Station	Water column Analyses		Sediment Analyses					
	D.O. & Temp.	Conductivity & pH	Metals (Cu, Zn, Pb, Cd, Cr, Ni, Hg)	AVS&SEM (Cu, Zn, Pb, Cd, Ni, Hg)	PAHs	PCBs & Pesticides	Dioxins	TOC
DAM001, Esmond Dam, North Providence	--	X	X	X	X	X	X	X
DAM002, Allendale Dam, North Providence	X	X	X	X	X	X	X	X
DAM003, Lymanville Dam, North Providence	X	X	X	X	X	X	X	X
DAM004, Manton Dam, Providence	X	X	X	X	X	X	X	X
DAM005, Dyerville Dam, Providence	X	X	X	X	X	X	X	X
DAM006, Olneyville Dam, Providence	X	X	X	X	X	X	X	X
DAM007, Lonigan Dam, Providence	X	X	X	X	X	X	X	X

Sampling sites were reached using a jon boat or wading into the stream near the center of the channel. Samples were collected at the deep holes near the outlets. Locational data for each sampling station was collected using Global Positioning System(GPS) referencing the NAD-83 Coordinate System. These locations are presented in table II.

Table II: Locational Data of Sites (± 2 meters)

Station #	Site	Latitude			Longitude		
		Deg	Min	Sec	Deg	Min	Sec
DAM001	Esmond Dam	41	51	58.68	71	29	33.49
DAM002	Allendale Mill Dam	41	51	4.28	71	28	53.68
DAM003	Lymansville Dam	41	50	24.36	71	28	38.95
DAM004	Manton Dam	41	50	6.19	71	28	19.98
DAM005	Dyerville Dam	41	49	40.76	71	27	47.39
DAM006	Olneyville Dam	41	49	6.67	71	26	56.43
DAM007	Lonigan Dam	41	49	19.3	71	26	31.39

Water Sampling

Field water quality measurements were made using an electronic multi-parameter monitor, YSI Model 30 for conductivity and temperature and an Orion Model 250 meter for pH. At the Esmond Dam site, conductivity was not recorded due to an instrument calibration problem. Field water quality measurements were collected at 0.2 meters below the water's surface.

Sediment Sampling

The sampling crew selected sampling sites in depositional areas with silty and clay bottoms. Areas such as this are likely to contain the highest concentration of contaminants due to the binding tendency of these substrates. A stainless steel Eckman dredge was used to collect sediment samples from the upper four inches of bottom substrate. The dredge was used several times at each site to obtain adequate sample volumes. Samples were emptied from the dredge into a clean plastic tray. Detritus and pebbles were removed and excess water was poured off. Samples for AVS/SEM and metal analyses were collected first with a new plastic spoon used at each site to scoop samples from the plastic tray into the sample jars. The sediment in the plastic tray was then mixed (homogenized) with a clean stainless steel spoon. From this homogenized sample, samples for PAHs, PCBs, pesticides and TOC analyses were taken. All samples were placed in precleaned containers. The dredge and stainless steel spoon were decontaminated between sampling stations with soapy water, deionized water, isopropanol rinse and deionized water rinse. Samples were collected according to OEME Standard Operating Procedures and the quality assurance project plan (QAPP).

DATA SUMMARY

Water Column Analysis

The field water quality data, found in Table III, met Ambient Water Quality Criteria. The pH difference of 2.2 s.u. between the Manton Dam to the Dyerville Dam may warrant further investigations to a possible point source discharger.

Table III: Water Quality Results

Site	Esmond Dam	Allendale Dam	Lymansville Dam	Manton Dam	Duplicate of Manton Dam	Dyerville Dam	Olneyville Dam	Longan Dam
Site	DAM001	DAM002	DAM003	DAM004	DAM04A	DAM005	DAM006	DAM007
pH(s.u.)	6.6	6.8	6.8	6.6	6.6	8.8	8.4	8.6
Temperature(°C)	10	11	11	11	11	9	8	9
Conductivity (µs/cm)	--	206	242	246	246	250	225	230

Sediment Analysis

Results of the sediment analysis were used for the development of an ecological and human health risk screen. For ecological risk screening purposes comparisons were made to biologically significant sediment quality guidelines. The human health risk screening was performed considering specific exposure scenarios with associated assumptions. For a detailed human health and ecological risk screening see Appendix B and D, respectively.

Sediment Analysis by Parameter

Acid Volatile Sulfide and Simultaneously Extracted Metals (AVS and SEM)

AVS and SEM concentrations were determined for each site. The SEM/AVS ratio can be used to predict the bioavailability and potential acute toxicity from nickel, zinc, cadmium, copper, and lead. Sulfides bind these metals to the sediment which reduces their availability to benthic biota. AVS is typically highest during summer months because warmer temperatures, increased microbial activity, and lower dissolved oxygen, produce an environment where sulfides predominate. In the winter time AVS is lower and these metals are more bioavailable. At any time of the year, if the SEM/AVS ratio is greater than one the above metals are potentially bioavailable and may cause toxicity. If the SEM/AVS ratio is less than one the metals are usually not bioavailable (W. Berry 1996). The Dyerville Dam site was the only site which had an SEM/AVS ratio greater than 1.0. The SEM/AVS ratio was 2.5.

Total Organic Carbon(TOC)

TOC concentrations were analyzed at each site. Examining the TOC component is important because of it's ability to bind non-polar hydrophobic organic compounds, thereby reducing their

bioavailability potential. The highest concentration measured was 10.9% at the Esmond Dam site. The Manton Dam Site had the lowest measured TOC of 3.8%.

Metals and Total Cyanide

The sediments were analyzed for metals and total cyanide at all sites. Elevated levels of heavy metals were detected at all site at varying concentrations and frequencies. Table IV below summarizes the inorganics detection frequency and concentration.

Table IV: Metals and Total Cyanide Results

Site	Esmond Dam	Allendale Dam	Lymansville Dam	Manton Dam	Dyerville Dam	Oneyville Dam	Longan Dam
Site	DAM001	DAM002	DAM003	DAM004	DAM005	DAM006	DAM007
Sample	6197	6198	6199	6200	6202	6203	6205
Aluminum (mg/kg)	18700	11100	18300	5490	10700	7300	5310
Antimony (mg/kg)	10u	11u	10u	10u	9u	10u	10u
Arsenic (mg/kg)	35.0u	10.6u	35.0u	10.4u	20.0u	9.9u	10.1u
Barium (mg/kg)	37.5	218	310	97.8	116	138	106
Beryllium (mg/kg)	5.4	2.5	3.8	1.0	1.5	1.2	0.9
Calcium (mg/kg)	4830	3480	4650	2160	2450	2750	2260
Cadmium (mg/kg)	4.2	3u	4.6	3u	4	3u	3u
Chromium (total) (mg/kg)	117	136	204	62.4	385	63	48.4
Cobalt (mg/kg)	18	12.6	17.4	7.5	9.1	9.2	6.8
Copper (mg/kg)	196	136	206	47.8	210	89.3	88.1
Iron (mg/kg)	29100	24700	25500	12300	15300	17200	15400
Lead (mg/kg)	317	250	414	128	307	205	275
Manganese (mg/kg)	1980	1340	997	500	598	1000	879
Magnesium (mg/kg)	2910	2260	3620	1450	2770	2130	1570
Mercury (total) (mg/kg)	0.63	0.5	0.73	0.16	1.06	0.26	0.36
Nickel (mg/kg)	53.4	38.4	76	27	35	29.1	26.2
Selenium (mg/kg)	10.0u	10.6u	10.0u	10.4u	8.6u	9.9u	10.1u
Silver (mg/kg)	3.0u	3.2u	5.0u	3.1u	2.6u	3.0u	3.0u
Thallium (mg/kg)	10.0u	10.6u	10.0u	10.4u	8.6u	9.9u	10.1u
Vanadium (mg/kg)	39.5	33	47.6	16.4	28.4	24.6	30.0u
Zinc (mg/kg)	616	568	757	237	1930	386	346
Total Cyanide (mg/kg)	12.8U	6.4U	7.5U	2.4U	2.6U	3.3U	2.8U
SEM/AVS Ratio (Cu,Zn,Pb,Cd,Cr,Hg,Ni)	0.45	0.8	0.71	0.68	2.5	0.38	0.83

u= not detected above associated reporting limit, approximate value

Chlorinated Pesticides and Polychlorinated Biphenyls

Polychlorinated biphenyls and chlorinated pesticides were analyzed at each site (see Table V). Several pesticides and their breakdown products were detected. PCB Arochlors 1242, 1254 and 1268 were also detected.

Table V: Pesticide/PCB Results

Site	Esmond Dam	Allendale Dam	Lymansville Dam	Manton Dam	Dyemile Dam	Oneymile Dam	Lonigan Dam
Site Sample	DAM001 6197	DAM002 6198	DAM003 6199	DAM004 6200	DAM005 6202	DAM006 6203	DAM007 6205
Aldrin	ND	ND	ND	ND	ND	ND	ND
alpha-BHC	ND	ND	ND	ND	ND	ND	ND
beta-BHC	ND	ND	ND	ND	ND	ND	ND
delta-BHC	ND	ND	ND	ND	ND	ND	ND
gamma-BHC	ND	ND	ND	ND	ND	ND	ND
Alpha Chlordane	15	34	40	13	11	21	24
gamma Chlordane	7.3	ND	18	7.3	ND	8.9	17
Chlordane (technical)	ND	ND	ND	ND	ND	ND	ND
2,2',4,4'-DDB	9.6	16	19	8.5	13	12	12
2,2',4,4'-DDE	17	25	35	10	2.8	12	11
2,2',4,4'-DDT	5.2	10	ND	ND	6.3	6.3	12
Dieldrin	ND	11	8.6	ND	30	5.7	4.4
Endosulfan I	ND	ND	ND	2.3	ND	ND	5
Endosulfan II	ND	ND	ND	13	ND	12	12
Endosulfan sulfate	ND	ND	ND	ND	11	ND	ND
Endrin	ND	ND	ND	ND	ND	ND	ND
Endrin aldehyde	ND	ND	ND	ND	ND	3.6	5.4
Endrin ketone	ND	23	ND	ND	ND	7.7	ND
Heptachlor	ND	ND	ND	ND	ND	ND	ND
Heptachlor epoxide	ND	ND	ND	ND	ND	ND	ND
Methoxychlor	ND	ND	ND	ND	ND	ND	ND
Toxaphene	ND	ND	ND	ND	ND	ND	ND
Aroclor 1016	ND	ND	ND	ND	ND	ND	ND
Aroclor 1221	ND	ND	ND	ND	ND	ND	ND
Aroclor 1232	ND	ND	ND	ND	ND	ND	ND
Aroclor 1242	ND	ND	ND	ND	ND	120	250
Aroclor 1248	ND	ND	ND	ND	ND	ND	ND
Aroclor 1254	120	590	1100	210	1300	290	250
Aroclor 1260	ND	ND	ND	ND	ND	ND	ND
Aroclor 1262	ND	ND	ND	ND	ND	ND	ND
Aroclor 1268	88	120	91	17	120	ND	ND
Total PCBs	208	710	1191	227	1420	410	500
Total Organic Carbon (%)	10.9	7.6	9.3	3.8	4.6	5	5.9

ND =Not Detected

ND=Not Detected

Units are in ug/Kg

Dioxins and HCX

Dioxins were detected at all seven locations sampled. Concentrations were considerably higher in samples taken upstream of and in close proximity to the Allendale and Lymansville Dams. Results were highest at the Allendale Dam and Lymansville Dam (See Table VI and note that the dioxin results reported are those from EPA's Region VII laboratory). Additional discussion on the dioxin analysis can be found in the attached Appendix C: "Memorandum: Woonasquatucket River Sediment - PCDD/Fs".

US EPA ARCHIVE DOCUMENT

Table VI: Dioxin Results

Sample Name	AA10001	AA10002	AA10003	AA10004	AA10005	AA10006	AA10007
Req ID	06197	06198	06199	06200	06202	06203	06205
Sample Description	Esmond Dam	Allendale Dam	Lymansville Dam	Manton Dam	Dyerville Dam	Olneyville Dam	Longan Dam
2,3,7,8-TCDD	11U	7350	8200	444	94.2	483	251
1,2,3,7,8-PeCDD	5U	5U	9	5U	5U	5U	5U
1,2,3,4,7,8-HxCDD	6.9	12.7	14	5U	13.1	9.5	7.6
1,2,3,6,7,8-HxCDD	24.5	45.7	45	11	32.1	23.8	23.5
1,2,3,7,8,9-HxCDD	28	43.1	42	8.5	36.8	25	23.8
1,2,3,4,6,7,8-HpCDD	583	916	1050	241	452	652	752
OCDD	3750	5580	6690	1790	1870	3940	7260
2,3,7,8-TCDF	11U	18U	29U	11U	62U	18U	14U
1,2,3,7,8-PeCDF	5U	6.3	9	5U	11.9	5U	5U
2,3,4,7,8-PeCDF	5	11	12U	5U	25.9	5U	5U
1,2,3,4,7,8-HxCDF	5U	34.2	5U	7.7	50.3	13.9	15.4
1,2,3,6,7,8-HxCDF	15.5	23.2	27	5U	36	10.6	9.1
1,2,3,7,8,9-HxCDF	5U	5U	5	5U	5U	5U	5U
2,3,4,6,7,8-HpCDF	9.7	16.3	19	5U	23	6.6	8.5
1,2,3,4,6,7,8,9-HpCDF	195U	333U	283U	79	343	66U	174U
1,2,3,4,7,8,9-HpCDF	5U	14	5U	5U	17.5	5U	11U
OCDF	162	328	386	79	43U	183	390

u=detection limit
Units are in pg/g

The compound 1,2,4,5,7,8-Hexachloro(9H)xanthene (HCX) was also detected at all seven of the sites (see Table VII). Again the highest concentrations were found at the Allendale and Lymansville Dams. The fluctuation in the concentration of HCX mimics the fluctuation in dioxin concentration from site to site.

Dioxin and HCX are both biproducts in the production of certain chemical products. As such the presence of these compounds may help in leading to the identification of potential sources. See Appendix C for further discussion.

Table VII: HCX vs. 2,3,7,8-TCDD Results

Sample Description	Esmond Dam	Allendale Dam	Lymansville Dam	Manton Dam	Dyerville Dam	Olneyville Dam	Longan Dam
HCX	1600	131000	182000	7760	2460	14000	5280
2,3,7,8-TCDD	11U	4170	8200	444	94.2	483	251

Units are in pg/g

Petroleum Aromatic Hydrocarbons(PAHs)

Numerous PAHs were detected at all seven locations sampled. Total PAHs which were calculated by adding the concentrations of the 16 individual compounds analyzed are listed in Table VIII. PAH concentrations were quite variable with no recognizable trend. The Allendale Dam site had the highest total PAH of 67,320 ug/Kg. The Dyerville Dam site had the lowest total PAH with 18,392 ug/Kg. See Appendix A-3 for analytical results compared to LEL and SEL site specific limits.

Table VIII: PAHs Results

Site	Esmond Dam	Allendale Dam	Lymansville Dam	Manton Dam	Dyerville Dam	Olneyville Dam	Logan Dam
Site #	DAM001	DAM002	DAM003	DAM004	DAM005	DAM006	DAM007
Sample #	6197	6198	6199	6200	6202	6203	6205
Acenaphthene	150	200	120	510	68	190	450
Acenaphthylene	110	320	280	140	270	160	130
Anthracene	410	770	490	2100	260	980	1100
Benzo(a)anthracene	1600	4500	2600	3800	1300	3700	3100
Benzo(b)fluoranthene	3700	9400	6000	5100	2800	6500	5300
Benzo(k)fluoranthene	1100	3300	2300	1700	890	2800	2000
Benzo(a)pyrene	2500	5400	3500	3500	1700	4200	3500
Benzo(ghi)perylene	1900	4500	3000	2100	1400	3200	2600
Chrysene	3000	7000	4400	4300	1900	5400	4200
Dibenzo(a,h)anthracene	470	700	560	590	250	380	390
Fluoranthene	5400	12000	7400	9000	2400	9300	8000
Fluorene	200	320	210	740	120	310	350
Indeno(1,2,3-cd)pyrene	2200	5400	3500	2700	1800	4000	3400
Naphthalene	86	110	67	150	64	60	230
Phenanthrene	2600	4800	2600	7000	870	4400	5200
Pyrene	4700	8600	6500	7300	2300	7700	7800
Total PAHs	30126	67320	43527	50730	18392	53280	47750
Total Organic Carbon (%)	10.9	7.6	9.3	3.8	4.6	5	5.9

Units: TOC is in %, all others in ug/Kg

Data Usability

Chain of custody records were maintained for all collected samples. Holding times were met for all parameters analyzed by EPA Region I. At site DAM004, blind duplicate samples were collected for all reported compounds. Laboratory blanks were analyzed for pesticides, PCBs and dioxins. All reported compounds from the duplicate samples met the relative percent difference goals established in the Quality Assurance Project Plan.

Dioxin samples were frozen at the Narragansett Lab when they were received. Low resolution mass spectrometry was performed by Narragansett. High Resolution analysis was performed by EPA's Region 7 laboratory in Kansas City, Kansas. Samples were shipped frozen between the two labs. Dioxin results were reviewed by EPA, Region I, Quality Assurance Unit.(see Appendix E)

Method blanks were analyzed for metals, PCBs, pesticides and dioxins. The results indicate no laboratory contamination.

Meeting the above QA parameters indicate that the use of the data resulting from this project for the purposes of risk screening and targeting future investigation is appropriate.

REFERENCES

W. Berry. 1996. An Overview of Sediment Assessment Methods For Metals Contaminated Sediments and the EPA Approach to Developing Metals Sediment Quality Criteria. USEPA, Atlantic Ecology Division. Narragansett, RI. 4 pp

Appendix A-1

INORGANIC ANALYTICAL RESULTS

Woonasquatucket Sediment Sampling
REGION I LABORATORY

█ =Above LEL

█ =Above SEL

Site Sample	Site							Residual	
	18700	11100	18300	5490	10700	7300	5310	LEL	SEL
Aluminum (mg/kg)	18700	11100	18300	5490	10700	7300	5310	NA	NA
Antimony (mg/kg)	10u	11u	10u	10u	9u	10u	10u	NA	NA
Arsenic (mg/kg)	35.0u	10.6u	35.0u	10.4u	20.0u	9.9u	10.1u	6	33
Barium (mg/kg)	37.5	218	310	97.8	116	138	106	NA	NA
Beryllium (mg/kg)	5.4	2.5	3.8	1.0	1.5	1.2	0.9	NA	NA
Calcium (mg/kg)	4830	3480	4650	2160	2450	2750	2260	NA	NA
Cadmium (mg/kg)		3u		3u	4	3u	3u	0.6	10
Chromium (total) (mg/kg)								26	110
Cobalt (mg/kg)	18.0	12.6	17.4	7.5	9.1	9.2	6.8	NA	NA
Copper (mg/kg)								16	110
Iron (mg/kg)				12300	15300	17200	15400	20000	40000
Lead (mg/kg)								31	250
Manganese (mg/kg)								460	1100
Magnesium (mg/kg)	2910	2260	3620	1450	2770	2130	1570	NA	NA
Mercury, Total (mg/kg)				0.16				0.2	2
Nickel (mg/kg)								16	75
Selenium (mg/kg)	10.0u	10.6u	10.0u	10.4u	8.6u	9.9u	10.1u	NA	NA
Silver (mg/kg)	3.0u	3.2u	5.0u	3.1u	2.6u	3.0u	3.0u	NA	NA
Thallium (mg/kg)	10.0u	10.6u	10.0u	10.4u	8.6u	9.9u	10.1u	NA	NA
Vanadium (mg/kg)	39.5	33.0	47.6	16.4	28.4	24.6	30.0u	NA	NA
Zinc (mg/kg)								120	820
Total Cyanide (mg/kg)	12.8U	6.4U	7.5U	2.4U	2.6U	3.3U	2.8U	NA	NA
SEM/AVS Ratio (Cu, Zn, Pb, Cd, Cr, Hg, Ni)	0.45	0.80	0.71	0.68	2.50	0.38	0.83		

u = not detected above associated reporting limit, approximate value

NA= Not Applicable

LEL and SEL Levels Obtained from: Persaud, D., R. Jaagumagi, and A. Hayton, Ontario Ministry of Environment and Energy, Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario, August 1993.

Sediment samples were collected 10/23-24/97.

Appendix A-2

Woonasquatucket Sediment Sampling PESTICIDE AND PCB ANALYTICAL RESULTS
 REGION I LABORATORY Units are in ug/kg except for TOC. [REDACTED] =Above LEL

[REDACTED]								
Aldrin	ND	ND	ND	ND	ND	ND	ND	ND
alpha-BHC	ND	ND	ND	ND	ND	ND	ND	ND
beta-BHC	ND	ND	ND	ND	ND	ND	ND	ND
delta-BHC	ND	ND	ND	ND	ND	ND	ND	ND
gamma-BHC	ND	ND	ND	ND	ND	ND	ND	ND
Alpha Chlordane								
gamma Chlordane		ND			ND			
Chlordane (technical)	ND	ND	ND	ND	ND	ND	ND	ND
4,4'-DDD								
4,4'-DDE					2.8			
4,4'-DDT	5.2		ND	ND	6.3	6.3		
Dieldrin	ND				ND			
Endosulfan-I	ND	ND	ND	2.3	ND	ND	5	
Endosulfan-II	ND	ND	ND	13	ND	12	12	
Endosulfan sulfate	ND	ND	ND	ND	11	ND	ND	
Endrin	ND	ND	ND	ND	ND	ND	ND	
Endrin aldehyde	ND	ND	ND	ND	ND	3.6	5.4	
Endrin ketone	ND	23	ND	ND	ND	7.7	ND	
Heptachlor	ND	ND	ND	ND	ND	ND	ND	
Heptachlor epoxide	ND	ND	ND	ND	ND	ND	ND	
Methoxychlor	ND	ND	ND	ND	ND	ND	ND	
Toxaphene	ND	ND	ND	ND	ND	ND	ND	
Aroclor-1016	ND	ND	ND	ND	ND	ND	ND	
Aroclor-1221	ND	ND	ND	ND	ND	ND	ND	
Aroclor-1232	ND	ND	ND	ND	ND	ND	ND	
Aroclor-1242	ND	ND	ND	ND	ND	120	250	
Aroclor-1248	ND	ND	ND	ND	ND	ND	ND	
Aroclor-1254								
Aroclor-1260	ND	ND	ND	ND	ND	ND	ND	
Aroclor-1262	ND	ND	ND	ND	ND	ND	ND	
Aroclor-1268	88	120	91	17	120	ND	ND	
Total PCBs								
Total Organic Carbon (%)	10.9	7.6	9.3	3.8	4.6	5.0	5.9	

ND = Not Detected

LEL Values Obtained from: Persaud, D., R. Jaagumagi, and A. Hayton, Ontario Ministry of Environment and Energy, Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario, August 1993. Sediment samples were collected 10/23-24/97.

Appendix A-3

SEMIVOLATILES (PAHs) ANALYTICAL RESULTS

Woonasquatucket Sediment Sampling
REGION I LABORATORY

██████████ =Above LEL

All units are in ug/Kg except TOC

Site							
Sample #							
Acenaphthene	150	200	120	510	68	190	450
Acenaphthylene	110	320	280	140	270	160	130
Anthracene							
Benzo(a)anthracene							
Benzo(b)fluoranthene	3700	9400	6000	5100	2800	6500	5300
Benzo(k)fluoranthene							
Benzo(a)pyrene							
Benzo(ghi)perylene							
Chrysene							
Dibenzo(a,h)anthracene							
Fluoranthene							
Fluorene					120		
Indeno(1,2,3-cd)pyrene							
Naphthalene	86	110	67	150	64	60	230
Phenanthrene							
Pyrene							
Total PAHs							
Total Organic Carbon (%)	10.9	7.6	9.3	3.8	4.6	5	5.9

Sediment samples were collected 10/23-24/97.

LEL &SEL levels obtained from: Persaud, D., R. Jaagumagi, and A. Hayton, Ontario Ministry of Environment and Energy, Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario, August 1993.

Appendix A-4

DIOXIN and HCX ANALYTICAL RESULTS

Woonasquatucket Sediment Sampling
USEPA Region 7 Analysis

Units are in PG/G DRY WT.
U=Detection Limit

	Toxicity Equivalent TEQs (TEQs)							
2,3,7,8-TCDD	1	11U	7350	8200	444	94.2	483	251
1,2,3,7,8-PeCDD	0.5	5U	5U	9	5U	5U	5U	5U
1,2,3,4,7,8-HxCDD	0.1	6.9	12.7	14	5U	13.1	9.5	7.6
1,2,3,6,7,8-HxCDD	0.1	24.5	45.7	45	11	32.1	23.8	23.5
1,2,3,7,8,9-HxCDD	0	28	43.1	42	8.5	36.8	25	23.8
1,2,3,4,6,7,8-HpCDD	0.01	583	916	1050	241	452	652	752
OCDD	0.0001	3750	5580	6690	1790	1870	3940	7260
2,3,7,8-TCDF	0.1	11U	18U	29U	11U	62U	18U	14U
1,2,3,7,8-PeCDF	0.05	5U	6.3	9	5U	11.9	5U	5U
2,3,4,7,8-PeCDF	0.5	5	11	12U	5U	25.9	5U	5U
1,2,3,4,7,8-HxCDF	0.1	5U	34.2	5U	7.7	50.3	13.9	15.4
1,2,3,6,7,8-HxCDF	0.1	15.5	23.2	27	5U	36	10.6	9.1
1,2,3,7,8,9-HxCDF	0.1	5U	5U	5	5U	5U	5U	5U
2,3,4,6,7,8-HxCDF	0.1	9.7	16.3	19	5U	23	6.6	8.5
1,2,3,4,6,7,8-HpCDF	0.01	195U	333U	283U	79	343	66U	174U
1,2,3,4,7,8,9-HpCDF	0.01	5U	14	5U	5U	17.5	5U	11U
OCDF	0.001	162	328	386	79	43U	183	390
Toxic Equivalent Concentrations		20.7						

█ = Exceed High Risk TCDD Concentrations

Sediment samples were collected 10/23-24/97.

HCX = 1,2,4,5,7,8-hexachloro(9H)xanthene

HCX	1600	131000	182000	7760	2460	14000	5280
2,3,7,8-TCDD	11U	7350	8200	444	94.2	483	251

Appendix A-5

Pest/PCB SEL CALCULATION WORKSHEET

Woonasquatucket Sediment Sampling

Pest/PCB LEL and SEL Values [1]

	Freshwater LEL	Freshwater SEL
Aldrin	2	NA
alpha-BHC	6	NA
beta-BHC	5	NA
delta-BHC	NA	NA
gamma-BHC	3	NA
Alpha Chlordane	7	6000
gamma-Chlordane	7	6000
Chlordane (technical)	7	6000
4,4'-DDD	8	6000
4,4'-DDE	5	19000
4,4'-DDT	8	71000
Dieldrin	2	91000
Endosulfan I	NA	NA
Endosulfan II	NA	NA
Endosulfan sulfate	NA	NA
Endrin	3	130000
Endrin aldehyde	NA	NA
Endrin ketone	NA	NA
Heptachlor	NA	NA
Heptachlor epoxide	5	NA
Methoxychlor	NA	NA
Toxaphene	NA	NA
Aroclor-1016	7	NA
Aroclor-1221	NA	NA
Aroclor-1232	NA	NA
Aroclor-1242	NA	NA
Aroclor-1248	30	150000
Aroclor-1254	60	34000
Aroclor-1260	5	24000
Aroclor-1262	NA	NA
Aroclor-1268	NA	NA
Total PCBs	70	530000

NA = Not Applicable

LEL Values are in ug/Kg.

SEL Values are in ug/KgOC

[1] Obtained from: Persaud, D., R. Jaagumagi, and A. Hayton, Ontario Ministry of Environment and Energy, Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario, August 1993.

Pest/PCB SEL Values Adjusted for Site Specific TOC

Units are in ug/kg.

	Site Specific TOC	Site Specific TOC	Site Specific TOC	Site Specific TOC	Site Specific TOC	Site Specific TOC	Site Specific TOC
Alpha Chlordane	654	456	558	228	276	300	354
gamma-Chlordane	654	456	558	228	276	300	354
Chlordane (technical)	654	456	558	228	276	300	354
4,4'-DDD	654	456	558	228	276	300	354
4,4'-DDE	2071	1444	1767	722	874	950	1121
4,4'-DDT	7739	5396	6603	2698	3266	3550	4189
Dieldrin	9919	6916	8463	3458	4186	4550	5369
Endrin	14170	9880	12090	4940	5980	6500	7670
Aroclor-1248	16350	11400	13950	5700	6900	7500	8850
Aroclor-1254	3706	2584	3162	1292	1564	1700	2006
Aroclor-1260	2616	1824	2232	912	1104	1200	1416
Total PCBs	57770	40280	49290	20140	24380	26500	31270
Total Organic Carbon (%)	10.9	7.6	9.3	3.8	4.6	5	5.9

Appendix A-6

PAH SEL CALCULATION WORKSHEET

Woonasquatucket Sediment Sampling

PAH LEL and SEL Values [1]

Compounds	Freshwater LEL	Freshwater SEL
Acenaphthene	NA	NA
Acenaphthylene	NA	NA
Anthracene	220	3.70E+005
Benzo(a)anthracene	320	1.48E+006
Benzo(b)fluoranthene	NA	NA
Benzo(k)fluoranthene	240	1.34E+006
Benzo(a)pyrene	370	1.44E+006
Benzo(ghi)perylene	170	3.20E+005
Chrysene	60	4.60E+005
Dibenz(a,h)anthracene	60	1.30E+005
Fluoranthene	750	1.02E+006
Fluorene	190	1.60E+005
Indeno(1,2,3-cd)pyrene	200	3.20E+005
Naphthalene	NA	NA
Phenanthrene	560	9.50E+005
Pyrene	490	8.50E+005
Total PAHs	4000	1.00E+007

NA = Not Applicable

LEL values are in ug/Kg.

SEL values are in ug/KgOC.

[1] Obtained from: Persaud, D., R. Jaagumagi, and A. Hayton, Ontario Ministry of Environment and Energy, Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario, August 1993.

PAH SEL Adjusted to Site Specific TOC

Compounds	TOC 10.9%	TOC 7.6%	TOC 9.3%	TOC 3.8%	TOC 4.6%	TOC 5.0%	TOC 5.9%
Anthracene	40330	28120	34410	14060	17020	18500	21830
Benzo(a)anthracene	148000	112480	137640	56240	68080	74000	87320
Benzo(k)fluoranthene	134000	101840	124620	50920	61640	67000	79060
Benzo(a)pyrene	144000	109440	133920	54720	66240	72000	84960
Benzo(ghi)perylene	32000	24320	29760	12160	14720	16000	18880
Chrysene	46000	34960	42780	17480	21160	23000	27140
Dibenz(a,h)anthracene	13000	9880	12090	4940	5980	6500	7670
Fluoranthene	102000	77520	94860	38760	46920	51000	60180
Fluorene	16000	12160	14880	6080	7360	8000	9440
Indeno(1,2,3-cd)pyrene	32000	24320	29760	12160	14720	16000	18880
Phenanthrene	95000	72200	88350	36100	43700	47500	56050
Pyrene	85000	64600	79050	32300	39100	42500	50150
Total PAHs	1000000	760000	930000	380000	460000	500000	590000
Total Organic Carbon (%)	10.9	7.6	9.3	3.8	4.6	5.0	5.9

Units are in ug/kg except for TOC.

**UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 1
JFK Federal Building, Boston, MA 02203-2211**

DATE: February 24, 1998

SUBJ: Human Health Risk Screening Analysis for a Recreational Exposure to sediments in the Woonasquatucket River, Providence, RI

FROM: Ann-Marie Burke, Toxicologist
Technical Support Section

TO: Woonasquatucket Team

INTRODUCTION

The following is a human health risk screening analysis for an older child or an adult who may be exposed to sediments in the Woonasquatucket river during recreational activities. A risk screening analysis is similar to a risk assessment in that similar formulas and methods are used to assess risk. The major difference is that the results of a risk screening are generally more uncertain than those of a risk assessment due to a) a limited data set (resulting in an uncertain exposure dose), b) limited information about exposure, and/or c) data of lower quality than is typically used in a risk assessment. In the case of the Woonasquatucket river this assessment is defined as a risk screening because it is based on limited data, (i.e. 7 samples collected over 7 miles of river in areas that are not very representative of actual exposure), and there is limited information about exposure, (i.e. who is exposed and how often?). Thus this risk screening analysis adopts conservative but reasonable estimates of exposure and toxicity. As a result the true risk is likely to be lower than that estimated here. The results of the risk screen indicate that adverse health effects from exposures to sediments along the river under a recreational scenario are unlikely. If you have any questions about this calculation, do not hesitate to call me at (617)223-5528.

BACKGROUND

In May, 1996 EPA collected sunfish and eel from the Woonasquatucket River and analyzed fillet and offal for cadmium, copper, chromium, nickel lead, zinc, mercury, PCB congeners,

hexachlorobenzene, DDE, DDD, DDT, lindane, chlordane, nonachlor and dioxin homologues¹. A risk screen was performed for a hypothetical subsistence fisherman who would harvest all the fish he ingests from the Woonasquatucket River. The results of the screen indicated that adverse cancer and noncancer health effects could occur in subsistence fishermen who ingested 70g/dy of whole eel or sunfish, (or fish similar to these), for a lifetime from the Woonasquatucket river. Estimated cancer risks in sunfish were due mainly to PCBs (1.3E-03), and 2,3,7,8-TCDD (equivalents) (2.5E-02). Noncancer risks were due mainly to mercury (HQ=1.9), PCBs (HQ=76), and lindane (HQ=1.5).

Over a year later limited sediment sampling was conducted along a seven mile stretch of the Woonasquatucket River. Samples were analyzed for metals, pesticides, total PCBs and congeners 77, 126 and 169, PAHs, and dioxins. Seven samples were collected from the top 4 inches of sediment in low flowing areas directly behind 7 dams in the river. Since there is an immediate need to assess whether exposure to river sediments should be restricted, I have conservatively assumed that the bottom sediment samples collected for this effort would have similar concentrations as the more accessible bank areas. NOTE: This is a very uncertain assumption and may result in an overestimate of the actual risk since most of the sediment samples collected are below water and in areas not likely to be accessed by recreational visitors, (i.e. middle of river instead of on banks).

HAZARD IDENTIFICATION

This screen is focussed on those chemicals which are expected to be the major contributors to excess cancer and noncancer risks. These chemicals are chosen by comparing the maximum concentrations detected in river sediments to a residential risk-based screening level. A residential risk-based screening level is a concentration in soil which is associated with a 1E-06 cancer risk or hazard quotient of 0.1 assuming a young child and adult would be exposed to these soils 350 days/yr for 30 years. These levels are considered to be protective of public health. The Woonasquatucket river is not a residential setting so screening with a risk-based concentration is conservative. The screen results in 7 contaminants of concern (COCs). These are PCBs, benzo(a)anthracene, benzo(b)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, and dioxins.

EXPOSURE ASSESSMENT

Receptor: The receptor for this analysis is an older child or adult who might use areas along the river to picnic, wade or walk. Since this is a screen I have assumed adult body weights, surface areas, and adherence factors for both the older child and adult, rather than conducting an age-

¹ Memo from A. Burke to I. Balkissoon, "Human Health Risk Screening Analysis for a Subsistence Fisherman in the Woonasquatucket River, Providence, RI," 9/30/96.

specific analysis. This type of analysis is unlikely to result in a big difference in risk estimates but could result in a slight underestimate of risk.

The City of Providence is developing areas around sections of the river as a "Greenway" or an area with grass, groomed paths and bikepaths. Since it is unknown where the Greenway will extend to and thus which parts of the river an individual might be exposed to, each dammed area along the river will be considered a discrete exposure area.

Pathway: A recreational user could be exposed to contaminated sediments in the Woonasquatucket river by coming in direct contact with sediments and by accidentally ingesting sediments which had adhered to the hands. These pathways are evaluated in this risk screen. The inhalation pathway is not expected to contribute significantly to the total risk from contaminated sediments since all of the COCs have low vapor pressures and would not be expected to volatilize to any great extent.

Frequency and Duration of Exposure: It will be assumed that the same individual will frequent a discrete exposure area consistently over the long term. This is a very conservative assumption since individuals are likely to visit different areas along the river over time. It was also assumed that an individual would visit the river twice a week during the summer months (June, July, August) and once a week during May, September and October. This results in an exposure frequency of 32 days/yr. A long term duration of 24 years (for ages 7-31) was assumed.

Ingestion Rate: Upper end estimates of the amount of soil that an adult would accidentally ingest approximate 100mg/dy. This is a typical default assumption for soil ingestion in residential settings. There is no information on how much sediment an adult or young child might accidentally ingest in a recreational scenario. Since this is a risk screen I have assumed the same ingestion rate as for residential soils. This is a *very* conservative assumption and actual sediment ingestion rates are likely to be much lower.

RISK SCREENING RESULTS

The equation for deriving a protective level of a contaminant in soil or sediment is described below. To estimate risk one simply puts in the site-specific contaminant concentration and solves for TR or target risk. The default value used in this assessment for each exposure parameter is listed next its' symbol below.

$$C_s \text{ (mg/kg)} = \frac{\text{TR} \times \text{BW} \times \text{At}_c}{\text{F} \times \text{D} \times \text{CPF} \left[\frac{\text{RAF}_o \times \text{IR}}{10^6 \text{ mg/kg}} + \frac{(\text{SA} \times \text{AF} \times \text{RAF}_d)}{10^6 \text{ mg/kg}} \right]}$$

Where:

C_s = contaminant concentration in soil = risk-based concentration (mg/kg)

TR = target excess lifetime cancer risk - 1E-06

Bwa = adult body weight (70kg)

AT_c = averaging time, carcinogen (70yrs x 365dys/yr) - 25550 days

CPF = cancer potency factor (chemical specific)

F = exposure frequency (32 dys/yr)

IR = soil ingestion rate, (100mg/dy) x FI (fraction ingested from source (1)

AF - soil adherence factor, Kissel et al (1996) - 0.23mg/cm² (reed gatherers)

RAF_o = oral relative absorption factor = amount absorbed from the oral route from the site/amt absorbed from tox study = chemical specific

RAF_{dermal} = dermal relative absorption factor = amount absorbed via the dermal route from the site/amt absorbed from tox study (chemical specific)

Tables 1 through 4 report the estimated cancer and noncancer risks for each contaminant of concern in the first four areas of the river, (i.e Esmond Dam, Allendale Dam, Lymansville Dam and Manton Dam). Risks were not calculated for other areas of the river due to time constraints but the risks in these sections of the river, (i.e. Dyerville, Olneyville and Lonigan Dams), are likely to be lower than the Manton Dam since concentrations of contaminants continue to drop off with distance from the Allendale Dam.

TABLE 1
RME CANCER RISK AND HAZARD QUOTIENT FOR DIRECT CONTACT TO
SEDIMENTS IN THE WOONASQUATUCKET RIVER
FROM RECREATIONAL EXPOSURES
ESMOND DAM

CHEMICAL	EXPOSURE PT. CONCENTRATION (MG/KG)	EXCESS CANCER RISK	HAZARD QUOTIENT
Total PCBs	0.21	5.1E-08	0.07
B(a)A	1.6	1.3E-07	NA
B(b)F	3.7	1.3E-07	NA
B(a)P	2.5	1.3E-06	NA
DBA	0.47	3.7E-07	NA
IP	2.2	1.8E-07	NA
TCDD TEQS	0.00003	2.7E-07	NA
TOTAL		3.3E-06	0.07

TABLE 2
RME CANCER RISK AND HAZARD QUOTIENT FOR DIRECT CONTACT TO
SEDIMENTS IN THE WOONASQUATUCKET RIVER
FROM RECREATIONAL EXPOSURES
ALLENDALE DAM

CHEMICAL	EXPOSURE PT. CONCENTRATION (MG/KG)	EXCESS CANCER RISK	HAZARD QUOTIENT
Total PCBs	0.71	1.7e-07	0.23
B(a)A	4.5	3.8E-07	NA
B(b)F	9.4	8E-07	NA
B(a)P	5.4	4.5E-06	NA
DBA	0.7	5.5E-07	NA
IP	5.4	4.5E-07	NA
TCDD TEQS	0.004	3.6E-05	NA
TOTAL		4.1E-06	0.07

TABLE 3
RME CANCER RISK AND HAZARD QUOTIENT FOR DIRECT CONTACT TO
SEDIMENTS IN THE WOONASQUATUCKET RIVER
FROM RECREATIONAL EXPOSURES
LYMANVILLE DAM

CHEMICAL	EXPOSURE PT. CONCENTRATION (MG/KG)	EXCESS CANCER RISK	HAZARD QUOTIENT
Total PCBs	1.2	2.9E-07	0.4
B(a)A	2.6	2.2E-07	NA
B(b)F	6.0	5.1E-07	NA
B(a)P	3.5	2.9E-06	NA
DBA	0.56	4.7E-07	NA
IP	3.5	2.9E-07	NA
TCDD TEQS	0.006	5.4E-05	NA
TOTAL		5.7E-06	0.07

TABLE 4
RME CANCER RISK AND HAZARD QUOTIENT FOR DIRECT CONTACT TO
SEDIMENTS IN THE WOONASQUATUCKET RIVER
FROM RECREATIONAL EXPOSURES
MANTON DAM

CHEMICAL	EXPOSURE PT. CONCENTRATION (MG/KG)	EXCESS CANCER RISK	HAZARD QUOTIENT
Total PCBs	0.23	5.5E-08	0.08
B(a)A	3.8	3.2E-07	NA
B(b)F	5.1	4.3E-07	NA
B(a)P	3.5	2.9E-06	NA
DBA	0.59	4.6E-07	NA
IP	2.7	2.2E-07	NA
TCDD TEQS	0.0004	3.6E-06	NA
TOTAL		7.8E-06	0.08

At the Esmond Dam (prior to the proposed source for dioxins) it can be seen that benzo(a)pyrene is responsible for the majority of the cancer risk. As one moves downstream past the Allendale Dam TCDD and benzo(a)pyrene are about equal in their contribution towards the total cancer risk. And finally by the time one reaches the Lymansville Dam (at which the highest concentrations of dioxins are measured, the majority of the cancer risk is from TCDD. After this the risks from benzo(a)pyrene and TCDD again are about equal (at the Manton Dam). All estimated cancer risks and hazard quotients are well within EPA's acceptable risk range for the Superfund program. Given the estimated cancer risk and HQ, adverse effects from recreational exposures to river sediments is unlikely. Although additional dams downstream of the Manton Dam were not quantitatively evaluated, the risks are expected to be less than the Manton dam since the concentrations of PAHs and TCDD decrease.

UNCERTAINTIES

There are several uncertainties in this risk screening evaluation which could result in an under- or overestimate of the actual risk, although most tend to overestimate the risk. These include the following;

1. Exposure Point Concentration - Since there were no sediment samples in areas where a recreational user might be exposed, (i.e. along the banks), it was assumed that sediment samples collected at the bottom of the river behind dams was representative of what an individual might be exposed to along the banks. This is a very conservative assumption which may overestimate the true risk since bank sediment samples may be much lower than those collected at depth in depositional areas.

2. Frequency and Duration of Exposure - Because there was limited sampling along the river, it was assumed that the area around each dam was a discrete exposure area and that an individual would visit the same spot 32 times per year. This is likely to overestimate actual exposure since it is more likely that an individual would visit different areas along the river over time. In addition, the duration assumed was 24 years when in fact the average individual doesn't live in one place more than 9 years.

3. Sediment ingestion rate - Since there is little to no information on sediment ingestion rates, it was assumed that the sediment ingestion rate would equal a residential soil ingestion rate. This is likely to overestimate the actual sediment intake since the exposure time in a recreational event is much shorter than in a residential event and the same types of activities (resulting in a higher ingestion rate), are not being performed.

4. Adult exposure parameters Because this is a screen and due to time constraints, an age-specific analysis was not conducted for the older child (ages 7-31). Instead adult parameters were adopted for the older child. Although this is not expected to result in a large difference in the estimated risk, it may result in a slight underestimate of risk.

5. Dioxins - acute exposure An acute exposure is defined as a short-term exposure to high concentrations of a chemical. A characteristic sign of acute exposures to dioxins is delayed lethality after a pronounced wasting syndrome. Dermal effects similar to chloracne are also a prominent sign of acute toxicity. The estimated dose for a recreational user exposed to dioxins in Woonasquatucket river sediments is not high enough to result in this type of acute toxicity.

6. Dioxins - Noncancer effects - Dioxins have been shown to result in a myriad of noncancer effects such as developmental toxicity, impaired reproduction, alterations in endocrine function, immunotoxicity, liver damage, etc. EPA does not currently quantitatively evaluate the health hazards for noncarcinogenic effects since some adverse effects might be occurring at or near background levels of exposure. Thus this risk screen may underestimate noncancer risks from exposures to dioxins. However, it is important to note that the estimated exposure dose for dioxin is very low even for many of the noncancer endpoints.

7. Dermal toxicity to carcinogenic PAHs Carcinogenic PAHs were present in fairly high concentrations in several stretches of the Woonasquatucket river. Although EPA quantitatively evaluates systemic effects from dermal exposure to PAHs, we are currently unable to evaluate dermal toxicity. Carcinogenic PAHs are known to cause skin cancer in laboratory animals.

B(a)P is used as a positive control for skin cancer in many animal bioassays. It is likely that skin cancer effects occur at lower levels than do systemic effects. Thus the potential for skin cancer may be underestimated in this risk screen.

SUMMARY AND CONCLUSIONS

This risk screen indicates that adverse health effects from recreational exposures to sediments in the Woonasquatucket river are unlikely for an older child or adult. There are several uncertainties in this assessment but most are likely to overestimate rather than underestimate exposure and thus risk. Perhaps the greatest uncertainty is what individuals are actually exposed to. I have taken the highest concentrations present in bottom sediments, which recreational users are not expected to be exposed to, and assumed these represent shoreline concentrations. If there are unexpected higher concentrations of contaminants in bank samples this would result in higher risks than those estimated in this screen.

In general, risks are expected to be low due to the low frequency of exposure inherent in this type of a recreational scenario. This is not the same type of exposure that would occur under a residential setting in which this type of contamination would be considered a health hazard. Very short term exposures, such as from a one day clean up of the river, are not expected to result in adverse effects. There is the potential, however, for skin irritation and it would be expected that anyone wading through the river would have protective thigh high rubber waders and rubber gloves.

DATA NEEDS: In order to more accurately assess exposure to a recreational user of the Woonasquatucket river shoreline sediment samples in areas of high access are necessary. Samples should be collected in areas where the proposed "Greenway" is expected to run and should include analysis for cPAHs, dioxins, PCBs and dioxin-like congeners.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
NATIONAL HEALTH AND ENVIRONMENTAL EFFECTS LABORATORY
ATLANTIC ECOLOGY DIVISION
27 TARZWELL DRIVE
NARRAGANSETT, RHODE ISLAND 02882

February 5, 1998

MEMORANDUM

SUBJECT: Woonasquatucket River Sediment - PCDD/Fs
FROM: Richard J. Pruell, Research Chemist
TO: Tim Bridges, EPA-Region I

The following is my preliminary assessment of our results for dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in the sediments collected from the Woonasquatucket River. Analysis of the sediment samples indicates the presence of several PCDD/F congeners, particularly 2,3,7,8-tetrachloro-*p*-dioxin, octachloro-*p*-dioxin and octachlorodibenzofuran. No PCDD/Fs were detected in either the Field Blank or Procedural Blank. A Certified Reference Material was also analyzed with this batch of samples. The concentrations measured in this sample were all within the ranges of the Certified levels. All of this indicates that the sediments collected from the river contain significant amounts of some PCDD/F congeners.

There can be many sources of PCDD/Fs to the environment including combustion processes, paper bleaching, chemical manufacturing, the use of chlorophenols and many more. Each source type tends to produce distinct congener distributions or ratios that can be used to fingerprint potential sources. The distributions of PCDD/F congeners in the Woonasquatucket River sediments are very unusual and do not appear to match any one source type. Instead, it appears that there may be two major source types contributing to these distributions.

The high molecular weight PCDD/Fs (hepta- and octachloro congeners) are probably associated with the use of pentachlorophenol. This compound has been widely used as a wood preservative and in the textile industry. Based on the concentrations measured in the sediments, this compound may have entered the river at several locations.

It appears that another source of PCDD/Fs may have been located between the Esmond and Allendale dams. This source was highly enriched in 2,3,7,8-tetrachloro-*p*-dioxin which indicates a chemical manufacturing process that involved the use of 2,4,5-trichlorophenol. Well known cases of 2,3,7,8-tetrachloro-*p*-dioxin contamination have resulted from the production of 2,4,5-trichlorophenol for use in herbicides and from the production of hexachlorophene.

Please call me at (401)782-3091 if you have any questions.

cc:N. Rubinstein
S. Schimmel
B. Taplin
R. McKinney

Woonasquatucket River Sediment Sampling
(3/1/98)
Preliminary Ecological Risk Screening Information

Individual surface sediment samples (0-10 cm) were taken at seven low energy locations along the Woonasquatucket River. From up to downstream they were the Esmond Dam, Allendale Dam, Lymansville Dam, Manton Dam, Dyerville Dam, Olneyville Dam and Lonigan Dam.

Analyses of these samples were performed at EPA's regional laboratory in Lexington, MA. for total metals, total cyanide, polyaromatic hydrocarbons (PAHs), pesticides, polychlorinated biphenyls (PCBs), total organic carbon, acid volatile sulfides (AVS) and the simultaneously extracted metals (SEM) Cu, Zn, Pb, Cd, and Ni. Analyses for dioxins and furans in sediment was performed at the EPA Narragansett Laboratory.

The following techniques were used to provide a preliminary screening of potential ecological risk from the above analytes to the biological community along this section of the river .

Where available, analytes detected were compared to sediment guidelines shown in Appendix A-1, A-5 and A-6 (Persaud et al. 1993). These include low effect levels (LELs) and severe effect levels (SELs). The LEL indicates a sediment is clean to marginally polluted and has no significant effect on a majority of freshwater benthos. Exceedance of these values may require additional study. The SEL indicates a sediment is likely to be heavily contaminated, and so, would impact a majority of benthos in the study area. Consequently, further examination would be required in an attempt to define the extent and magnitude of impact.

One vehicle used to better define the risk potential associated with metals at these locations is SEM/AVS ratios. The SEM/AVS ratio is a means to attempt to evaluate the bioavailability potential. It reflects the solid phase sulfides ability to bind certain metals. This ratio will be used to identify the potential for metals associated toxicity.

A second vehicle used particularly in the evaluation of non- polar organics is normalization to site specific organic carbon content. TOC is being used in conjunction with SEL values to establish location specific sediment effects benchmarks.

Organics

Comparison to site specific SEL values in Appendix A-6 show no exceedances. Comparison to LEL values show significant exceedances of numerous PAHs, pesticides and Arochlor 1254 (see Appendixes A-5 and A-6). Furthermore, total PAH values far exceed i.e. >10x the total PAH LEL value. This may give some indication of the additive or synergistic effects potential. The same can be seen for total PCB values.

An attempt was made to better define the impact potential that is reflected by an exceedance of one threshold value i.e. LELs, by incorporating a comparison to two other sediment quality benchmarks. These values are the threshold effect concentration (TEC) and the probable effect concentration (PEC) developed for the USEPA under the Assessment and Remediation of Contaminated Sediment (ARCS) project (USEPA 1996). TEC values are associated with the upper concentration showing little or no effect. The PEC value is that concentration that is almost always associated with adverse impacts to benthic species. As discussed in (Jones et al 1997), the TEC and PEC values for PAHs have a moderate to high confidence rating. The PAH compounds benzo(a)pyrene, fluoranthene, indeno(1,2,3-cd) pyrene, pyrene and total PAHs exceed both the TEC and PEC at all locations sampled. From the ARCS project, only a total PCB benchmark value was available. The PEC of 245 ug/Kg was exceeded at all but the Esmond and Manton Dam locations.

Dioxins

Available sediment data (Appendix A-4) indicates that 2,3,7,8 TCDD has been detected in samples from Allendale, Lymanville, Manton, Olneyville and Lonigan Dams. Concentrations in dry weight range from 8200pg/g at Lymanville Dam to 94.2pg/g at Dyerville Dam. There was no 2,3,7,8 TCDD detected at Esmond Dam. Other dioxins and furans were detected in the sediments as well. As seen in Appendix A-4 the detected isomers and congeners of both the dioxins and furans were equated to 2,3,7,8 TCDD using toxicity equivalency factors (TEFs) (USEPA 1993a). These values were then compared to 2,3,7,8, TCDD sediment values associated with predictions of low and high risk to sensitive fish species i.e. 60 pg/g and 100 pg/g, respectively (USEPA 1993b). These sediment quality values were developed from sensitive fish effects data and a biota to sediment accumulation factor (BSAF) of 0.3. Generally speaking, more tolerant aquatic species appear to be at a lesser risk, perhaps in the range of 10 times less than sensitive species. In addition, these values are based on a sediment organic carbon concentration of 3%. Comparison of TEF concentrations from Appendix A-4 indicate that all locations except Esmond Dam and Dyerville Dam show exceedances of the high risk screening value.

Additional documents were consulted in an attempt to gauge the 2,3,7,8 TCDD guidelines identified in the above paragraph.

According to the equilibrium partitioning (EqP) theory, sediment quality values (SQV) can be calculated for non-polar hydrophobic organic chemicals. The equation for such a calculation is $SQV(ug/goc) = Koc(L/Kg) * FCV(ug/L) * 1Kg/1goc$. National chronic ambient water quality criteria (AWQC) for 2,3,7,8 TCDD is <0.00001 ug/L and for the acute value is 0.01 ug/L. These criteria values are actually a lowest observed effect level (LOEL) because there is not enough data to support the determination of actual AWQC values. A Koc value of 10^7 was estimated based on analysis of measurements and models (USEPA 1993b). Based on this information and a 0.01 ug/L acute value, an acute SQV of 100 ug/g(oc) would result. TOC normalized acute SQV values would range from 3800 ug/Kg for 3.8%TOC to 10,900 ug/Kg for 10.9% TOC. Based on chronic WQC a chronic SQV of 0.1 ug/g(oc) would be calculated. This

would result in a TOC normalized range of 3.8 - 10.9 ug/Kg for chronic criteria. Dioxins sediment concentrations detected at this site would appear not to pose an acute significant risk to the benthic invertebrate community based on these calculated site specific SQVs. However, based on the chronic calculated SQVs, chronic impacts to the benthic community would be expected.

A 10 ug/g(oc) sediment criteria for the protection of the benthic community was proposed for use in New York (New York Bureau of Environmental Protection 1989) and was based on aquatic toxicity data. Normalizing this value to site specific organic carbon data would result in a criteria range of 380 - 1090 ug/Kg. Calculated sediment criteria or guidelines based on Koc values have its own uncertainty associated with it. Some would say that because of the uncertainty involved, bounds of 1 order of magnitude to either side is appropriate (New York Bureau of Environmental Protection 1989). This is to say that sediment concentrations approaching 10 times the New York criteria would likely result in chronic impacts to benthos. Values exceeding 100 times (assuming an acute to chronic factor of 10) the New York guidance values are likely to elicit acute effects. Using this criteria, again acute impacts to benthic organisms would not be expected. As for chronic impacts this range of error would suggest a lack of chronic impacts as well.

Though the sediment quality guidance is mixed, the fact that the "low" and "high" risk values of 50 and 100 pg/g for sediment are based on a back calculation of impacts to a sensitive fish species (one not expected in this area of the Woonasquatucket River) coupled with the fact that benthic invertebrates that have been tested are less sensitive than fish in general would suggest that these values may be conservative. Use of the EqP method because of its growing acceptance within a critical scientific community may provide a better range of appropriate guidance values for protection to the benthic community.

Another level of the aquatic community that was examined was the pelagic fish community. A publication of the Society of Environmental Toxicology and Chemistry (SETAC) (SETAC 1996) provides a compilation of calculated body burden effects data for various fish species and effects endpoints. These endpoints are associated with early and adult life-stages. Calculated body burden data from this document were selected based on the fish species caught in the river for tissue analysis or those expected to inhabit this area. Lethal effects in adult stages were associated with a calculated effect body burden range of 5 -16 ug/Kg in older fish. A lethal body burden of 5 ug/Kg for Bullhead Catfish was calculated from LD50 data. A calculated effect body burden of 11 ug/Kg for Largemouth Bass LC50 data was listed. A 16 ug/Kg effect body burden for Bluegill Sunfish based on LD50 data was also identified. Calculated sublethal body burden concentrations were also listed. A 0.08 ug/Kg effect body burden based on a no observable effect concentration (NOEC) for Guppy fin necrosis was calculated. An effect body burden concentration of 8 ug/Kg associated with a growth and survival NOEC was also calculated.

Proper comparison of this information to site specific fish tissue data collected would require sample weights. This was not currently available.

A general comparison of this information with fish tissue data for 2,3,7,8 TCDD would seem to indicate that a significant acute lethality issue, at least to adult fish, may not be present. However, the possibility of sublethal effects is present. **Note that because of increased sensitivity, early life stage effects concentrations can be much lower.**

Another point should be made that the fish tissue data used for this comparison was taken from a location which has, relatively speaking, dioxin sediment concentrations on the low end of the data range. It would be safe to say that an increase in tissue concentrations would be expected in fish from areas of higher sediment concentrations. The likely increase in fish tissue concentrations would increase the likelihood of chronic and possibly acute impacts to fish species in these areas.

Due to its propensity to biomagnify in the foodchain, protective sediment values for 2,3,7,8 TCDD suggested for the protection of piscivores i.e. fish eating birds and mammals, is in some cases lower than for either fish or benthos. A sediment criteria value of 0.0002 ug/goc based on wildlife residues was proposed (New York Bureau of Environmental Protection 1989). Based on this, site sediment values exceeding 0.008 to 0.022 ug/Kg would pose a risk. Low and high risk sediment values associated with upper food chain piscivores were identified (USEPA 1993b) as 0.0025 and 0.025 ug/Kg for mammalian species and 0.021 to .210 ug/Kg for avian species. These values again were based on sensitive species.

Comparison of these values with site sediment concentration would certainly indicate a chronic, and very possibly, an acute risk to upper trophic level species.

Inorganics

Various metals detected in the sediment samples exceeded their associated LEL and SEL values (AppendixA-1). SEL exceedances at the Esmond Dam were identified for chromium, copper, lead and manganese. Exceedance of the same metals were found at the Allendale Dam. SEL exceedances of chromium, copper, lead and nickel were identified at the Lysmanville Dam. The sample from the Dyerville Dam exceeded the SEL for chromium, copper, lead and zinc. Lastly, the lead SEL was exceeded at the Lonigan Dam. There were no SEL exceedances at either Manton or Olneyville Dams.

Bulk sediment chemistry in itself is not likely to present a clear picture of actual risk. Actual effects may be governed by other chemical and physical factors associated with sediment. One such factor is the sulfides, in particular, acid volatile sulfides. An SEM/AVS ratio in $\mu\text{mol/g}$ of ≤ 1.0 can accurately predict the lack of acute toxicity from detected SEM divalent metals (Hansen et al 1996). Based on this research and the sediment data provided, the highest likelihood of toxicity from metals would be found at the Dyerville Dam location with a SEM/AVS ratio of 2.5. All other location have SEM/AVS ratios well below 1, which indicates a lack of significant acute risk to benthos from SEM metals. Currently SEM/AVS screening is not applicable to other metals such as mercury and chromium. However, based on the assumption

that the total chromium detected is not in the hexavalent form, significant acute risk from chromium is unlikely.

As for mercury, again acute risk is unlikely but one must keep in mind chronic impacts and that mercury, primarily methylmercury, does have the potential to biomagnify in the foodchain.

Uncertainty Analysis

Various uncertainties are associated with this evaluation. Attempts were made to reduce at least some of them through the use of site specific information. It is also pertinent to keep in mind that this is a screening level risk evaluation using limited data.

The first is the amount of data available. Risk to aquatic life is based on the use of one sediment sample at each of the seven locations. The spatial extent of the contamination is not known. Additionally, fish tissue analyses is from one location and any extrapolation of risk estimates to other locations is limited.

A second point is that there is no background data available and so this evaluation is site specific with no relative comparison to similar lotic systems.

For PAH, pesticide, PCB and dioxin evaluation, comparison was made to TOC normalized criteria guidelines. Other physical and chemical characteristics of the site may influence an over or underestimation of the actual effects posed to biota associated with the site.

The evaluation of dioxin is based on values associated with an early life stage of a sensitive fish species. The extrapolation to sediment "low" and "high" risk values are done so with a non site specific TOC value of 3 % and a BSAF from a sensitive fish species that is not be found in this urban setting. The species of fish likely to be found at the site may be less sensitive. This would mean that any estimation of ecological risk to the aquatic environment based solely on these guidelines is likely to be an overestimation. In addition, the actual organic carbon content at each location is greater than 3 again likely to lead to an over estimation.

The Koc value used is an estimated average. The literature reports a range of values. The Koc value selected may over or underestimate the actual risk potential.

TEC and PEC values used were based on a compilation of sediment toxicity data. Site specific characteristics may mean the use of these values could potentially over or underestimate the actual risk.

The evaluation of risk from bioaccumulation and biomagnification in the foodchain was limited. This is due to limited data related to contaminants in fish tissue and habitat suitability and use.

Inorganics were evaluated through the use of SEM/AVS ratios. While ratios may exceed 1, actual toxicological impacts may not be present due to other binding factors. In addition,

while SEM/AVS ratio <1 provide a good indication of a lack of acute toxicity, chronic effects may be present and impacts while not likely may be caused by other metals .

With mixtures of chemicals synergistic, additive and/or antagonistic effects may lead to an over or underestimation of actual risk.

Summary

The screening level ecological risk evaluation is limited primarily due to limited information. However, based on the sediments and fish tissue data available the following points can be made.

The inorganic fraction based on SEM/AVS data would pose little if any immediate acute risk. This is not to say that there is not risk from other inorganics which are not evaluated through SEM/AVS ratios.

At this time it appears the majority of risk from chemical contaminants to the aquatic community in this study area would be from the organic component. Individual and total PAHs exceeded guidelines used in this screening risk evaluation. Total PCBs also exceeded its associated guideline values. Impacts to the benthic community from both PAHs and PCBs seem possible. Based on the information reviewed, dioxin would appear to be at least one possible cause of chronic impacts to the benthic community in the river. The pelagic community may also be at risk from chronic exposure to dioxin. More uncertain are the impacts to upper trophic level species. A primary reason for this is the lack of information on available habitat and the use of this river area by mammalian and avian piscivores for feeding. If significant use is probable, then based on the sediment concentrations of dioxin impacts may be likely.

Recommendations

The present sediment sampling data is limited both in lateral and vertical extent. Due to the risk and the source of that risk it would be important to better define this extent through additional sampling. Analysis of these sediments should include inorganics and organics as well as TOC and SEM/AVS. Co-located surface water sampling should also be performed with analysis of both the total and dissolved fractions.

Historical fish tissue data was based on samples taken from a location showing a lower level of dioxin contamination. Since higher levels are probable in fish that would be taken from those areas with higher levels of dioxin additional fish sampling should also be considered. Fish sampling undertaken in the future should be done in such a way that ecological, as well as human health risk evaluations can be performed.

Due to the complexed nature of sediment chemical and physical impacts on contaminants detected, it would be prudent to attempt to confirm or deny with biosurveys and/or toxicity testing the actual predicted through any risk assessment.

For exposure assessment purposes an evaluation of habitat quality and availability is also necessary.

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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MEMORANDUM

DATE: June 8, 1998

SUBJ: Review of Woonasquatucket Dioxin/Furan Results

FROM: Steve Stodola, QA Chemist

TO: Tim Brigdes, Environmental Scientist

As we discussed, a preliminary review of the dioxin/furan results from Region 7 has been completed. These results from Region 7 covered the analysis of the sediment samples which were taken from the Woonasquatucket River in the fall of 1997. The samples were initially analyzed for dioxin/furan by the National Health and Environmental Effects Laboratory (NHEEL) in Narragansett, RI. The samples were split and portions were sent to EPA Region 7 in Kansas City for analysis of the 17 standard dioxin/furan congeners as well as hexachloroxanthene (HCX). The purpose of the work at Region 7 was to confirm the screening results from NHEEL. Region 7 was also expected to quantitate more accurately the results for HCX.

A full data validation on the data package was not done at this time. The Data Quality Record: Organic Form from Region 7 was reviewed and no major problems were found. However, several specific items need to be drawn to your attention as you incorporate these results into your final report for this project.

- The analyses done at NHEEL were done by low resolution GC/MS, while the ones done in Region 7 were done by high resolution GC/MS. Low resolution GC/MS can be considered a screening method confirmed done by the high resolution method. Also, the low resolution method will have higher detection limits for the analytes than the high resolution GC/MS. The extraction procedures for these samples were essentially equivalent, both used an acetone/hexane mixture for the extraction.
- The sediment samples were oven dried by NHEEL before analysis. The split samples were dried by Region 7 in an air stream in a hood at room temperature overnight. This removed all but 5% (approximately) of the moisture as observed by visual inspection by the Region 7 analyst. This small amount of excess moisture could lead to slightly lower results when compared to the same samples analyzed by NHEEL. However, given the variability in sediment sample composition this uncertainty is not significant.

- Region 7 reported their EMPC (Estimated Maximum Possible Concentration) values as "U", non-detected results. These items are marked on the attached tables with an "*". Even if these "U" values had been reported as EMPC values, the interpretation of the 2378-TCDD Total Equivalency (TEQ) would not be changed. Namely, the two sediment samples with TEQ values higher than 1000 ng/kg (1ppb) will still be significant. The five samples with TEQ's less than 1000 ng/kg (1ppb) will remain below that level. Therefore, we recommend keeping the "U" qualifiers as reported by Region 7. A value of 1000 ng/kg (1ppb) is often used as an action level for remediation in dioxin/furan work.
- The HCX results reported by NEEHL should not be used since these values were calculated using an estimated response factor. NEEHL did not have an analytical standard to use in their analysis.
- Region 7 had HCX contamination in their method blank. As a result, the detection limits for HCX had to be raised in reporting the results for this compound. Therefore, only the high levels of HCX in samples 002, 003, and 006 can be considered reportable at this time.
- The Region 7 PE sample results were acceptable.

The results from NHEEL and Region 7 can be compared if these items mentioned above are taken into account. The results from Region 7 are summarized on the attached tables. The Percent Differences (%D) were calculated for all of the analytes that had positive results from both laboratories. The %D's for each of the seven samples were then averaged to give an indication of how favorably the results compared. The results can be summarized as follows:

<u>Location</u>	<u>% Difference</u>
Esmond Dam	79%
Allendale Dam	40%
Water Street Dam	53%
Manton Dam	30%
Dyerville Dam	18%
Olneyville Dam	50%
Lonigin Dam	46%

The averages ranged from 79% to 18%. For the two samples (002 and 003) with the highest TEQ values, the average %D's were 40% and 53%, respectively. This degree of comparability is acceptable for sediment samples given the amount of handling that the samples went through during the laboratory splitting operation and the fact that two different mass spectrometer methods were used.

Another important pattern to note is the relative concentrations of OCDD and OCDF in the samples. In all seven samples from both

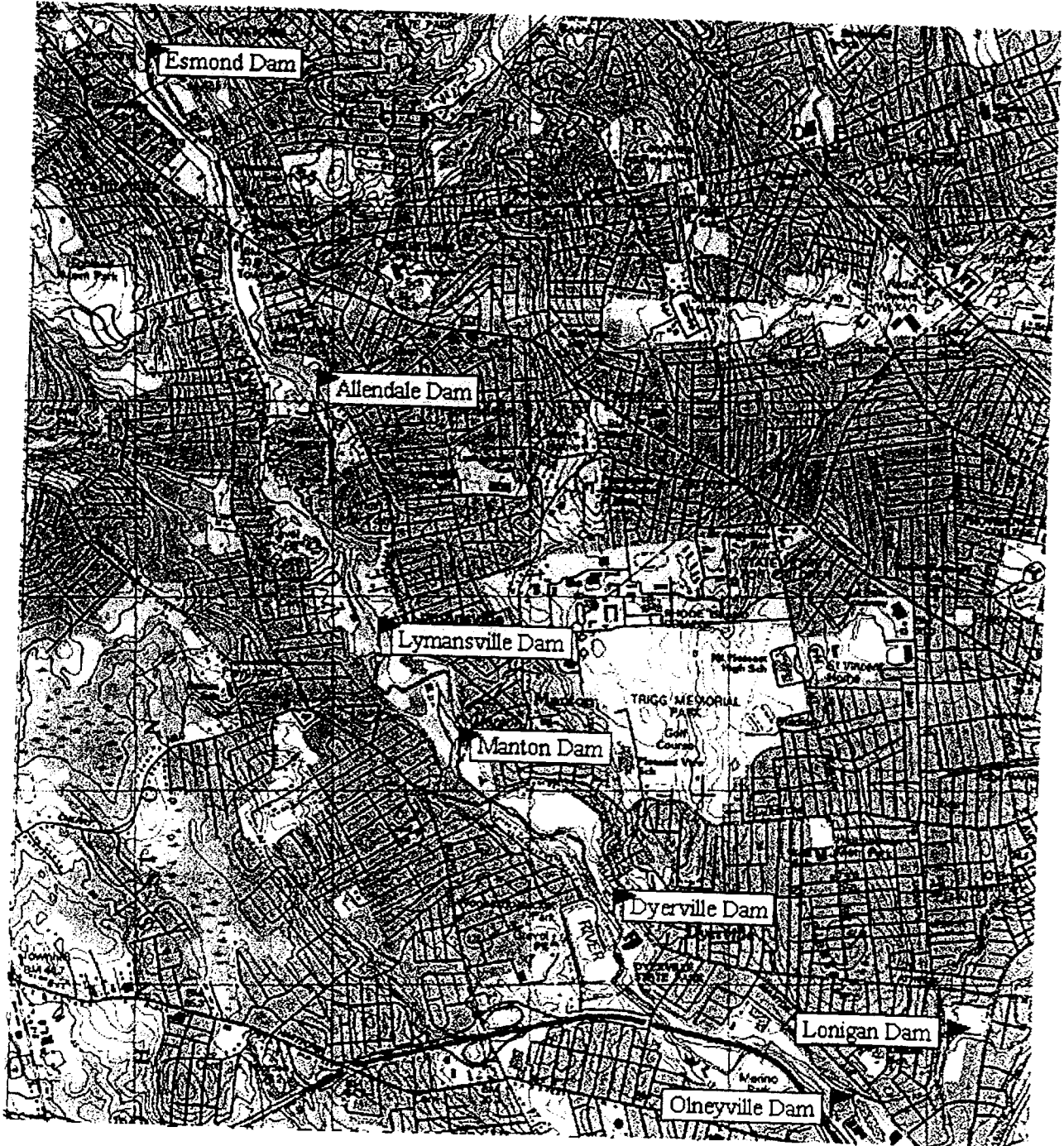
laboratories, the concentrations of OCDD are significantly higher than the OCDF concentrations. This indicates that the two mass spectrometer methods are producing consistent results across the set of seven samples.

Summary

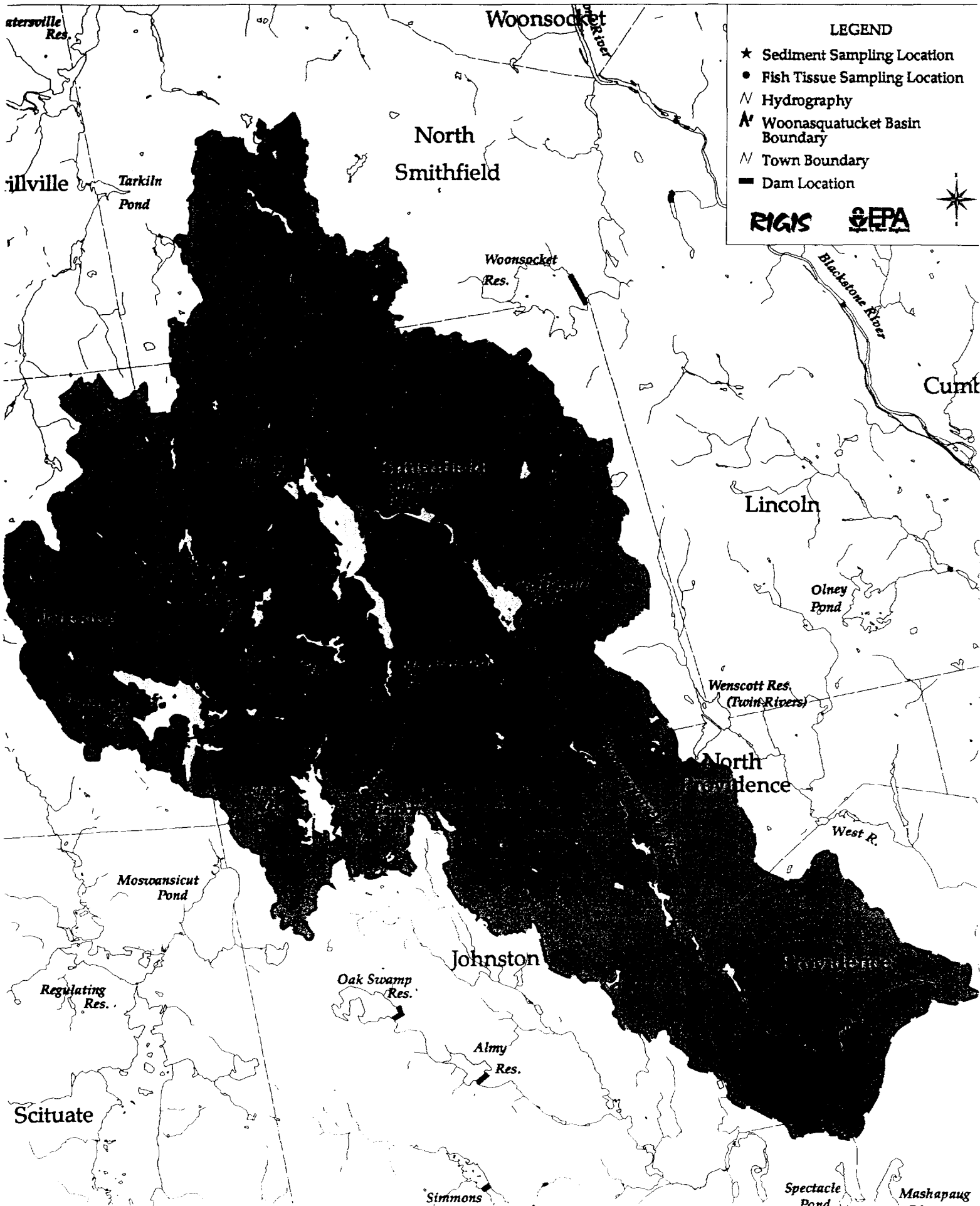
- The results from NHEEL and Region 7 agree reasonably well for sediment samples.
- The High Resolution GC/MS analyses performed at Region 7 confirm the Low Resolution GC/MS screening results from NHEEL.
- The fact that the two sets of data compared as closely as they do and that no major data quality issues were found with the Region 7 data indicates that the Region 7 results can be incorporated into your final report in order to meet the final goals of the project.
- The HCX results from Region 7 should be used and not the one from NHEEL since NHEEL did not have an adequate analytical standard for HCX.
- In the next phase of the project the dioxin/furan results should be submitted along with a full CLP-like deliverables package and a Tier III data validation be performed on the data.

If you have any questions, please call me at 781-860-4634.

cc: A. Beliveau, OEME
N. Barmakian, OEME
C. Wood, OEME




Appendix G: Basin M.



LEGEND

- ★ Sediment Sampling Location
- Fish Tissue Sampling Location
- ~ Hydrography
- ▬ Woonasquatucket Basin Boundary
- - - Town Boundary
- ▬ Dam Location

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