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The Use of Semipermeable Membrane Devices (SPMDS) for Monitoring Dioxin Levels in Maine Rivers

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THE USE OF SEMIPERMEABLE MEMBRANE DEVICES (SPMDS) FOR MONITORING DIOXIN LEVELS IN MAINE RIVERS

By

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Thesis Advisor: Dr. Howard Patterson

An Abstract of the Thesis Presented
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Maine's Department of Environmental Protection has been monitoring dioxin/furan levels in Maine rivers using fish tissue analysis since the 1980's. Effective December 31, 2002, pulp and paper mills in Maine must not discharge any toxic congeners of dioxins/furans into local surface water. The test prescribed in the law (38 M.R.S.A. §420) requires the concentration of dioxins or furans in fish (or surrogate) collected downstream of a mill cannot exceed fish monitored upstream from a mill. The purpose of this project is to determine if SPMDs are a better procedure for monitoring dioxin levels in accordance with the upstream/downstream test.

Effective analytical and field methods were developed at the Environmental Chemistry Laboratory at the University of Maine to determine dissolved dioxin/furan concentrations in SPMD sampling matrix. Water temperature, biofouling, and flow velocity are environmental conditions that can affect the uptake kinetics of SPMDs. Assuming isotropic exchange kinetics, a permeability reference compound (PRC) can be spiked into the SPMD prior to deployment to calibrate the rate change of dioxin/furan

uptake caused by environmental conditions (Huckins et al., 2002a). Thus, more accurate concentrations can be determined utilizing these passive samplers instead of using destructive fish tissue analysis.

The results of this thesis conclude the levels of most dioxin/furan congeners are consistently at or below the detection limit and PRCs are effective at correcting for the environmental conditions. 2,3,7,8-TCDF has been quantified in each of the three deployments on the Androscoggin River at both the upstream and downstream locations. In 2002, both toxic PeCDFs were quantified along with TCDF allowing a comparison of the upstream and downstream sites for those three congeners. The rest of the seventeen toxic dioxin/furan congeners were not consistently detected. Using the Mann-Whitney U test, a significant difference in concentration ($p=0.05$) was determined between the two sites with the upstream site greater than the downstream site. There are three possible explanations for the lower trend in furan concentrations downstream. 1. The downstream location is too far from the point of discharge leading to dilution of the furans. 2. The discharged dioxin/furans are not in dissolved form upon release from the mill. 3. The pulp and paper mill assessed is in compliance with the upstream/downstream law and is not releasing dioxin/furans in excess of the background concentrations in the Androscoggin river based on the SPMD protocol established in this thesis.

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INTRODUCTION

Maine's Dioxin Monitoring Program (DMP) is investigating sampling procedures for dioxin to attain the best possible upstream/downstream (U/D) test for the 1997 Dioxin Law. The legislation mandates that the dioxin concentration in fish downstream from a pulp and paper mill shall not exceed the concentration upstream after December 31, 2002 (38 M.R.S.A. §420-A). The DMP has utilized fish tissue analysis to determine dioxin levels in Maine rivers. The impetus for this research project is to determine whether the SPMD sampling technique is an appropriate surrogate procedure for the U/D test. This chapter provides introductory information and outlines the project objectives.

1.1. Dioxin

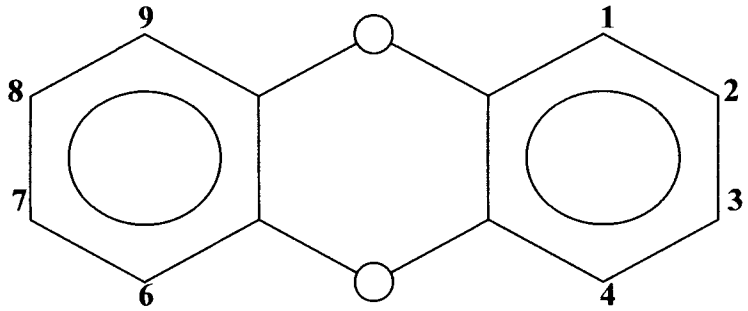
Dioxin is a colloquial term for polychlorinated dibenzo-*para*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), a group of organic compounds that are ubiquitous in the environment. The toxicity and unique characteristics of these compounds have created considerable interest in monitoring the concentrations in different environmental matrices (i.e. biota, water, soils). Dioxins are naturally produced in the environment (Ferrario et al, 2000). However, within the last 60 years, additional anthropogenic sources have elevated the levels of dioxin to the point where regulatory action has been taken (Czuczwa and Hites, 1984).

1.1.1. Dioxin Physical and Chemical Properties

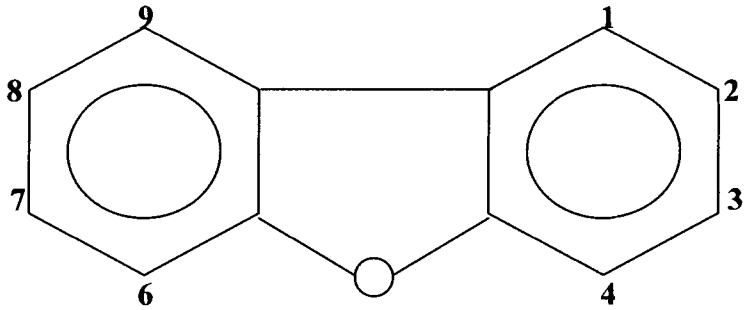
Dioxins are hydrophobic, lipophilic, stable molecules. There are 75 dibenzo-*para*-dioxin and 135 dibenzofuran congeners (EPA, 2000). A dioxin/furan congener is a compound with the same structural backbone with differing amounts and/or positions of chlorine atoms. There are eight possible sites on dioxins for the chlorine arrangement (Figure 1.1). Only 17 of the 210 congeners are considered toxic (EPA, 2000). All toxic congeners have chlorination at the 2,3,7, and 8 positions on the molecule (EPA, 2000). For simplicity, the seventeen toxic congeners will be designated by the term 'dioxins' for the remainder of this thesis. Also, acronyms are used when discussing a certain congener. For instance, 2,3,7,8 TCDD is 2,3,7,8 tetrachlorodibenzo-*para*-dioxin.

The estimated half-life of dioxins in the environment is ten to twelve years (Birnbaum and DeVito, 1995). The solubility range for dioxins is 19.3 ng/L for 2,3,7,8-TCDD to 0.74 ng/L for OCDD and the log octanol-water equilibrium coefficients (K_{OW}) range from 6.64 for 2,3,7,8-TCDD to 8.2 for OCDD (Mackay et al. 1992). Therefore dioxins are insoluble in polar solvents (i.e. water). The vapor pressure of dioxins range from 10^{-8} mm Hg for 2,3,7,8-TCDD to 10^{-12} mm Hg for OCDD meaning the compounds are classified as semi-volatile to non-volatile (Eitzer and Hites, 1988). Dioxins are small compounds ranging from 306 atomic mass units (amu) to 460 amu.

Figure 1.1. The Chemical Structure of Dioxins



Dibenzo-*para*-dioxin



Dibenzofuran

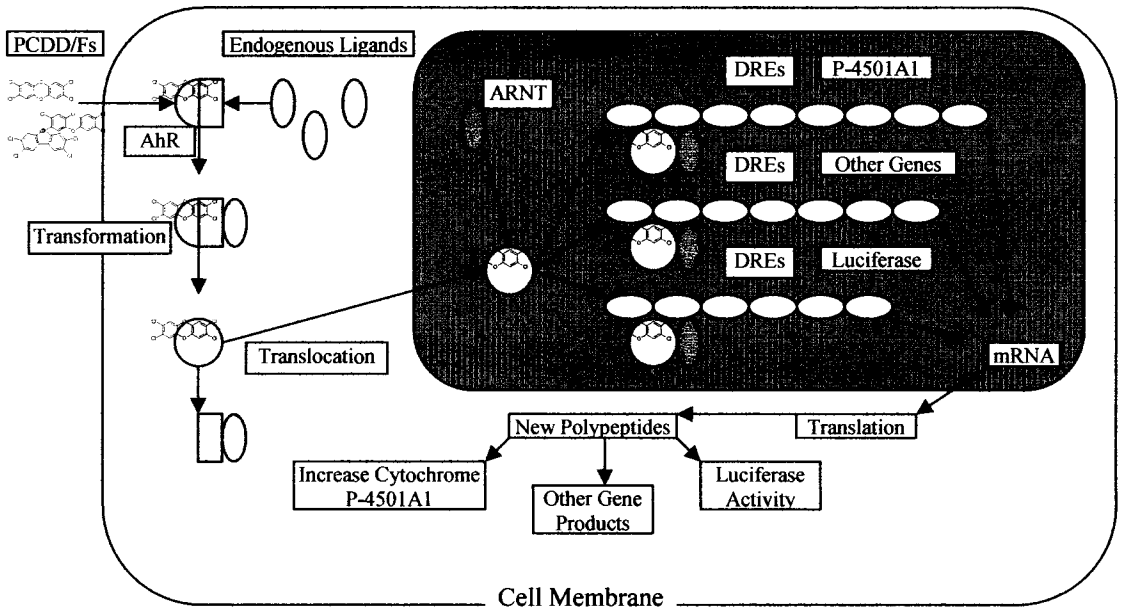
1.1.2. Dioxin Toxicity

Dioxins produce many carcinogenic, immunotoxic, and reproductive effects in the host organism. Since dioxin is ubiquitous, there are background levels in humans at an average body burden of 9 ng/kg (EPA, 1994). In adult humans, the estimated half-life is 7.78 years for 2,3,7,8-TCDD, 12.6 years for 1,2,3,7,8-PeCDD, 26-45 years for HxCDDs, 80-102 for HpCDDs, and 112-132 years for OCDD (Geyer et al, 2002). The majority of human accumulation originates from the diet (95%) with smaller percentages deriving from inhalation and dermal exposure (Gilman et al. 1991). In humans, elevated levels of dioxin exposure have been associated with chloracne at an estimated body burden of 45-3000 ng/kg, cancer at 109-7000 ng/kg, decreased testosterone at 83 ng/kg, decreased testis size at 14 ng/kg, and altered glucose tolerance at 14-110 ng/kg (EPA, 1994). Recently, dioxin has been labeled as an endocrine disrupter in laboratory animals as well (Maczka et al. 2000). However, the mechanisms of toxicity have not been fully characterized leading to some debate on whether there is enough information to appropriately regulate dioxin.

The most studied biochemical pathway for dioxin toxicity is recognition and binding by the Ah (aryl hydrocarbon) receptor protein (AhR) leading to translocation into the cell nucleus (Figure 1.2). Once inside, the AhR-dioxin complex binds with the Ah receptor nuclear translocator (ARNT) increasing the binding affinity to DNA. The complex then binds to the dioxin responsive element (DRE) on the DNA strand upstream from the response genes (i.e. Luciferase, P-450s). This leads to DNA bending, chromatin disruption, nucleosome disruption, increased promoter accessibility, and increased rates of response gene production (Hankinson, 1995). Toxic dioxin congeners have

chlorination at the 2, 3, 7, and 8 positions implying their importance in the recognition and binding by the Ah Receptor.

Figure 1.2. Ah Receptor-mediated Dioxin Mechanism of Toxicity (adapted from iDenison and Heath-Pagliuso, 1998)



The World Health Organization (W.H.O.) has developed a ranking of the toxic congeners based on the binding affinity to the Ah receptor protein to assess the potency of a mixture of dioxins (Van den Berg and Birnbaum, 1988). Toxic equivalency factors (TEF) are used to calculate the toxic equivalency quotient (TEQ) for environmental samples by multiplying the amount of each congener by the corresponding TEF and then summing the values to obtain the total TEQ value. The entire system is based on the toxicity of 2,3,7,8-TCDD (Table 1.1.).

Table 1.1. World Health Organization's (W.H.O.) Toxic Equivalency Factors (TEF) for Mammals (Van den Berg and Birnbaum, 1988).

CONGENER	W.H.O. TEF
2,3,7,8-Tetrachlorodibenzo-p-dioxin	1.0
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	1.0
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	0.1
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	0.1
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	0.1
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	0.01
Octachlorodibenzo-p-dioxin	0.0001
2,3,7,8-Tetrachlorodibenzofuran	0.1
1,2,3,7,8-Pentachlorodibenzofuran	0.05
2,3,4,7,8-Pentachlorodibenzofuran	0.5
1,2,3,4,7,8-Hexachlorodibenzofuran	0.1
1,2,3,6,7,8-Hexachlorodibenzofuran	0.1
2,3,4,6,7,8-Hexachlorodibenzofuran	0.1
1,2,3,7,8,9-Hexachlorodibenzofuran	0.1
1,2,3,4,6,7,8-Heptachlorodibenzofuran	0.01
1,2,3,4,7,8,9-Heptachlorodibenzofuran	0.01
Octachlorodibenzofuran	0.0001

1.1.3. Dioxin Sources

The EPA lists five major sources of dioxin: anthropogenic and natural combustion and incineration, metal production, chemical manufacturing, biological and photochemical reactions and remobilization from the reservoir sources (sediments, soils, and organic matter) (EPA, 1998). To form dioxin molecules, a system requires elevated temperatures, organic material, and chlorine atoms. The majority of dioxin formation is a result of human activities. Dioxin formation is an incidental occurrence meaning it is not produced for any human application. Dioxin is also naturally produced by forest fires, biotransformation, photochemical reactions, and volcanoes (Ferrario et al, 2000). Natural dioxin formation is usually not significant enough to cause a contamination problem unless anthropogenic sources become a contributor.

In Table 1.2, the EPA lists the sources of dioxin-like compounds throughout the United States. The largest source of dioxin originates from combustion and incineration processes accounting for 96% of total emissions in 1995. In comparison, water discharge and land application only constitutes 0.6% and 3.4% respectively. The once prominent discharge of dioxin from pulp and paper mills was dramatically reduced 95% from 1987 to 1995.

Table 1.2. Inventory of Sources of Dioxin-like Compounds in the United States for Air (*), Land (^), and Water (#) (EPA, 2000)

SOURCES	1987 (g/yr TEQ)	1995 (g/yr TEQ)	PERCENT REDUCTION
Municipal Solid Waste Incineration*	8877.0	1250.0	86%
Backyard Refuse Barrel Burning*	604.0	628.0	-4%
Medical Waste Incineration*	2590.0	488.0	81%
Secondary Copper Smelting*	983.0	271.0	72%
Cement Kilns*	131.5	173.9	-32%
Sewage Sludge/land applied^	76.6	76.6	0%
Residential Wood Burning*	89.6	62.8	30%
Coal-fired Utilities*	50.8	60.1	-18%
Diesel Trucks*	27.8	35.5	-28%
Secondary Aluminum Smelting*	16.3	29.1	-79%
2,4-D^	33.4	28.9	13%
Iron Ore Sintering*	32.7	28.0	14%
Industrial Wood Burning*	26.4	27.6	-5%
Bleached Pulp and Paper Mills#	**356.0**	**19.5**	**95%**
Sewage Sludge Incineration*	6.1	14.8	-143%
EDC/Vinyl chloride*	NA	11.2	NA
Oil-fired Utilities*	17.8	10.7	40%
Crematoria*	5.5	9.1	-65%
Unleaded Gasoline*	3.6	5.6	-56%
Hazardous Waste Incineration*	5.0	5.8	-16%
Lightweight Ag kilns, haz waste*	2.4	3.3	-38%
Commercial Sewage Sludge^	2.6	2.6	0%
Kraft Black Liquor Boilers*	2.0	2.3	-15%
Petrol Refine Catalyst Reg.*	2.24	2.21	-1%
Leaded Gasoline*	37.5	2.0	95%
Secondary Lead Smelting*	1.29	1.72	-33%
Paper Mill Sludge^	14.1	1.4	90%
Cigarette Smoke*	1.0	0.8	20%
EDC/Vinyl Chloride^	NA	0.73	NA
Primary Copper*	0.5	0.5	0%
EDC/Vinyl Chloride#	NA	0.43	NA
Boilers/Industrial Furnaces*	0.78	0.39	50%
Tire Combustion*	0.11	0.11	0%
Drum Reclamation*	0.1	0.1	0%
Carbon Reactivation Furnace*	0.08	0.06	25%
TOTALS	**13,998**	**3,255**	**77%**

NA = Not Available

In Table 1.3, the inventory of sources of dioxin in Maine is obtained through direct measuring and by models with varying levels of confidence (Wright et al, 2001). The estimates do not take into account out-of-state sources. A large discrepancy can occur in the mass balance of dioxin in Maine due to the atmospheric deposition from out-of-state sources since most of the dioxin produced in the United States is from combustion and incineration processes. Like the rest of the country, the sources in Maine are mainly attributed to air emissions and solid waste at 15.43 (29%) and 35.39 (66.4%) grams/year respectively. The 2.5 (4.6%) grams/year that are directly from water discharge is a relatively small value compared to other sources. However, even at that level, burial in the sediment and uptake by organisms can lead to unacceptable biota concentrations.

1.1.4. History of Dioxin Formation in Bleached Kraft Pulp and Paper Mills

As early as the 1970's, scientists hypothesized that bleached kraft pulp and paper mills were possible dioxin point sources in the United States. However, due to poor analytical abilities, confirmation of this hypothesis did not occur until 'The Five Mill Study' (EPA, 1988). During this time period, most paper mills were using elemental chlorine as their bleaching agent. Elemental chlorine is an oxidizing agent used to bleach high grade paper and tissue. The Five Mill Study was followed by the more comprehensive '104 Mill Study' (Anderson et al, 1990). This study validated the previous result that paper mills produced dioxin in the bleaching process. Also, the study demonstrated dioxins were released in the wastewater effluent (sludge and direct discharge) as well as the pulp itself.

Table 1.3. Dioxin Source Inventory for the State of Maine (Wright et al, 2001)

SOURCE	GRAMS TEQ	PERCENTAGE
Residential; bituminous	0.0136	0.09
Residential; #2 fuel oil	0.182	1.18
Residential wood consumption	3.17	20.55
Back Yard Burning	4.05	26.25
Subtotal/Residential Combustion	**7.4156**	**48.06**
Wood, industrial non P&P mills	0.177	1.15
Residual Commercial Oil	0.0328	0.21
Wood – P&P Mills	2.88	18.67
Tire waste combustion (paper mills)	0.00509	0.03
Subtotal/Commercial & Industrial	**3.09489**	**20.06**
Wood - Utility	1.1	7.13
Oil-fired Utility Boilers	0.0401	0.26
Subtotal/Utility Boilers	**1.1401**	**7.39**
Municipal Waste Incinerators	1.95	12.64
Medical Waste Incinerators	1.68	10.89
Crematories	0.00263	0.01
Cement Production, Wet Process	0.109	0.71
Chlorine Production	0.00000000902	0.00
On Road Vehicles	0.372	0.24
Subtotal/Other	**4.11363**	**24.5**
TOTAL FOR AIR EMISSIONS	***15.42942***	***100***
Solid Waste Incinerators	34.11	96
Pulp & Paper mills (sludge)	.923	0.03
Pulp & Paper mills (ash)	0.07	0.00
Sewage Treatment Sludge	0.06	0.00
Biomass power generation	0.074	0.00
Subtotal for Landfill Solid Waste	**35.24**	**99.995**
Solid Waste Incinerators (ash)	0.00	0.00
Pulp & Paper mills (sludge)	0.009	0.00
Pulp & Paper mills (ash)	0.005	0.00
Sewage Treatment plant sludge	0.132	0.004
Biomass Power Generation	0.013	0.00
Tannery, Textiles (sludge)	0.00	0.00
Subtotal for Reused Solid Waste	**0.159**	**0.005**
TOTAL FOR SOLID WASTE	***35.396***	***100***
Municipal Wastewater Discharges	Trace	Trace
Pulp & Paper Mill Discharges	**2.3**	**91**
Other Industrial Discharges	Est. 0.01	<1
Non Point Source Discharges	0.2	8
TOTAL FOR WATER DISCHARGE	***2.5***	***100***

Beginning in the early 1990's, researchers discovered that substituting chlorine dioxide for elemental chlorine reduced dioxin discharge dramatically by reducing the atomic chlorine to wood fiber ratio (Voss et al, 1998). Therefore, by reducing the amount of precursor chlorine in the bleaching process, the mills could reduce the amount of dioxin formation. The use of chlorine dioxide (ClO_2) is termed elemental chlorine free (ECF) bleaching. Numerous studies have investigated dioxin formation in ECF plants with the results typically below the detection limit with the exceptions of TCDF, OCDF, and OCDD (N. McCubbin Consultants Inc., 2003). Other oxidizing agents like hydrogen peroxide and ozone can be utilized to bleach paper as well. These processes are coined total chlorine free (TCF) bleaching due to the lack of chlorine atoms in the bleaching reagent. TCF bleaching does not produce any dioxin (EPA, 1998). Mills can also reduce dioxin formation by reducing organic precursors (i.e. phenols, non-chlorinated dioxins) in the processing steps leading up to bleaching by using alternative washing techniques and defoaming agents (N. McCubbin Consultants Inc., 2003). Also, mills can further reduce dioxin discharge by controlling the amount of suspended solids in their effluents using better management techniques, increasing operator knowledge, and utilizing specialized equipment (N. McCubbin Consultants Inc., 2003).

The six bleached kraft pulp and paper mills in Maine are International Paper in Riley, Mead/Westvaco in Rumford, SAPPI-Somerset, Lincoln Pulp and Paper, Georgia-Pacific in Old Town, and SAPPI-Westbrook (Figure 1.2.). All together these mills produce about 5,000 tons/day with an average fiberline of 600 tons/day. All the bleached kraft pulp and paper mills in Maine have converted to the ECF bleaching process.

Figure 1.3. U.S.G.S. Map of the Bleached Kraft Pulp and Paper Mill Locations in Maine

1.1.5. Dioxin Fate and Transport

The fate and transport of dioxin follows many complex and poorly understood pathways. In the atmosphere, dioxin travels by sorbing to particulates and aerosols. The EPA has discovered the estimated amount of dioxin released by emissions is less than the amount that is being precipitated by deposition (EPA, 1998). More than likely, this discrepancy is a result of a lack of reliable monitoring rather than formation in the atmosphere. Nonetheless, researchers are attempting to determine possible photochemical formation in the atmosphere (Whitefield et al, 1995). The ultimate sinks for dioxin are soils, sediments, and organic matter (Czuczwa and Hites, 1986). For the purposes of this thesis, the factors affecting fate and transport in Maine rivers will be interpreted.

Dioxin transport in surface water is partially understood. Since dioxin is highly insoluble in water, theoretically it would precipitate through the water column directly to the sediment. However, due to dioxin's high partitioning affinity to natural organic material (NOM), it can be transported effectively in the water column. Therefore, transport of dioxin in surface water is a function of biotic, physical, hydrodynamic, and chemical properties.

Natural Organic Matter (NOM) is a collective term for the biogenic molecules in aqueous systems. NOM consists of particulate organic matter (POM > 0.45 μm) and dissolved organic matter (DOM < 0.45 μm). NOM has hydrophilic and hydrophobic domains. Typically, NOM in the aqueous environment exhibits polarity due to the oxygen and nitrogen functional groups (Aikens et al, 1985). Though numerous elements constitute NOM (nitrogen, oxygen, hydrogen etc.), organic carbon is the element most readily measured in the laboratory. Hence, NOM is typically referred to in the literature

as either total organic carbon (TOC), particulate organic carbon (POC), or dissolved organic carbon (DOC) with the same operational definition as NOM, POM, and DOM. While NOM can be made up of numerous components (carbohydrates, fatty acids, peptides, amino acids), these are usually metabolized relatively fast by biota in the aquatic system (Koelmans et al, 2001). Therefore the components that compose the majority of measured TOC are recalcitrant, typically smaller molecules. As illustrated in Table 1.4., DOC is usually the dominant fraction of TOC in all types of freshwater systems.

Table 1.4. Median Organic Carbon Content of Surface Waters (Wetzel, 2001)

HABITAT	TOC (mg/l)	DOC (mg/l)	POC (mg/l)	DOC:POC
Rivers	7.0	5.0	2.0	3:1
Eutrophic Lakes	12.0	10.3	1.7	6:1
Wetlands	17.0	15.3	1.7	9:1
Oligotrophic Lakes	2.2	2	0.2	10:1
Bogs	33.0	30.3	2.7	11:1

Aqueous dioxin sorption to NOM can either occur by adsorption (chemical process on a two-dimensional plane) or absorption (physical process into a three-dimensional matrix) (Schwarzenbach et al, 2002). Absorption can only occur with NOM of adequate size. Therefore absorption usually exists within POM or colloidal DOM (ie. large macromolecules or microparticulates). Meanwhile adsorption can manifest on any size distribution of NOM. Organic matter can adsorb onto larger particles (i.e. other suspended solids, minerals, and biota), aggregate into larger particles, and be sequestered by biota (Koelmans et al, 2001). The main chemical characteristic of dioxin that contributes to the association with NOM is the hydrophobicity of the compound. Therefore, the main mechanism of sorption is the hydrophobic interactions between the

dioxin molecule and the hydrophobic domain of NOM. Dioxin association with organic matter exists by this interaction resulting in a non-linear sorption isotherm described by the following equations:

Equation 1.1. Concentration of Sorbed Dioxin (C_S) (adapted from Accardi-Dey and Gschwend, 2002)

$$C_S = f_{OC}K_{OC}C_W + f_{BC}K_{BC}C_W^n$$

Where, f_{OC} is the fraction of organic carbon

K_{OC} is the organic carbon normalized distribution coefficient for dioxin

C_W is the dissolved dioxin concentration in the water

f_{BC} is the fraction of black carbon (soot)

K_{BC} is the black carbon normalized distribution coefficient

n is the Freundlich exponent

Equation 1.2. Dioxin Solid-Water Distribution Coefficient (C_S/C_W) (adapted from Accardi-Dey and Gschwend, 2002)

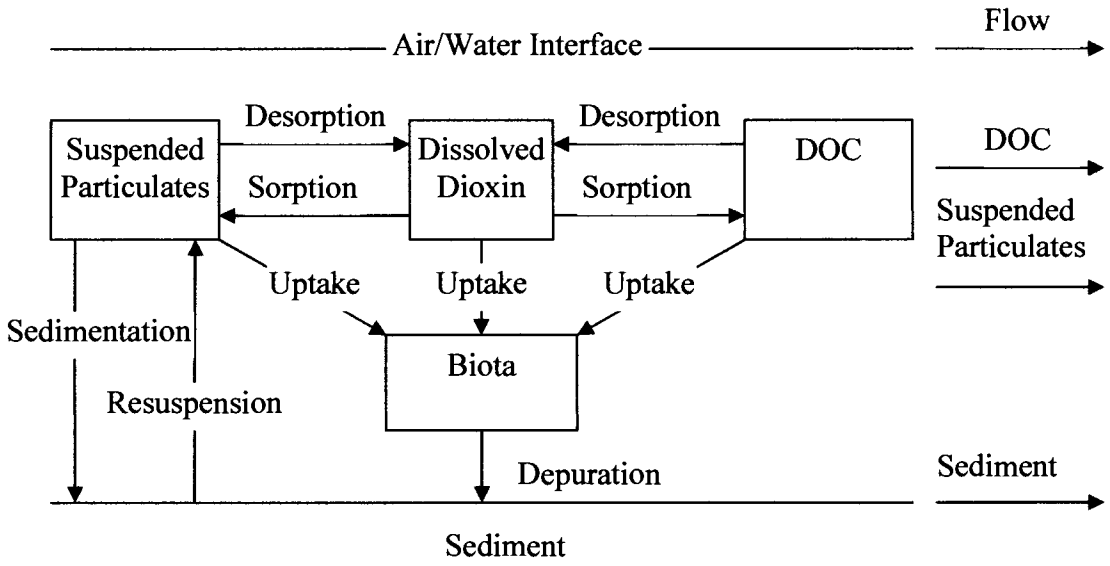
$$K_d = f_{OC}K_{OC} + f_{BC}K_{BC}C_W^{n-1}$$

The equations above introduce the concept of black carbon (a.k.a. soot, glassy carbon, rigid carbon) explaining the deviation from the linear sorption of dioxin onto/into NOM. The black carbon fraction can constitute up to 10% of the total NOM in sediments (Gustafsson et al, 1997). In essence, the black carbon fraction accounts for the complex distribution of dioxin in the aquatic environment due to the variability in NOM structure. In a study using a soot-column cosolvency method, the log K_{BC} was calculated to be approximately 6.37 for dibenzo-*para*-dioxin and 4.94 for dibenzofuran while the log K_{OC} was only 4.01 and 3.18 respectively (Barring et al, 2002). This is further evidence that the

hydrophobic interactions between black carbon-like compounds and dioxin regulate the sorption onto/into NOM. This means that the more planar and hydrophobic regions constituting TOC, the higher affinity TOC has for dioxin molecules. Therefore, characterization of the total dioxin concentration at any given point in the river requires knowledge of the amount and type of TOC.

In a modeling study utilizing a Monte Carlo simulation, the equilibrium distribution of TCDD in the water column for a small river was calculated to be 6.5% dissolved, 8.5% associated with DOC, and 85% sorbed with POC (Giri et al, 2001). This means at any one time or position in the river greater than 90% of the total dioxin concentration is sorbed to NOM assuming equilibrium. The advection component of a riverine system creates a less uniform and larger spatial distribution of dioxin within the water body. Figure 1.4. is a diagram of the mechanisms of transport for dioxin. Whether the source is from effluent discharges or atmospheric deposition, natural organic matter (i.e. suspended solids, resuspended sediments, or DOC) act as carrier compounds to redistribute dioxin downstream from the point source of contamination. This solubility enhancement of dioxin has been well documented (Chiou et al, 1986, Kim et al, 2002). The ability of the NOM to circulate dioxin is due to the solubility and size of the associated organic matter. Therefore, DOC, which is smaller and more polar than other forms of NOM, is typically a better carrier compound.

Figure 1.4. Distribution Diagram of Dioxin in a River



The classic assumption of dioxin uptake by biota from the water body is passive diffusion resulting in bioconcentration. Bioconcentration is where compounds permeate through bio-membranes making the concentration in the animal greater than the environment (Servos et al, 1989). Dioxin is concentrated in the lipose tissue of organisms due to its lipophilic properties. Most organisms, including bacteria, phytoplankton, zooplankton, benthic and pelagic biota, accumulate dioxin in this manner (Koelmans et al, 2001). NOM inhibits the freely dissolved uptake mechanism considerably by associating with that fraction of dioxin in the water column (Servos et al, 1989). Once associated to NOM, dioxin can be considered physically part of the NOM which is too large to diffuse through cell membranes.

Once in the organism, dioxin exhibits a long half-life before depuration or metabolism. For example, the estimated half-life of dioxin in fish varies from 2 months to 2 years (Frakes et al, 1993). Due to the persistence of dioxin in organisms,

biomagnification within the food web occurs. Biomagnification is the process by which species higher on the trophic scale of the ecosystem have increased body burdens of dioxin due to diet. Laboratory derived bioconcentration factors (BCFs) for fish have been determined based solely on the molecular diffusion uptake mechanism from freely dissolved concentrations in water (Branson et al, 1985). Though this may work in a laboratory, the environment cannot be so easily modeled. To address this incongruity, researchers attempted to derive bioaccumulation factors (BAFs). A BAF is the ratio of dioxin in fish to dioxin in the environment resulting from contaminated food, water, and sediment (Frakes et al, 1993). Unfortunately, limitations to the BAF model are numerous. For example, there are uncertainties arising from a lack of knowledge about the food web structure, the actual bioavailability of dioxin , the lipid content of the species, exposure conditions (chemical and physical), and biodegradation along the food chain (Koelmans et al, 2001).

1.2. Monitoring for Dioxin

There are many different procedures for monitoring dioxin. Each technique has some benefits and drawbacks. Even at contaminated sites, concentrations of dioxin are low resulting in most methods being complex, expensive and time-consuming. The six main approaches for dioxin monitoring are chemical analysis, immunoassays, biosensors, in vivo biomarkers of exposure, in vivo bioassays, and in vitro bioassays (Hahn, 2002).

The most developed and commonly used monitoring method is chemical analysis of environmental samples. This involves extraction, clean-up, and quantification with either gas chromatograph-electron capture detection (GC-ECD) or a high-resolution gas chromatograph high-resolution mass spectrometry (HRGC-HRMS) (Liem et al, 1992).

The environmental samples can be either biotic (mussels, fish, mammals etc.), passive samplers (SPMDs, PISCEs etc.), sediment cores, effluents/sludges, or concentrated water samples. The advantage to chemical analysis is the sensitivity and specificity allowing for quantification of all seventeen toxic congeners thereby enabling the use of the W.H.O. TEQ system. However, the process is time consuming and expensive. For example, each type of sample requires a certain extraction technique with multiple clean-up steps before analysis. Developing the proper procedure can be the difference between quantification and a non-detect in an environmental sample.

Table 1.5. Techniques for Chemical Analysis of Dioxin (Liem et al, 1992)

Sample Types	Extraction Techniques	Clean-up Techniques	Analysis
Biota Passive Samplers Sediment Cores Effluents/Sludges Water Samples	Solid-Phase (column) Solvent Soxhlet Liquid-liquid Partitioning Dialysis	Adsorption Chromatography (AC) on silica AC on carbon AC on alumina AC on Florisil Gel Permeation Chromatography	HRGC/MS HRGC/ECD

The other techniques available for dioxin monitoring were developed from a biochemical perspective. Immunoassays utilize antibodies that recognize dioxin-like compounds by the affinity for the Ah receptor. These are called enzyme-linked immunosorbent assays (ELISA) (Hahn, 2002). Similarly, biosensor technology use antibodies attached to probes that transduce antigen-antibody interactions into electrochemical signals that can be detected within the environmental matrix (Hahn, 2002). Both these methods are usually quicker and cheaper than chemical analysis. These techniques measure the endpoint of toxicity meaning the method can only reveal the

sample toxicity and cannot quantify the exact compounds that are producing the toxic effect.

Biomarkers and bioassays can be utilized to measure the toxicity of dioxin-like compounds in the environment. Biomarkers are *in situ* biochemical, biological, or physiological changes from dioxin-like compounds causing measurable effects in organisms. Usually, this is accomplished by measuring the induction of the enzymes cytochrome P450 1A (CYP1A) or ethoxyresorufin *O*-deethylase (EROD) (Hahn, 2002). Similarly, in vivo and in vitro bioassays measure the same activity except outside of the environmental medium in laboratory exposures and cell cultures, respectively (Hahn, 2002). These are indiscriminate tests indicating that the sample is toxic, but are unable to quantify the compounds of interest. An advantage of these techniques is that synergistic or antagonistic toxicological effects from dioxin-like compounds can be measured. Direct chemical analysis cannot account for these types of mechanisms of toxicity. The most comprehensive monitoring of dioxin would include chemical analysis and one or more of the biochemical tests.

1.2.1. Maine's Dioxin Monitoring Program

In 1988, Maine's Dioxin Monitoring Program (DMP) was enacted to determine the dioxin contamination level in the waters and fisheries of the state. The Department of Environmental Protection (DEP) is required to sample no more than 12 possible point sources of dioxin throughout the state. DEP is advised by the Surface Water Ambient Toxics (SWAT) Monitoring Program Technical Advisory Group and must report all results to the Joint Standing Committee on Natural Resources by March 31st of each year. The main objective of the program is to monitor fish for ecological and human health

risk. The second goal is to determine trends, monitor the dioxin reduction, and initiate changes when required. The DMP is obligated to develop an appropriate upstream/downstream test for the 1997 Dioxin Law.

The law requires an upstream/downstream (U/D) test that is representative of the particular facility, has a uniform exposure time, and has enough sensitivity to detect relatively small differences between the two locations. Since 1988, the DMP has used numerous types of biotic samples to attempt to estimate the levels of dioxin in accordance with the U/D test. Species include smallmouth bass, white suckers, caged freshwater mussels and brown trout. The tissues include fillets, whole body, and livers (Mower, personal communication). While their attempts have been comprehensive, each biotic matrix has inherent problems. The difficulties with biotic samples are:

1. Mobility – fish are non-uniformly distributed in the environment and exposures are variable.
2. Dioxin concentrations in tissue vary with age.
3. Different species are assumed to accumulate, metabolize, and depurate dioxin differently.
4. Bioaccumulation and biomagnification are a measure of historical dioxin as well as current discharge from the mill.
5. Biotic samples typically aren't homogeneous.
6. High variability – with all the aforementioned problems, larger sample sizes are required to demonstrate a significant difference between sites.

1.2.2. SPMD Special Studies

In 1999, the DMP started a special studies project examining the feasibility of Semipermeable Membrane Devices (SPMDs) as a surrogate procedure for fish tissue analysis in an attempt to address the U/D test requirement. The project has been executed in a collaborative effort by Maine's Department of Environmental Protection, the Senator George J. Mitchell Center for Environmental and Watershed Research, and the Environmental Chemistry Laboratory at the University of Maine. Heather Shoven matriculated and managed the SPMD research project from June 1999 to June 2001. During her Master's work, she determined that SPMDs are effective at sequestering all toxic congeners of dioxin when deployed in Maine rivers for 28 days. These results demonstrated that SPMDs have promise as a possible surrogate procedure for destructive fish tissue analysis thereby maintaining fish populations and circumventing complications when using biotic samples for monitoring dioxin levels.

1.3. SPMD Design

Semipermeable Membrane Devices (SPMDs) are passive *in situ* sampling devices consisting of low-density polyethylene (LDPE) tubing enclosing a thin layer of the model lipid triolein (Huckins et al, 1993). The technology was developed and patented (Huckins et al., U.S. Patents, #5,098,573 and #5,395,426) by researchers at the Columbia Environmental Research Center in Columbia, MO and is marketed by Environmental Sampling Technologies, Inc. in St. Joseph, MO. The specifications of the standard SPMD are in Table 1.6. The lengths and widths can be altered on a standard SPMD as long as the lipid to membrane mass ratio is $\cong 0.2$.

Table 1.6. Specifications of the Standard SPMD

Width	2.5 cm
Height	91.4 cm
Weight	4.5 g
Surface Area	450 cm^2 or 100 cm^2/g of SPMD
Membrane Thickness	70-95 μm
99.9% Pure Triolein	0.915 g
Volume	$5.2 * 10^{-3}$ L

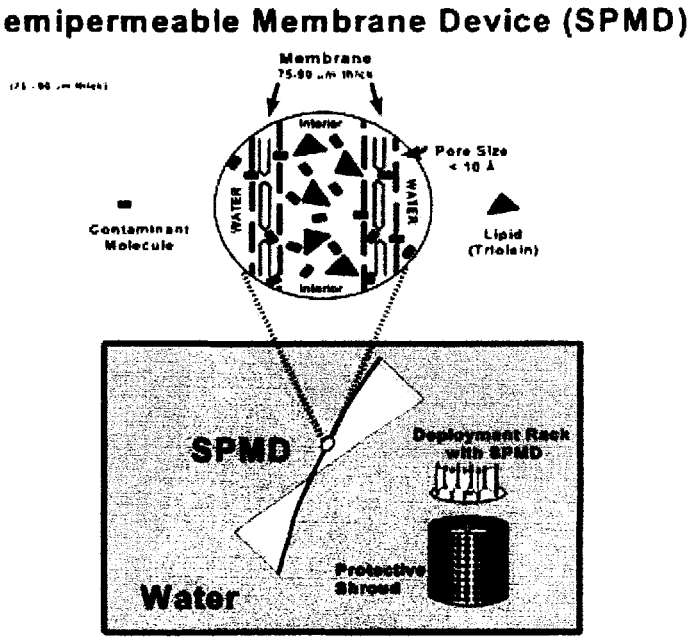
There are three compartments to the SPMD matrix, the aqueous diffusion layer, the low-density polyethylene (LDPE) membrane and the synthesized lipid triolein (1,2,3-tri[(cis)-9-octadecenoyl] glycerol) (Gale, 1998). The aqueous diffusion layer is a thin layer of laminar water molecules surrounding the membrane. The LDPE membrane is nonporous, but experiences transient cavities of approximately 10 Å due to thermal motions of the polymer chains (Hwang and Kammermeyer, 1984). These transient cavities mimic the estimated 9.8 Å size limit for gill membranes in fish (Opperhuizen et al, 1985). The ephemeral holes allow compounds of <600 amu to passively diffuse through the membrane (Huckins et al, 1990). Triolein is utilized since it is commonly found in organisms as a storage fat. There are some physiochemical advantages to using triolein over other lipids. These are:

1. A high purity (95-99%)
2. A melting point of 0°C allowing exposures in cold water
3. The ability to solubilize non-polar organics
4. A close correlation between the equilibrium triolein-water partition coefficient (K_{LW}) and the equilibrium octanol water partition coefficient (K_{OW}) of hydrophobic contaminants (Chiou, 1985)

5. A low LDPE membrane permeability ensuring no loss of lipid during exposure and dialysis (Huckins et al, 1990; 1993; 1995; 1996; 2002b; Meadows et al, 1993).

Once past the aqueous diffusion layer and in contact with the membrane wall, contaminants will either diffuse through the membrane and partition to the triolein or adsorb to the membrane itself. Studies have shown that as much as 50% of the compounds sequestered by a SPMD are recovered from the membrane (Gale, 1998). The contaminants will remain partitioned until either equilibrium is reached with the ambient environmental concentration or the SPMD is analyzed. The entire system mimics bioconcentration meaning SPMDs sequester only dissolved compounds from the water column (Huckins et al, 1993).

Figure 1.5. Diagram of a SPMD (Huckins et al, 2002b)



The lipid containing semipermeable membrane device (SPMD) and a typical deployment apparatus.

1.3.1. SPMD Uptake Theory

Since there are three compartments to the SPMD, two mass transfer steps are required to ensure liquid-liquid partitioning of a contaminant. The aqueous diffusion layer is the first obstacle for a dissolved compound to pass through. The second mass transfer step is the contaminants diffusion through the membrane wall (Gale, 1998). The environmental factors that affect the uptake kinetics of SPMDs are flow velocity, biofouling, and temperature (Petty et al, 2000). Increased flow velocity (i.e. turbulence) increases the amount of water sampled per day by the SPMD. Biofouling (periphytic growth) on the SPMD during the exposure can expand the width of the membrane increasing the amount of energy required to impregnate the matrix, thereby slowing the uptake rate. The biofouling itself can sequester dioxin, but is removed from the matrix prior to analysis. The uptake increases as the temperature increases in the laboratory. However, Shoven (2001) correlated increased temperature with increased biofouling. Therefore, biofouling and temperature are confounding environmental factors that affect uptake rates. Water chemistry (i.e. pH, salinity etc.) can affect the speciation of the analyte of interest in the environment, but does not alter the uptake rates of the SPMD (Huckins et al, 2002b). Regardless of the contaminants concentration in the environmental medium, SPMDs sample the same amount of water for each calibrated compound (Gale, 1998; Huckins et al, 1990; 1993; 1995; 1996, 2002b).

Analytes of interest can be grouped into two rate-limiting SPMD uptake models. In one model, compounds under membrane control are characterized by a log K_{OW} value less than 4.4. In the other model, compounds are under aqueous diffusion layer control with a log K_{OW} value greater than 4.4 (Booij et al, 1997, 1998; Huckins et al, 2002b).

Membrane controlled compounds typically reach equilibrium in a short period of time while aqueous diffusion layer controlled compounds do not reach equilibrium during typical exposure periods. The cut off (log K_{OW} = 4.4) for the two groups of compounds is estimated and can change due to the environmental conditions of the exposure. However, for extremely hydrophobic compounds like dioxin (log K_{OW} > 6), the aqueous diffusion layer is the rate limiting step (Huckins et al, 2002b).

SPMDs can be used as integrative samplers for hydrophobic compounds (log K_{OW} > 4.4) meaning the sequestering phase is linear and equilibrium is not approached during the exposure period. The linearity of the uptake allows for calculation of the ambient dioxin concentration in the water assuming calibration data is available. In order to ensure that SPMDs are integrative samplers for dioxin, the length of the linear uptake phase was determined. The linear uptake phase ends approximately at one half-time ($t_{1/2}$) which is half the time to equilibrium (Huckins et al, 1999). The half-time was calculated by using Equation 1.6. Before calculation of the half-time is possible, the researcher must be able to estimate some physiochemical parameters for dioxin. These parameters are the membrane-water equilibrium partition coefficient (K_{MW}), the triolein-water equilibrium partition coefficient (K_{TW}), and the SPMD-water equilibrium partition coefficient (K_{SPMD}) for dioxin (Huckins et al, 1999). All these coefficients can be derived from the K_{OW} for dioxin congeners using linear regressions seen in Equations 1.3, 1.4 and 1.5.

Equation 1.3. The Calculation of the Membrane-Water Equilibrium Partition Coefficient (Hofmans, 1998)

$$\log K_{MW} = -0.0956 * (\log K_{OW})^2 + 1.7643 * (\log K_{OW}) - 1.9$$

Equation 1.4. The Calculation of the Triolein-Water Equilibrium Partition Coefficient (Hofmans, 1998)

$$\log K_{TW} = -0.1257 * (\log K_{OW})^2 + 1.9405 * (\log K_{OW}) - 1.46$$

Equation 1.5. The Calculation of the SPMD-Water Equilibrium Partition Coefficient (Huckins et al, 1999b)

$$K_{SPMD} = (K_{MW} * V_M + K_{TW} * V_T) / V_{SPMD}$$

Where, K_{MW} is the Membrane-Water Equilibrium Partition Coefficient

V_M is the Volume of the Membrane = 0.0042 L

K_{TW} is the Triolein-Water Coefficient

V_T is the Volume of the Triolein = 0.001 L

V_{SPMD} is the Volume of the SPMD = 0.0052 L

Equation 1.6. The Calculation of the Half-Time to Equilibrium for Dioxin (adapted from Huckins et al, 1999)

$$t_{1/2} = [-\ln(0.5) * K_{SPMD} * V_{SPMD}] / R_S$$

Where, K_{SPMD} is the SPMD-water equilibrium partition coefficient

V_{SPMD} is the volume of the SPMD = $5.2 * 10^{-3}$ L

R_S is the SPMD sampling rate for TCDD at 19°C = 3.8 L/day

Table 1.7. Calculation of the Half-Times for Sixteen Toxic Congeners

CONGENER	K_{OW}	K_{MW}	K_{TW}	K_{SPMD}	R_S[e]	$T_{1/2}$
TCDD	2630267.99[a]	306561.89	656309.24	373821	3.8	354.5756
PeCDD	4365158.32[a]	398094.56	763584.81	468381.1	3.4	496.5343
1,2,3,4,7,8-HxCDD	63095734.4[b]	1109777.7	1067362.6	1101621	4	992.6611
1,2,3,6,7,8-HxCDD	63095734.4[b]	1109777.7	1067362.6	1101621	3.2	1240.826
1,2,3,7,8,9-HxCDD	63095734.4[b]	1109777.7	1067362.6	1101621	2.9	1369.188
HpCDD	100000000[b]	1247383.5	1045201.4	1208502	2.2	1979.947
OCDD	158489319[b]	1377577.4	1000073.7	1304981	3	1567.876
TCDF	3388441.56[a]	350274.85	710401.5	419530	3.7	408.6863
1,2,3,7,8-PeCDF	6165950.02[a]	469942.84	833123.97	539785.4	3.8	511.9957
2,3,4,7,8-PeCDF	8317637.71[a]	538289.81	889077.3	605748.9	4.2	519.843
1,2,3,4,7,8-HxCDF	10000000[c]	583042.21	920873.55	648009.8	2.7	865.0607
1,2,3,6,7,8-HxCDF	10000000[c]	583042.21	920873.55	648009.8	2.9	805.4014
2,3,4,6,7,8-HxCDF	10000000[c]	583042.21	920873.55	648009.8	3	778.5547
1,2,3,7,8,9-HxCDF	10000000[c]	583042.21	920873.55	648009.8	2.3	1015.506
HpCDF	83176377.1[a]	1192922.3	1056942.9	1166772	2.7	1557.583
OCDF	93325430.1[d]	1227080.2	1050044.9	1193035	1.8	2388.963

(a) Sijm et al, 1989
(b) Shiu et al, 1988
(c) Mackay et al, 1992
(d) Doucette and Andren, 1988
(e) Rantalainen et al, 2000

The R_S values (uptake rates) were determined in a laboratory flow through experiment at 19°C and 10°C (Rantalein et al, 2000) (Table 1.7.). The uptake rates at 19°C are more representative of the average ambient temperature for Maine rivers during the summer so those values were used in this study. At that temperature, the shortest half-time is for TCDD at 354 days. Therefore, it can be safely assumed that the uptake of dioxin is in the linear phase for any deployment period up to approximately a year regardless of ambient dioxin concentration in the water. However, depending on the environmental medium, biofouling of the membrane becomes a serious complication (uptake becomes non-linear) when SPMDs are deployed for extended periods of time (Richardson et al, 2002). Since the uptake of dioxin is considered linear, the calculation of the estimated dioxin concentration in the water is straightforward assuming biofouling impedance is minimal.

Equation 1.7. Calculation for Dissolved Dioxin Concentrations in the Water Column (Huckins et al, 2002b)

$$C_W = (C_{SPMD} * M_{SPMD}) / (R_S * t)$$

Where, C_W is the dioxin concentration in the water

C_{SPMD} is the dioxin concentration in the SPMD

M_{SPMD} is the mass of the SPMD

R_S is the sampling rate for the congener

t is the duration of the deployment

The dissolved dioxin concentration is only one aspect of the total speciation of dioxin in the environmental medium. As mentioned in the Dioxin Fate and Transport Section, most of the dioxin in the water column is adsorbed onto natural organic matter. Therefore, Equation 1.8 was developed for the total contaminant concentration in the water column accounting for the total organic carbon fraction (i.e. NOM). The accuracy of this calculation is a limited estimate because of the lack of reliable K_{OC} values for the dioxin congeners. As mentioned earlier the exact structural components (i.e. hydrophobic domains) of organic carbon are molecule specific. The exact K_{OC} value will be unique to each environment. Therefore, to more accurately determine the total dioxin concentration in the water, the TOC of Maine rivers must be characterized by separate experiments.

Equation 1.8. Calculation of the Total Contaminant Concentration in the Water Column (Meadows et al, 1998)

$$C_{W\text{-}TOT} = (1 + TOC * K_{OC} / M_W) * C_W$$

Where, $C_{W\text{-}TOT}$ is the total dioxin concentration in the water column

TOC is the total organic carbon

K_{OC} is the organic carbon-water equilibrium coefficient

M_W is the mass of water

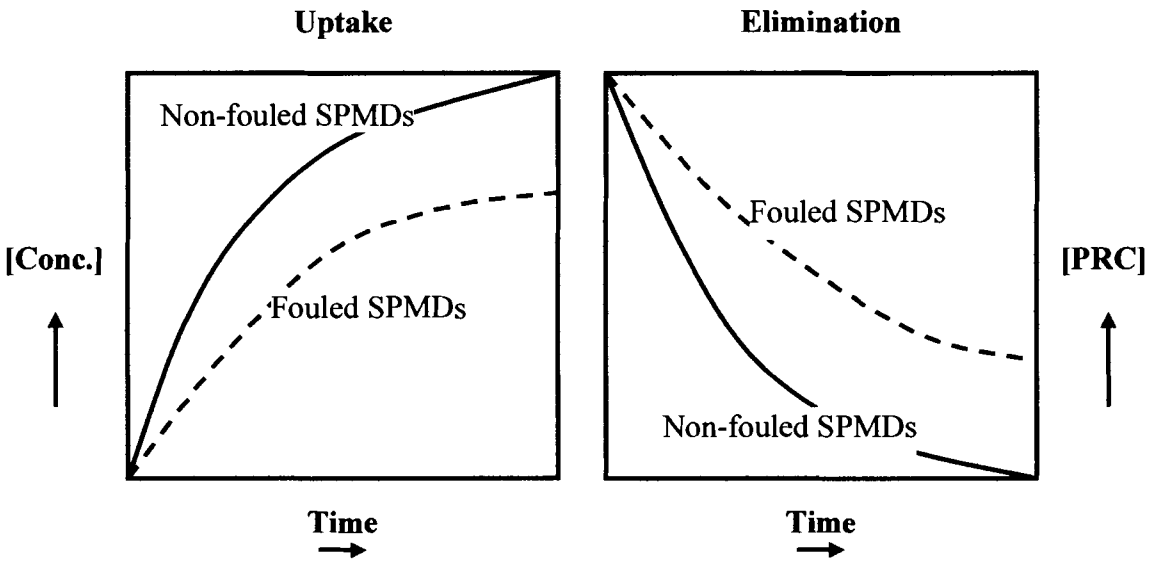
C_W is the dissolved dioxin concentration in the water

1.3.2. Calibrating SPMDs for Dioxin Field Investigations using PRCs

In order to calculate the dioxin concentration in surface water (Equations 1.7 and 1.8), the investigator needs to have calibration data for the contaminants to be estimated. Typically this is determined by running laboratory experiments with flow through exposures and known concentrations of the analytes of interest. In order to properly calibrate for uptake rates of dioxin in this study, monitors need to have calibration data for the specific flow velocity, amount of expected biofouling impedance, and the average temperature for each site. Obtaining this much calibration data from controlled laboratory experiments is not possible for the scope of this thesis. To address this problem, the developers of SPMDs have suggested using Permeability Reference Compounds (PRCs). These compounds are an *in situ* calibration approach. PRCs are analytically non-interfering compounds with relatively high SPMD fugacity which are spiked in the SPMDs prior to exposure in the field (Huckins et al, 2002a). This calibration technique is based on the assumption of isotropic exchange kinetics meaning the uptake rate of an analyte is equal to the elimination rate (Huckins et al, 2002a). This can be seen in Figure

1.6. where the area in between the non-fouled SPMD and the fouled SPMD uptake curve is the same as the area between the elimination curves. This assumption is mainly theoretical, but there exists some calibration data which support the hypothesis (Huckins et al, 1994; 1997; 2002a; 2002b).

Figure 1.6. Theory of Isotropic Exchange Kinetics (adapted from Huckins et al, 2002b)



Choosing the proper PRC to correct for the analyte of interest can be difficult. The compound must differ from procedural and instrumental internal standards. The compounds should be compatible with the analytical procedure for the analyte of interest. The PRCs cannot be found in the sampled water column at confounding concentrations. The compounds should represent the same rate-controlling mechanism as the target analyte (i.e. the aqueous diffusion layer or the membrane layer). PRCs should have recoveries between 20 to 80 percent of the spiked amount (Huckins et al, 2002b). However, information can still be gained by PRCs which are completely eliminated or do not dissipate at all (see the Discussion chapter).

After quantification of the PRC-spiked SPMDs, calculations can be used to determine an exposure adjustment factor (EAF). First, the investigator needs to calculate the elimination rate for the PRC. In Equation 1.9, a two-point derivation is used to calculate the elimination rate assuming first order kinetics. This assumption is valid if the SPMD was spiked immediately before the deployment and the rate-limiting step for the PRC is the aqueous diffusion layer (Huckins et al, 2002b). As seen in Equation 1.10., the EAF is a ratio between the calibrated elimination rate in the laboratory and the measured elimination rate in the field.

Equation 1.9. Calculation of the Elimination Rate for PRCs (Huckins et al, 2002b)

$$k_{e\text{-}PRC} = \ln (C_{SPMD\text{-}0} / C_{SPMD}) / t$$

Where, $k_{e\text{-}PRC}$ is the elimination rate for the PRC

$C_{SPMD\text{-}0}$ is the initial PRC concentration spiked into the SPMD

C_{SPMD} is the PRC concentration in the retrieved SPMD

t is the time of the deployment

Equation 1.10. Calculation of the Exposure Adjustment Factor (Huckins et al, 2002b)

$$EAF = k_{e\text{-}PRC} / k_{e\text{-}cal}$$

Where, $k_{e\text{-}PRC}$ is the elimination rate for PRC

$k_{e\text{-}cal}$ is the calibrated eliminate rate

With the use of PRCs, investigators now have the ability to do an *in situ* calibration for their analytes of interest thereby allowing them to use previously determined calibration data to calculate water concentration estimates more accurately. Typically, PRCs are of the same chemical class as the analyte of interest (i.e. deuterated

PAHs as PRCs for PAHs in the environment). However, Huckins et al (2002a) suggested that it is possible to use compounds of different classes to calibrate for other compounds as long as both classes have the same uptake/elimination rate-limiting mechanism. For example, compounds with log K_{OW} of 4.4 to 5.5 can be used to estimate more hydrophobic compounds like dioxin (log K_{OW} 6.4 to 8). Using extremely hydrophobic compounds as PRCs is not feasible because the elimination rate from the SPMD is so slow that the dissipation will not be significant. Therefore, the best compounds to use for aqueous diffusion layer controlled analytes of interest are PRCs with the log K_{OW} range of 4.4 to 5.5 (Huckins et al, 2002a).

1.3.3. Field Investigations using SPMDs

In the past thirteen years, SPMDs have been researched extensively all over the world. Investigators have focused on four different types of research; SPMD calibration and theory, SPMD comparisons with other monitoring techniques, screening with SPMDs using toxicity tests, and SPMD performance assessing different contaminants of concern. Most of the relevant calibration and theory papers have been discussed, so in this section the focus will be on reviewing comparison studies and research involving related organic contaminants.

Prest et al (1992) completed a study at three sites on the Sacramento/San Joaquin River Delta to measure organic contaminants using SPMDs in concert with freshwater clams (*Corbicula fluminea*) for two months. The authors analyzed for pesticides, polychlorinated biphenyls (PCBs), and dioxins. The SPMDs were not standard (5 X 229 cm, with 5 ml of triolein) and only the triolein was analyzed in this study. OCDD dominated the congener profile in both clams and SPMDs. However, much higher levels

of TCDD were found in the SPMDs (32% of the congener profile) compared to the clams (<1% of the congener profile) suggesting the matrices have different uptake mechanisms.

The most applicable study related to this research project at the University of Maine was executed at an EPA superfund site in Bayou Meto, Arkansas (Lebo et al, 1995). The investigators exposed SPMDs for 28 days to measure all seventeen toxic congeners of dioxin upstream and downstream from a known point source using gas chromatography/mass spectrometry (GC/MS) and a H4IIE bioassay. They used 4 replicates of 17 gram SPMDs (non-standard) for each analysis. At the upstream site, only traces of HpCDDs (35 +/- 4 pg) and OCDD (642 +/- 94 pg) were discovered. At the downstream site, however, the samples averaged 1550 +/- 80 pg of TCDD, 1640 +/- 80 pg of TCDF, and lower concentrations for all other toxic congeners. The results from the H4IIE bioassay agreed well with the GC/MS results. The authors estimated the water concentration for TCDF and TCDD to be at 2 pg/L using calibration data for similar PCBs.

SPMDs and blue mussels (*Mytilus edulis*) were simultaneously deployed for 60 days in Corio Bay, Victoria, Australia to measure PCBs and pesticides (Prest et al, 1995). The study design was similar to that of Prest et al, 1992. Both matrices displayed similar results about the relative levels of contamination. However, the PCB congener profile differed dramatically between SPMDs and mussels. As in 1992, the lower-chlorinated congeners were much higher in the SPMDs than in the mussels. The authors attributed this to contaminant solubility, partitioning to TOC, and biotransformation. Also, they discovered more unidentified halogenated hydrocarbons in the SPMDs than the mussels,

suggesting that SPMDs may be better samplers of the total organic contaminant load in the water column.

Another comparison study was done on ten sites in the Upper Mississippi River with SPMDs (2.54 X 183 cm, 2 ml triolein), tangential-flow ultrafilter permeates, caged fish (3 sites), and feral fish (3 sites) (Ellis et al, 1995). The analytes of interest were pesticides (chlordanes, pentachloroanisole, dieldrin, lindane, dacthal, aldrin, and heptachlor epoxide) which are no longer applied in agriculture causing the expected water concentrations to be minute. The SPMDs and caged fish were deployed for 28 days. The researchers determined there was a 'reasonable' agreement between the SPMD-derived water concentration and the ultrafilter permeate. The caged and feral fish were unsuccessful at accumulating the organic contaminants during the short period of deployment. SPMDs proved much more adept at sequestering a greater number of organic contaminants than any of the other methods.

SPMDs (2.5 X 152 cm, 2 ml triolein, 17 g total mass) were deployed for 28 days at five sites on the Lower Missouri River to assess pesticide contamination (Petty et al, 1995). The authors determined that organochlorine pesticides were present at all sites. The highest concentrations were chlordane, heptachlor epoxide, toxaphene, and dieldrin with concentrations ranging from below calibration to 800 ng per sample. The coefficient of variations for the sample sets were in-between 10-35 percent.

Following the same protocol as Prest et al (1992 and 1995), Finnish scientists exposed SPMDs and caged lake mussels (*Anodonta piscinalis*) simultaneously for 28 days in 4 lake watercourses in Central Finland as part of annual monitoring program (Herve et al, 1995). The authors were interested in assessing the organochlorine

contamination from nearby pulp and paper mills. The mussels only sequestered chlorohydrocarbons (CHCs) while the SPMDs were able to concentrate CHCs, chlorophenols (PCPs), chloroanisoles (PCAs), and chloroveratroles (PCVs). The compound profile of each matrix demonstrated SPMDs sequester lower chlorinated compounds better than the mussels and vice versa for the higher-chlorinated congeners.

A preliminary assessment of the potential of SPMDs to monitor pulp mill effluents was conducted by the University of British Columbia (Rohr et al, 1996). The study included a laboratory exposure of four commonly found contaminants in mill effluents (2,2',5,5'-tetrachlorobiphenyl, dehydroabietic acid, guaiacol, and α-pinene) and direct measurement of collected mill effluent. SPMDs sequestered all of the commonly found contaminants except guaiacol (polar). The sampling of the mill effluents recovered numerous organic contaminants proving the ability of SPMDs to be used as a monitoring tool. The authors concluded SPMDs show much more promise than biotic samples as a monitoring technique for mill effluents.

Dioxins and PCBs were assessed in the Saginaw River in Michigan using SPMDs, caged channel catfish (*Icatalurus punctatus*), and sediment-derived water concentration estimates (Gale et al, 1997). The SPMDs (2.5 X 1.52 cm, 1.64 g triolein, 8.35 g total mass) were deployed simultaneously with the catfish for 28 days. Analytes accumulated by SPMDs were proportional to actual analyte water concentrations while the biotic and inferred sediment samples did not show the same accuracy. The authors concluded that the elevated levels of lower-chlorinated congeners in SPMDs indicate non-passive sampling by biota can produce 50-500% error due to biotransformation and elimination.

SPMDs (3.3 X 110 cm, 1 ml triolein) were exposed in the sediments and the water column for 62 days in the Lower Fraser River in British Columbia to compare the results with the levels of Dioxins and PCBs obtained by an Infiltrex resin column water sampler and benthic fish tissue analysis (Rantalein et al, 1998). The congener profile elucidated multiple sources of the contaminants including pulp mills, pentachlorophenol formulation, and deposition from combustion. The estimated water concentrations and congener profiles from the SPMD data compared fairly well with the Infiltrex system and the fish tissue. However, the levels in each matrix were noticeably different.

Blue mussels (*Mytilus edulis*) and SPMDs (5 X 90 cm, 25 μm thick, 0.5 g triolein) were deployed at 5 sites in New Bedford Harbor, MA for 30 days to accumulate pesticides and PCBs (Hofelt and Shea, 1997). The authors demonstrated an excellent correlation between the K_{OW} and BAF for mussels and the K_{OW} and AF (accumulation factor) for SPMDs with the accumulation in mussels being 2-fold higher when the concentrations were based on lipid basis. The correlation was better than in previous research because the investigators modified the original SPMD design demonstrating the ability of monitors to adjust the physical parameters of SPMDs (surface area, membrane thickness, and lipid volume) to optimize the uptake rate and equilibrium point for specific applications.

The uptake rate constants for standard SPMDs and brown trout (*Salmo trutta*) were estimated from a 0, 7, 14, and 28-day deployment in a PCB contaminated spring in Pennsylvania (Meadows et al, 1998). PCB concentrations in the water were assessed with a 4 L water sample at each interval. The samples were corrected for TOC to obtain the estimated freely dissolved PCB-water concentration. The estimated uptake rates were

similar for both matrices with the equilibrium constants of SPMDs ranging from one to two times higher than those of brown trout. The congener profile was similar for both sampling techniques.

Standard SPMDs were deployed for 35 days at 9 main stem and 7 tributary sites on the Lower Columbia River to assess the distribution of organochlorine contaminants (dioxins, PCBs, chlorinated pesticides, and transformation products) and PAHs over a span of 700 miles during low flow conditions in 1997 and high flow conditions in 1998 (McCarthy and Gale, 1999). They concluded: (1) SPMDs can reveal contamination at levels much lower than conventional water sampling, (2) the distribution of organic contaminants in the streambed is not necessarily representative of the dissolved-phase, (3) the elevated contaminant concentrations in tributaries are significantly reduced by confluence to the main stem, (4) during times of high flow rate the concentrations in the dissolved phase are dramatically reduced, (5) the elevated levels of contaminants in the Portland/Vancouver area are indicative of local contamination, not upstream sources, and (6) without significant additional sources, volatilization, dilution, and precipitation of contaminant-sorbed particles reduces the dissolved-phase concentration along the flow regime.

In a Lithuanian study, SPMDs (2.5 X 50 cm, 0.455 g triolein) were deployed for 28 days in the Ula and the Vilnia Rivers (Sabaliunas et al, 1999). The SPMD dialysates were analyzed by a Microtox™ assay for toxicity. The relatively clean Ula River samples demonstrated three times more toxicity than the more polluted Vilnia River. The dialysates were fractionated with a silica gel column and analyzed by various analytical techniques to identify the contaminants providing the toxicity. The most toxic of the

fractions was the one containing oleic acid which is the major impurity in triolein. The amount of oleic acid in the Ula site samples was three times the amount in the Vilnia samples implying the difference in toxicity was from that impurity. Once the oleic acid fraction was discarded, the toxicity of the two rivers was better characterized. The authors recommend using SPMD dialysates in biochemical toxicity screening, but a clean-up step is required to remove the interfering oleic acid impurity.

In a similar study, standard SPMDs were deployed on two rivers in Lithuania to assess the potential of numerous types of biochemical techniques for toxicity screening (Sabaliunas et al, 2000). The SPMD dialysates were fractionated with gel permeation chromatography (GPC) with the PAH and organochlorine pesticide fraction as the main focus. The fraction was characterized by GC/MS and bioassays including Microtox™, Mutatox™, *Daphnia pulex* immobilization assay and the sister chromatid exchange (SCE) in human lymphocytes *in vitro* test. The most sensitive test proved to be the Mictotox™. The toxicity of one GPC fraction was due to SPMD sampled elemental sulfur from the sediment which complicates the investigator's ability to assess the toxicity of whole samples which typically displayed much higher responses. In this study, the authors demonstrated the potential and limitations of using SPMDs in bioscreening tests.

Standard SPMDs, caged channel catfish (*Ictalurus punctatus*) were deployed for 28 days at five sites in the Saginaw River to assess PCB contamination (Echols et al, 2000). The relative PCB patterns from fish, sediment, and SPMDs were compared using principal component analysis. Sediment and SPMD data demonstrated complementary information because sediments represent historical accumulation while SPMDs only

reflect the current dissolved PCB fraction during the deployment period. The congener profile in the fish and SPMD differed significantly due to the biotic samples ability to depurate and metabolize lower-substituted PCBs. The PCB profile for the fish and sediment were nearly identical suggesting that fish are possibly more representative of historical PCB contamination.

In a PAH-contaminated aquifer, standard SPMDs were deployed for 29 days to compare the potential for groundwater assessments with three conventional sampling techniques (bailing, low-flow, and bailing with filtering) (Gustavson and Harkin, 2000). The SPMD-derived PAH concentrations were similar to the conventional sampling results. SPMDs were able to bioconcentrate lower levels of certain PAHs better than the other water sampling techniques. The authors demonstrate SPMDs have a high potential for groundwater monitoring because of the higher sensitivity and accurate estimations of dissolved concentrations.

Sediment samples, standard SPMDs, and blue mussels (*Mytilus edulis*) were used in a study assessing hexachlorobenzene (HCB), chlorophenol, and PCB contamination on the coast of Sweden (Granmo et al, 2000). The SPMDs and mussels were deployed in a gradient design from the point source for 30 days. The estimated water concentrations from each matrix were determined and compared to each other with the sediment results highest in concentration. The authors concluded, when combining SPMD, mussel, and sediment data, assessors can detect short-term environmental loads of hydrophobic organic pollutants with relative confidence.

In a similar project, mussels (*Perna viridis*) and standard SPMDs were exposed for 30 days in a gradient scheme in Hong Kong coastal waters to monitor trace

organochlorine contaminants (Richardson et al, 2001). Both matrices resulted in contaminant concentrations with different rankings of the various sites. However, SPMDs were able to circumvent some of the inherent problems associated with biotic samples. For instance, at one highly polluted site, the caged mussels experienced high mortality leading to a decreased sample size. Therefore, the investigators concluded SPMDs are a valuable monitoring technique to assess dissolved concentrations of organochlorine contaminants.

Researchers in the Netherlands used SPMDs (2.5 X 30 cm, 270 mg triolein) to estimate the levels of HCB and PCBs in the atmosphere, sea-surface microlayer, and the water column (Booij and Drooge, 2001). PRCs (1,3,5-trichlorobenzene, PCB 29, PCB 4) were used to calibrate the *in situ* exchange kinetics. The results demonstrated PCBs were in equilibrium between the atmosphere and water column, HCB was super saturated in the atmosphere by a factor of 6-10, and the sea-surface microlayer has no toxicological significance. The PRCs allowed the authors to interpret the data more accurately. However, the lack of PRC data at many temperatures decreases that accuracy.

In order to validate uptake rates obtained by Huckins et al (1999) and increase the number of compounds in the database, researchers performed two laboratory calibration experiments and one field verification with standard SPMDs sampling 28 PAHs and 19 homologues (Luellen and Shea, 2002). PAHs sampling rates in both studies were similar. The field verification of the uptake rates agreed well with the laboratory data within a factor of 2 for most compounds and within a factor of 4 for all PAHs. Typically, more hydrophobic PAHs displayed more deviation. PRCs (anthracene d-10, flourene d-10, and pyrene d-10) were used as an *in situ* uptake rate calibration and were compared to

laboratory elimination rates with no significant difference between the laboratory rates and field rates.

Standard SPMDs were deployed for 55 days in the Fraser River, British Columbia, to evaluate the possible sources of polybrominated diphenylethers (PBDEs) (Rayne and Ikonomou, 2002). The authors investigated 36 PBDEs including all homologue groups ranging from mono- through hexa-brominated compounds. Using the SPMD data for the dissolved form of PBDEs, the researchers utilized an EcoFate multimedia mass balance aquatic simulation model to estimate the possible source mixtures. It was concluded that the SPMD patterns more closely matched the composite technical mixture of penta- and octa-BDE.

Standard SPMDs were exposed for 28 days in conjunction with destructive fish tissue analysis and sediment samples to examine the PCB, substituted benzene, pesticide, and PAH contamination present at two sites on the Huaihe River, China (Wang et al, 2002). The estimated log-transformed water concentrations from each matrix were well correlated (r^2 = 0.881 to 0.986). The authors discovered the correlation was strongest with less hydrophobic organic contaminants suggesting that SPMD exposures will better estimate biotic concentrations for moderate to low K_{OW} compounds.

The National Council for Air and Stream Improvement (NCASI) and Oregon State University executed a study investigating the proper interpretation of SPMD field data (Louch et al, 2003). The researchers exposed three SPMD canisters containing five standard SPMDs at three sites transecting the Long Tom River in Oregon. The deployment was 62 days and various PAHs were determined. The PAHs with log K_{OW} values > 4.4 displayed a significant difference across the transect with relative differences

of 10 to 54%. For compounds with log K_{OW} less than 4.4, there was no difference. The temperature at each site was statistically the same, there were no qualitative differences in biofouling, and the flow velocities could not account for the differences in PAH concentrations. This evidence indicates that, when interpreting SPMD data, spatial variability in the water column must be accounted for and the investigators should not assume homogeneous concentrations in a river (Louch et al, 2003).

1.4. Research Objectives of this SPMD Project

The main goal of this thesis was to assist the Maine Department of Environmental Protection in determining whether SPMD technology is an appropriate surrogate procedure for the U/D test compared to fish tissue analysis outlined on page 20 of this chapter. This objective was maintained throughout the research project. To meet this goal, the methods and secondary objectives were altered several times to address complications as problems surfaced and new ideas were proposed. In chronological order, the objectives will be outlined within the context of accomplishing the main goal of the SPMD project.

1.4.1. The 2001 Objectives

The main objective of the 2001 field season was to validate or improve the previous work of Shoven (2001). The experimental design was to use the same field and analytical procedures in two separate deployments at the same sites around the Rumford mill. The goals of the first year of research were to:

(1) Validate or improve the previous SPMD research project.

(2) Measure a significant difference between sites by increasing the sample size at each site.

(3) Decrease the variability between samples thereby increasing the sensitivity of the U/D test.

(4) Estimate ambient water concentrations.

(5) Compare the SPMD results to those of fish tissue analysis.

An option for decreasing variability and the number of non-detects was to increase the number of SPMDs per sample from two to five. The second deployment at Jay, ME in September had a sample size of eight with five SPMDs in each sample. This was done to determine whether increased composites of SPMDs per sample will decrease variability among samples. Also, the field deployment scheme from the July exposure was vandalized, so a new deployment scheme was developed to ensure sample security. The feasibility of this new deployment scheme was evaluated as well.

1.4.2. The 2002 Objectives

Most of the goals (2-5 previous page) of the project remained the same in 2002. Complications from 2001 caused new concerns that needed to be addressed. The first was the analytical method which, after reviewing the 2001 data, was determined to be inadequate for the levels of dioxin in Maine rivers. A new standard operating procedure (SOP) was developed and tested. In conjunction with a new analytical procedure, a method detection limit study was executed to determine the detection limits of the new SOP. Secondly, vandalism marred both exposures in 2001, so alterations to the Jay deployment scheme were tested. Finally, permeability reference compounds were used as an *in situ* calibration during the deployment for the first time in the project. To complement the dioxin analyses, some goals were outlined for the experiments involving permeability reference compounds.

The objectives for the PRCs were:

(1) Evaluate the performance of various deuterated PAHs as PRCs.

(2) Determine whether the two Rumford sites were statistically different with regards to the environmental factors affecting SPMD uptake rates.

(3) Calculate the elimination rate for each PRC.

(4) Calculate an exposure adjustment factor (EAF) from PRC calibration data.

Chapter 2

MATERIALS AND METHODS

2.1. Field Methods

2.1.1. Androscoggin River at Rumford 2001

The SPMD deployment on the Androscoggin River was chosen to validate the previous work done by Shoven (2001). Forty SPMDs were exposed at each upstream and downstream site around the Mead Paper Mill in Rumford, ME from July 13 to August 10, 2001. Two SPMDs were combined into one sample, so there were 20 samples per location. Each SPMD canister holds 5 SPMDs. All standard SPMDs, deployment canisters, and spiders were rented or purchased from Environmental Sampling Technologies of St. Joseph, MO. Two vertical deployment schemes were placed at each location with 4 canisters attached (Figure 2.3.). The relative positions in the river and the deployment scheme were the same as the 2000 study (Shoven, 2001). This location was chosen to coincide with DMP fish sampling sites and to ensure that the mill effluent was well mixed with the river water.

Depth, flow velocity, temperature, total organic carbon, dissolved organic carbon, and specific conductivity were determined at each site. The flow velocity was measured using a Global Water velocity meter after anchoring the boat during deployment and retrieval. Hourly temperature readings throughout the exposure were measured using an Onset optic stowaway temperature logger. Two liters (two high-density polyethylene one liter bottles) of river water were sampled during deployment and retrieval for water chemistry parameters.

Before transportation to the field, SPMDs were loaded onto the deployment carriers in a regulatory level M-3.5 clean room (Figure 2.1.A.) and sealed in solvent rinsed, gallon-sized cans to circumvent any contamination. The sealed cans were kept in coolers on ice during transit. Upon arrival, the carriers were placed into the deployment canisters and submerged in the water (Figure 2.1.B and 2.1.C.). While the sealed cans were opened and the canisters were lowered into the water, trip blank SPMDs in pint-sized, solvent rinsed, sealed cans were uncovered for the same length of time to quantify any contamination from the ambient air. The number of trip blank SPMDs equated to the number of SPMDs combined into one sample. Loading time was under 20 minutes for all the deployments. Global positioning system waypoints were acquired for each location (Table 2.1.).

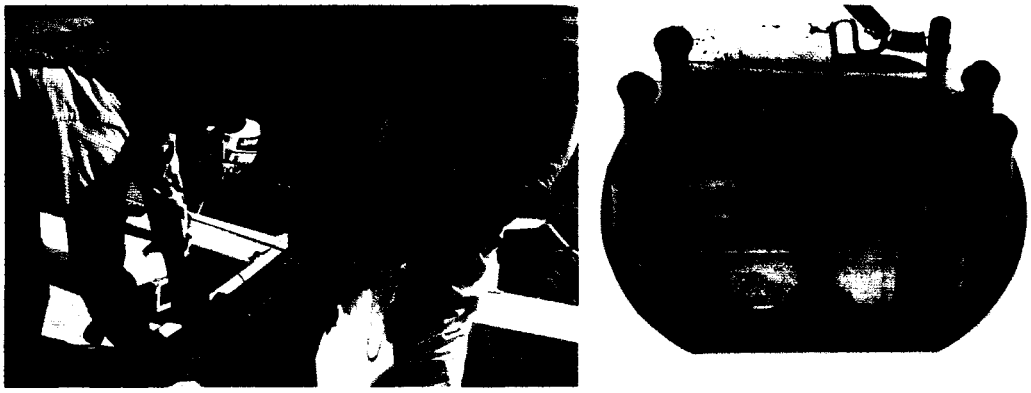
Table 2.1. Global Positioning System (GPS) Waypoints for Deployment Sites

SITE	LATITUDE	LONGITUDE
2001 Rumford Upstream	N44°31'04"	W70°33'05"
2001 Rumford Downstream	N44°30'10"	W70°23'53"
2001 Jay Upstream	N44°28'42.4"	W70°16'18.7"
2001 Jay Downstream	N44°29'06.2"	W70°12'13.8"
2002 Rumford Upstream	N44°31'04"	W70°33'03"
2002 Rumford Downstream	N44°30'11"	W70°23'51"

Figure 2.1. Photographs of a SPMD Field Deployment

A. Loaded Carrier B. Loaded Canister

C. Lowering the Canisters D. Deployed Canisters



E. Retrieval F. Biofouled SPMD

Figure 2.2. U.S.G.S. Topographical Map of the Rumford Location

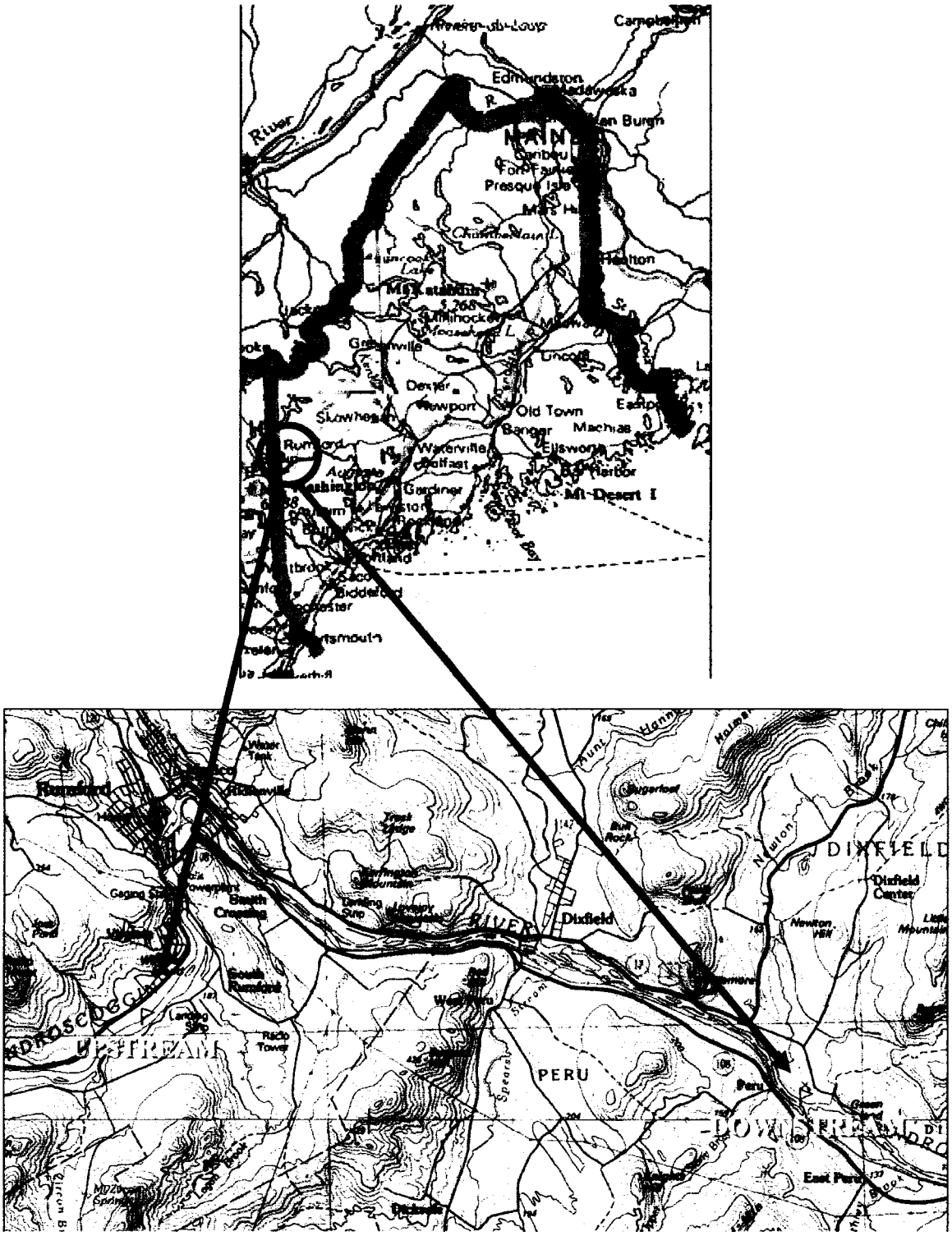
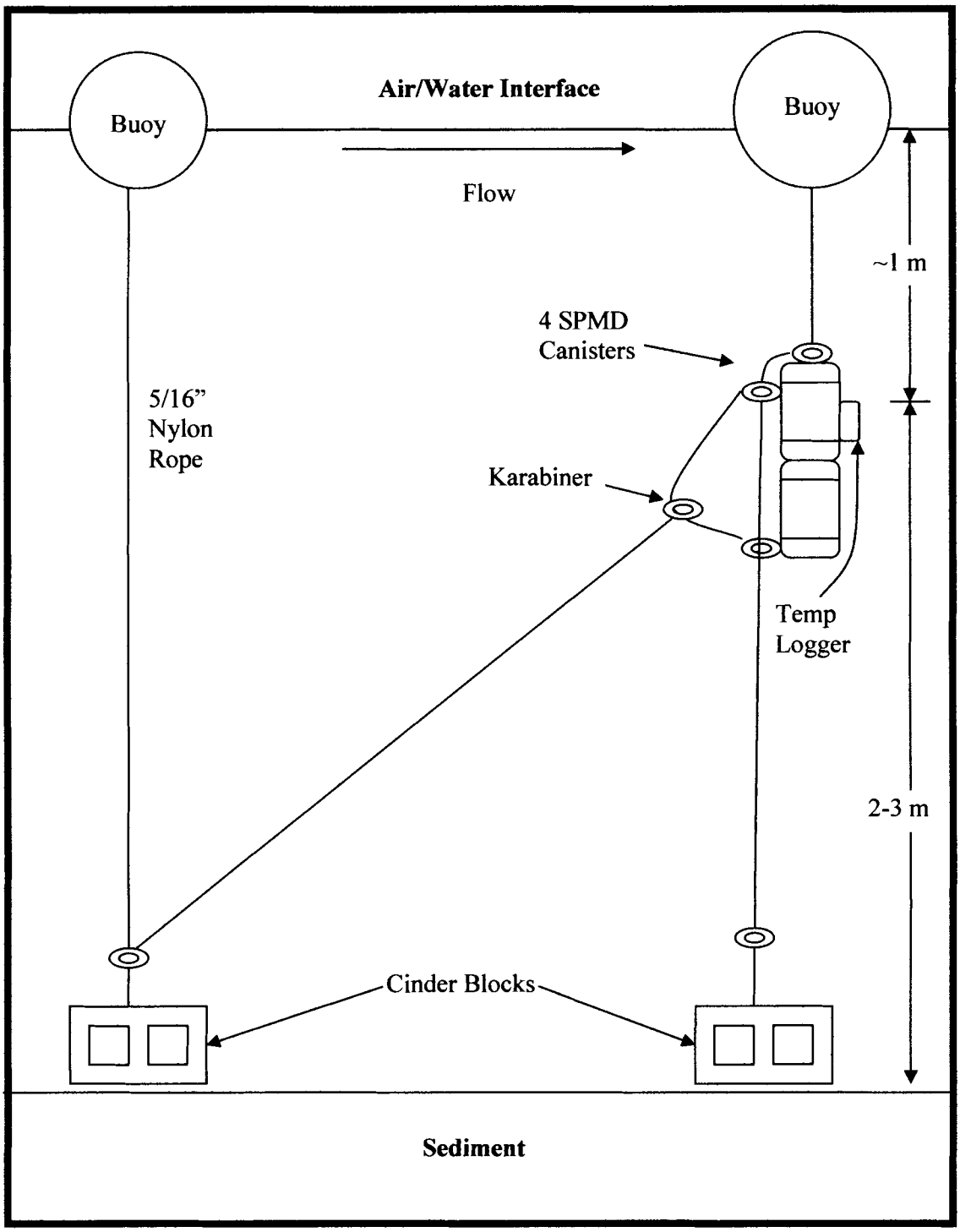


Figure 2.3. Vertical Deployment Scheme (Shoven, 2001)



2.1.2. Androscoggin River at Jay 2001

Before deployment, the carriers and canisters were cleaned. The devices were scrubbed of all debris under tap water using a scouring pad and allowed to dry. Then the devices were placed in a muffle furnace and baked at 440°C for 6 hours. After cooling, the pieces were dipped into dilute HCl (1 N – 2 N) to remove any oxidized material on the surface. The devices were rinsed under tap water and allowed to dry. After drying, the carriers and canisters were rinsed with acetone, isopropyl alcohol, and hexane. The carriers were stored in the clean room and the canisters in a metal closet.

The Jay site was chosen as an alternate as a result of the Rumford mill shutdown during the scheduled sampling in September. Forty SPMDs were deployed at upstream and downstream locations of the mill in Jay, ME. The sampling transpired from September 22 to October 20, 2001. Five SPMDs were combined to create one sample. There were 8 samples at each location. The composites were increased in number to decrease the chance of non-detects for key congeners. Due to vandalism with the vertical deployment scheme, the system was altered to a submersed buoy, static line arrangement to hide the deployed SPMDs (Figure 2.5.). Instead of using surface buoys, empty milk jugs were utilized as floatation devices within the water column. Four buoy systems were deployed in a cluster (5 m X 5 m). Both Jay sites were characterized for the same chemical parameters as the Rumford deployment. The same necessary precautions were done for quality control in the field.

Figure 2.4. U.S.G.S. Topographical Map of the Jay Site

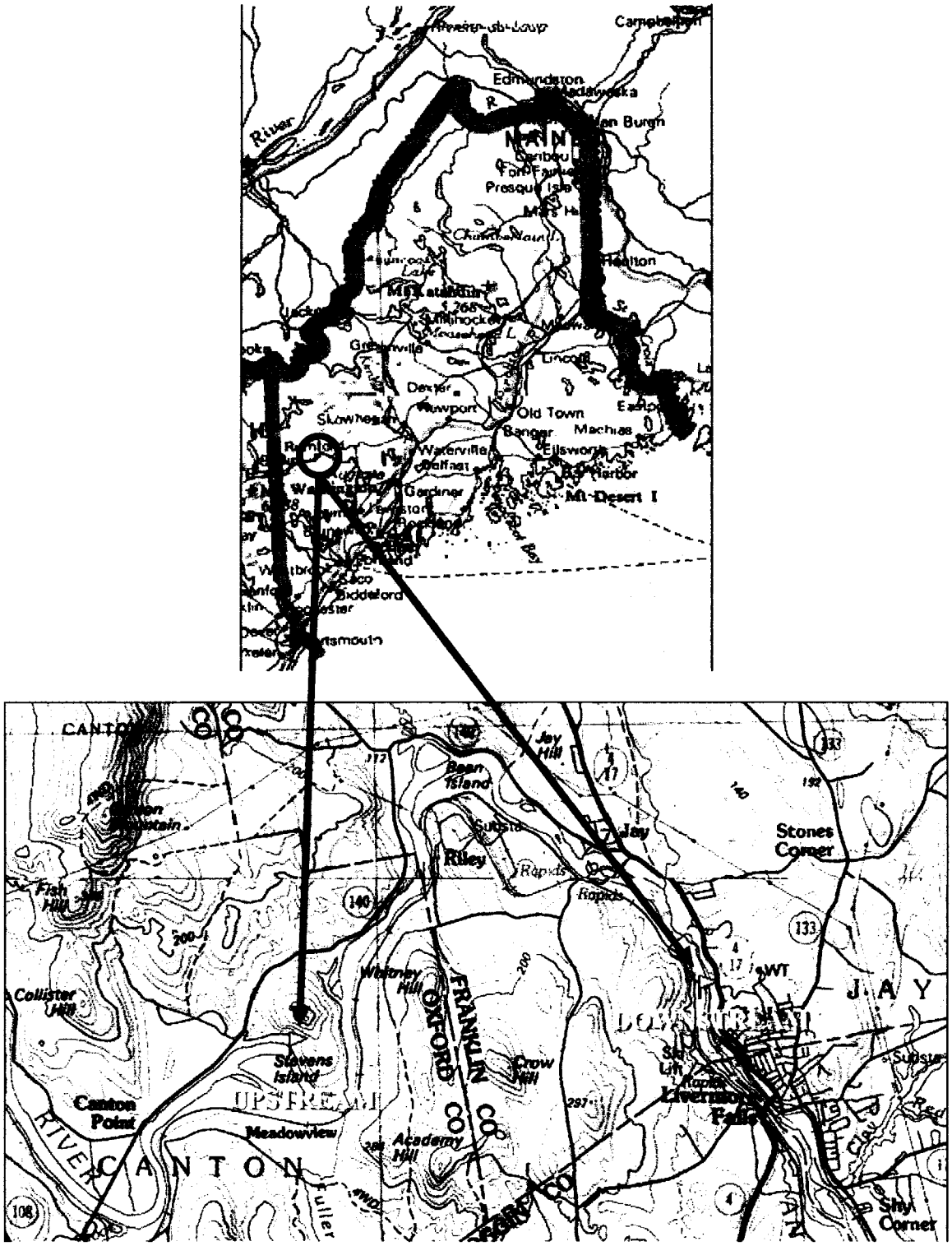
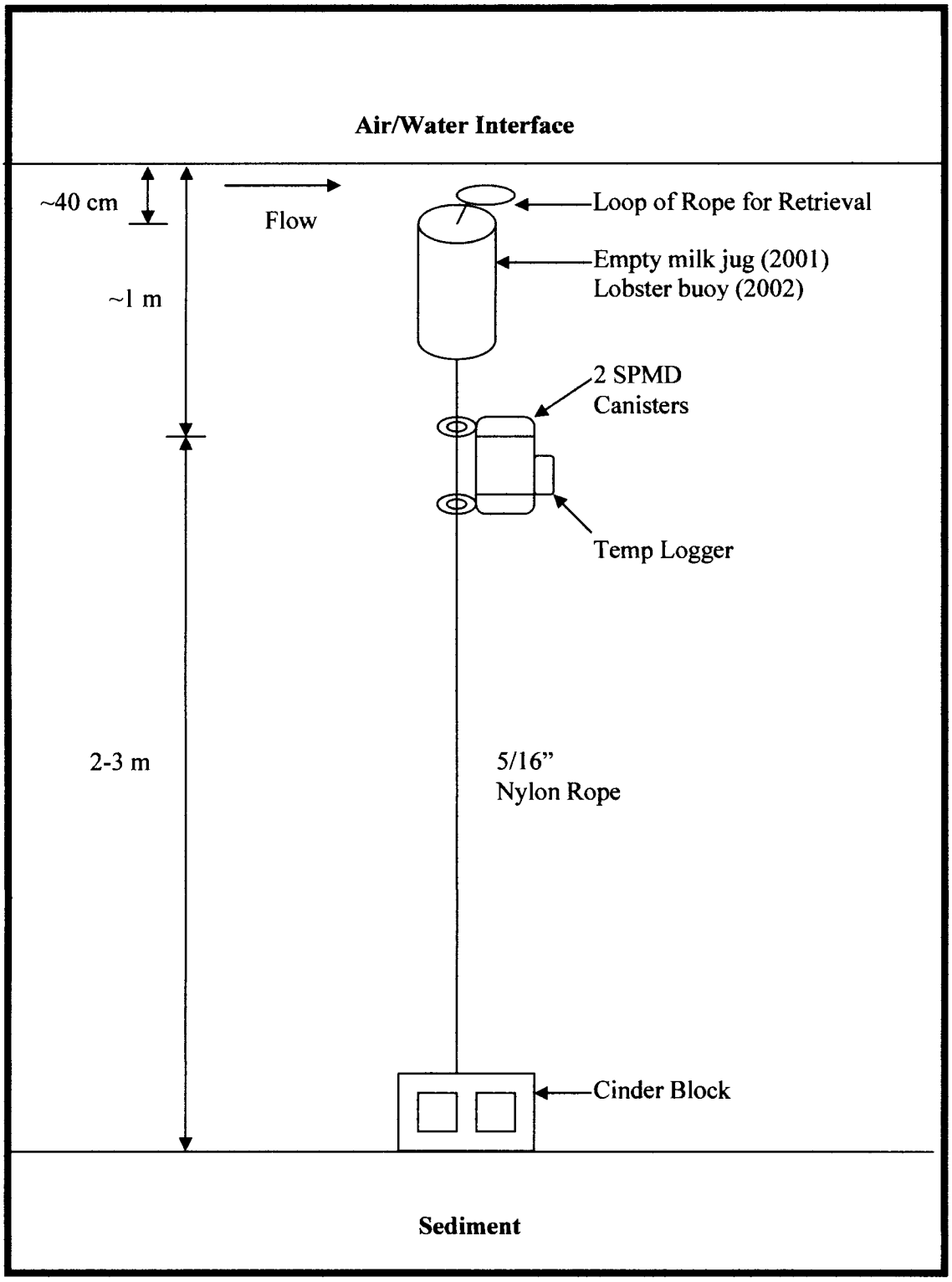


Figure 2.5. Submersed Buoy, Static Line Deployment Scheme



2.1.3. Androscoggin River at Rumford 2002

For the 2002 field season, the SPMD project returned to the same Rumford locations sampled in 2001 and 2000. The deployment occurred from August 9 to September 6, 2002. Similar to the Jay 2001 deployment, the submersed buoy, static line system was utilized with lobster buoys instead of milk jugs as floats. The same chemical parameters were characterized as before with the exception of specific conductivity. Specific conductivity was not measured since previous data already revealed that the site was within the plume of the mill.

Prior to deployment, 2 μg of deuterated polyaromatic hydrocarbons (PAHs) (Cambridge Isotope Laboratories, Andover, MA) were spiked into sixteen SPMDs in a clean room before transportation to the field. The elimination of the PAHs from the SPMD matrix during deployment was used to determine environmental factors affecting SPMD uptake rates. The deuterated PAHs were chosen for their relative similarity in physical-chemical characteristics to dioxin (Table 2.2.), affordability, and the existence of calibration data. Each deployment canister contained four SPMDs for dioxin analysis and one PAH-spiked SPMD for PRC quantification. Four SPMDs were combined to make one dioxin sample, so each site had 8 PAH-spiked samples and 8 dioxin samples. All PAH-SPMDs were loaded into the canisters in the field shaded from the sunlight by using a large, black trash bag. This precaution was taken because PAHs are highly UV sensitive (Orazio et al, 2002).

Table 2.2. The Molecular Weights and Octanol-Water Equilibrium Coefficients for the Selected PAH Compounds (Huckins et al, 1999)

COMPOUND	MOLECULAR WEIGHT	LOG K_{OW}
Acenaphthene D-10	164.28	4.22
Phenanthrene D-10	188.30	4.46
Pyrene D-10	212.33	5.30
Benzo(b)Fluoranthene D-12	264.40	5.78

2.2. Analytical Methods

The water samples were analyzed using the standard operating procedures determined by the Mitchell Center and the Environmental Chemistry Lab (ECL). Similar to the field methods, the analytical procedure for dioxin samples was a process of continual refinement. Each set of samples were analyzed in a different way. However, all dioxin procedures were based on EPA Method 1613-B (Telliard, 1994). The PAH method was determined from previous research executed by Luellen and Shea (2002) and Wang et al (1994).

2.2.1. Water Samples

After returning from the field, the water samples were refrigerated until analysis. Samples were analyzed within the allowed two week holding time. The Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC; 0.4 micron filtered) were determined employing the same analytical method. The samples were first acidified using two drops of 1:1 water:sulfuric acid per 60 ml of sample. After acidification, the samples were quantified utilizing an OI Model 700 Total Organic Carbon Analyzer. This machine functions by measuring the amount of carbon dioxide released by persulfate oxidation of the organic carbon in the sample. Specific conductance was quantified using a Yellow

Springs Instrument (YSI) Model Number 35 digital conductivity meter and a YSI probe 3401 at 25°C.

2.2.2. SPMD Quality Control Samples

Extra samples were analyzed to ensure the quality of the field and analytical methods. All quality control (QC) samples were quantified using the same method (SOP) utilized for that particular deployment. The QC samples consisted of the upstream trip blank, the downstream trip blank, a dialysis blank, a procedural blank, and a precision and recovery (PAR) standard spike (Table 2.3.). The trip blanks were described earlier in the field method section. The dialysis blanks mimicked the entire procedure but lacked a SPMD to ensure no contamination due to glassware or instruments. A procedural blank underwent the entire method with a blank SPMD to check for contamination within the manufactured SPMDs. A 10 µl PAR standard spiked sample was analyzed to determine the accuracy of the analyses.

2.2.3. The 2001 Rumford Dioxin Samples

The 2001 Rumford dioxin samples were analyzed using the same procedure developed in Shoven (2001). Upon retrieval, SPMDs were removed from the carriers in the clean room and placed in solvent rinsed paint cans. The cans were then kept in a minus 20°C freezer until dialysis. The SPMDs were separated only by location (i.e. upstream or downstream). The composites were combined randomly with the assumption that all SPMDs are uniform.

2.2.3.1 SPMD Dialysis

After the 28-day deployment, the SPMDs were biofouled with the downstream SPMDs usually more heavily biofouled. The first step in the laboratory was to perform an

Table 2.3. Precision and Recovery Standard in Nonane (EDF-7999 from Cambridge Isotope Laboratories, Andover, MA)

COMPOUND	CONC. (ng/ml)
2,3,7,8-TCDD	40
2,3,7,8-TCDF	40
1,2,3,7,8-PeCDD	200
1,2,3,7,8-PeCDF	200
2,3,4,7,8-PeCDF	200
1,2,3,4,7,8-HxCDD	200
1,2,3,6,7,8-HxCDD	200
1,2,3,7,8,9-HxCDD	200
1,2,3,4,7,8-HxCDF	200
1,2,3,6,7,8-HxCDF	200
1,2,3,7,8,9-HxCDF	200
2,3,4,6,7,8-HxCDF	200
1,2,3,4,6,7,8-HpCDD	200
1,2,3,4,6,7,8-HpCDF	200
1,2,3,4,7,8,9-HpCDF	200
OCDD	400
OCDF	400

exterior cleaning of the membrane. This was accomplished by scrubbing the SPMD with a soft-bristled toothbrush under lukewarm tap water. The SPMD was then swirled in a beaker of ~450 ml of 1 N HCl (Fisher Scientific, Fairlawn, NJ) for 30 seconds, rinsed with tap water, and dried with a Kimwipe (Kimberly-Clark, Roswell, GA). Then one end of the SPMD was snipped and spiked with the appropriate amount of dioxin surrogate standard (Table 2.3.) and PCB surrogate standard (though no PCB analysis was done). The 2001 Rumford SPMDs were mistakenly spiked with 10 µl (5 µl would have matched lab protocol). The snipped end of the SPMD was resealed using a Seal-N-Save (Sears, Roebuck and Co., Chicago, IL). After resealing, the SPMDs were rinsed with acetone (Fisher Scientific, Fairlawn, NJ) and isopropyl alcohol (LabChem, Inc., Pittsburgh, PA).

The SPMDs were then air dried, coiled and placed into solvent-rinsed, one liter Mason jars for dialysis with ~150 ml of optimum grade hexane (Burdick and Jackson, Muskegon, MI). Once full, the Mason jars were covered with solvent rinsed aluminum foil and the jar lid. The dialysis was a two-stage, 48 hour procedure at sub-ambient temperature (~18 C^{o}). Elevated temperatures can cause the triolein to co-dialysize with the analyte of interest (Huckins et al, 1993). After the first 24 hours, the hexane (dialysate) was decanted and another 150 ml were added to the Mason jar for the final 24 hours. The SPMD was then triple rinsed with hexane, removed, dried in the hood and discarded. Both 24-hour dialysates were concentrated using a Kuderna-Danish (KD) apparatus with boiling chips to ~5 ml.

Table 2.4. Isotope Dilution Method Labeled Standards in Nonane (EDF-8999, EDF-6999*, and EDF-5999^ from Cambridge Isotope Laboratories, Andover, MA)

LABELED COMPOUNDS	(ng/ml)	FUNCTION
2,3,7,8-TCDD ($^{13}C_{12}$, 99%)	100	Surrogate Standard
2,3,7,8-TCDF ($^{13}C_{12}$, 99%)	100	Surrogate Standard
1,2,3,7,8-PeCDD ($^{13}C_{12}$, 99%)	100	Surrogate Standard
1,2,3,7,8-PeCDF ($^{13}C_{12}$, 99%)	100	Surrogate Standard
2,3,4,7,8-PeCDF ($^{13}C_{12}$, 99%)	100	Surrogate Standard
1,2,3,4,7,8-HxCDD ($^{13}C_{12}$, 99%)	100	Surrogate Standard
1,2,3,6,7,8-HxCDD ($^{13}C_{12}$, 99%)	100	Surrogate Standard
!,2,3,4,7,8-HxCDF ($^{13}C_{12}$, 99%)	100	Surrogate Standard
1,2,3,6,7,8-HxCDF ($^{13}C_{12}$, 99%)	100	Surrogate Standard
1,2,3,7,8,9-HxCDF ($^{13}C_{12}$, 99%)	100	Surrogate Standard
2,3,4,6,7,8-HxCDF ($^{13}C_{12}$, 99%)	100	Surrogate Standard
1,2,3,4,6,7,8-HpCDD ($^{13}C_{12}$, 99%)	100	Surrogate Standard
1,2,3,4,6,7,8-HpCDF ($^{13}C_{12}$, 99%)	100	Surrogate Standard
1,2,3,4,7,8,9-HpCDF ($^{13}C_{12}$, 99%)	100	Surrogate Standard
OCDD ($^{13}C_{12}$, 99%)	200	Surrogate Standard
2,3,7,8-TCDD ($^{37}Cl_4$, 96%)*	0.8	Clean Up Standard
1,2,3,4-TCDD ($^{13}C_{12}$, 99%)^	200	Internal Standard
1,2,3,7,8,9-HxCDD ($^{13}C_{12}$, 99%)^	200	Internal Standard

2.2.3.2. Clean-Up Procedure

After concentrating, the dialysates were ready for the acidified silica gel slurry clean-up method. The purpose of this procedure is to hydrolyze the remaining triolein after dialysis and degrade possible interfering compounds with sulfuric acid. A four point stir bar, 100 ml of GC-grade hexane (Fisher Scientific, Fairlawn, NJ), 500 ml of dioxin clean-up standard (Table 2.3), and the triple-rinsed sample were added to a 200 ml beaker. The beaker was placed onto a magnetic stir plate and ~15 g of acidified silica gel (30% H_2SO_4) was added. Solvent-rinsed aluminum foil covered the beaker to ensure the sample did not spill. The stir plate was set so the sample was well mixed for one hour. During mixing, a glass funnel was plugged with glass wool and topped with ~15 g of anhydrous sodium sulfate. After the allotted time, the sample was removed from the stir plate and filtered through the funnel rinsing three times with hexane into a KD flask and concentrator tube. The sample was concentrated to dryness using the KD and then nitrogen gas in a sand bath. Once dry, the sample was filtered through a 0.45 micron Whatman Puradisc^{TM} disposable filter using dichloromethane (Fisher Scientific, Fairlawn, NJ) into a Gel Permeation Chromatography (GPC) tube.

The final clean up step for the 2001 Rumford samples was GPC or Size Exclusion Chromatography (SEC). GPC is a method that separates analytes mainly by size. In theory, GPC would eliminate any leftover interferents after the acidified silica gel slurry (i.e. triolein or hydrolyzation by-products). The procedure was performed on an O.I. Analytical GPC Autoprep 2000 using an Envirobead SX-3 high capacity column. Before each set of samples were run, the machine was calibrated by injecting 300 µl of stock solution (Table 2.5) to determine the collection time for dioxin. The compounds would

elute with corn oil (large compounds) first and sulfur (small compounds) last. A UV detector set at 254 nm would chart the elution of each compound. The collection time was calculated by subtracting the average of the corn oil and bis(2-ethylhexyl)phthalate peaks from the average of the perylene and sulfur peaks. The collection time usually started around 22 minutes and would last for approximately 25 minutes. The system was run at a flow rate of 5 ml/min in 100% dichloromethane. Typically, 10 samples were in each batch.

Table 2.5. GPC Calibration Solution in Dichloromethane

COMPOUND	CONC. (mg/l)
Corn Oil	25,000
Bis(2-ethylhexyl)phthalate	1,000
Methoxychlor	200
Perylene	20
Sulfur	80

2.2.3.3. Final Volume

After the GPC, the samples were concentrated using a KD apparatus. The concentrated samples were transferred using a pipette to a tapered test tube, placed into a sand bath under a stream of nitrogen gas and allowed to dry completely. The samples were transferred to an injection vial using dichloromethane and allowed to totally evaporate under the same conditions. Finally, 5 µl of internal standard (Table 2.4.) and 5 µl of nonane (Fisher Scientific, Fairlawn, NJ) were added to the injection vial and capped. The samples are ready for quantification by HRGC/HRMS.

2.2.3.4. Analysis by HRGC/HRMS

In this project, the isotope dilution method for all seventeen toxic congeners of dioxin was used to quantify a given sample. Isotope dilution works by adding a known

amount of labeled dioxins (surrogates in Table 2.4.) before dialysis and clean-up. By measuring the recovery of those surrogates, corrections can be made for native compounds in the sample matrix. In conjunction with the surrogates, an internal standard is spiked into the sample prior to analysis to quantify the surrogates thereby determining the amount of native dioxin. A HRGC/HRMS is a coupled instrument used for accurate congener-specific dioxin analysis. A CarloErba 8000 high-resolution gas chromatograph (Micromass, Manchester, U.K.) was used to separate the dioxin congeners before entering into the mass spectrometer source. High resolution is required due to the congeners near equal mass and the inability of the mass spectrometer to quantify complex mixtures. Two microliters of the ten microliter sample is introduced into the DB-5 fused silica, open tubular, capillary column (60 m long, 0.32 mm diameter, 0.25 μm film thickness) (J&W Scientific, Folsom, CA) in splitless injection mode by a CTC 200S Autosampler (Micromass, Manchester, U.K.). The temperature program for the HRGC is initially 150°C with a 2°C per minute increase to 200°C (25 minutes), then a 6°C per minute increase to 300°C (4 minutes), and an interface temperature of 290°C. UHP helium gas at 30 PSI elutes the congeners from the lowest substituted (TCDD) to the highest substituted congeners (OCDD).

Once eluted, the congeners reach the source of the Autospec-UltimaE Mass Spectrometer (Micromass, Manchester, U.K.). The HRMS is tuned at 10,000 resolution in selective ion monitoring (SIM) mode. At the source, the ionization is under positive conditions, the temperature set at 260°C, and the vacuum pressure at 6×10^{-6} mbar. At this point, the congeners are fractured into ion fragments (M+) by a potential between a

tungsten filament and an electron beam of 29 eV. The newly charged masses are forced through the source slit into the flight tube by an electric potential difference.

In order for the machine to recognize the proper ion fragments, perfluorokerosene (PFK) is used as a reference compound. The five constant lock masses produced by the fragmentation of PFK correct for any mass drifts during the runs (Table 2.6.). Two electrostatic analyzers (ESAs) and a magnet sector analyzer (MSA) direct the tuned (PFK-like) ion beams towards the collector slit where the detector generates the mass spectrum. The undesired ion fragments will collide with the walls of the flight tube which is periodically baked to remove this unwanted residue. At the beginning of each run, the PFK lock mass of 304.9824 was used to tune the machine at a minimal resolution of 10,000 by adjusting the various lenses, ESAs, and MSAs.

Table 2.6. Descriptor Ions (Telliard, 1994)

DESCRIPTOR	ION EXACT m/z	IDENTITY
1	303.9016	TCDF (M)
	305.8987	TCDF (M+2)
	315.9419	$^{13}C_{12}$ TCDF (M)
	316.9824	PFK Lock Mass
	317.9389	$^{13}C_{12}$ TCDF (M+2)
	319.8936	TCDD (M)
	321.8936	TCDD (M+2)
	327.8847	$^{37}Cl_4$ TCDD
	331.9368	$^{13}C_{12}$ TCDD (M)
	333.9339	$^{13}C_{12}$ TCDD (M+2)
	375.8364	Hexachlorodiphenylether
2	339.8597	PeCDF (M+2)
	341.8568	PeCDF (M+4)
	351.9000	$^{13}C_{12}$ PeCDF (M+2)
	353.8970	$^{13}C_{12}$ PeCDF (M+4)
	355.8546	PeCDD (M+2)
	357.8521	PeCDD (M+4)
	366.9792	PFK Lock Mass
	367.8948	PeCDD (M+2)
	369.8919	PeCDD (M+4)
	409.7974	Heptachlorodiphenylether
3	373.8207	HxCDF (M+2)
	375.8178	HxCDF (M+4)
	380.9760	PFK Lock Mass
	383.8639	$^{13}C_{12}$ HxCDF (M)
	385.8610	$^{13}C_{12}$ HxCDF (M+2)
	389.8156	HxCDD (M+2)
	391.8127	HxCDD (M+4)
	401.8559	$^{13}C_{12}$ HxCDD (M+2)
	403.8530	$^{13}C_{12}$ HxCDD (M+4)
	445.7555	Octachlorodiphenylether
4	407.7818	HpCDF (M+2)
	409.7788	HpCDF (M+4)
	417.8253	$^{13}C_{12}$ HpCDF (M)
	419.8220	$^{13}C_{12}$ HpCDF (M+2)
	423.7767	HpCDD
	425.7737	HpCDD
	430.9728	PFK Lock Mass
	435.8169	$^{13}C_{12}$ HpCDD (M+2)
	437.8140	$^{13}C_{12}$ HpCDD (M+4)
	479.7165	Nonachlorodiphenylether
5	441.7428	OCDF (M+2)
	443.7398	OCDF (M+4)
	454.9728	PFK Lock Mass
	457.7377	OCDD (M+2)
	459.7348	OCDD (M+4)
	469.7780	$^{13}C_{12}$ OCDD (M+2)
	471.7750	$^{13}C_{12}$ OCDD (M+4)
	513.6775	Decachlorodiphenylether

The descriptor ions are grouped by elution profile from the HRGC (retention time). Descriptor ions 1 through 5 have retention times of 31:00 to 51:45, 51:45 to 61:45, 61:45 to 66:30, 66:30 to 71:00, and 71:00 to 75:00, respectively. Throughout all the groups, the HRMS was continuously scanning for these ions. Diphenylethers were included in the profile because of their common interference with dioxin analysis.

Before any samples can be quantified using the isotope dilution method, a five-point (CS1-CS5) calibration curve is run (Table 2.6.). The curve should encompass the range of expected concentrations in the samples. The relative response (RR) and response factors (RF) of the HRGC/HRMS should correlate linearly with the standard concentrations. If the relative responses and response factors are within a coefficient of variation of 20%, then an average relative response can be used to calculate samples. Otherwise, a new calibration curve is run. A daily calibration mix (CS3) is analyzed at the beginning and end of each set of samples (<10) to ensure the RRs and RFs do not deviate from the averages in the calibration curve.

In order to quantify the native dioxin, the analyst first calculates the relative response of the native dioxin to its surrogate by using the responses of both the primary and secondary m/z's (mass to charge ratios) (Equation 2.1.). Similarly, the response factor is determined by calculating the response of the surrogates to its internal standard (Equation 2.2.).

Equation 2.1. Calculation of the Relative Response (Telliard, 1994)

$$RR = (A1_n + A2_n)*C_s / (A1_s + A2_s)*C_n$$

Where: $A1_n$ and $A2_n$ are the m/z's for the native dioxin

$A1_s$ and $A2_s$ are the m/z's for the labeled surrogate

C_s is the concentration of the surrogate in the calibration standard

C_n is the concentration of the native dioxin in the calibration standard

Equation 2.2. Calculation of the Response Factor (Telliard, 1994)

$$RF = (A1_s + A2_s)*C_{is} / (A1_{is} + A2_{is})*C_s$$

Where: $A1_s$ and $A2_s$ are the m/z's for the labeled surrogate

$A1_{is}$ and $A2_{is}$ are the m/z's for the internal standard

C_{is} is the concentration of the internal standard

C_s is the concentration of the surrogate in the calibration standard

Table 2.7. Method 1613 Calibration Solution in Nonane (EDF-9999 from Cambridge Isotope Laboratories, Andover, MA) (all concentrations in ng/ml)

COMPOUND	CS1/2*	CS1	CS2	CS3	CS4	CS5
2,3,7,8-TCDD	0.25	0.5	2.0	10	40	200
2,3,7,8-TCDF	0.25	0.5	2.0	10	40	200
1,2,3,7,8-PeCDD	1.25	2.5	10	50	200	1000
1,2,3,7,8-PeCDF	1.25	2.5	10	50	200	1000
2,3,4,7,8-PeCDF	1.25	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDD	1.25	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDD	1.25	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDD	1.25	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDF	1.25	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDF	1.25	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDF	1.25	2.5	10	50	200	1000
2,3,4,6,7,8-HxCDF	1.25	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDD	1.25	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDF	1.25	2.5	10	50	200	1000
1,2,3,4,7,8,9-HpCDF	1.25	2.5	10	50	200	1000
OCDD	2.50	5.0	20	100	400	2000
OCDF	2.50	5.0	20	100	400	2000
1,2,3,4-TCDD ($^{13}C_{12}$, 99%)	100	100	100	100	100	100
2,3,7,8-TCDD ($^{13}C_{12}$, 99%)	100	100	100	100	100	100
2,3,7,8-TCDD ($^{37}Cl_4$, 96%)	0.25	0.5	2.0	10	40	200
2,3,7,8-TCDF ($^{13}C_{12}$, 99%)	100	100	100	100	100	100
1,2,3,7,8-PeCDD ($^{13}C_{12}$, 99%)	100	100	100	100	100	100
1,2,3,7,8-PeCDF ($^{13}C_{12}$, 99%)	100	100	100	100	100	100
2,3,4,7,8-PeCDF ($^{13}C_{12}$, 99%)	100	100	100	100	100	100
1,2,3,4,7,8-HxCDD ($^{13}C_{12}$, 99%)	100	100	100	100	100	100
1,2,3,6,7,8-HxCDD ($^{13}C_{12}$, 99%)	100	100	100	100	100	100
1,2,3,7,8,9-HxCDD ($^{13}C_{12}$, 99%)	100	100	100	100	100	100
!,2,3,4,7,8-HxCDF ($^{13}C_{12}$, 99%)	100	100	100	100	100	100
1,2,3,6,7,8-HxCDF ($^{13}C_{12}$, 99%)	100	100	100	100	100	100
1,2,3,7,8,9-HxCDF ($^{13}C_{12}$, 99%)	100	100	100	100	100	100
2,3,4,6,7,8-HxCDF ($^{13}C_{12}$, 99%)	100	100	100	100	100	100
1,2,3,4,6,7,8-HpCDD ($^{13}C_{12}$, 99%)	100	100	100	100	100	100
1,2,3,4,6,7,8-HpCDF ($^{13}C_{12}$, 99%)	100	100	100	100	100	100
1,2,3,4,7,8,9-HpCDF ($^{13}C_{12}$, 99%)	100	100	100	100	100	100
OCDD ($^{13}C_{12}$, 99%)	200	200	200	200	200	200

* CS1/2 was used only in the 2002 analyses

Numerous acceptance criteria are required for calibration verification. The m/z abundance ratios must fall within EPA limits (Table 2.8.). The peaks representing the compounds in the daily mix must have a signal to noise ratio of at least 10. The relative retention times must be within the prescribed limits (Table 2.9.). The peaks representing different congeners must have a valley not exceeding 25% of the total abundance. Finally, the concentrations computed from the RRs and RFs must equal the standard concentration within the designated limits (Table 2.10.) (Equation 2.3.). If any of these acceptance criteria are not accomplished by the analyst, the calibration verification needs to be rerun. If, after several attempts, the calibration still does not meet these standards, then the calibration curve needs to be rerun and new average RR/RFs should be calculated.

Equation 2.3. The Calculation of Native Dioxin Concentration in the Extract (C_{ex}) (ng/ml) (Telliard, 1994)

$$C_{ex} = (A1_n + A2_n)*C_s / (A1_s + A2_s)*RR$$

Where: The terms are defined in Equation 2.1. and 2.2.

Terms can be substituted to calculate the surrogate using a RF

Table 2.8. Theoretical and Acceptable Ion Abundance Ratios (Telliard, 1994)

NUMBER OF CHOLORINE ATOMS	M/Z'S FORMING RATIO	THEORETICAL RATIO	UPPER AND LOWER QC LIMITS
4	M/(M+2)	0.77	0.65-0.89
5	(M+2)/(M+4)	1.55	1.32-1.78
6	(M+2)/(M+4)	1.24	1.05-1.43
6[1]	M/(M+2)	0.51	0.43-0.59
7	(M+2)/(M+4)	1.05	0.88-1.20
7[2]	M/(M+2)	0.44	0.37-0.51
8	(M+2)/(M+4)	0.89	0.76-1.02

[1] $^{13}C_{12}$-HxCDF only [2] $^{13}C_{12}$-HpCDF only

Table 2.9. Retention Time References, Quantitation References, and Acceptable Relative Retention Times for Dioxin Analysis (Telliard, 1994)

DIOXIN CONGENER	RETENTION TIME AND QUANTITATION REFERENCE	RELATIVE RETENTION TIME
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	0.999-1.003
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	0.999-1.002
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF	0.999-1.002
2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,3,4,7,8-PeCDF	0.999-1.002
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	0.999-1.002
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD	0.923-1.103
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.976-1.043
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.989-1.052
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.425
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.011-1.526
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.567
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	0.999-1.001
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	0.997-1.005
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	0.999-1.001
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	0.999-1.001
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	0.999-1.001
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	0.998-1.004
1,2,3,7,8,9-HxCDD	*	1.000-1.019
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	0.999-1.001
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	0.999-1.001
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	0.999-1.001
OCDF	$^{13}C_{12}$-OCDF	0.999-1.008
OCDD	$^{13}C_{12}$-OCDD	0.999-1.001
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.944-0.970
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.949-0.975
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977-1.047
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.959-1.021
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977-1.000
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.981-1.003
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.043-1.085
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.057-1.151
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.086-1.110
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.032-1.311

* Referenced by $^{13}C_{12}$-1,2,3,6,7,8-HxCDD and quantified by the average responses of $^{13}C_{12}$-1,2,3,4,7,8-HxCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD

Table 2.10. Acceptance Criteria for Calibration Verification (Telliard, 1994)

COMPOUND	CS3 (ng/ml)	ACCEPTANCE RANGE
2,3,7,8-TCDD	10	7.8-12.9
2,3,7,8-TCDF	10	8.4-12.0
1,2,3,7,8-PeCDD	50	39-65
1,2,3,7,8-PeCDF	50	41-60
2,3,4,7,8-PeCDF	50	41-61
1,2,3,4,7,8-HxCDD	50	39-64
1,2,3,6,7,8-HxCDD	50	39-64
1,2,3,7,8,9-HxCDD	50	41-61
1,2,3,4,7,8-HxCDF	50	45-56
1,2,3,6,7,8-HxCDF	50	44-57
1,2,3,7,8,9-HxCDF	50	45-56
2,3,4,6,7,8-HxCDF	50	44-57
1,2,3,4,6,7,8-HpCDD	50	43-58
1,2,3,4,6,7,8-HpCDF	50	45-55
1,2,3,4,7,8,9-HpCDF	50	43-58
OCDD	100	79-126
OCDF	100	63-159
$^{13}C_{12}$-2,3,7,8-TCDD	100	82-121
$^{13}C_{12}$-2,3,7,8-TCDF	100	71-140
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	62-160
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	76-130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	77-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	85-117
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	85-118
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	76-131
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	70-143
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	74-135
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	73-137
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	72-138
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	78-129
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	77-129
$^{13}C_{12}$-OCDD	200	96-415
$^{37}Cl_4$-2,3,7,8-TCDD	10	7.9-12.7

Assuming acceptable RR/RFs are calculated from the calibration curve and the calibration verification has been executed, the analyst may start injecting samples. The HRGC is injected with 2 µl of sample with the same HRGC/HRMS procedure. Nonane (Fisher Scientific, Fairlawn, NJ) blanks are placed intermittently throughout the run to check for carryover of analytes. Similar to the calibration stock solutions, the SPMD samples must pass a series of quality assurance criteria. The m/z abundance ratios must fall within the same limits outlined in Table 2.8. The peaks representing the surrogate and native compounds in the sample must have a signal to noise ratio of 10:1 and 2.5:1, respectively, and maximize within the same two seconds of retention time. The relative retention times must be within the prescribed limits in Table 2.9. Finally, surrogate recoveries must exceed minimum values (Table 2.11.). If any of the acceptance criteria are not met, the data can not be reported for regulatory purposes.

The peaks in the mass spectra were auto-integrated by the Opus Program or integrated manually by the analyst. The spectra consist of ion abundance (Y-axis) versus retention time (X-axis). The ion abundance areas (peaks) were entered into a Microsoft Excel Spreadsheet to calculate the concentration in the extract using the RR/RFs from the calibration curve (Equation 2.3.). The retention times of the peaks were also entered into the spreadsheet to check the QA criteria. Once the concentration in the extract (C_{ex}) was determined, the units were converted to mass of native dioxin per mass of SPMD which are the reported values (Equation 2.4.). The W_{SPMD} varied with deployment depending on how many SPMDs were combined into one sample. Since the surrogate amount was mistakenly doubled (20 µl per sample, instead of 10 µl), the C_s in Equation 2.3. was doubled as well.

Table 2.11. Acceptance Criteria for Surrogate Concentrations and Recoveries (Telliard, 1994)

SURROGATE		RECOVERY RANGE	
COMPOUND	**(ng/ml)**	**(ng/ml)**	**PERCENT**
$^{13}C_{12}$-2,3,7,8-TCDD	100	25-164	25-164
$^{13}C_{12}$-2,3,7,8-TCDF	100	24-169	24-169
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25-181	25-181
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24-185	24-185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21-178	21-178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32-141	32-141
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	28-130	28-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26-152	26-152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26-123	26-123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	29-147	29-147
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	28-136	28-136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23-140	23-140
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28-143	28-143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26-138	26-138
$^{13}C_{12}$-OCDD	200	34-313	17-157
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.5-19.7	35-197

Equation 2.4. Conversion to Reported Values (Huckins et al, 1999a)

$$C_{SPMD} = (C_{ex} * V_{ex}) / W_{SPMD}$$

Where: C_{SPMD} is the concentration of dioxin in a SPMD (pg/g)

V_{ex} is the volume of extract (µl)

W_{SPMD} is the weight of the SPMD/s (4.5 g per SPMD)

2.2.4. The 2001 Jay Dioxin Samples

Most of the procedure remained the same for the 2001 Jay dioxin samples. Some of the 2001 Rumford samples were quantified before the 2001 Jay samples were started. The interferences and background noise in the chromatograms from 2001 Rumford deployment provided evidence of an ineffective clean-up procedure, so modifications had to be made in an attempt to obtain reportable data. Possible interferents causing the unacceptable data were excess triolein, PCBs, and/or diphenylethers. In the following section, the improvements made for the 2001 Jay samples will be described.

As previously mentioned, the composites for the 2001 Jay samples consisted of 5 SPMDs. Knowing that the composite of 2 SPMDs from the 2001 Rumford samples were not sufficiently cleaned using the previous method, the 2001 Jay SPMDs were combined in intervals throughout the clean up procedure. After dialysis, one sample was split into two aliquots (2 SPMDs and 3 SPMDs) each with 10 μl of surrogate. Isotope labeled clean up standard for dioxin and the PCB surrogates were not used in the Jay dioxin samples. The aliquots underwent acidified silica gel slurry and GPC clean up before being combined into one sample. At this point, it was assumed there was no leftover triolein in the sample. However, even without triolein, a new clean-up procedure was needed before HRGC/HRMS analysis to decrease diphenylether and PCB interference.

The sample was put through an ENVI-Carb Reversible SPE Cartridge (Supelco Inc., Belafonte, PA). The pre-packed SPE cartridges were filled with 250 mg of Carbopack-B adsorbent (120-400 mesh). Carbon adsorbents are used as a fractionation procedure to remove closely related planar compounds based on a charge transfer mechanism (Concejero et al, 2001). To start the procedure, the reversible SPE cartridges

are mounted onto a vacuum manifold (J.T. Baker, Phillipsburg, NJ). The cartridges are washed with 20 ml of optimum grade toluene (Burdick and Jackson, Muskegon, MI) in the forward direction and 20 ml of GC-grade hexane (Fisher Scientific, Fairlawn, NJ) in the reverse direction with a flow rate of ~ 2 ml/min. The triple rinsed sample is pipetted into the cartridge making sure the carbon adsorbent does not dry. The di, tri, and tetra-ortho PCBs are eluted with 15 ml of hexane; the mono-ortho PCBs are eluted with 20 ml of hexane:toluene (99:1); and the non-ortho PCBs are eluted with 20 ml of hexane:toluene (75:25). The PCB fractions were not collected for analysis in this study. Finally, the dioxins are eluted with 60 ml of toluene in the reverse direction (Concejero et al, 2001). The sample is now ready for final volume and analysis by HRGC/HRMS. The final volume and HRGC/HRMS procedure was the same as the 2001 Rumford dioxin samples.

2.2.5. The 2002 Rumford PAH Samples

The 2002 Rumford deployment had 8 PAH samples upstream and downstream to investigate the impact environmental factors had on SPMD uptake rates. Luellen and Shea (2002) and Huckins et al (2000), spiked the PRCs directly into the SPMD which was to be used as the sampler for the analyte of interest. In this study, PAH and dioxin samples were kept separate during analysis. The reasons for this are:

(1) Chemical analysis of PAHs is different than dioxins. The acidified silica column in the dioxin clean-up would remove the deuterated atoms on the PAH molecules thereby making the quantification of the PRCs impossible.

(2) The PAH compounds were spiked at a much higher concentration than the native dioxin concentrations in the SPMDs. This large difference in

concentration could make the dioxin concentrations more difficult to quantify due to possible PAH interference.

(3) The PAH-SPMDs were not combined into composite samples like the dioxin samples.

Therefore, the elimination rates of the PAHs (and thereby the dioxin uptake rates) at each site were assumed to be affected by the environmental factors identically. After retrieval from the field, the PAH-spiked SPMDs were separated by location and kept in a solvent-rinsed can at –20°C until analysis.

2.2.5.1. PAH-Spiked SPMD Dialysis

The exterior cleaning of the membrane was the same as the dioxin procedure. The surrogates were spiked into each sample at 1 μg per SPMD after exterior cleaning (Table 2.13.). The two-stage forty-eight hour dialysis was done in ~200 ml of hexane (Burdick and Jackson, Muskegon, MI). The dialysates were concentrated in a KD apparatus with boiling chips to ~5 ml. At this point, the samples were filtered through a 0.45 micron Whatman Puradisc using dichloromethane (Fisher Scientific, Fairlawn, NJ) as the triple rinse solvent.

Table 2.12. Surrogates (^) and Internal Standards (*) for the PAH-spiked SPMD Samples (Cambridge Isotope Laboratories, Andover, MA)

COMPOUND	MOLECULAR WEIGHT	LOG K_{OW}
Acenaphthylene D-8^	160.26	4.08
Fluorene D-10^	176.29	4.38
Anthracene D-10^	188.32	4.54
Benzo[A]Pyrene D-12^	264.40	6.35
Naphthalene D-8*	136.24	3.45
Chrysene D-12*	240.39	5.61

2.2.5.2. Clean-Up Procedure

The clean-up procedure for the PAH samples was a two step process; Gel Permeation Chromatography and an activated silica gel gravimetric column. Before the samples could be injected into the GPC, the keeper solvent was changed from a hexane:dichloromethane mixture to 100% dichloromethane. This was accomplished by evaporating the samples down to 0.5 ml using the Turbo-Vap Concentration Workstation, transferring to a GPC tube, rinsing the sample three times with dichloromethane, and bringing the volume to 5 ml with dichloromethane. The Turbo-Vap system works by placing 200 ml concentrator tubes into a temperature controlled water bath with a lid that contains a nitrogen gas line. The gas line concentrates the samples to a calibrated point where a sensor automatically turns off the apparatus preventing complete dryness.
The GPC calibration was the same as the dioxin samples. However, PAHs usually elute later than dioxin, so the collection time was lengthened another 5 minutes on average depending on the cessation of the last peak (the PAHs) in the chart recorder. The O.I. Analytical Autoprep 2000 was dismantled after 2001 by the Environmental Chemistry Laboratory, so a Waters PrepLC 4000 (Millipore, Bilerica, MA) single injection GPC was used with the same Envirobead SX-3 column. After the GPC, the samples underwent another solvent exchange this time from dichloromethane back to hexane using the Turbo-Vap Concentration Workshop. The samples were now ready for the silica gel gravimetric column.

Before the columns were used, the silica gel (100-200 mesh, pore size 150 A, pore 1.2 cm^3/g, active surface 320 m^2/g) (Fisher Scientific, Fairlawn, NJ) was prepared by rinsing 3 times with ~250 ml of acetone (Fisher Scientific, Fairlawn, NJ), hexane, and

dichloromethane. The silica gel was allowed to dry overnight in the hood. The silica gel was activated at 150°C for 24 hours and kept in a dessicator until used. The chromatographic column (250 X 10.5-mm i.d.) with a Teflon stopcock (Kimble/Kontes, Vineland, NJ) was plugged with glass wool and rinsed with dichloromethane, toluene and hexane. After the column dried, it was dry-packed with 3 grams of activated silica gel and ~0.5 cm of anhydrous sodium sulfate. The column was conditioned with 20 ml of hexane making sure the anhydrous sodium sulfate layer was not exposed to the air. The sample was then applied to the column with a triple rinse of hexane. The aliphatic hydrocarbons were eluted with 12 ml of hexane and discarded. Then the aromatic hydrocarbons were eluted with 15 ml of dichloromethane and collected in Zymark concentration tubes. The samples were brought to final volume (1 ml) using the Turbo-Vap Concentration Workshop with 1 μg of internal standards added (Table 2.13.).

2.2.5.3. Analysis by GC/MS

A method was developed to identify and quantify the samples with Chemstation software using a coupled Hewlett Packard 6890+ Gas Chromatograph and a Hewlett Packard 5973 Mass Selective Detector (Agilent, Palo Alto, CA). The specifications of the GC were an initial temperature of 100°C increasing at 10 degrees per minute until 300°C with a run time of 46 minutes. The DB-5 capillary column (60 m length, 250 μm diameter, 0.25 μm film thickness) was in splitless mode with an initial temperature of 290°C and a pressure of 16.11 psi. The carrier gas was helium.

Before the Chemstation Program could quantify the samples by selective ion monitoring (SIM) mode, the compounds needed to be characterized by retention time, primary ions, and secondary ions (Table 2.13.). Therefore a standard solution (2 ppm)

was made of all ten PAH compounds. The solution was injected into the GC at 2 μl to identify the parameters needed for quantification. The MS was in scan mode to detect all the ion fragments up to 500 amu. The aforementioned parameters were deciphered and manually entered into the Chemstation software enabling the detector to scan the correct ion fragments at the correct retention time in SIM mode.

Table 2.13. Parameters to Identify and Quantify the Deuterated PAHs by GC/MS

Compound	Retention Time (min)	Primary Ion	Secondary Ion
Naphthalene D-8	6.772	136	108
Acenaphthylene D-8	10.477	160	162
Acenaphthene D-10	10.891	164	162
Fluorene D-10	12.192	176	174
Phenanthrene D-10	14.700	188	187
Anthracene D-10	14.829	188	94
Pyrene D-10	18.451	212	106
Chrysene D-12	21.688	240	236
Benzo(b)Fluoranthene D-12	24.875	264	260
Benzo[A]Pyrene D-12	26.062	264	260

Similar to the HRGC/HRMS, a five-point calibration was run for the compounds of interest. Stock solutions of five different concentrations were made of the eight deuterated PAHs used as surrogates and natives. The concentrations were 0.050 μg/ml, 0.100 μg/ml, 0.500 μg/ml, 1.000 μg/ml, and 2.000 μg/ml. The internal standard was kept at 1.000 μg/ml in each stock solution enabling the program to determine the response factor for each analyte by using a response ratio calculated from a linear fit. The responses were used to quantify the PAH-spiked SPMD samples. Before the PAH-spiked SPMD samples were run, the instrument was tuned using the auto-tune function of the Chemstation program. The three lock masses that the machine tunes on are 69.10, 218.90,

and 502.00 amu. The analyst must make sure the peak widths are equal and the electron multiplier volts are less than 2000 before running the sample sequence.

2.2.6. The 2002 Rumford Dioxin Samples

In the summer of 2002, the new procedures of the Environmental Chemistry Laboratory slowed the progress considerably of the SPMD sample analyses due to the method validation process for fish tissue analysis, but the improvements in dioxin analysis for both matrices are demonstrable.

2.2.6.1. SPMD Dialysis

The general dialysis procedure remained the same for the 2002 Rumford dioxin samples. For the first time in this project, the proper amount of surrogate was spiked into the samples (10µl/sample or 2.5 µl/SPMD). Therefore no corrections were needed in calculating the concentration in extract after HRGC/HRMS. The SPMDs were combined immediately after dialysis (4 SPMDs/sample) in the KD apparatus. The concentrated samples were then filtered through a 0.45 micron Whatman Puradisc ™ before clean-up was executed.

2.2.6.2. Clean-Up Procedure

The clean-up of the dioxin samples was completely changed. Two automated Power Prep ™ Systems were purchased by the Environmental Chemistry Lab from Fluid Management Systems (FMS) Inc., Watertown, MA. The Power Prep ™ system is a series of pressurized pre-packed chromatographic columns engineered to process dioxin samples mechanically. Normally, processing a sample can take weeks of laborious steps. The Power Prep ™ can shorten the process to an hour and a half. Not only is the system efficient, it is mechanized decreasing the probability of human error in the clean-up

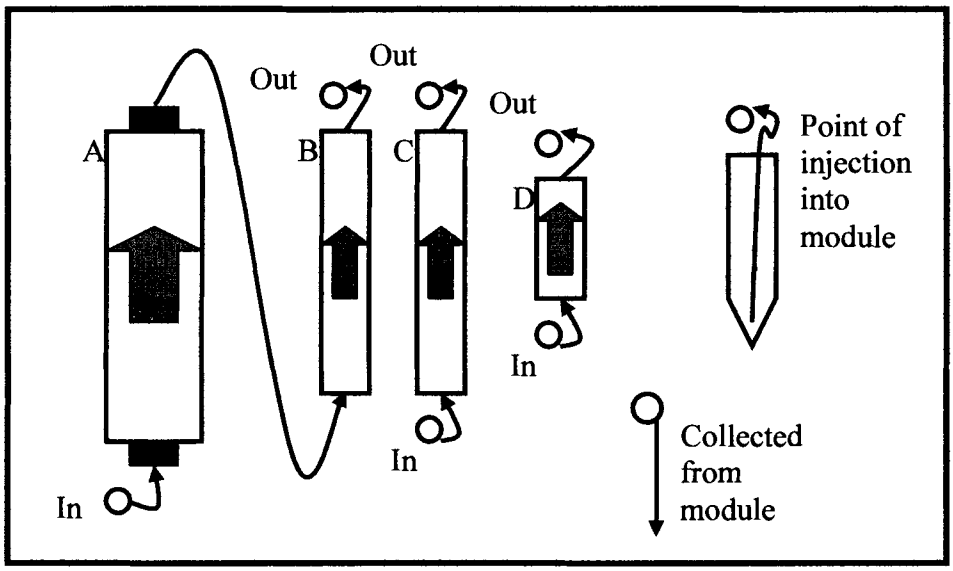
procedure. The efficiency of the Power Prep ™ enabled the SPMD project to add the appropriate clean-up steps to remove most interferents. An extensive study evaluating the Power Prep ™ System was completed demonstrating acceptable surrogate recoveries for all toxic congeners (>55%) and good comparability to manually run samples (Abad et al, 2000). Method validation was also performed by the Environmental Chemistry Lab.

The SPMD samples were run through a high capacity disposable acidic silica column to remove lipids, a disposable acid/base/neutral silica column to ensure lipid elimination, a disposable basic alumina (11 g) column to remove diphenylethers, and a disposable carbon/celite (0.34 g) column to fractionate PCBs (Figure 2.6.). All the columns were purchased from FMS. Before starting the procedure, all glassware is triple-rinsed and 200 µl of dioxin clean up standard is added to the sample (Table 2.4.). The column components (i.e. frits, fittings, injection lines, tubes) were triple rinsed and sonicated before injection of the sample. The entire elution program (Table 2.12.) is controlled by a desktop computer with DMS 6000 software. After completing the dioxin program, the columns are removed, dried and discarded. The module is then cleaned using two separate wash programs to ensure no carryover between samples.

The samples are collected from the Power Prep ™ module into 200 ml Zymark concentration tubes and evaporated in a Turbo-Vap II Concentration Workstation (Zymark, Hopkinton, MA). For the dioxin samples, the water bath is set at 50°C, the gas pressure is in between 6-12 psi, and the endpoint is set for 0.75 ml. The sample is then concentrated for another 5 minutes to reach the desired 0.5 ml. Into a final volume vial, 10 µl of tridecane (Supelco, Belafonte, PA), 5 µl of internal standard (Table 2.4.), and the triple rinsed (with DCM) 0.5 ml sample are added to a silanized final volume vial (Sun-

SRI, Wilmington, NC). The solution is then concentrated using a Mini-Vap Evaporator (Supelco, Belafonte, PA) with nitrogen gas to the final volume of 10 µl. The sample vial is capped and ready for HRGC/HRMS.

Figure 2.6. Diagram of the Power Prep ™ with (A) High Capacity Acidic Silica Column, (B) Acid/Base/Neutral Silica Column, (C) Basic Alumina Column, and (D) Carbon-Celite Column



Originally, the 2002 standard operating procedure did not incorporate the gel permeation chromatography clean-up due to time constraints and poor previous performance by the GPC. However, when the samples were brought to final volume without the GPC step, a cloudy residue was noticeable in the final volume vials. After referral to SPMD literature, the residue was determined to be polyethylene waxes which should easily be removed using the GPC (Jim Petty, personal communication). These polyethylene waxes are formed by break down of the SPMD low-density polyethylene membrane. Essentially, the waxes are oligomers and polymeric chains of various sizes. Therefore, the samples were run through the GPC using the same protocol as the PAH

method. The final volume procedure was duplicated and no visible waxes were seen in the final volume vials after the GPC clean up.

2.2.6.3. Analysis by HRGC/HRMS

A new high resolution Hewlett Packard 6890+ Gas Chromatograph was purchased (Agilent, Palo Alto, CA) in 2002. Also, a new column was used (DB-5MS, 60 m length, 0.25 mm diameter, 0.25 μm film thickness). Therefore a new GC program for dioxin was established. The temperature profile started initially at 180°C for 2 minutes, increased at 5°C per minute holding at 220°C for 16 minutes, then increased at 5°C per minute holding at 235°C for 11 minutes, and finally increased at 5°C per minute holding at 320°C for 6 minutes. The head pressure was set at 25 psi. The injector, line and interface temperatures were all set at 280°C. Helium was the carrier gas.

Before samples were run through the GC, an isomer specificity solution for TCDF was analyzed to ensure there was sufficient separation from possible co-eluting peaks. Normally, on other GC columns (like the DB-5 used in the 2001 analyses), a confirmatory column needs to be installed to confirm PCDD/PCDF quantification. However, with the DB-5MS, no confirmatory column is needed to ensure that there is adequate separation between the toxic and non-toxic isomers.

Unlike the 2001 analyses, a six point calibration curve was executed. By using the one half calibration standard (CS1/2), the lower limit of calibration was decreased 2 fold. The minimum levels are 0.139 pg/g for tetrachlorinated congeners, 0.694 pg/g for penta through heptachlorinated congeners, and 1.389 pg/g for octachlorinated congeners. The coefficient of variations for all congener relative response factors were under 10% with the maximum allowed by EPA 1613B being 25%. The lock masses for the instrument

Table 2.14. SPMD Dioxin Sample Program for the Power Prep™

STEP	FLOW (ml/min)	SOLVENT (ml)	PURPOSE
1	10	Hexane (60)	Leak Test for Silica Column
2	10	Hexane (10)	Flush Bypass Lines
3	10	Hexane (12)	Wet Alumina Column
4	10	Hexane (20)	Wet Carbon Column
5	10	Hexane (200)	Condition Silica Column
6	10	Toluene (12)	Solvent Change
7	10	Toluene (40)	Pre-elute Carbon Column
8	10	50% EA:Toluene (12)	Solvent Change
9	10	50% EA:Toluene (10)	Pre-elute Carbon Column
10	10	50% DCM:Hexane (12)	Solvent Change
11	10	50% DCM:Hexane (20)	Pre-elute Carbon Column
12	10	Hexane (12)	Solvent Change
13	10	Hexane (30)	Pre-elute Carbon Column
14	5	Hexane (16)	Add Sample
15	10	Hexane (300)	Elute Silica Column
16	12	2% DCM:Hexane (12)	Solvent Change
17	10	2% DCM:Hexane (60)	Elute Alumina Column
18	10	50% DCM:Hexane (12)	Solvent Change
19	7	50% DCM:Hexane (120)	Elute Alumina Column
20	10	50% EA:Toluene (12)	Solvent Change
21	10	50% EA:Toluene (16)	Elute Carbon Column
22	10	Hexane (12)	Solvent Change
23	10	Hexane (10)	Flush Carbon Column
24	10	Toluene (12)	Solvent Change
25	5	Toluene (90)	Elute Dioxins from Carbon Column

were the same as the 2001 analyses with the exception of the PeCDD window which used the M/M+2 ions instead of the M+2/M+4 ions outlined by EPA 1613B. This modification was performed to eliminate a reoccurring interference with the same mass as the M+4 ion. The ion abundance ratio was subsequently changed from 1.55 to 0.62. The MS instrument tuning parameters are in Table 2.15.

Table 2.15. Vg AutoSpec Ultima Mass Spectrometer Tuning Parameters

Source Vacuum	7.2 E -7 mbar
Analyzer Vacuum	1.05 E -7 mbar
Source Temperature	280 °C
Trap Current	750 μA
Electron Energy	35.8 V
Ion Energy	-13.2
Multiplier	360 kV
Y Focus	5.27
Resolution at M/z	> 10,000

2.3. Method Detection Limit (MDL) Study

The analysis of dioxin samples requires determination of the detection limits of the analytical procedure. Therefore, a method detection limit study was performed for the SPMD matrix using the 2002 dioxin procedure. The method detection limit is the minimum concentration of dioxin that can be measured by the HRGC/HRMS with 99% confidence that the value is greater than zero. The Environmental Chemistry Lab estimates the lowest possible detectable concentration for TCDD is 0.1 ng/ml at final volume (μl) with a signal to noise ratio greater than 10 (Elizabeth Damaske, personal communication). The concentration in the matrix using 25 g of fish tissue is 40 pg/kg. The MDL study for SPMDs was spiked at similar concentrations since it is based on the limit of detection (LOD) for the instrument.

A total of seven blank samples (4 SPMDs) were spiked with 24 µl of diluted PAR (Table 2.3) stock solution (TCDD = 0.04 ng/ml). The final concentration in the matrix (4 SPMDs) was 0.053 pg/g for TCDD/F, 0.267 pg/g for PeCDD/F-HpCDD/F, and 0.533 pg/g for OCDD/F. The MDL samples underwent the same analytical procedure for dioxin as the 2002 Rumford Samples. The standard deviation of the seven MDL samples was multiplied by the appropriate t-statistic (3.14 for seven samples). This calculation determines the method detection limit for the current procedure.

2.4. Statistical Methods

To test if two sites (i.e. population means) are different in dioxin concentration from one another, a parametric statistical test would be preferred. The assumptions for a parametric test are the data fits a normal distribution and the variances are equal. When these assumptions are not met, non-parametric statistical tests are used. Parametric tests are more robust than non-parametric tests meaning more confidence can be put into the results. In the instance of the upstream/downstream legislation, the level of confidence of the assessor is important. The upstream/downstream test should be able to accurately determine the presence of an actual difference in dioxin concentration with as high a level of confidence as possible.

The most common approach of statistical inference is hypothesis testing. For the upstream/downstream test, the null hypothesis is that the upstream and downstream dioxin concentrations are the same and the alternative hypothesis is the upstream and downstream dioxin concentrations are different. There are two significance levels relating to the hypotheses which are chosen by the monitor before the statistical tests are executed, the alpha level and the beta level. The alpha (α) level is representative of the

probability of a Type I error. In this case, the Type I error is the chance of detecting a statistical difference when there is not an actual difference in dioxin concentration. The goal of the Maine's Dioxin Monitoring Program is an alpha level of 0.05 (B. Mower, personal communication). The beta (β) level is the probability of a making a Type II error. A Type II error occurs when the dioxin concentrations between the two locations are different, but the null hypothesis is not rejected. In either instance, the ramification of whether or not the pulp and paper industry is in compliance with the upstream/downstream legislation can be falsely determined. The overall power of the statistical test is the probability that the null hypothesis will be rejected when some alternative hypothesis is true (power = β-1). The goal of Maine's DMP is to obtain a power of 90 percent on the parametric statistic used. The power of the statistical test is directly related to the sample size. The larger the sample size the greater the power of the statistical test.

Before the first deployment in July of 2001, statistical analyses were performed on the data from the 2000 Rumford deployment to estimate the sample size required to obtain a significant difference between the upstream and downstream sites. The computer program PC-SIZE version 2.0 (Dallal, 1985) was used at an alpha level of 0.05 and a power of 0.9 using the standard deviations from the previous TEQ values. Three interpretations of the non-detects in the 2000 Rumford data were utilized (non-detects (ND) equal zero, ND equal half the detection limit (DL), and ND equal to the DL) (Shoven, 2001). The sample sizes determined by the program were 66,000 (ND=0), 14 (ND=0.5DL), and 8 (ND=DL). Sixty-six thousand samples are not feasible. A sample size of twenty was selected.

To evaluate the data obtained from 2001 and 2002, numerous statistical methods and programs were utilized. The raw data (pg-congener /g-SPMD) was entered into a Microsoft Excel™ spreadsheet. The mean, standard deviation and coefficient of variation were calculated using the basic statistical functions of the program. For all congeners that were consistently detected and passed quality assurance criteria at both the upstream and downstream sites, the sample populations were entered into a Systat™ program and tested for a normal distribution using the One Sample Kolmogorov-Smirnov Test function. If the sample population distribution were determined to be Gaussian with 95% confidence for both sites, then parametric statistics were used. If the distribution was not normal, then the data were transformed by both the natural logarithm and square root functions. If a normal distribution was achieved by either transformation, then the variances were tested for equality. Assuming equal variance and a normal distribution, the data from the two sites underwent a paired t-test with an alpha level of 0.05 to determine any significant differences between mean concentrations. If a normal distribution could not be obtained by transformation, a Mann-Whitney U test was performed on the congener concentrations to determine if there were significant differences with a confidence level of 95%. .

Chapter 3

RESULTS

3.1. The 2001 Rumford Deployment on the Androscoggin River

The sample names are acronyms. For example, **R**umford **D**ownstream 200**1** **D**ioxin sample number **3** is RD1D3. With the exception of 2,3,7,8-TCDF, most of the congeners concentrations were below the calibration of the instrument and the method detection limit determined by Shoven (2001). The lower end of the calibration curve was 0.556 pg-dioxin/g-SPMD for tetra-, 2.778 pg/g for penta- through hepta-, and 5.556 pg/g for octa-chlorinated congeners. The percent surrogate recoveries (Table 3.6., 3.7., and 3.11.) are well within the quality assurance limits with the notable exception of the penta-chlorinated congeners which in some cases went undetected by the mass spectrometer. Samples RD1D1, RD1D2, RD1D19, RU1D1, RU1D6, RU1D7, RU1D8, RU1D10, RU1D13, RU1D14, RU1D15, and RU1D16 were not quantified due to time constraints at the laboratory. The TEQ values were calculated using only concentrations greater than the calibration lower limit and the method detection limit. Therefore, the two reportable mean concentrations in the sample set are 2,3,7,8-TCDF and the TEQ value which is one-tenth the TCDF value with the exception of two OCDD contributions in RD1D4 and RD1D20.

The statistical analysis of the data from this deployment determined extremely high levels of variance. The coefficient of variation ranged from 34% to 412% for the congeners, using zero for values less than the detection limit. For TCDF, the coefficient of variation was 37% for the downstream samples and 34% for the upstream samples.

The TEQ values exhibited a coefficient of variation of 37% for the downstream samples and 50% for the upstream samples. The data and the transformed data failed the test for a normal distribution, so non-parametric statistics were used. Both TCDF and the TEQ values showed no significant differences between the upstream and downstream locations using the Mann-Whitney U test (95% confidence). The general spatial trend from the calculated means is that the concentration of toxic congeners decreases from upstream to downstream. With variance this high in a relatively small sample population, it is difficult to infer anything, let alone obtain statistical significance. However, one inference that can easily be made is that the analytical procedure needs refinement. The levels of dissolved dioxin contamination in Maine rivers is extremely low according to these results. In order to obtain a statistically significant difference in mean concentrations between the upstream and downstream sites, the variability among the sample population must decrease. This can be accomplished by refining the analytical procedure thereby decreasing the detection level and background noise as well as eliminating interfering compounds.

The results from the 2001 Rumford quality control samples are shown in Table 3.12. Concentrations of PCDD/Fs in both trip blanks were less than the method detection limit for all congeners with the exception of the OCDD concentration on RD1TB. The precision and recovery matrix spike showed consistent over-estimation of the actual standard concentration which is cause for concern when interpreting the data. No procedural or dialysis blank quality control samples were analyzed for this deployment.

Table 3.1. Water Quality Data from the 2001 Rumford Deployment

PARAMETER	DOWNSTREAM	UPSTREAM
DOC 7/17	6.03 mg/l	4.50 mg/l
TOC 7/17	6.23 mg/l	4.51 mg/l
Specific Conductivity 7/17	95.26 $\mu s/cm^2$	55.57 $\mu s/cm^2$
Flow Velocity 7/17	0.79 m/s	0.55 m/s
DOC 8/10	6.2 mg/l	4.50 mg/l
TOC 8/10	6.3 mg/l	4.6 mg/l
Specific Conductivity 8/10	115.3 $\mu s/cm^2$	61.80 $\mu s/cm^2$
Flow Velocity 8/10	0.40 m/s	0.15 m/s
Average Temperature	23.79 °C	19.34 °C
Average DOC	6.12 mg/l	4.50 mg/l
Average TOC	6.27 mg/l	4.55 mg/l
Depth	4.39 m	3.84 m

Table 3.2. SPMD Concentrations (pg/g) for RD1D3 through RD1D7

CONGENER	MDL*	RD1D3	RD1D4	RD1D5	RD1D6	RD1D7	DATA FLAGS
2,3,7,8-TCDF	0.8	7.110	11.622	10.874	2.113 ^	12.966	^ M/z
1,2,3,7,8-PeCDF	2.08	<DL	<DL	<DL	<DL	<DL	
2,3,4,7,8-PeCDF	3.13	<DL	<DL	<DL	<DL	<DL	
1,2,3,4,7,8-HxCDF	2.59	<DL	<DL	<DL	<DL	<DL	
1,2,3,6,7,8-HxCDF	2.46	<DL	<DL	<DL	<DL	<DL	
2,3,4,6,7,8-HxCDF	2.88	<DL	<DL	<DL	<DL	<DL	
1,2,3,7,8,9-HxCDF	1.68	<DL	<DL	<DL	<DL	<DL	
1,2,3,4,6,7,8-HpCDF	2.65	<DL	<DL	<DL	<DL	3.068 ^	^ M/z
1,2,3,4,7,8,9-HpCDF	1.56	<DL	<DL	ND	ND	<DL	
OCDF	7.18	<DL	ND	ND	<DL	ND	
2,3,7,8-TCDD	2.1	<DL	<DL	<DL	<DL	<DL	
1,2,3,7,8-PeCDD	2.14	ND	ND	<DL	ND	ND	
1,2,3,4,7,8-HxCDD	3.08	<DL	<DL	<DL	<DL	<DL	
1,2,3,6,7,8-HxCDD	1.22	<DL	<DL	<DL	<DL	<DL	
1,2,3,7,8,9,-HxCDD	2.84	<DL	<DL	<DL	<DL	<DL	
1,2,3,4,6,7,8-HpCDD	2.31	<DL	<DL	<DL	<DL	<DL	
OCDD	6.7	<DL	8.310	<DL	<DL	<DL	
TEQ		**0.711**	**1.163**	**1.087**	**0.211**	**1.327**	

* Method Detection Limit from Shoven (2001)
ND = Non Detects
M/z = Ion Ratio outside QA limits (EPA 1613B)
Calibration Lower Limit = 0.556 pg/g for tetra-, 2.778 pg/g for penta- through hepta-, and 5.556 pg/g for octa-chlorinated congeners

Table 3.3. SPMD Concentrations (pg/g) for RD1D8 through RD1D12

CONGENER	MDL*	RD1D8	RD1D9	RD1D10	RD1D11	RD1D12
2,3,7,8-TCDF	0.8	9.503	7.640	9.915	7.505	6.803
1,2,3,7,8-PeCDF	2.08	<DL	<DL	<DL	<DL	<DL
2,3,4,7,8-PeCDF	3.13	<DL	<DL	<DL	<DL	ND
1,2,3,4,7,8-HxCDF	2.59	<DL	<DL	<DL	<DL	<DL
1,2,3,6,7,8-HxCDF	2.46	<DL	<DL	<DL	<DL	<DL
2,3,4,6,7,8-HxCDF	2.88	<DL	<DL	<DL	<DL	<DL
1,2,3,7,8,9-HxCDF	1.68	<DL	<DL	<DL	<DL	<DL
1,2,3,4,6,7,8-HpCDF	2.65	<DL	<DL	<DL	<DL	<DL
1,2,3,4,7,8,9-HpCDF	1.56	<DL	ND	<DL	ND	<DL
OCDF	7.18	<DL	<DL	<DL	ND	<DL
2,3,7,8-TCDD	2.1	<DL	<DL	<DL	<DL	<DL
1,2,3,7,8-PeCDD	2.14	ND	ND	ND	ND	ND
1,2,3,4,7,8-HxCDD	3.08	<DL	<DL	<DL	<DL	<DL
1,2,3,6,7,8-HxCDD	1.22	<DL	<DL	<DL	<DL	<DL
1,2,3,7,8,9,-HxCDD	2.84	<DL	<DL	<DL	<DL	<DL
1,2,3,4,6,7,8-HpCDD	2.31	<DL	<DL	<DL	<DL	<DL
OCDD	6.7	<DL	<DL	<DL	<DL	<DL
TEQ		**0.950**	**0.764**	**0.992**	**0.751**	**0.680**

* Method Detection Limit from Shoven (2001)
ND = Non Detects
Calibration Lower Limit = 0.556 pg/g for tetra-, 2.778 pg/g for penta- through hepta-, and 5.556 pg/g for octa-chlorinated congeners

Table 3.4. SPMD Concentrations (pg/g) for RD1D13 through RD1D17

CONGENER	MDL*	RD1D13	RD1D14	RD1D15	RD1D16	RD1D17	DATA FLAGS
2,3,7,8-TCDF	0.8	4.733	4.529	7.177	6.874	9.484	
1,2,3,7,8-PeCDF	2.08	<DL	<DL	<DL	<DL	<DL	
2,3,4,7,8-PeCDF	3.13	<DL	ND	<DL	ND	<DL	
1,2,3,4,7,8-HxCDF	2.59	<DL	<DL	<DL	<DL	<DL	
1,2,3,6,7,8-HxCDF	2.46	<DL	<DL	<DL	<DL	<DL	
2,3,4,6,7,8-HxCDF	2.88	<DL	<DL	<DL	<DL	<DL	
1,2,3,7,8,9-HxCDF	1.68	<DL	<DL	ND	<DL	<DL	
1,2,3,4,6,7,8-HpCDF	2.65	<DL	<DL	3.448 ^	<DL	<DL	^ M/z
1,2,3,4,7,8,9-HpCDF	1.56	<DL	<DL	ND	<DL	<DL	
OCDF	7.18	<DL	<DL	<DL	<DL	<DL	
2,3,7,8-TCDD	2.1	<DL	<DL	<DL	<DL	<DL	
1,2,3,7,8-PeCDD	2.14	ND	ND	ND	ND	<DL	
1,2,3,4,7,8-HxCDD	3.08	<DL	<DL	<DL	<DL	<DL	
1,2,3,6,7,8-HxCDD	1.22	<DL	<DL	<DL	<DL	<DL	
1,2,3,7,8,9,-HxCDD	2.84	<DL	<DL	ND	<DL	<DL	
1,2,3,4,6,7,8-HpCDD	2.31	<DL	<DL	<DL	<DL	<DL	
OCDD	6.7	<DL	<DL	<DL	<DL	<DL	
TEQ		**0.473**	**0.453**	**1.041**	**0.687**	**0.948**	

* Method Detection Limit from Shoven (2001)
ND = Non Detects
M/z = Ion Ratio outside QA limits (EPA 1613B)
Calibration Lower Limit = 0.556 pg/g for tetra-, 2.778 pg/g for penta- through hepta-, and 5.556 pg/g for octa-chlorinated congeners

Table 3.5. SPMD Concentrations (pg/g) for RD1D18 and RD1D20, Mean, Standard Deviation (S.D.), and Coefficient of Variation (C.V.) for all 2001 Rumford Downstream Samples

CONGENER	MDL*	RD1D18	RD1D20	MEAN	S. D.	C.V.
2,3,7,8-TCDF	0.8	8.823	3.987	7.745	2.870	37.054
1,2,3,7,8-PeCDF	2.08	2.429	<DL	0.143	0.589	412.311
2,3,4,7,8-PeCDF	3.13	<DL	ND	0	0	0
1,2,3,4,7,8-HxCDF	2.59	<DL	<DL	0	0	0
1,2,3,6,7,8-HxCDF	2.46	<DL	<DL	0	0	0
2,3,4,6,7,8-HxCDF	2.88	<DL	<DL	0	0	0
1,2,3,7,8,9-HxCDF	1.68	<DL	<DL	0	0	0
1,2,3,4,6,7,8-HpCDF	2.65	<DL	<DL	0.383	1.084	282.833
1,2,3,4,7,8,9-HpCDF	1.56	<DL	<DL	0	0	0
OCDF	7.18	ND	<DL	0	0	0
2,3,7,8-TCDD	2.1	<DL	<DL	0	0	0
1,2,3,7,8-PeCDD	2.14	<DL	ND	0	0	0
1,2,3,4,7,8-HxCDD	3.08	<DL	<DL	0	0	0
1,2,3,6,7,8-HxCDD	1.22	2.083	<DL	0.123	0.505	412.311
1,2,3,7,8,9,-HxCDD	2.84	<DL	<DL	0	0	0
1,2,3,4,6,7,8-HpCDD	2.31	<DL	<DL	0	0	0
OCDD	6.7	<DL	14.044	1.315	3.848	292.626
TEQ		**0.882**	**0.400**	**0.778**	**0.290**	**37.277**

* Method Detection Limit from Shoven (2001)
ND = Non Detects
Calibration Lower Limit = 0.556 pg/g for tetra-, 2.778 pg/g for penta- through hepta-, and 5.556 pg/g for octa-chlorinated congeners

Table 3.6. Percent Surrogate Recoveries for the 2001 Rumford Downstream Samples

C^{13} LABELLED SURROGATE	SAMPLE NUMBER									
	3	4	5	6	7	8	9	10	11	Q.A. LIMITS
2,3,7,8-TCDF	79	71	73	65	75	77	66	64	65	24-169
1,2,3,7,8-PeCDF	73	64	39	65	44	71	60	79	67	24-185
2,3,4,7,8-PeCDF	30	36	43	68	42	27	112	137	26	21-178
1,2,3,4,7,8-HxCDF	71	74	79	66	84	55	96	60	65	26-152
1,2,3,6,7,8-HxCDF	64	68	68	63	79	59	91	58	58	26-123
2,3,4,6,7,8-HxCDF	64	55	67	63	74	62	77	72	47	29-147
1,2,3,7,8,9-HxCDF	81	70	84	70	90	75	90	72	75	28-136
1,2,3,4,6,7,8-HpCDF	88	99	101	64	116	81	83	66	84	28-143
1,2,3,4,7,8,9-HpCDF	83	53	57	49	61	67	78	67	49	26-138
2,3,7,8-TCDD	79	67	73	63	72	80	56	61	80	25-164
1,2,3,7,8-PeCDD	104	68	67	110	61	65	69	76	63	25-181
1,2,3,4,7,8-HxCDD	54	61	50	57	53	51	99	98	55	32-141
1,2,3,6,7,8-HxCDD	42	71	80	69	88	50	77	63	62	28-130
1,2,3,4,6,7,8-HpCDD	97	92	89	60	100	88	74	74	76	23-140
OCDD	108	36	36	44	37	32	63	62	26	17-157

Table 3.7. Percent Surrogate Recoveries for the 2001 Rumford Downstream Samples (Bold indicates values not within QC limits)

C^{13} LABELLED SURROGATE	SAMPLE NUMBER								
	12	13	14	15	16	17	18	20	Q.A. LIMITS
2,3,7,8-TCDF	67	71	71	59	64	54	66	87	24-169
1,2,3,7,8-PeCDF	70	69	69	68	64	54	43	73	24-185
2,3,4,7,8-PeCDF	**4**	**10**	**4**	30	**5**	86	47	**5**	21-178
1,2,3,4,7,8-HxCDF	51	47	57	85	55	64	81	74	26-152
1,2,3,6,7,8-HxCDF	58	57	55	81	49	60	61	68	26-123
2,3,4,6,7,8-HxCDF	58	54	57	61	67	69	67	69	29-147
1,2,3,7,8,9-HxCDF	73	64	73	74	79	75	87	86	28-136
1,2,3,4,6,7,8-HpCDF	79	68	76	110	83	68	111	92	28-143
1,2,3,4,7,8,9-HpCDF	63	65	65	59	76	76	62	84	26-138
2,3,7,8-TCDD	75	78	81	59	65	52	63	90	25-164
1,2,3,7,8-PeCDD	**1**	ND	ND	55	ND	65	78	ND	25-181
1,2,3,4,7,8-HxCDD	42	41	39	36	43	84	63	47	32-141
1,2,3,6,7,8-HxCDD	64	58	64	99	73	74	78	74	28-130
1,2,3,4,6,7,8-HpCDD	84	78	85	103	97	74	94	103	23-140
OCDD	30	82	87	107	99	56	37	99	17-157

Table 3.8. SPMD Concentrations (pg/g) for RU1D2, RU1D3, RU1D4, RU1D5, and RU1D9

CONGENER	MDL*	RU1D2	RU1D3	RU1D4	RU1D5	RU1D9	DATA FLAGS
2,3,7,8-TCDF	0.8	11.815	7.814	11.072	8.941	ND	
1,2,3,7,8-PeCDF	2.08	<DL	<DL	<DL	<DL	<DL	
2,3,4,7,8-PeCDF	3.13	<DL	<DL	<DL	<DL	<DL	
1,2,3,4,7,8-HxCDF	2.59	<DL	<DL	<DL	<DL	<DL	
1,2,3,6,7,8-HxCDF	2.46	<DL	<DL	<DL	<DL	<DL	
2,3,4,6,7,8-HxCDF	2.88	<DL	<DL	<DL	<DL	<DL	
1,2,3,7,8,9-HxCDF	1.68	<DL	<DL	<DL	<DL	<DL	
1,2,3,4,6,7,8-HpCDF	2.65	<DL	<DL	<DL	2.896 ^	3.051 ^	^ M/z
1,2,3,4,7,8,9-HpCDF	1.56	ND	<DL	ND	<DL	ND	
OCDF	7.18	ND	<DL	ND	<DL	ND	
2,3,7,8-TCDD	2.1	<DL	<DL	<DL	<DL	<DL	
1,2,3,7,8-PeCDD	2.14	<DL	ND	<DL	<DL	<DL	
1,2,3,4,7,8-HxCDD	3.08	<DL	<DL	<DL	<DL	ND	
1,2,3,6,7,8-HxCDD	1.22	<DL	<DL	<DL	<DL	<DL	
1,2,3,7,8,9,-HxCDD	2.84	ND	<DL	<DL	<DL	<DL	
1,2,3,4,6,7,8-HpCDD	2.31	<DL	<DL	<DL	<DL	ND	
OCDD	6.7	<DL	<DL	<DL	<DL	<DL	
TEQ		**1.182**	**0.781**	**1.107**	**0.923**	**0.031**	

* Method Detection Limit from Shoven (2001)
ND = Non Detects
M/z = Ion Ratio outside QA limits (EPA 1613B)
Calibration Lower Limit = 0.556 pg/g for tetra-, 2.778 pg/g for penta- through hepta-, and 5.556 pg/g for octa-chlorinated congeners

Table 3.9. SPMD Concentrations (pg/g) for RU1D11, RU1D12, RU1D17, RU1D18, and RU1D19

CONGENER	MDL*	RU1D11	RU1D12	RU1D17	RU1D18	RU1D19
2,3,7,8-TCDF	0.8	11.079	10.818	12.816	13.735	12.083
1,2,3,7,8-PeCDF	2.08	<DL	<DL	<DL	<DL	<DL
2,3,4,7,8-PeCDF	3.13	<DL	<DL	<DL	<DL	<DL
1,2,3,4,7,8-HxCDF	2.59	<DL	<DL	<DL	<DL	<DL
1,2,3,6,7,8-HxCDF	2.46	<DL	<DL	<DL	<DL	<DL
2,3,4,6,7,8-HxCDF	2.88	<DL	<DL	<DL	<DL	<DL
1,2,3,7,8,9-HxCDF	1.68	<DL	<DL	<DL	<DL	<DL
1,2,3,4,6,7,8-HpCDF	2.65	<DL	<DL	<DL	<DL	<DL
1,2,3,4,7,8,9-HpCDF	1.56	<DL	<DL	<DL	<DL	<DL
OCDF	7.18	ND	ND	<DL	<DL	<DL
2,3,7,8-TCDD	2.1	<DL	<DL	<DL	<DL	<DL
1,2,3,7,8-PeCDD	2.14	<DL	<DL	ND	<DL	<DL
1,2,3,4,7,8-HxCDD	3.08	<DL	<DL	<DL	<DL	<DL
1,2,3,6,7,8-HxCDD	1.22	<DL	<DL	<DL	<DL	1.484
1,2,3,7,8,9,-HxCDD	2.84	<DL	<DL	<DL	<DL	<DL
1,2,3,4,6,7,8-HpCDD	2.31	<DL	<DL	<DL	<DL	<DL
OCDD	6.7	<DL	<DL	<DL	<DL	<DL
TEQ		**1.108**	**1.082**	**1.282**	**1.374**	**1.618**

* Method Detection Limit from Shoven (2001)
ND = Non Detects
Calibration Lower Limit = 0.556 pg/g for tetra-, 2.778 pg/g for penta- through hepta-, and 5.556 pg/g for octa-chlorinated congeners

Table 3.10. SPMD Concentrations (pg/g) for RU1D20, Mean, Standard Deviation (S.D.), and Coefficient of Variation (C.V.) for all 2001 Rumford Upstream Samples

CONGENER	MDL*	RU1D20	MEAN	S. D.	C.V.
2,3,7,8-TCDF	0.8	1.623	10.180	3.468	34.069
1,2,3,7,8-PeCDF	2.08	<DL	0.251	0.834	331.662
2,3,4,7,8-PeCDF	3.13	<DL	0	0	0
1,2,3,4,7,8-HxCDF	2.59	<DL	0	0	0
1,2,3,6,7,8-HxCDF	2.46	<DL	0	0	0
2,3,4,6,7,8-HxCDF	2.88	<DL	0	0	0
1,2,3,7,8,9-HxCDF	1.68	<DL	0	0	0
1,2,3,4,6,7,8-HpCDF	2.65	<DL	0.541	1.203	222.578
1,2,3,4,7,8,9-HpCDF	1.56	<DL	0	0	0
OCDF	7.18	<DL	0	0	0
2,3,7,8-TCDD	2.1	<DL	0	0	0
1,2,3,7,8-PeCDD	2.14	<DL	0	0	0
1,2,3,4,7,8-HxCDD	3.08	<DL	0	0	0
1,2,3,6,7,8-HxCDD	1.22	<DL	0.135	0.447	331.662
1,2,3,7,8,9,-HxCDD	2.84	<DL	0	0	0
1,2,3,4,6,7,8-HpCDD	2.31	<DL	0	0	0
OCDD	6.7	<DL	0	0	0
TEQ		**0.162**	**0.957**	**0.469**	**49.033**

* Method Detection Limit from Shoven (2001)
ND = Non Detects
Calibration Lower Limit = 0.556 pg/g for tetra-, 2.778 pg/g for penta- through hepta-, and 5.556 pg/g for octa-chlorinated congeners

Table 3.11. Percent Surrogate Recoveries for the 2001 Rumford Upstream Samples (Bold indicates values not within QC limits)

C^{13} LABELLED SURROGATE	SAMPLE NUMBER											
	2	3	4	5	9	11	12	17	18	19	20	Q.A. LIMITS
2,3,7,8-TCDF	53	49	70	51	ND	50	54	65	54	43	52	24-169
1,2,3,7,8-PeCDF	53	70	80	65	**419**	68	67	80	76	63	65	24-185
2,3,4,7,8-PeCDF	57	78	40	80	**458**	79	61	28	73	59	37	21-178
1,2,3,4,7,8-HxCDF	74	62	83	63	33	65	63	71	58	50	58	26-152
1,2,3,6,7,8-HxCDF	79	48	79	63	30	52	61	63	60	48	52	26-123
2,3,4,6,7,8-HxCDF	73	67	84	61	29	60	59	67	60	49	60	29-147
1,2,3,7,8,9-HxCDF	80	71	95	69	34	73	68	81	79	59	64	28-136
1,2,3,4,6,7,8-HpCDF	106	67	112	65	31	64	63	75	69	54	58	28-143
1,2,3,4,7,8,9-HpCDF	55	62	58	66	31	59	59	68	61	48	59	26-138
2,3,7,8-TCDD	55	57	68	58	163	57	61	74	67	52	59	25-164
1,2,3,7,8-PeCDD	59	123	71	114	678	75	124	79	284	124	17	25-181
1,2,3,4,7,8-HxCDD	56	92	62	72	35	68	65	67	58	50	60	32-141
1,2,3,6,7,8-HxCDD	71	57	85	68	27	57	57	65	61	50	50	28-130
1,2,3,4,6,7,8-HpCDD	89	71	95	65	32	64	62	73	67	55	61	23-140
OCDD	27	68	27	71	26	61	49	73	68	56	48	17-157

Table 3.12. SPMD Concentrations (pg/g) for the 2001 Rumford Quality Control Samples

CONGENER	MDL*	RD1TB	RU1TB	PAR01	[PAR]	DATA FLAGS
2,3,7,8-TCDF	0.8	<DL	<DL	58.244	40	
1,2,3,7,8-PeCDF	2.08	<DL	<DL	287.367	200	
2,3,4,7,8-PeCDF	3.13	<DL	<DL	289.349	200	
1,2,3,4,7,8-HxCDF	2.59	<DL	<DL	249.66	200	
1,2,3,6,7,8-HxCDF	2.46	<DL	<DL	255.734	200	
2,3,4,6,7,8-HxCDF	2.88	<DL	<DL	259.642	200	
1,2,3,7,8,9-HxCDF	1.68	<DL	<DL	245.013	200	
1,2,3,4,6,7,8-HpCDF	2.65	ND	ND	254.363	200	
1,2,3,4,7,8,9-HpCDF	1.56	ND	ND	266.5	200	
OCDF	7.18	<DL	ND	665.295	400	
2,3,7,8-TCDD	2.1	ND	ND	62.172	40	
1,2,3,7,8-PeCDD	2.14	ND	ND	696.266 ^	200	^ M/z
1,2,3,4,7,8-HxCDD	3.08	ND	ND	255.502	200	
1,2,3,6,7,8-HxCDD	1.22	ND	ND	338.597	200	
1,2,3,7,8,9,-HxCDD	2.84	<DL	ND	227.108	200	
1,2,3,4,6,7,8-HpCDD	2.31	<DL	<DL	285.87	200	
OCDD	6.7	8.047	<DL	597.925	400	

* Method Detection Limit from Shoven (2001)
ND = Non Detects
M/z = Ion Ratio outside QA limits (EPA 1613B)
RD1TB = Rumford Downstream 2001 Trip Blank
RU1TB = Rumford Upstream 2001 Trip Blank
PAR01 = Precision and Recovery Standard Matrix Spike

Table 3.13. Percent Surrogate Recoveries for the 2001 Rumford Quality Control Samples (Bold indicates values not within QC limits)

C^{13} LABELLED SURROGATE	SAMPLE NUMBER			
	RU1TB	RD1TB	PAR01	Q.A. LIMITS
2,3,7,8-TCDF	100	102	69	24-169
1,2,3,7,8-PeCDF	67	78	63	24-185
2,3,4,7,8-PeCDF	70	70	61	21-178
1,2,3,4,7,8-HxCDF	94	103	75	26-152
1,2,3,6,7,8-HxCDF	95	111	73	26-123
2,3,4,6,7,8-HxCDF	101	125	73	29-147
1,2,3,7,8,9-HxCDF	98	**137**	76	28-136
1,2,3,4,6,7,8-HpCDF	110	127	74	28-143
1,2,3,4,7,8,9-HpCDF	109	134	75	26-138
2,3,7,8-TCDD	61	61	50	25-164
1,2,3,7,8-PeCDD	95	89	53	25-181
1,2,3,4,7,8-HxCDD	52	41	83	32-141
1,2,3,6,7,8-HxCDD	64	68	58	28-130
1,2,3,4,6,7,8-HpCDD	104	118	59	23-140
OCDD	38	99	53	17-157

3.2. The 2001 Jay Deployment on the Androscoggin River

The sample names are acronyms using the same identification system. With the exception of 2,3,7,8-TCDF, all the congeners concentrations were below the calibration of the instrument which was 0.222 pg-dioxin/g-SPMD for tetra-, 1.111 pg/g for penta- through hepta-, and 2.222 pg/g for octa-chlorinated congeners. No method detection limit study was completed for the analytical procedure used in this deployment. Therefore, the data are not quality assured and cannot be reported for compliance with the upstream/downstream test as presented in this thesis.

The percent surrogate recoveries for the downstream site (Table 3.17.) are within the quality assurance limits. However, for the upstream location (Table 3.20.), three samples (JU1D2, JU1D3, and JU1D8) are less than the required limits for percent surrogate recoveries for numerous congeners. For JU1D2 and JU1D3, approximately half of each sample was spilled during the GPC clean up step leading to the recovery problems. The surrogate issues for JU1D8 were caused by not having enough carrier solvent in the reservoir of the GPC, so the last compounds to elute (lower molecular masses) were lost at the end of the last sample run. The TEQ values were calculated using only concentrations greater than the calibration lower limit. Therefore, the two reportable mean concentrations in the sample set are 2,3,7,8-TCDF and the TEQ value. None of the quality control samples were analyzed from this exposure.

The statistical analysis of the Jay deployment required some manipulation. JU1D2 and JU1D3 were greater than two standard deviations from the mean, so those samples were considered outliers and were not used in the basic statistics for the upstream location. Also, the problems with surrogate recoveries made those data even less reliable.

The coefficient of variation varied from 6% to 56% for all congeners. The coefficient of variation for TCDF was 10% and 6% for the downstream and upstream locations, respectively. The TEQ values showed the same variation. The samples did not fit a normal distribution. There was a significant difference using the Mann-Whitney U test (95% confidence) with the TCDF and TEQ mean concentrations greater at the upstream site.

Table 3.14. Water Quality Data from the 2001 Jay Deployment

PARAMETER	DOWNSTREAM	UPSTREAM
DOC 9/22	5.26 mg/l	3.82 mg/l
TOC 9/22	5.39 mg/l	4.19 mg/l
Specific Conductivity 9/22	76.94 $\mu s/cm^2$	45.03 $\mu s/cm^2$
Flow Velocity 9/22	0.23 m/s	0.24 m/s
DOC 10/20	7.74 mg/l	5.93 mg/l
TOC 10/20	7.83 mg/l	6.39 mg/l
Specific Conductivity 10/20	134.6 $\mu s/cm^2$	95.22 $\mu s/cm^2$
Flow Velocity 10/20	0.20 m/s	0.43 m/s
Average Temperature	15.61 °C	15.16 °C
Average DOC	6.5 mg/l	4.88 mg/l
Average TOC	6.61 mg/l	5.29 mg/l
Depth	5.21 m	4.85 m

Table 3.15. SPMD Concentrations (pg/g) for JD1D1 through JD1D6

CONGENER	JD1D1	JD1D2	JD1D3	JD1D4	JD1D5	JD1D6	DATA FLAGS
2,3,7,8-TCDF	0.759	0.711	0.781	0.770	0.640	0.656	
1,2,3,7,8-PeCDF	0.547	0.350	0.312	0.324	0.265	0.264	
2,3,4,7,8-PeCDF	0.519	0.304	0.293	0.359	0.297	0.262	
1,2,3,4,7,8-HxCDF	0.450	0.287	0.241	0.263	0.263	0.231	
1,2,3,6,7,8-HxCDF	0.276	0.170	0.152	0.125	0.119	0.160	
2,3,4,6,7,8-HxCDF	0.253	0.104	0.144	0.134	0.088	0.118	
1,2,3,7,8,9-HxCDF	0.255	0.091	0.104	0.117	0.088	0.101	
1,2,3,4,6,7,8-HpCDF	0.301	0.293	0.317 ^	0.255	0.229 ^	0.241	^ M/z
1,2,3,4,7,8,9-HpCDF	0.232	0.157 ^	0.103	0.114	0.060	0.128	^ M/z
OCDF	0.405	0.371	0.344	0.333	0.287	0.368	
2,3,7,8-TCDD	0.213	0.174	0.116	0.093	0.083	0.086 ^	^ M/z
1,2,3,7,8-PeCDD	0.351	0.158	0.142	0.115	0.101	0.148 ^	^ M/z
1,2,3,4,7,8-HxCDD	0.193	0.096	0.100 ^	0.097 ^	0.101	0.087	^ M/z
1,2,3,6,7,8-HxCDD	0.890	0.499	0.482	0.731 ^	0.535	0.723	^ M/z
1,2,3,7,8,9,-HxCDD	0.354	0.198	0.154 ^	0.157	0.152	0.156 ^	^ M/z
1,2,3,4,6,7,8-HpCDD	0.453	0.461	0.503	0.415	0.386	0.368	
OCDD	1.786	1.503	1.602	1.471	1.175	1.137	
TEQ	**0.076**	**0.071**	**0.078**	**0.077**	**0.064**	**0.066**	

ND = Non Detects
M/z = Ion Ratio outside QA limits (EPA 1613B)

Table 3.16. SPMD Concentrations (pg/g) for JD1D7, JD1D8, Mean, Standard Deviation (S.D.), and Coefficient of Variation (C.V.) for all 2001 Jay Downstream Samples

CONGENER	JD1D7	JD1D8	DATA FLAGS	MEAN	S.D.	C.V.
2,3,7,8-TCDF	0.612	0.613		0.693	0.071	10.279
1,2,3,7,8-PeCDF	0.258	0.201		0.315	0.105	33.171
2,3,4,7,8-PeCDF	0.262	0.266		0.320	0.086	26.985
1,2,3,4,7,8-HxCDF	0.221	0.223 ^	^ M/z	0.272	0.075	27.654
1,2,3,6,7,8-HxCDF	0.100	0.082		0.148	0.060	40.426
2,3,4,6,7,8-HxCDF	0.061	0.055 ^	^ M/z	0.120	0.063	52.348
1,2,3,7,8,9-HxCDF	0.074	0.052		0.110	0.062	56.013
1,2,3,4,6,7,8-HpCDF	0.188	0.165		0.249	0.054	21.787
1,2,3,4,7,8,9-HpCDF	0.060	0.068		0.115	0.059	50.833
OCDF	0.304	0.228		0.330	0.056	16.943
2,3,7,8-TCDD	0.086	0.102 ^	^ M/z	0.119	0.048	40.519
1,2,3,7,8-PeCDD	0.100	0.097		0.152	0.084	55.478
1,2,3,4,7,8-HxCDD	0.0745	0.082		0.104	0.037	35.862
1,2,3,6,7,8-HxCDD	0.483	0.541		0.611	0.152	24.844
1,2,3,7,8,9,-HxCDD	0.131	0.099		0.175	0.077	44.198
1,2,3,4,6,7,8-HpCDD	0.343	0.303		0.404	0.067	16.502
OCDD	1.211	0.975		1.358	0.274	20.215
TEQ	**0.061**	**0.061**		**0.069**	**0.007**	**10.279**

ND = Non Detects

M/z = Ion Ratio outside QA limits (EPA 1613B)

Table 3.17. Percent Surrogate Recoveries for the 2001 Jay Downstream Samples

C^{13} LABELLED SURROGATE	SAMPLE IDENTIFICATION								
	JD1D1	JD1D2	JD1D3	JD1D4	JD1D5	JD1D6	JD1D7	JD1D8	Q.A. LIMITS
2,3,7,8-TCDF	50	35	48	46	50	54	57	51	24-169
1,2,3,7,8-PeCDF	43	30	38	46	42	46	54	55	24-185
2,3,4,7,8-PeCDF	39	27	35	45	43	41	50	52	21-178
1,2,3,4,7,8-HxCDF	56	45	50	64	62	60	61	70	26-152
1,2,3,6,7,8-HxCDF	56	46	50	61	58	56	58	68	26-123
2,3,4,6,7,8-HxCDF	54	41	48	55	53	52	49	60	29-147
1,2,3,7,8,9-HxCDF	59	51	58	68	61	61	66	72	28-136
1,2,3,4,6,7,8-HpCDF	61	73	46	66	59	63	70	73	28-143
1,2,3,4,7,8,9-HpCDF	60	83	56	64	57	62	69	68	26-138
2,3,7,8-TCDD	51	36	48	45	47	53	56	50	25-164
1,2,3,7,8-PeCDD	35	24	32	42	42	39	49	49	25-181
1,2,3,4,7,8-HxCDD	57	46	56	56	52	59	64	59	32-141
1,2,3,6,7,8-HxCDD	57	46	57	60	51	65	61	64	28-130
1,2,3,4,6,7,8-HpCDD	39	59	41	55	50	57	41	60	23-140
OCDD	49	72	48	58	50	61	52	59	17-157

Table 3.18. SPMD Concentrations (pg/g) for JU1D1 through JU1D6

CONGENER	JU1D1	JU1D2	JU1D3	JU1D4	JU1D5	JU1D6	DATA FLAGS
2,3,7,8-TCDF	2.319	2.374 *	2.849 *	2.522	2.238	2.124	* S.R.
1,2,3,7,8-PeCDF	0.606	0.999 *	0.941 *	0.683	0.709	0.610	* S.R.
2,3,4,7,8-PeCDF	0.772	1.120 *	1.027 *	0.847	0.739	0.732	* S.R.
1,2,3,4,7,8-HxCDF	0.399	0.838 *	0.548 *	0.459	0.376	0.384	* S.R.
1,2,3,6,7,8-HxCDF	0.145	0.469	0.182 *	0.144	0.156	0.101	* S.R.
2,3,4,6,7,8-HxCDF	0.126	0.373	0.225 *	0.146	0.125	0.094	* S.R.
1,2,3,7,8,9-HxCDF	0.057	0.390	0.128 *	0.043	0.071	0.048	* S.R.
1,2,3,4,6,7,8-HpCDF	0.273	0.819 ^	0.363 #	0.262 ^	0.230	0.184	^ M/z; # M/z, S.R.
1,2,3,4,7,8,9-HpCDF	0.080	0.422	0.175 *	0.107	0.134	0.058	* S.R.
OCDF	0.206	0.887	0.358 *	0.256	0.271	0.186	* S.R
2,3,7,8-TCDD	0.115 ^	0.238 *	0.158 *	0.141 ^	0.095	0.127	^ M/z; * S.R.
1,2,3,7,8-PeCDD	0.098	0.447 *	0.186 *	0.079	0.135 ^	0.069	^ M/z; * S.R.
1,2,3,4,7,8-HxCDD	0.076	0.368	0.103 *	0.061	0.109	0.076	* S.R.
1,2,3,6,7,8-HxCDD	0.626	1.058	0.321 #	0.655	0.655	0.472	# M/z, S.R.
1,2,3,7,8,9,-HxCDD	0.137 ^	0.561	0.310 *	0.190	0.270	0.172	^ M/z; * S.R.
1,2,3,4,6,7,8-HpCDD	0.603	0.921 *	0.687 *	0.582	0.553	0.555	* S.R.
OCDD	1.444	2.205	1.754 *	1.528	1.253	1.305	
TEQ	**0.232**	**0.237**	**0.285**	**0.252**	**0.224**	**0.212**	

ND = Non Detects
M/z = Ion Ratio outside QA limits (EPA 1613B)
S.R. = Surrogate Recoveries outside QA limits (EPA 1613B)
JU1D2 and JU1D5 were deployed for 37 days
Calibration lower limit = 0.222 pg/g for tetra-, 1.111 pg/g for penta- through hepta-, and 2.222 pg/g for octa-chlorinated

Table 3.19. SPMD Concentrations (pg/g) for JU1D1, JU1D6, Mean, Standard Deviation (S.D.), and Coefficient of Variation (C.V.) for all 2001 Jay Upstream Samples (Statistics do not include JU1D2 and JU1D3)

CONGENER	JU1D7	JU1D8	DATA FLAGS	MEAN	S.D.	C.V.
2,3,7,8-TCDF	2.228	2.187 *	* S.R.	2.270	0.139	6.134
1,2,3,7,8-PeCDF	0.675	0.683 *	* S.R.	0.661	0.043	6.452
2,3,4,7,8-PeCDF	0.860	0.724		0.779	0.060	7.717
1,2,3,4,7,8-HxCDF	0.455	0.398		0.412	0.036	8.757
1,2,3,6,7,8-HxCDF	0.130	0.146		0.137	0.019	14.229
2,3,4,6,7,8-HxCDF	0.097	0.088		0.113	0.023	20.408
1,2,3,7,8,9-HxCDF	0.045	0.043		0.051	0.011	21.566
1,2,3,4,6,7,8-HpCDF	0.399 ^	0.240	^ M/z	0.265	0.073	27.475
1,2,3,4,7,8,9-HpCDF	0.103	0.066 ^	^ M/z	0.091	0.029	31.289
OCDF	0.255	0.207		0.230	0.035	15.079
2,3,7,8-TCDD	0.131 ^	0.190 *	* S.R., ^ M/z	0.133	0.032	24.032
1,2,3,7,8-PeCDD	0.113 ^	0.074 ^	^ M/z	0.095	0.026	27.160
1,2,3,4,7,8-HxCDD	0.105	0.071 ^	^ M/z	0.083	0.019	23.380
1,2,3,6,7,8-HxCDD	0.853	0.547		0.635	0.129	20.266
1,2,3,7,8,9,-HxCDD	0.200	0.165		0.189	0.045	23.958
1,2,3,4,6,7,8-HpCDD	0.658	0.522		0.579	0.048	8.223
OCDD	1.446	1.275		1.375	0.112	8.162
TEQ	**0.223**	**0.219**		**0.227**	**0.014**	**6.134**

ND = Non Detects
M/z = Ion Ratio outside QA limits (EPA 1613B)
S.R. = Surrogate Recoveries outside QA limits (EPA 1613B)
JU1D7 and JU1D8 were deployed for 37 days
Calibration lower limit = 0.222 pg/g for tetra-, 1.111 pg/g for penta- through hepta-, and 2.222 pg/g for octa-chlorinated

Table 3.20. Percent Surrogate Recoveries for the 2001 Jay Upstream Samples (Bold indicates values not within QC limits)

C^{13} LABELLED SURROGATE	SAMPLE IDENTIFICATION								
	JU1D1	JU1D2	JU1D3	JU1D4	JU1D5	JU1D6	JU1D7	JU1D8	Q.A. LIMITS
2,3,7,8-TCDF	49	**11**	**13**	39	37	39	57	**11**	24-169
1,2,3,7,8-PeCDF	41	**15**	**14**	36	35	30	39	**22**	24-185
2,3,4,7,8-PeCDF	38	**19**	**16**	40	38	29	44	31	21-178
1,2,3,4,7,8-HxCDF	44	29	**20**	51	57	62	74	47	26-152
1,2,3,6,7,8-HxCDF	55	29	**20**	51	51	53	72	46	26-123
2,3,4,6,7,8-HxCDF	49	**28**	**17**	45	50	49	66	45	29-147
1,2,3,7,8,9-HxCDF	60	33	**21**	57	60	64	83	57	28-136
1,2,3,4,6,7,8-HpCDF	61	32	**21**	57	58	66	80	57	28-143
1,2,3,4,7,8,9-HpCDF	60	33	**19**	54	56	63	78	59	26-138
2,3,7,8-TCDD	48	**10**	**14**	38	38	39	57	**11**	25-164
1,2,3,7,8-PeCDD	35	**17**	**15**	39	34	25	37	29	25-181
1,2,3,4,7,8-HxCDD	54	**29**	**17**	46	47	55	71	47	32-141
1,2,3,6,7,8-HxCDD	52	28	**19**	49	49	59	63	44	28-130
1,2,3,4,6,7,8-HpCDD	49	27	**18**	47	46	42	53	46	23-140
OCDD	55	31	**18**	52	49	50	67	56	17-157

3.3. 2002 Method Detection Limit Study

The actual concentration in the matrix determined by the standard is in the second column (headed by [PAR]). Comparing the actual concentration with the mean values for samples one through seven, exhibits acceptable precision. There are many M/z ion ratio data flags. However, this is common for method detection limit studies since the 'true' concentrations are as close to the background noise as possible. The MDL values seen in the last column of Table 3.23., are derived by multiplying the standard deviation by the t-statistic for a sample size of seven. All surrogate recoveries were within quality assurance limits though barely with some of the heavier congeners.

Table 3.21. SPMD Concentrations (pg/g) for the 2002 Method Detection Limit Study Samples

CONGENER	[PAR]	MDL 1	MDL 2	MDL 3	MDL 4	MDL 5	DATA FLAGS
2,3,7,8-TCDF	0.056	0.137 ^	0.149	ND	0.167	0.146	^ M/z
1,2,3,7,8-PeCDF	0.278	0.352	0.268	ND	0.345	0.381	
2,3,4,7,8-PeCDF	0.278	0.305	0.324	0.303	0.327	0.316 ^	^ M/z
1,2,3,4,7,8-HxCDF	0.278	0.352	0.330	0.229 ^	0.334 ^	0.361	^ M/z
1,2,3,6,7,8-HxCDF	0.278	0.292 ^	0.257 ^	ND	0.295 ^	0.334 ^	^ M/z
2,3,4,6,7,8-HxCDF	0.278	0.317	0.303	0.179	0.285 ^	0.352	^ M/z
1,2,3,7,8,9-HxCDF	0.278	0.500	0.331 ^	0.285 ^	0.537 ^	0.418	^ M/z
1,2,3,4,6,7,8-HpCDF	0.278	0.388	0.358	0.405 ^	0.353	0.341 ^	^ M/z
1,2,3,4,7,8,9-HpCDF	0.278	0.349	0.332	0.504	0.373	0.330 ^	^ M/z
OCDF	0.556	0.718	0.678	ND	0.653 ^	0.987 ^	^ M/z
2,3,7,8-TCDD	0.056	0.201 ^	0.163	0.117 ^	0.193	0.178 ^	^ M/z
1,2,3,7,8-PeCDD	0.278	0.349 ^	0.314 ^	0.131 ^	0.334	0.324 ^	^ M/z
1,2,3,4,7,8-HxCDD	0.278	0.292 ^	0.222	ND	0.212 ^	0.289	^ M/z
1,2,3,6,7,8-HxCDD	0.278	0.660 ^	0.198	0.168 ^	0.454	0.503	^ M/z
1,2,3,7,8,9,-HxCDD	0.278	0.657	0.229	ND	0.419 ^	0.456	^ M/z
1,2,3,4,6,7,8-HpCDD	0.278	0.412 ^	0.445 ^	ND	0.716	0.465	^ M/z
OCDD	0.556	0.821	0.831	ND	0.949	1.335	

ND = Non Detects

M/z = Ion Ratio outside QA limits (EPA 1613B)

Table 3.22. SPMD Concentrations (pg/g), Mean, Standard Deviation (S.D.), and the Method Detection Limit (MDL) for the 2002 Dioxin Samples

CONGENER	[PAR]	MDL 6	MDL 7	DATA FLAGS	MEAN	S.D.	MDL
2,3,7,8-TCDF	0.056	ND	0.141 ^	^ M/z	0.106	0.073	0.229
1,2,3,7,8-PeCDF	0.278	0.184 ^	0.347 ^	^ M/z	0.268	0.136	0.427
2,3,4,7,8-PeCDF	0.278	ND	0.382		0.280	0.126	0.396
1,2,3,4,7,8-HxCDF	0.278	ND	0.320 ^	^ M/z	0.275	0.129	0.405
1,2,3,6,7,8-HxCDF	0.278	0.425	0.318 ^	^ M/z	0.274	0.132	0.414
2,3,4,6,7,8-HxCDF	0.278	0.379	0.429		0.321	0.079	0.249
1,2,3,7,8,9-HxCDF	0.278	ND	0.516 ^	^ M/z	0.370	0.189	0.593
1,2,3,4,6,7,8-HpCDF	0.278	ND	0.507		0.336	0.158	0.497
1,2,3,4,7,8,9-HpCDF	0.278	ND	0.537 ^	^ M/z	0.346	0.174	0.547
OCDF	0.556	ND	0.557 ^	^ M/z	0.513	0.375	1.176
2,3,7,8-TCDD	0.056	ND	0.179 ^	^ M/z	0.147	0.070	0.221
1,2,3,7,8-PeCDD	0.278	0.163 ^	0.389 ^	^ M/z	0.286	0.099	0.309
1,2,3,4,7,8-HxCDD	0.278	ND	0.339		0.193	0.139	0.437
1,2,3,6,7,8-HxCDD	0.278	ND	0.358		0.334	0.226	0.711
1,2,3,7,8,9,-HxCDD	0.278	0.131 ^	0.443	^ M/z	0.334	0.224	0.705
1,2,3,4,6,7,8-HpCDD	0.278	ND	0.598 ^	^ M/z	0.377	0.277	0.871
OCDD	0.556	ND	1.088 ^	^ M/z	0.718	0.520	1.634

ND = Non Detects

M/z = Ion Ratio outside QA limits (EPA 1613B)

Table 3.23. Percent Surrogate Recoveries for the 2002 Method Detection Limit Samples

C^{13} LABELLED SURROGATE	SAMPLE IDENTIFICATION							
	MDL 1	MDL 2	MDL 3	MDL 4	MDL 5	MDL 6	MDL 7	Q.A. LIMITS
2,3,7,8-TCDF	64	67	62	65	66	65	67	24-169
1,2,3,7,8-PeCDF	57	63	41	46	57	44	46	24-185
2,3,4,7,8-PeCDF	63	69	49	54	63	55	56	21-178
1,2,3,4,7,8-HxCDF	75	68	75	82	70	68	74	26-152
1,2,3,6,7,8-HxCDF	72	73	75	67	57	79	73	26-123
2,3,4,6,7,8-HxCDF	71	69	70	71	60	69	67	29-147
1,2,3,7,8,9-HxCDF	67	64	56	54	52	56	53	28-136
1,2,3,4,6,7,8-HpCDF	62	58	38	39	44	37	37	28-143
1,2,3,4,7,8,9-HpCDF	61	57	36	34	40	38	33	26-138
2,3,7,8-TCDD	67	66	59	61	57	57	60	25-164
1,2,3,7,8-PeCDD	65	74	51	57	69	57	61	25-181
1,2,3,4,7,8-HxCDD	98	99	82	86	80	76	81	32-141
1,2,3,6,7,8-HxCDD	48	35	72	65	51	93	74	28-130
1,2,3,4,6,7,8-HpCDD	61	58	37	38	44	39	35	23-140
OCDD	49	48	18	19	28	22	19	17-157

3.4. The 2002 Rumford Deployment on the Androscoggin River

The sample acronyms follow the same code as previous years. Again, most of the congener concentrations are below the calibration of the instrument and the method detection limit. However, at both sites, the toxic tetra- and pentachlorinated dibenzofurans are greater than the detection limits and consistently passed the quality assurance criteria. The upstream site also had relatively consistent quantification for toxic hepta- and octachlorinated dibenzo-*para*-dioxins. The lower end of the calibration curve was 0.139 pg-dioxin/g-SPMD for tetra-, 0.694 pg/g for penta- through hepta-, and 1.389 pg/g for octa-chlorinated congeners. The percent surrogate recoveries (Table 3.28. and 3.31.) are within the quality assurance limits with the exception of 1,2,3,6,7,8-HxCDF in RD2D3 and OCDD in RD2D7. The TEQ values were calculated using concentrations greater than the method detection limit and at or above the lower end of the calibration curve. Therefore, the reportable mean concentrations in the sample set are 2,3,7,8-TCDF and the PeDCFs for both sites. The downstream site also included reportable means for 1,2,3,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDD, and OCDD.

The statistical analysis of the 2002 deployment was manipulated similar to the 2001 Jay data set. RD2D7 was much greater than two standard deviations from the mean, so that sample was considered an outlier and was not used in the basic statistics. Also, the congener profile of RD2D7 was markedly different than the other samples. This is a common sign of contamination during the analytical procedure. The coefficient of variation varied from 11% to 282% for all congeners. The coefficient of variation ranged from 11% to 17% for the congeners detected at both sites. The other detected congeners at the upstream site did not show the same variation with the coefficients of variation

ranging from 26% to 70% implying possible contamination. The data do not fit a normal distribution even after transformation, so non-parametric statistics were utilized. The Mann-Whitney U test determined the concentrations between the two sites were significantly different at 95% confidence for all values.

All of the appropriate quality control samples were analyzed for the 2002 Rumford deployment (Table 3.32.). With the exception of the downstream trip blank (RD1TB), all quality control samples were below the method detection limit or non-detections. RD1TB showed contamination with 2,3,7,8-TCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, and 2,3,7,8-TCDD. All of those congeners were not quantified on a consistent basis except for 2,3,7,8-TCDF, so the contamination was not a problem that affected analysis of those congeners. However, for 2,3,7,8-TCDF some of the mass abundance may come from the ambient air during the deployment, if the assumption behind trip blanks is valid. The matrix spike (PAR02) displays excellent precision.

Table 3.24. Water Quality Data from the 2002 Rumford Deployment

PARAMETER	DOWNSTREAM	UPSTREAM
DOC 8/9	6.43 mg/l	4.45 mg/l
TOC 8/9	6.54 mg/l	4.57 mg/l
Total Suspended Solids 8/9	1.4	< 1
Flow Velocity 8/9	0.42 m/s	0.25 m/s
DOC 9/6	7.17 mg/l	4.48 mg/l
TOC 9/6	7.22 mg/l	4.55 mg/l
Total Suspended Solids 9/6	1.5	1.3
Flow Rate 9/6	0.35 m/s	0.24 m/s
Average Temperature	23.32 °C	22.90 °C
Average DOC	6.80 mg/l	4.47 mg/l
Average TOC	6.88 mg/l	4.56 mg/l
Depth	4.60 m	4.97 m

Table 3.25. SPMD Concentrations (pg/g) for RD2D1 through RD2D5

CONGENER	MDL	RD2D1	RD2D2	RD2D3	RD2D4	RD2D5	DATA FLAGS
2,3,7,8-TCDF	0.229	7.029	7.175	7.097	6.735	8.298	
1,2,3,7,8-PeCDF	0.427	0.637	0.550	0.639	0.851 ^	0.796	^ M/z
2,3,4,7,8-PeCDF	0.396	1.217	0.892	1.182	1.074	1.461	
1,2,3,4,7,8-HxCDF	0.405	< DL	< DL	0.470 ^	< DL	0.540	^ M/z
1,2,3,6,7,8-HxCDF	0.414	< DL	ND	< DL	< DL	< DL	
2,3,4,6,7,8-HxCDF	0.249	< DL	< DL	< DL	< DL	ND	
1,2,3,7,8,9-HxCDF	0.593	< DL	< DL	< DL	< DL	< DL	
1,2,3,4,6,7,8-HpCDF	0.497	< DL	< DL	< DL	< DL	< DL	
1,2,3,4,7,8,9-HpCDF	0.547	< DL	< DL	ND	< DL	< DL	
OCDF	1.176	ND	< DL	0.293	0.580	ND	
2,3,7,8-TCDD	0.221	0.287	< DL	< DL	ND	< DL	
1,2,3,7,8-PeCDD	0.309	< DL	ND	ND	< DL	< DL	
1,2,3,4,7,8-HxCDD	0.437	< DL	ND	< DL	< DL	0.447	
1,2,3,6,7,8-HxCDD	0.711	< DL	ND	ND	< DL	< DL	
1,2,3,7,8,9,-HxCDD	0.705	ND	ND	ND	ND	< DL	
1,2,3,4,6,7,8-HpCDD	0.871	< DL	< DL	< DL	< DL	< DL	
OCDD	1.634	< DL	< DL	< DL	< DL	< DL	
TEQ		**1.630**	**1.164**	**1.333**	**1.253**	**1.600**	

ND = Non Detects

M/z = Ion Ratio outside QA limits (EPA 1613B)

Calibration lower limit = 0.139 pg/g for tetra-, 0.694 pg/g for penta- through hepta-, and 1.389 pg/g for octachlorinated congeners

Table 3.26. SPMD Concentrations (pg/g) for RD2D6, RD2D7, RD2D8, Mean, Standard Deviation (S.D.), and Coefficient of Variation (C.V.) for all 2002 Rumford Downstream Samples (Statistics do not include RD2D7)

CONGENER	MDL	RD2D6	RD2D7	RD2D8	DATA FLAGS	MEAN	S.D.	C.V.
2,3,7,8-TCDF	0.229	6.544	2.165 ^	5.624	^ M/z	6.929	0.802	11.579
1,2,3,7,8-PeCDF	0.427	0.710	ND	0.624		0.687	0.106	15.371
2,3,4,7,8-PeCDF	0.396	1.094	0.783	0.924		1.121	0.193	17.194
1,2,3,4,7,8-HxCDF	0.405	< DL	3.647 ^	< DL	^ M/z	0.077	0.204	264.575
1,2,3,6,7,8-HxCDF	0.414	< DL	3.148 ^	< DL	^ M/z	0	0	0
2,3,4,6,7,8-HxCDF	0.249	< DL	ND	< DL		0	0	0
1,2,3,7,8,9-HxCDF	0.593	< DL	ND	< DL		0	0	0
1,2,3,4,6,7,8-HpCDF	0.497	< DL	13.508	< DL		0	0	0
1,2,3,4,7,8,9-HpCDF	0.547	< DL	16.704	< DL		0	0	0
OCDF	1.176	< DL	10.815 ^	< DL	^ M/z	0	0	0
2,3,7,8-TCDD	0.221	< DL	< DL	< DL		0.048	0.117	244.949
1,2,3,7,8-PeCDD	0.309	< DL	ND	< DL		0	0	0
1,2,3,4,7,8-HxCDD	0.437	< DL	ND	< DL		0.075	0.182	244.949
1,2,3,6,7,8-HxCDD	0.711	< DL	ND	< DL		0	0	0
1,2,3,7,8,9,-HxCDD	0.705	< DL	ND	< DL		0	0	0
1,2,3,4,6,7,8-HpCDD	0.871	< DL	17.922	< DL		0	0	0
OCDD	1.634	< DL	16.312 *	< DL	* S.R.	0	0	0
TEQ		**1.268**	**1.772**	**1.0556**		1.325	0.216	16.324

ND = Non Detects
M/z = Ion Ratio outside QA limits (EPA 1613B)
S.R. = Surrogate Recovery outside QA limits (EPA 1613B)
Calibration lower limit = 0.139 pg/g for tetra-, 0.694 pg/g for penta- through hepta-, and 1.389 pg/g for octachlorinated congeners

Table 3.27. Percent Surrogate Recoveries for the 2002 Rumford Downstream Samples (Bold indicates values not within QC limits)

C^{13} LABELLED SURROGATE	SAMPLE IDENTIFICATION								
	RD2D1	RD2D2	RD2D3	RD2D4	RD2D5	RD2D6	RD2D7	RD2D8	Q.A. LIMITS
2,3,7,8-TCDF	77	71	88	68	73	66	65	75	24-169
1,2,3,7,8-PeCDF	63	62	77	74	67	75	32	87	24-185
2,3,4,7,8-PeCDF	66	65	82	75	70	75	47	85	21-178
1,2,3,4,7,8-HxCDF	118	106	116	100	94	89	74	97	26-152
1,2,3,6,7,8-HxCDF	106	106	**127**	110	116	85	114	101	26-123
2,3,4,6,7,8-HxCDF	106	98	113	95	100	83	87	93	29-147
1,2,3,7,8,9-HxCDF	89	89	107	80	92	82	78	86	28-136
1,2,3,4,6,7,8-HpCDF	70	74	88	85	79	81	99	87	28-143
1,2,3,4,7,8,9-HpCDF	66	73	86	65	75	74	123	75	26-138
2,3,7,8-TCDD	79	73	89	80	78	80	71	88	25-164
1,2,3,7,8-PeCDD	62	59	ND	77	63	77	32	88	25-181
1,2,3,4,7,8-HxCDD	97	107	56	81	48	78	111	85	32-141
1,2,3,6,7,8-HxCDD	80	105	ND	96	110	74	109	88	28-130
1,2,3,4,6,7,8-HpCDD	54	62	72	72	65	73	113	77	23-140
OCDD	30	46	54	43	48	59	**181**	52	17-157

Table 3.28. SPMD Concentrations (pg/g) for RU2D1 through RU2D5

CONGENER	MDL	RU2D1	RU2D2	RU2D3	RU2D4	RU2D5	DATA FLAGS
2,3,7,8-TCDF	0.229	8.412	9.302	9.701	10.622	13.408	
1,2,3,7,8-PeCDF	0.427	1.358	1.327	1.300	1.200	1.001 ^	^ M/z
2,3,4,7,8-PeCDF	0.396	2.007	2.175	2.047	2.222	3.262	
1,2,3,4,7,8-HxCDF	0.405	0.911	0.689	0.678	0.905	1.285	
1,2,3,6,7,8-HxCDF	0.414	< DL	< DL	< DL	< DL	0.428	
2,3,4,6,7,8-HxCDF	0.249	0.306 ^	0.253	< DL	0.291	0.596 ^	^ M/z
1,2,3,7,8,9-HxCDF	0.593	< DL	< DL	< DL	< DL	0.978	
1,2,3,4,6,7,8-HpCDF	0.497	0.700	< DL	< DL	0.524	1.902	
1,2,3,4,7,8,9-HpCDF	0.547	< DL	< DL	< DL	< DL	1.755	
OCDF	1.176	< DL	< DL	< DL	< DL	1.775	
2,3,7,8-TCDD	0.221	0.267	< DL	< DL	< DL	0.389 ^	^ M/z
1,2,3,7,8-PeCDD	0.309	< DL	< DL	ND	< DL	< DL	
1,2,3,4,7,8-HxCDD	0.437	< DL	< DL	< DL	< DL	< DL	
1,2,3,6,7,8-HxCDD	0.711	< DL	< DL	< DL	< DL	< DL	
1,2,3,7,8,9,-HxCDD	0.705	< DL	< DL	< DL	< DL	< DL	
1,2,3,4,6,7,8-HpCDD	0.871	1.222	< DL	< DL	0.913	2.817	
OCDD	1.634	1.902	1.557	1.672	2.024	5.522 ^	^ M/z
TEQ		**2.313**	**2.160**	**2.133**	**2.333**	**3.703**	

ND = Non Detects
M/z = Ion Ratio outside QA limits (EPA 1613B)
Calibration lower limit = 0.139 pg/g for tetra-, 0.694 pg/g for penta- through hepta-, and 1.389 pg/g for octachlorinated congeners

Table 3.29. SPMD Concentrations (pg/g) for RU2D6, RU2D7, RU2D8, Mean, Standard Deviation (S.D.), and Coefficient of Variation (C.V.) for all 2002 Rumford Upstream Samples

CONGENER	MDL	RU2D6	RU2D7	RU2D8	DATA FLAGS	MEAN	S.D.	C.V.
2,3,7,8-TCDF	0.229	11.086	9.585	12.906		10.628	1.762	16.584
1,2,3,7,8-PeCDF	0.427	1.543	1.394	1.721		1.356	0.215	15.871
2,3,4,7,8-PeCDF	0.396	2.464	2.308	2.830		2.414	0.431	17.851
1,2,3,4,7,8-HxCDF	0.405	0.825	0.763	1.268		0.916	0.239	26.113
1,2,3,6,7,8-HxCDF	0.414	< DL	< DL	0.506		0.149	0.217	145.099
2,3,4,6,7,8-HxCDF	0.249	0.287	0.288	0.544		0.321	0.184	57.315
1,2,3,7,8,9-HxCDF	0.593	< DL	< DL	1.410 ^	^ M/z	0.299	0.565	189.161
1,2,3,4,6,7,8-HpCDF	0.497	< DL	< DL	1.989		0.639	0.851	133.079
1,2,3,4,7,8,9-HpCDF	0.547	< DL	< DL	1.793		0.499	0.802	160.763
OCDF	1.176	< DL	< DL	1.930		0.463	0.859	185.380
2,3,7,8-TCDD	0.221	< DL	< DL	0.711		0.171	0.266	155.552
1,2,3,7,8-PeCDD	0.309	< DL	< DL	< DL		0	0	0
1,2,3,4,7,8-HxCDD	0.437	< DL	< DL	< DL		0	0	0
1,2,3,6,7,8-HxCDD	0.711	< DL	< DL	< DL		0	0	0
1,2,3,7,8,9,-HxCDD	0.705	< DL	< DL	0.850		0.106	0.301	282.843
1,2,3,4,6,7,8-HpCDD	0.871	< DL	< DL	2.879		1.344	0.944	70.232
OCDD	1.634	< DL	1.876	3.719		2.089	1.829	87.561
TEQ		**2.507**	**2.267**	**3.923**		2.667	0.718	26.932

ND = Non Detects

M/z = Ion Ratio outside QA limits (EPA 1613B)

Calibration lower limit = 0.139 pg/g for tetra-, 0.694 pg/g for penta- through hepta-, and 1.389 pg/g for octachlorinated congeners

Table 3.30. Percent Surrogate Recoveries for the 2002 Rumford Upstream Samples (Bold indicates values not within QC limits)

C^{13} LABELLED SURROGATE	SAMPLE IDENTIFICATION								
	RU2D1	RU2D2	RU2D3	RU2D4	RU2D5	RU2D6	RU2D7	RU2D8	Q.A. LIMITS
2,3,7,8-TCDF	82	84	76	96	63	65	74	73	24-169
1,2,3,7,8-PeCDF	89	95	88	87	42	74	82	59	24-185
2,3,4,7,8-PeCDF	92	98	91	89	46	75	84	63	21-178
1,2,3,4,7,8-HxCDF	99	101	102	135	106	85	100	99	26-152
1,2,3,6,7,8-HxCDF	105	102	108	**135**	108	89	99	102	26-123
2,3,4,6,7,8-HxCDF	96	96	99	128	96	81	93	96	29-147
1,2,3,7,8,9-HxCDF	91	94	86	118	83	71	90	86	28-136
1,2,3,4,6,7,8-HpCDF	100	100	75	99	56	74	89	71	28-143
1,2,3,4,7,8,9-HpCDF	88	94	58	96	55	60	81	68	26-138
2,3,7,8-TCDD	97	100	89	102	70	80	92	78	25-164
1,2,3,7,8-PeCDD	92	101	92	81	62	80	86	57	25-181
1,2,3,4,7,8-HxCDD	83	93	83	135	88	76	93	90	32-141
1,2,3,6,7,8-HxCDD	101	95	98	**132**	82	84	82	73	28-130
1,2,3,4,6,7,8-HpCDD	89	94	64	79	45	67	81	58	23-140
OCDD	67	77	39	59	30	45	66	42	17-157

Table 3.31. SPMD Concentrations (pg/g) for 2002 Quality Control Samples (Bold indicates problematic detections)

CONGENER	MDL	RU2TB	RD2TB	PB2002	DB2002	PAR02	[PAR]	DATA FLAGS
2,3,7,8-TCDF	0.229	<DL	**0.475**	<DL	<DL	5.164	4.444	
1,2,3,7,8-PeCDF	0.427	ND	ND	<DL	<DL	24.682	22.222	
2,3,4,7,8-PeCDF	0.396	ND	<DL	<DL	<DL	23.061	22.222	
1,2,3,4,7,8-HxCDF	0.405	<DL	<DL	<DL	<DL	21.752	22.222	
1,2,3,6,7,8-HxCDF	0.414	<DL	<DL	<DL	<DL	23.312	22.222	
2,3,4,6,7,8-HxCDF	0.249	<DL	ND	ND	<DL	22.450	22.222	
1,2,3,7,8,9-HxCDF	0.593	<DL	**0.609**	ND	ND	21.397	22.222	
1,2,3,4,6,7,8-HpCDF	0.497	<DL	**0.599**	<DL	<DL	22.298	22.222	
1,2,3,4,7,8,9-HpCDF	0.547	<DL	**0.782** ^	ND	<DL	22.022	22.222	^ M/z
OCDF	1.176	<DL	<DL	<DL	<DL	46.343	44.444	
2,3,7,8-TCDD	0.221	<DL	**0.453** ^	<DL	<DL	3.913	4.444	^ M/z
1,2,3,7,8-PeCDD	0.309	<DL	<DL	ND	<DL	22.717	22.222	
1,2,3,4,7,8-HxCDD	0.437	ND	ND	ND	<DL	21.366	22.222	
1,2,3,6,7,8-HxCDD	0.711	ND	ND	<DL	<DL	24.409	22.222	
1,2,3,7,8,9,-HxCDD	0.705	ND	<DL	<DL	<DL	21.746	22.222	
1,2,3,4,6,7,8-HpCDD	0.871	<DL	<DL	<DL	<DL	23.056	22.222	
OCDD	1.634	ND	<DL	<DL	<DL	45.244	44.444	

ND = Non Detects
M/z = Ion Ratio outside QA limits (EPA 1613B)
RU2TB = Rumford Upstream 2002 Trip Blank
RD2TB = Rumford Downstream 2002 Trip Blank
PB2002 = Procedural Blank
DB2002 = Dialysis Blank
PAR02 = Precision and Recovery Matrix Spike 2002
[PAR] = Precision and Recovery Standard

Table 3.32. Percent Surrogate Recoveries for the 2002 Rumford Quality Control Samples

C^{13} LABELLED SURROGATE	SAMPLE NUMBER					
	RU2TB	RD2TB	PB2002	DB2002	PAR02	Q.A. LIMITS
2,3,7,8-TCDF	82	82	86	82	77	24-169
1,2,3,7,8-PeCDF	67	67	71	73	82	24-185
2,3,4,7,8-PeCDF	69	70	72	74	85	21-178
1,2,3,4,7,8-HxCDF	119	109	110	106	88	26-152
1,2,3,6,7,8-HxCDF	111	109	108	112	92	26-123
2,3,4,6,7,8-HxCDF	106	104	104	104	82	29-147
1,2,3,7,8,9-HxCDF	96	92	93	94	71	28-136
1,2,3,4,6,7,8-HpCDF	77	80	80	82	79	28-143
1,2,3,4,7,8,9-HpCDF	72	77	74	80	62	26-138
2,3,7,8-TCDD	81	80	82	82	87	25-164
1,2,3,7,8-PeCDD	64	65	68	68	88	25-181
1,2,3,4,7,8-HxCDD	114	105	118	130	81	32-141
1,2,3,6,7,8-HxCDD	72	74	61	128	89	28-130
1,2,3,4,6,7,8-HpCDD	64	65	65	70	71	23-140
OCDD	41	42	46	50	46	17-157

3.5. 2002 Permeability Reference Compound Results

The results from the PRC samples fit a normal distribution in some instances, but the Gaussian distribution could not be obtained for both the upstream and downstream sites for all statistical comparisons. Therefore a Mann-Whitney U test (95% confidence) was used to determine whether there was a statistical difference between the upstream and downstream mean concentrations. No statistical difference in mean concentrations for any of the PRCs was determined between the two sample locations. No detections were quantified in the method blank quality control samples. Quality assurance criteria were passed for all samples.

Deuterated acenaphthene (ACE-d10) was almost completely eliminated from the SPMD matrix with all concentrations below the instrument calibration and detection capabilities. The mean concentration of deuterated phenanthrene (PHE-d10) was 0.730 mg-PAH/ml-extract for the downstream site and 0.713 mg/ml for the upstream site. Therefore, the sites exhibited a 64% and 65% loss, respectively. The coefficients of variation were 8% for the downstream site and 6% for the upstream site. The mean concentration of deuterated pyrene (PYR-d10) was 0.649 mg/ml downstream and 0.496 mg/ml upstream exhibiting 68% and 75% losses respectively. The coefficients of variations were higher than the other PRCs used in this study with the downstream value at 23% and the upstream value equaling 34%. Finally, deuterated benzo(b)fluoranthene (B(b)F-d12) losses were only 17% for the downstream site and 16% for the upstream site with mean concentrations of 1.660 and 1.674 mg/ml, respectively. The coefficients of variation were 7% downstream and 6% upstream.

Table 3.33. PRC Concentrations in Extract (mg/ml) for the Downstream 2002 Rumford Deployment

PRC	SAMPLE NUMBER								MEAN	S.D.	C.V.
	1	2	3	4	5	6	7	8			
ACE-d10	B.C.	B.C.	B.C.	B.C.	N.D.	N.D.	B.C.	B.C.			
PHE-d10	0.71	0.72	0.82	0.69	0.77	0.76	0.67	0.70	0.730	0.050	6.790
PYR-d10	0.52	0.67	0.81	0.80	0.82	0.63	0.53	0.41	0.649	0.154	23.786
B(b)F-d12	1.59	1.54	1.79	1.59	1.6	1.63	1.67	1.88	1.660	0.116	6.979

B.C. = Below Calibration
N.D. = Non Detect
Surrogate Recoveries > 50%
Q-Value for all analytes > 90%
Method Blank had no detections

Table 3.34. PRC Concentrations in Extract (mg/ml) for the Upstream 2002 Rumford Deployment

PRC	SAMPLE NUMBER								MEAN	S.D.	C.V.
	1	2	3	4	5	6	7	8			
ACE-d10	N.D.	N.D.	N.D.	N.D.	N.D.	B.C.	N.D.	N.D.			
PHE-d10	0.68	0.62	0.73	0.78	0.79	0.68	0.73	0.69	0.713	0.057	7.931
PYR-d10	0.84	0.29	0.57	0.42	0.50	0.50	0.52	0.33	0.496	0.169	34.078
B(b)F-d12	1.57	1.56	1.71	1.73	1.72	1.87	1.63	1.6	1.674	0.104	6.233

B.C. = Below Calibration
N.D. = Non Detect
Surrogate Recoveries > 50%
Q-Value for all analytes > 90%
Method Blank had no detections

Chapter 4

DISCUSSION

The overall goal of the project is to determine if SPMD sampling is an appropriate surrogate procedure to replace fish tissue analysis for the upstream/downstream (U/D) test in compliance with the 1997 Dioxin legislation. The results, research objectives and future directions for the SPMD project are discussed in this chapter. The objectives are:

(1) Validate or improve the SPMD research project of Shoven (2001)

(2) Determine methods to decrease the variability among samples

(3) Determine if there is a significant difference in mean concentrations between upstream and downstream locations

(4) Estimate the dioxin concentrations in the ambient water

(5) Compare the results of SPMDs with fish tissue analysis

(6) Evaluate the use of permeability reference compounds (PRCs)

  (a) Determine whether the elimination rates are significantly different at the upstream and downstream sites

  (b) Evaluate deuterated PAH performance

  (c) Calculate the elimination rate for each PRC

  (d) Calculate the Exposure Adjustment Factor (EAF)

4.1. Objective One: Validate or Improve the Previous SPMD Research Project

The initial field and analytical procedures were inherited from the work of Shoven (2001). The purchase of a new O.I. Analytical Gel Permeation Chromatography Autoprep 2000 was intended to correct some analytical problems encountered by Shoven (2001). However, the results from the first 2001 deployment revealed a need for changes in the field and analytical protocol. In the following paragraphs, these problems and alterations will be discussed.

During the deployment, vandals compromised the integrity of the sampling scheme. One set of buoys (10 samples) was punctured and sunk to the bottom of the river at the upstream site. When deploying SPMDs, the assessor wants to avoid direct contact with the sediment since the majority of historical dioxin contamination is buried in the riverbed. SPMD sampling of sediments represent historical dioxin concentrations, while water column sampling is more representative of the current dioxin discharge. In this case, the biofouling on the bottom of the buoy indicated that the buoys were recently sunk maintaining the proper positioning in the water column for most of the exposure period. Therefore, the dioxin uptake from the sediment that possibly occurred was considered to be minute. The 2001 samples that were analyzed after retrieval from the river bottom were RU1D31, RU1D32, RU1D37, RU1D38, RU1D39, and RU1D40. Since the data from the 2001 Rumford deployment has so much variation; there are no obvious signs of concentration differences between the vandalized and un-vandalized samples.

A simplified deployment scheme was implemented to make positioning SPMDs more user-friendly without sacrificing sample security. A submersed buoy scheme was incorporated during the subsequent deployments. The first attempt at a submersed buoy

scheme failed. In the 2001 Jay Deployment, empty, sealed milk jugs were used as the floatation devices. Two sets of buoys at the upstream site proved incapable of retaining positive buoyancy. A dive team was needed to search the riverbed for the lost SPMDs. JU1D2, JU1D5, JU1D7, and JU1D8 were recovered after 37 days of exposure. There is no way of determining at what point during the deployment the milk jugs lost positive buoyancy, so the integrity of those samples is purely speculative. Judging from the results, the extra exposure time did not noticeably affect the variability among samples. It's possible the water was so cold by the end of the deployment that the uptake rate was significantly lowered. Also, the biofouling may have impeded any further dioxin uptake.

The analytical procedure used for the 2001 Rumford samples proved inadequate for quantifying extremely low dioxin levels in Maine rivers. The key to accurately quantifying low levels of any contaminant is to increase the signal to noise ratio on the HRGC/HRMS chromatograms as much as possible. The lower the noise in a sample, the lower the detection limits for the analyte of interest. The results from the 2001 Rumford deployment displayed high background noise, retention time shifts, and co-eluting interference peaks (mass abundances). In many cases, the ion fragments had to be manually integrated by the analyst on a congener by congener basis. The co-eluting peaks, retention time shifts and the elevated background noise are a result of unsuccessful clean-up steps. Quantifying the pentachlorinated congeners was difficult in 2001 which later proved to be a result of the quantification parameters of the HRGC/HRMS instrument instead of the sample clean-up. The M/M+2 ions for PeCDD were used instead of M+2/M+ 4, due to a reoccurring interfering ion with the M+4 mass. The ion ratio quality assurance was changed from 1.55 to 0.62.

The surrogate recoveries from the 2001 Rumford samples were within the EPA limits, so other clean-up options were considered before analyzing the 2001 Jay samples. Florisil Solid-Phase Extraction (SPE) columns (J.T. Baker, Phillipsburg, NJ) were unsuccessfully attempted in 1999 (Shoven, 2001). Therefore, a carbon adsorbent column and an alumina column were researched as possible additions. The alumina columns are excellent at removing diphenylethers (Telliard, 1994), but are difficult to calibrate (Huckins, personal communication). Researchers at the Columbia Environmental Research Center in Missouri used a radioactive PCB to calibrate their alumina column (Lebo et al, 1995). The Environmental Chemistry Lab at the University of Maine does not currently have the capability to do radioactive work, so the alumina column was not utilized. However, the adsorbent carbon column was added for the 2001 Jay analytical procedure and provided much cleaner samples for quantification.

SPMDs are excellent at sequestering non-polar, lipophilic compounds. Therefore in the initial standard operating procedure (SOP), polychlorinated biphenyl (PCB) surrogate was spiked into the SPMD matrix in case the samples were analyzed for PCBs in conjunction with the toxic dioxin congeners. This was similar to the analytical procedure in the Dioxin Monitoring Program fish tissue analysis. However, PCBs are known interferents for dioxin analysis and a fractionation of those two compounds is necessary to accurately determine either (Molina et al, 2000). Therefore it was concluded to focus all efforts on quantifying dioxin concentrations and remove any other analytes of interest, surrogates and internal standards.

4.2. Objective Two: Decrease Variability

The need to reduce the amount of variability among samples is paramount when considering the upstream/downstream (U/D) test. Typically, the coefficient of variation for this type of analysis ranges from 20% to 50% (Telliard, 1994). With this much variation in a sample population, the investigator needs to use a large number of samples to achieve statistical significance. One of the goals of this project was to develop ways to reduce the variability among samples. There are three ways to approach variability reduction for the U/D test: (1) decrease analytical variability, (2) increase the sample size to reduce statistical variance, and (3) increase the number of SPMDs per composite to decrease the detection limit.

Reduction of variability can be achieved in the laboratory by refining the analytical procedure. By eliminating interferences and background noise on the HRGC/HRMS, the analyst will obtain more consistent values. The improvements in the standard operating procedure during 2001 are already discussed. Throughout the second year of the project, the analytical procedure continued to be refined. The Power Prep™ automated clean up system has the potential to reduce variability among samples. The Power Prep™ can reduce variability by mechanization of the clean-up steps reducing the probability of human error (i.e. spilling, heterogeneous column packing etc.). The efficiency of the Power Prep™ clean up system allows for the analyst to implement all the appropriate clean-up steps economically and easily. In previous years, adding the carbon or alumina column was difficult due to the time constraints in the laboratory.

The coefficient of variation results from the 2001 and 2002 deployments show the ability of a refined analytical procedure to reduce variability for the U/D test. In Figures

4.1 and 4.2., the majority of the variation can be explained by the detection limits of the instrument. The congeners with the greatest variation are the ones that are below the calibration of the instrument and the method detection limit. Therefore, one of the best ways for reducing variability is to collect detectable levels of dioxin or lower the detection limits of the instrument. The coefficients of variation are usually less than 20% when using SPMDs for congeners that pass quality assurance and are greater than the method detection limit.

The most costly, but effective, way of dealing with the variability is to increase the sample size. Obtaining statistical significance is much easier when the sample size is over 30 instead of 8. Most statisticians consider a sample size of over 30 a large sample size. However, collecting 30 samples at each upstream and downstream site is not within the economic feasibility of this project. The computer program PC-SIZE version 2.0 (Dallal, 1985) determined that a large sample size is not needed when the coefficient of variations are small enough (10-20%). A sample size of 5 is required for a significant difference in congener concentration using the 2002 TCDF data in the sample size computer program. The statistical parameters were set at an alpha level of 0.05 and a power of 0.9. This result depends greatly on the detectable difference needed by the monitor. The detected difference for the 2002 TCDF data was relatively large (~ 3.7 pg/g). As the concentrations between the upstream and downstream site become numerically closer (i.e. the detectable difference becomes smaller), the coefficient of variations must decrease as well. For example, if the detected difference for TCDF was 1 pg/g instead of 3.7 pg/g in 2002, the monitor would need to have 35 samples to have a

Figure 4.1. Mean Dioxin Concentration versus Coefficient of Variation for the 2002 Rumford Deployment

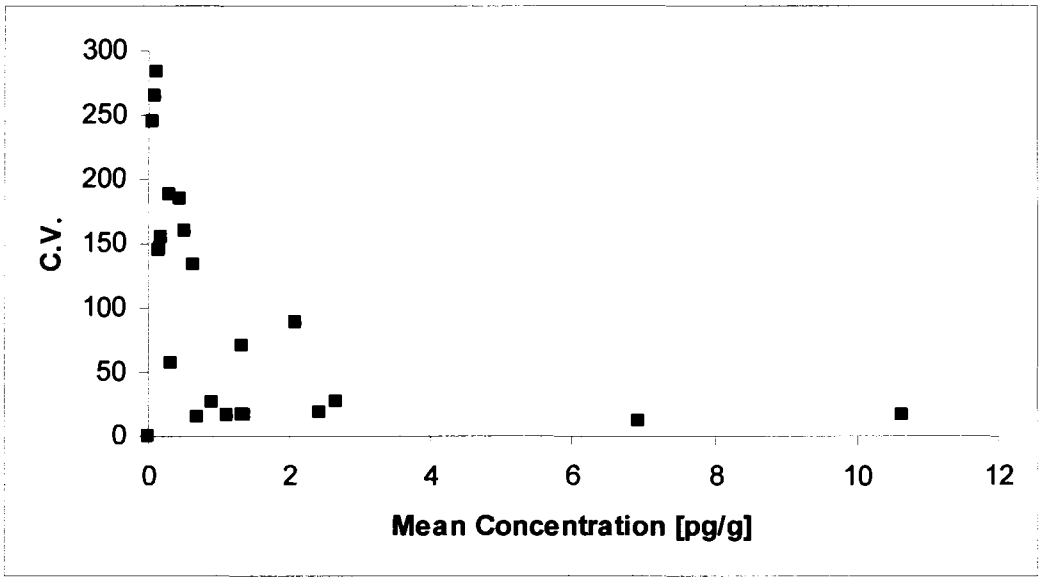
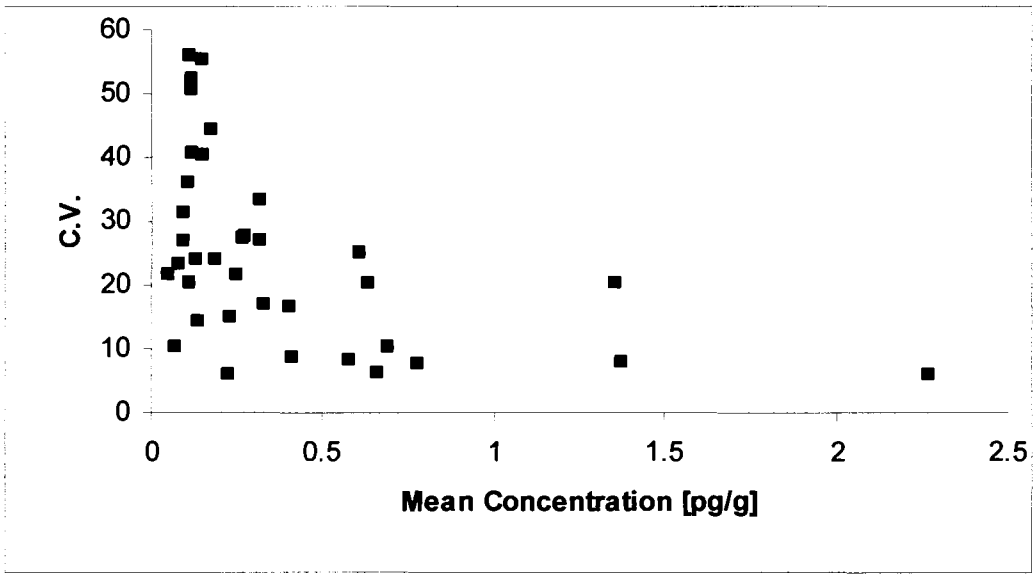


Figure 4.2. Mean Dioxin Concentration versus Coefficient of Variation for the 2001 Jay Deployment



power of 0.9 at an alpha level of 0.05. This is an example of the sample size increasing beyond the financial capacities of the monitor.

During this project, the number of SPMDs per composite sample was increased from 2 to 4 in an attempt to lower the variability by decreasing the detection limit of the sampler. The doubling of mass of SPMD per sample results in an increase in the mass of dioxin sequestered by each sample. This enables the analyst to lower detection limits by amplifying the mass abundance to background noise ratio in the mass spectrometer chromatograms. However, the greater SPMD mass increases the amount of interferents, triolein, and polyethylene waxes needing to be removed by the clean-up procedure.

4.3. Objective Three: Detecting Significant Differences for the U/D Test

The results from this study suggest that only certain congeners are greater than the detection limits for both the upstream and downstream sites. For comparisons between sites, only congeners that passed quality assurance limits can be used to determine a difference in dioxin levels. Even though there is not a method detection limit for the 2001 Jay analytical procedure, the TCDF mean concentrations were used in a comparison of upstream and downstream sites because all values greater than the lower end of the calibration curve are assumed to be more than the method detection limit. A statistical difference was obtained between the upstream and downstream sites. The opposite of what was expected was discovered. The upstream sites have higher levels than the downstream sites for both the 2001 Jay and 2002 Rumford data (Figure 4.3. and 4.4.). This means there could be a source of dioxin upstream from the mill in Rumford. This source may be the mill in Berlin, New Hampshire.

Figure 4.3. Significant Differences between the Downstream Site (blue hues) and Upstream Site (red hues) for the 2002 Rumford Deployment (Error bars are representative of the 95% confidence interval for each value)

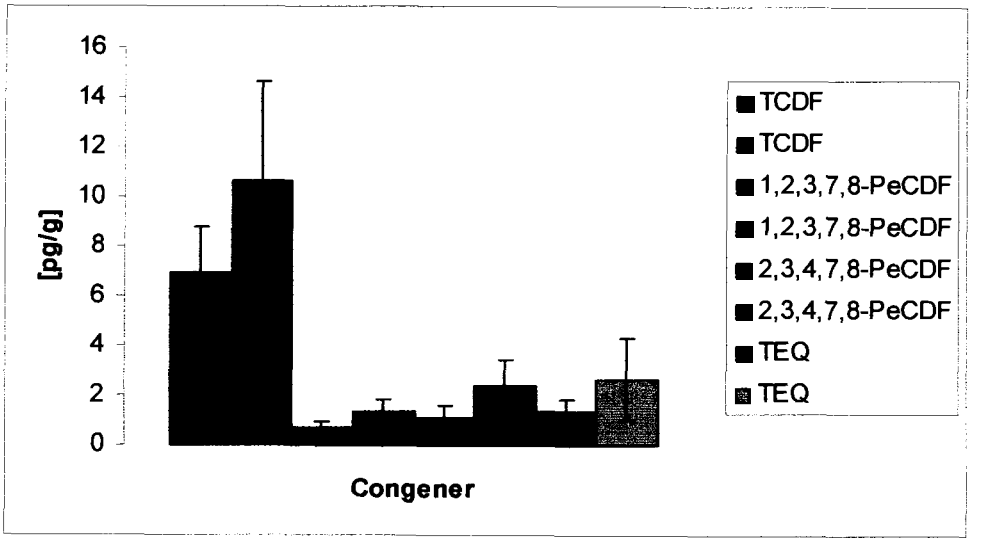
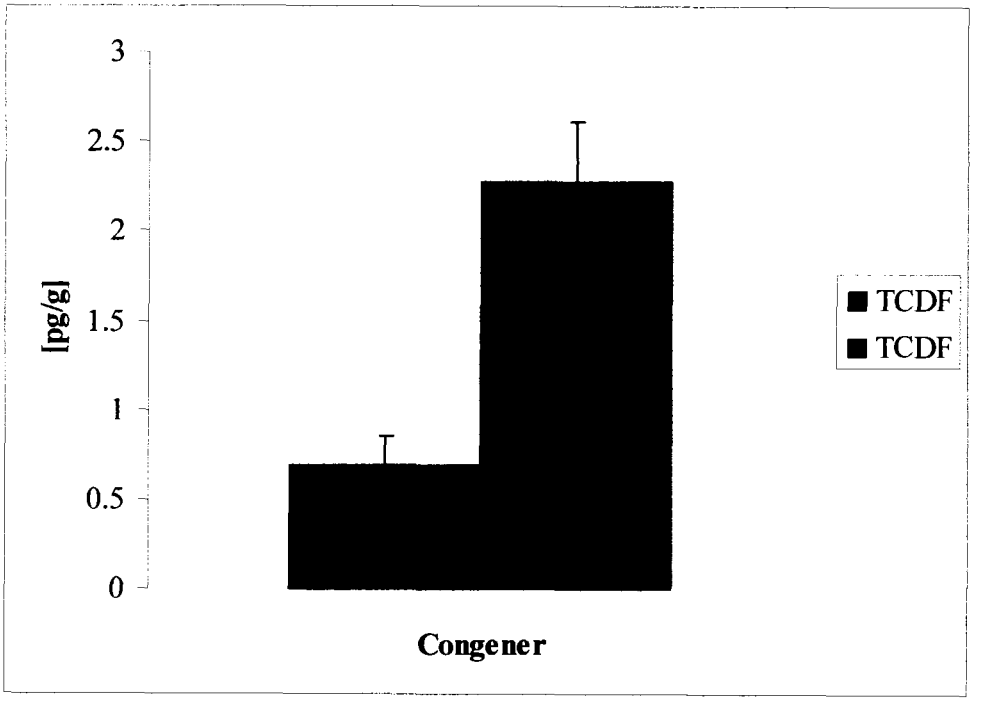
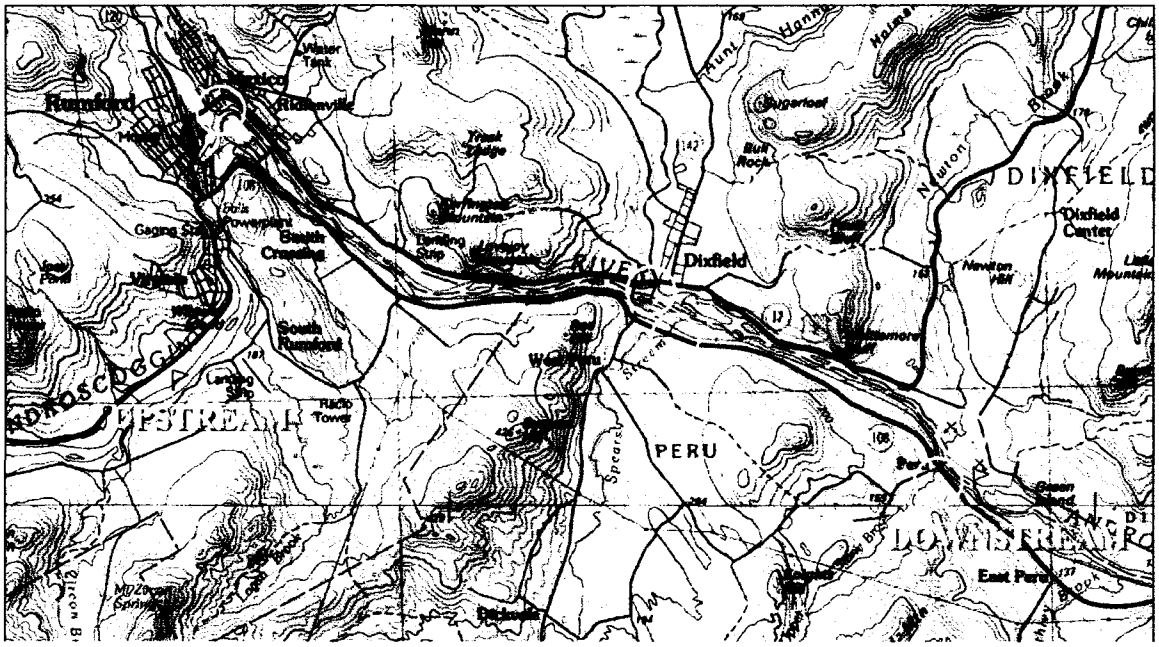


Figure 4.4. Significant Difference between the Downstream Site (blue) and Upstream Site (red) for the 2001 Jay Deployment (Error bars are representative of the 95% confidence interval)



There are at least two possible explanations for the decreasing dioxin levels in the Androscoggin River. The most obvious would be a dilution factor. Five tributaries contribute to the dilution of the Androscoggin River below the mill discharge and above the Rumford downstream sampling site; Newton Brook, Spears Stream, Upper Stone Brook, Webber River, and the Swift River (Figure 4.5.). The United States Geological Survey has stream flow gauges at Rumford and Auburn, ME. At Rumford, the average mean flow for July, 2002 was 2,355 cubic feet per second (CFS) while the average mean flow for Auburn was 3,367 CFS. Auburn is located approximately 40 miles downstream from Rumford. Therefore, some dilution must be occurring by the time the effluent reaches the downstream site which is approximately seven miles from the mill. There currently are not enough hydrological data available to accurately quantify the dilution factor.

Figure 4.5. U.S.G.S. Topographical Map of the Rumford Site with the Confluence Points of Five Tributaries Encircled



Another possible explanation for the lower concentration at the downstream site is that most of the discharged dioxin from the mill is sorbed to suspended solids and dissolved organic matter. Examining the water chemistry data from the past two years, an increase in total organic carbon and suspended solids is apparent from upstream to downstream even at the far distance of the existing site. Does the sorption of dioxin to natural organic matter interfere with the uptake of discharged dioxin being monitored by SPMDs? If this is the case, then fish tissue analysis should also show the same trend since the assumed main mechanism of dioxin uptake by fish is diffusion through the gill membranes which is mimicked by SPMD uptake.

The significant differences in dioxin levels should be viewed with caution. The statistic used was the non-parametric Mann-Whitney U test. In this case, the Mann-Whitney U test concludes that if all the values at one site are greater than the other, then the difference is significant. The standard deviation of the population is not taken into account by this statistical test. Examining the 95% confidence intervals for the 2002 Rumford deployment suggests that using a parametric test may not yield the same statistically significant result for some of the congeners. The Mann-Whitney U test is the one used by Maine's Dioxin Monitoring Program, so it was used for consistency. Parametric statistical tests such as the Student's t-test and the Analysis of Variance are more robust and powerful than non-parametric statistical tests.

The problem with the experimental design in this study is the sample sizes are small (<10). A normal distribution, which is a required assumption of parametric tests, is not obtained with a small sample size. Unfortunately, sample size is limited due to costs. This study determined that by reducing variability among samples a statistical

significance can be achieved with a relatively small sample size. However, the question of achieving the required assumptions of parametric statistical tests is much more difficult. So how many samples does a dioxin monitor need to have a normal distribution? This depends mainly on the variability and symmetry of the data which are very difficult to predict.

4.4. Objective Four: Estimated Dioxin Water Concentrations

Equation 1.7. was used to estimate the dissolved dioxin concentration in the Androscoggin River. The formula was entered into the spreadsheets containing the data from the three deployments. The uptake rates (R_s) from Rantalein et al (2000) at 19 C^o were used for both Rumford deployments since the averaged temperatures for those deployments were reasonably close to the calibration data. Averaged uptake rates from the 19 C^o and 11C^o R_s values from Rantalein et al (2000) were used for the 2001 Jay deployment data. It was assumed that the actual R_s value would be somewhere in-between those two values, since the average temperature for that deployment was 15 C^o. These values are estimates, so the water concentration should not be used for comparing upstream and downstream sites. Estimated concentrations were calculated for all the congeners whether or not the data met quality assurance since this estimate is speculative anyway (ND=0).

The ambient water concentration water quality criterion for TCDD in Maine is 0.013 pg/l. The TCDD values for all the deployments were estimated to be about 2-3 fold higher than the water quality criterion (Table 4.1.). However, the dioxin sorbed to organic matter in the river would be much higher. For instance, if 90% of the dioxin in a river is sorbed to organic matter (suggested by Giri et al, 2001), the total TCDD water

concentration would be 10 times greater than originally estimated. In conclusion, the calculations for water concentrations suggest there is still a dioxin contamination problem in Maine rivers.

Table 4.1. The Calculated Dioxin Concentrations (pg/l) in the Androscoggin River (R = Rumford, J = Jay, U = upstream, D = downstream, and the number = the year)

CONGENER	RD1	RU1	JD1	JU1	RD2	RU2
2,3,7,8-TCDF	0.673	0.884	0.177	0.588	1.204	1.847
1,2,3,7,8-PeCDF	0.067	0.088	0.078	0.183	0.116	0.229
2,3,4,7,8-PeCDF	0.085	0.093	0.077	0.205	0.172	0.370
1,2,3,4,7,8-HxCDF	0.087	0.130	0.102	0.170	0.089	0.218
1,2,3,6,7,8-HxCDF	0.033	0.048	0.051	0.054	0.033	0.071
2,3,4,6,7,8-HxCDF	0.026	0.036	0.038	0.043	0.031	0.075
1,2,3,7,8,9-HxCDF	0.026	0.030	0.044	0.025	0.050	0.138
1,2,3,4,6,7,8-HpCDF	0.217	0.193	0.114	0.125	0.072	0.196
1,2,3,4,7,8,9-HpCDF	0.029	0.063	0.047	0.043	0.0475	0.139
OCDF	0.076	0.058	0.223	0.161	0.126	0.251
2,3,7,8-TCDD	0.034	0.024	0.027	0.034	0.023	0.041
1,2,3,7,8-PeCDD	0.026	0.012	0.038	0.029	0.012	0.029
1,2,3,4,7,8-HxCDD	0.021	0.029	0.027	0.025	0.021	0.019
1,2,3,6,7,8-HxCDD	0.056	0.061	0.199	0.222	0.032	0.051
1,2,3,7,8,9,-HxCDD	0.041	0.046	0.057	0.072	0.033	0.064
1,2,3,4,6,7,8-HpCDD	0.148	0.126	0.220	0.321	0.169	0.393
OCDD	0.537	0.355	0.484	0.514	0.248	0.533

4.5. Objective Five: Comparison of SPMD Data with Fish Tissue Analysis

The 2002 fish tissue data were not complete at the time of publication, so the smallmouth bass data were not included in the comparison (Tables 4.2., 4.3., and 4.4.). The TCDF congener provided the most consistent parameter in all samples. The values for TCDF are different from year to year and matrix to matrix. This was expected because the literature states that biotic and abiotic matrices sequester dioxin differently. Also, some of that incongruity could be due to the ever-changing analytical methods at the Environmental Chemistry Laboratory. In general, the fish sequestered more toxic congeners than SPMDs in 2001 with the opposite occurring in 2002.

The comparison of the spatial trend is confounding. In the Rumford data for 2001 (Table 4.2.), the smallmouth bass exhibited a decreasing pattern downstream for TCDF. This resembled the results of the SPMD data though the values were smaller for the fish data. Conversely, the white sucker data demonstrated a much higher concentration at the downstream site. In the Jay data for 2001 (Table 4.3.), all the matrices had decreasing patterns for TCDF except the smallmouth bass which had a nearly 70% percent increase. In 2002 (Table 4.3.), white suckers and SPMDs showed a 55% and a 35% decrease in TCDF concentrations downstream, respectively. Even though there is some conflicting evidence, in general, the spatial patterns are similar (Figure 4.6. through Figure 4.9.). This would suggest that SPMDs are good at mimicking the uptake mechanism of fish and therefore could adequately act as a surrogate procedure for fish tissue analysis.

Table 4.2. 2001 Mean SPMD and Fish Tissue Concentration Data (pg/g) for the Rumford Site

CONGENER	ARP-SMB	ARP-WHS	SPMD UPSTREAM	ARF-SMB	ARF-WHS	SPMD DOWNSTREAM
2,3,7,8-TCDF	4.22	3.87	10.18	1.41	11.80	7.74
1,2,3,7,8-PeCDF	<DL	0.24	<DL	0.33	0.51	<DL
2,3,4,7,8-PeCDF	0.42	0.30	<DL	0.32	0.82	<DL
1,2,3,4,7,8-HxCDF	<DL	<DL	<DL	<DL	<DL	<DL
1,2,3,6,7,8-HxCDF	0.28	0.22	<DL	0.32	0.44	<DL
2,3,4,6,7,8-HxCDF	<DL	<DL	<DL	<DL	<DL	<DL
1,2,3,7,8,9-HxCDF	<DL	<DL	<DL	<DL	<DL	<DL
1,2,3,4,6,7,8-HpCDF	0.37	0.33	<DL	0.35	0.82	<DL
1,2,3,4,7,8,9-HpCDF	<DL	<DL	<DL	<DL	<DL	<DL
OCDF	0.77	0.13	<DL	<DL	0.37	<DL
2,3,7,8-TCDD	0.32	0.10	<DL	0.22	0.27	<DL
1,2,3,7,8-PeCDD	<DL	<DL	<DL	<DL	<DL	<DL
1,2,3,4,7,8-HxCDD	<DL	<DL	<DL	<DL	<DL	<DL
1,2,3,6,7,8-HxCDD	<DL	<DL	<DL	<DL	<DL	<DL
1,2,3,7,8,9-HxCDD	<DL	<DL	<DL	0.29	<DL	<DL
1,2,3,4,6,7,8-HpCDD	<DL	<DL	<DL	<DL	1.51	<DL
OCDD	1.89	1.52	<DL	0.59	1.63	<DL
TEQ	0.97	0.66	0.97	0.54	1.95	0.80

ARP = Androscoggin Rumford Point = SPMD Upstream
ARF = Androscoggin Below Rumford = SPMD Downstream
SMB = Smallmouth Bass
WHS = White Sucker

Table 4.3. 2001 Mean SPMD and Fish Tissue Concentration Data (pg/g) for the Jay Site

CONGENER	ARY-SMB	ARY-SSMB	ARY-WHS	SPMD UPSTREAM	ALV-SMB	ALV-SSMB	ALV-WHS	SPMD DOWN
2,3,7,8-TCDF	2.10	2.57	9.56	2.270	3.54	2.35	6.72	0.693
1,2,3,7,8-PeCDF	<DL	<DL	0.38	0.661	<DL	<DL	0.50	0.315
2,3,4,7,8-PeCDF	0.45	<DL	0.68	0.779	0.45	<DL	0.42	0.320
1,2,3,4,7,8-HxCDF	<DL	<DL	<DL	0.412	<DL	<DL	0.28	0.272
1,2,3,6,7,8-HxCDF	<DL	<DL	0.32	0.137	<DL	<DL	<DL	0.148
2,3,4,6,7,8-HxCDF	<DL	<DL	<DL	0.113	<DL	<DL	0.34	0.120
1,2,3,7,8,9-HxCDF	<DL	<DL	<DL	0.051	<DL	<DL	0.62	0.110
1,2,3,4,6,7,8-HpCDF	0.74	0.78	0.44	0.265	<DL	<DL	0.46	0.249
1,2,3,4,7,8,9-HpCDF	<DL	<DL	<DL	0.091	<DL	<DL	<DL	0.115
OCDF	<DL	<DL	<DL	0.230	0.79	0.66	1.15	0.330
2,3,7,8-TCDD	0.19	0.14	0.26	0.133	0.31	0.08	0.29	0.119
1,2,3,7,8-PeCDD	0.18	<DL	0.29	0.095	<DL	<DL	0.29	0.152
1,2,3,4,7,8-HxCDD	<DL	<DL	<DL	0.083	0.58	<DL	0.40	0.104
1,2,3,6,7,8-HxCDD	<DL	<DL	<DL	0.635	<DL	<DL	<DL	0.611
1,2,3,7,8,9-HxCDD	<DL	<DL	<DL	0.189	<DL	<DL	<DL	0.175
1,2,3,4,6,7,8-HpCDD	<DL	0.76	<DL	0.579	<DL	<DL	0.56	0.404
OCDD	1.14	1.57	2.49	1.375	1.13	1.86	1.25	1.358
TEQ	0.80	0.40	1.90	0.227	0.90	0.27	1.64	0.069

ARY = Androscoggin at Riley = SPMD Upstream
ALV = Androscoggin at Livermore Falls = SPMD Downstream
SMB = Smallmouth Bass
SSMB = Small Smallmouth Bass (1+ years)
WHS = White Sucker
* The SPMD data is speculative due to the lack of a method detection

Figure 4.6. Congener Profiles of the 2001 Jay Downstream Site

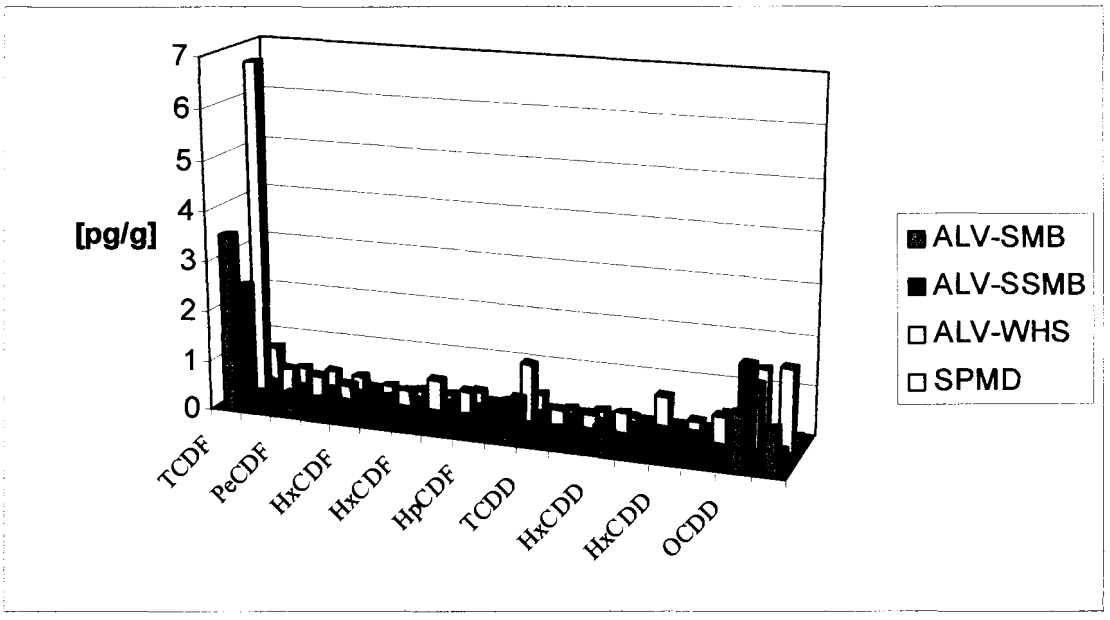


Figure 4.7. Congener Profiles of the 2001 Jay Upstream Site

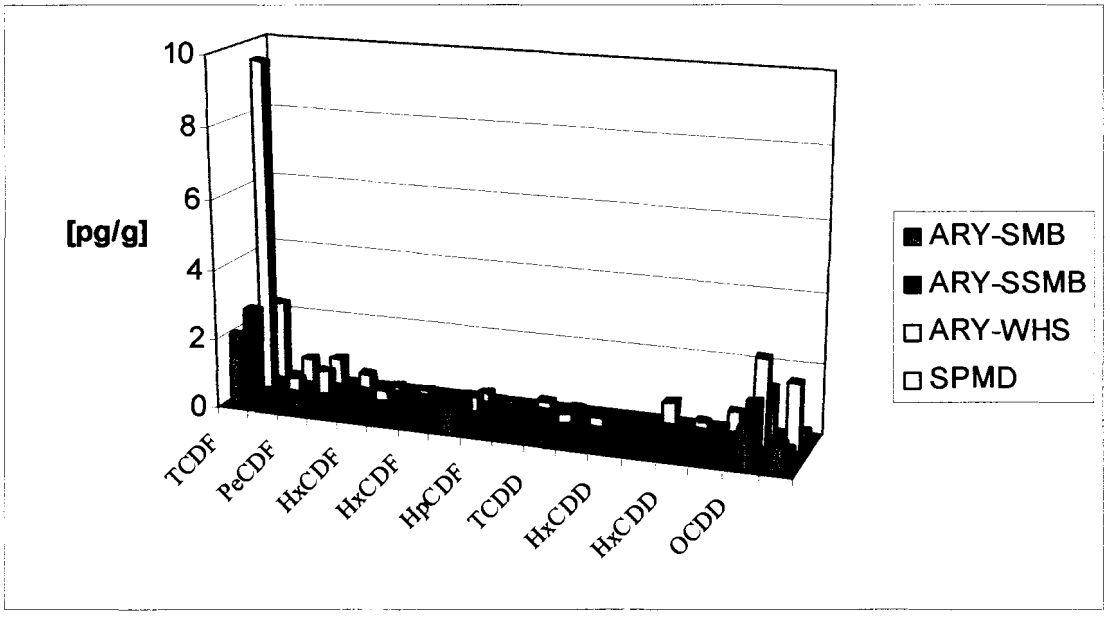


Table 4.4. 2002 Mean SPMD and Fish Tissue Concentration Data (pg/g) for the Rumford Site

CONGENER	ARP-WHS	SPMD UPSTREAM	ARF-WHS	SPMD DOWNSTREAM
2,3,7,8-TCDF	7.230	10.628	3.258	6.929
1,2,3,7,8-PeCDF	0.718	1.356	0.151	0.687
2,3,4,7,8-PeCDF	1.040	2.414	0.160	1.121
1,2,3,4,7,8-HxCDF	<DL	0.916	<DL	0.077
1,2,3,6,7,8-HxCDF	<DL	0.149	<DL	<DL
2,3,4,6,7,8-HxCDF	<DL	0.321	<DL	<DL
1,2,3,7,8,9-HxCDF	<DL	0.299	<DL	<DL
1,2,3,4,6,7,8-HpCDF	<DL	0.639	<DL	<DL
1,2,3,4,7,8,9-HpCDF	<DL	0.499	<DL	<DL
OCDF	<DL	0.463	<DL	<DL
2,3,7,8-TCDD	0.096	0.171	0.037	0.048
1,2,3,7,8-PeCDD	<DL	<DL	<DL	<DL
1,2,3,4,7,8-HxCDD	<DL	<DL	<DL	0.075
1,2,3,6,7,8-HxCDD	<DL	<DL	<DL	<DL
1,2,3,7,8,9-HxCDD	<DL	0.106	<DL	<DL
1,2,3,4,6,7,8-HpCDD	0.300	1.344	<DL	<DL
OCDD	0.665	2.089	1.128 *	<DL
TEQ	1.350	2.667	0.448	1.325

ARP = Androscoggin Rumford Point = SPMD Upstream
ARF = Androscoggin Below Rumford = SPMD Downstream
SMB = Smallmouth Bass
WHS = White Sucker
* Result of contamination

Figure 4.8. Congener Profiles of the 2002 Rumford Downstream Site

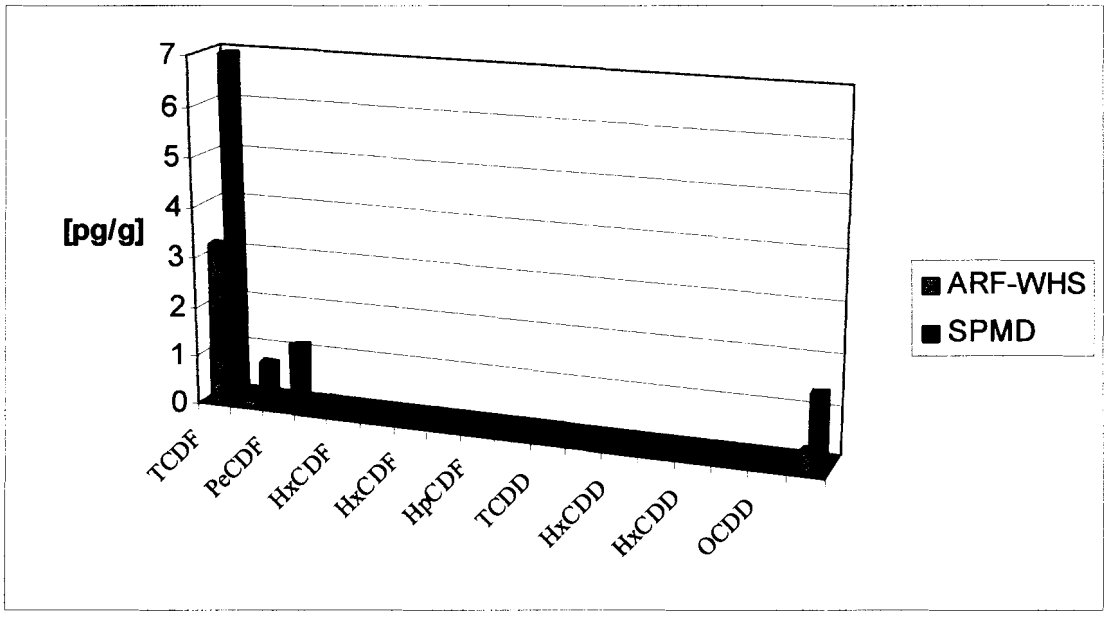


Figure 4.9. Congener Profiles of the 2002 Rumford Upstream Site

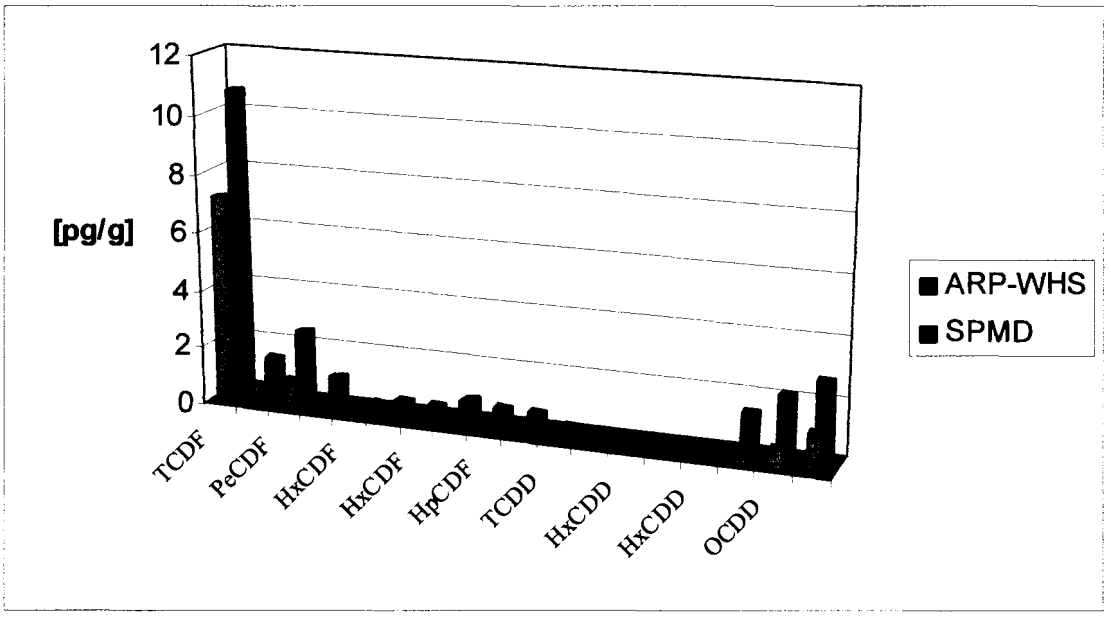


Table 4.5. Summed Toxic Isomer Profile Comparison of SPMD Concentrations for the 2002 Rumford Data (upstream (U), downstream (D) and White Sucker (WHS))

	TETRA pg/g (%)	PENTA pg/g (%)	HEXA pg/g (%)	HEPTA pg/g (%)	OCTA pg/g (%)
SPMD U	10.80 (50.5)	3.77 (17.6)	1.79 (8.4)	2.48 (11.6)	2.55 (11.9)
WHS U	7.33 (72.9)	1.76 (17.5)	0	0.30 (3.0)	0.67 (6.6)
SPMD D	6.98 (78.1)	1.81 (20.2)	0.15 (1.7)	0	0
WHS D	3.29 (91.4)	0.31 (8.4)	0	0	0

The relative percentages of each isomer are more similar than expected (Table 4.5.). The biotic samples exhibit higher levels of the heavier congeners while SPMDs typically sequester more of the less chlorinated congeners (Prest et al 1992, 1995; Gale et al 1997). In this case, the percentages of each toxic isomer display similar profiles with the lower chlorinated congeners actually higher in percentage for the fish than the SPMD. The opposite is demonstrated in the 2001 data, the SPMDs have higher percentages of the lower chlorinated congeners than do the fish. This should be viewed with caution because the only measurable congener was TCDF for the SPMD matrix.

Most of the early comparison studies (Prest et al 1992, 1995; Gale et al 1997) only analyzed the triolein fraction of the SPMD ignoring the membrane compartment of uptake. Since the membrane compartment sequesters up to 50% of the total contaminant concentration (Gale et al, 1998), a significant fraction of the congener profile is not accounted for in those earlier studies. The heavier congeners would more likely be sequestered by the membrane since the larger molecular size would promote entrapment in the ephemeral holes in the membrane while smaller molecules would permeate more easily. TCDF, TCDD and OCDD/F congeners typically are representative of pulp and paper mill pollution (N. McCubbin Consultants, Inc. 2003). In either matrix, the absence of the heavier congeners is puzzling.

4.6. Objective Six: Evaluation of Permeability Reference Compounds

One of the major objectives of this project was to evaluate the use of permeability reference compounds (PRCs). Biofouling, temperature and flow velocity affect the uptake rates of the analytes of interest. Therefore, calibrating for those environmental factors is necessary for determining whether SPMD technology is an appropriate surrogate procedure for the upstream/downstream test. PRCs were used in the SPMD project beginning in 2002. Without the *in situ* calibration, the project was unable to determine whether the upstream and downstream sites were actually sequestering dioxin at the same rate other than subjectively comparing water quality parameters. In the following paragraphs, the performance of deuterated PAHs as PRCs is discussed.

4.6.1. Performance of each Deuterated PAH

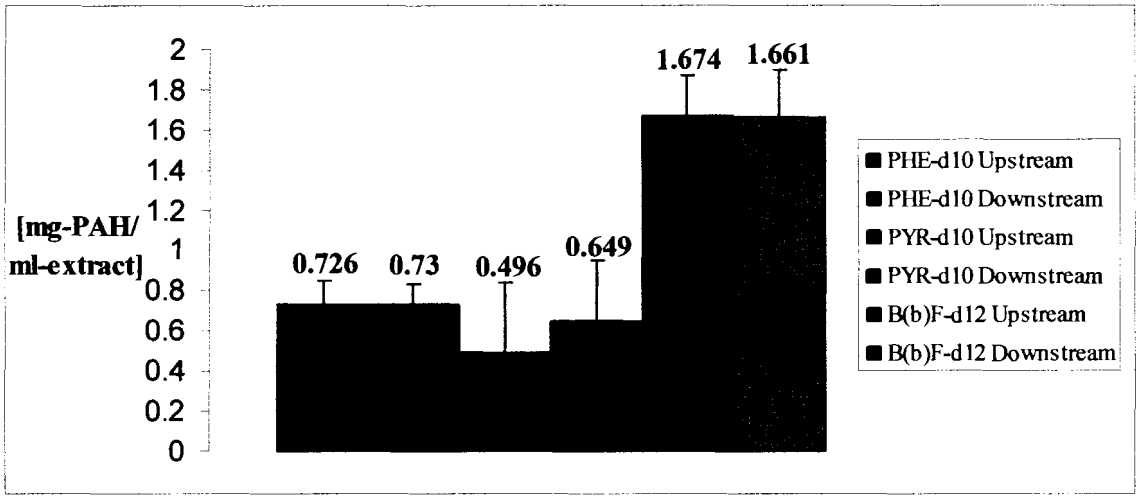
Deuterated acenaphthene was completely eliminated from the SPMD matrix during the exposure. This was expected since the log K_{OW} value is 4.22 meaning the uptake mechanism was membrane controlled. Membrane controlled analytes typically reach equilibrium in less than a month of exposure. However, if biofouling impedance was large enough at either site, then the elimination of acenaphthene would not have been complete. Since it actually was eliminated, the uptake/elimination impedance by biofouling did not significantly alter the membrane controlled analytes uptake mechanism. Continued use of acenaphthene as a PRC is not recommended since it exhibits a different uptake mechanism than dioxin.

Deuterated phenanthrene and pyrene were eliminated from the SPMD matrix during the exposure within the suggested percentage losses (>20% and < 80%) (Huckins et al, 2002a) (Figure 4.10.). Both analytes are under aqueous diffusion layer control

matching the uptake mechanism of dioxin. Neither PRC showed a significant difference in elimination rates between the above and below sites. Pyrene displayed higher variation than the other PRC compounds. The performance of deuterated pyrene is inconclusive so more research should be conducted before the compound is recommended as a PRC for dioxin monitoring. Phenanthrene had excellent coefficients of variation. Therefore, the use of phenanthrene is recommended for analytes under aqueous diffusion layer control.

Deuterated benzo(b)flouranthene was not eliminated from the SPMD at an acceptable level (~17%) during the exposure (Figure 4.10.). Therefore, continued use of benzo(b)flouranthene as a PRC is not recommended for the U/D test. The log K_{OW} of this compound is 5.78. The log K_{OW} range of chemicals that are recommended for use as PRCs when measuring dioxin in Maine rivers is 4.4 to 5.5. The PRC results from this study support the previous research of Huckins et al (2002a). However, some debate on whether or not PAHs are appropriate PRCs for dioxin monitoring has been put forth. Huckins et al (2002a) claims compounds of different classes can be PRCs as long as the uptake mechanism is the same for both the analyte of interest and the PRC. Other scientists have proposed that this assumption is too robust. This controversy cannot be resolved based on this study.

Figure 4.10. PRC Upstream/ Downstream Comparisons



4.6.2. Upstream/Downstream Evaluation of Sampling Rates

The results from this study conclude that the upstream and downstream locations are equivalent with regards to the environmental factors that effect uptake/elimination rates. The Mann-Whitney U test determined the populations were the same with a p-value of 0.05. Even though the sample populations did not fit a normal distribution, parametric statistics were utilized to support the non-parametric results. The variances are equal, so a student's t-test was executed with the same result (p=0.05). The present upstream and downstream sites for the Mead mill in Rumford can be considered equally suitable for the U/D test. This conclusion is not surprising. The water quality parameters for the locations are similar. Qualitatively, the downstream biofouling was more pronounced than the upstream site, but apparently not enough to significantly alter the uptake rates for dioxins.

4.6.3. Determination of the k_e and EAF

The calibration data for elimination rates for each PRC (Equation 1.9) are from Huckins et al (1999). At the 2002 Rumford deployment, the environmental factors increased the elimination rate of the PRCs from the SPMD matrix. In the case of

benzo(b)flouranthene, the k_e was increased three fold. The EAF (Equation 1.10.) is a simple ratio of the calibrated elimination constant ($k_{e\text{-}cal}$) and the *in situ* elimination constant ($k_{e\text{-}PRC}$). The EAF is then multiplied by the calibrated uptake rate to determine the actual, *in situ* uptake rate.

Theoretically, each PRC derived EAF would be equal in value for a particular location assuming that compounds with different log K_{OW} values actually can correct for each other as long as the uptake mechanism (i.e. aqueous diffusion or membrane layer) is the same. However, if the assumption that smaller log K_{OW} compounds can adjust for larger log K_{OW} compounds is not accepted, these results support the need to choose PRC compounds that bracket the range of log K_{OW} values.

Table 4.6. Elimination Constant (ke) and the Exposure Adjustment Factor (EAF) for the 2002 Rumford PRCs

PRC	$k_{E\text{-}PRC}$	$k_{E\text{-}CAL}$	EAF
PHE-d10 Upstream	0.0362	0.029	1.24
PYR-d10 Upstream	0.0498	0.024	2.07
B(b)F-d12 Upstream	0.0064	0.002	3.18
PHE-d10 Downstream	0.0360	0.029	1.24
PYR-d10 Downstream	0.0402	0.024	1.68
B(b)F-d12 Downstream	0.0066	0.002	3.31

The appropriate EAF for the environmental variables must be chosen since there are three different values for the two sites in this study. Deuterated pyrene had too much variation in the sample population, so those numbers are less trustworthy. Also, the upstream and downstream EAFs are different even though a statistical difference was not determined. Deuterated benzo(b)flouranthene was not eliminated within the recommended percent losses, so that EAF value was not used either. In this instance, the best EAF value to use is the one calculated from deuterated phenanthrene. The water

concentrations (Table 4.1.) were over-estimated by using the calibrated uptake rates from Rantalein et al (2001). However, the recalculated numbers suggest the water concentration is still greater than the water quality criterion limits set by the Maine DEP. The water concentration estimates do not change drastically using the EAF procedure (Table 4.7.).

Table 4.7. Recalculation of the 2002 Water Concentrations using the EAF (R = Rumford, D = Downstream, U = Upstream)

CONGENER	RD2	EAF-RD2	RU2	EAF-RU2
2,3,7,8-TCDF	1.204	0.971	1.847	1.489
1,2,3,7,8-PeCDF	0.116	0.094	0.229	0.185
2,3,4,7,8-PeCDF	0.172	0.138	0.370	0.298
1,2,3,4,7,8-HxCDF	0.089	0.072	0.218	0.176
1,2,3,6,7,8-HxCDF	0.033	0.026	0.071	0.057
2,3,4,6,7,8-HxCDF	0.031	0.025	0.075	0.060
1,2,3,7,8,9-HxCDF	0.050	0.040	0.138	0.111
1,2,3,4,6,7,8-HpCDF	0.072	0.058	0.196	0.158
1,2,3,4,7,8,9-HpCDF	0.048	0.038	0.139	0.112
OCDF	0.126	0.102	0.251	0.202
2,3,7,8-TCDD	0.023	0.018	0.041	0.033
1,2,3,7,8-PeCDD	0.012	0.009	0.029	0.024
1,2,3,4,7,8-HxCDD	0.021	0.017	0.019	0.015
1,2,3,6,7,8-HxCDD	0.032	0.026	0.051	0.041
1,2,3,7,8,9,-HxCDD	0.033	0.026	0.064	0.052
1,2,3,4,6,7,8-HpCDD	0.169	0.137	0.393	0.317
OCDD	0.248	0.200	0.533	0.430

Regardless of the small alteration to the estimated water concentrations the *in situ* EAF provides, for the context of the U/D test, PRCs answer the question: Are these two locations different with regards to the environmental factors that affect uptake rates? The use of PRC removes the need to have calibration data for each compound at each temperature, flow velocity, or level of biofouling impedance. If the above site is used as the reference site, the below locations can be evaluated by the difference, or lack there of,

in the elimination rate of PRCs. As long as the duration of the deployment is in the linear uptake phase for the analyte of interest (< 100 days for all compounds with a log K_{OW} greater than 4.4), the calculated EAF will correct the slope of the uptake curve to represent the environmental conditions relative to the reference (i.e. upstream) site. This proves to be an invaluable tool for environmental assessors.

4.7. Future SPMD Research Considerations

The SPMD project has made giant strides in the last few years from the initial deployments by Shoven (2001) in the Penobscot River in 1999 to the use of PRCs at the Rumford site in 2002. However, there are some remaining questions. These include further investigation of the fate and transport of dioxin in Maine rivers, validation of the developed analytical procedure, and further evaluation of permeability reference compounds.

- The results from this study suggest there is a dilution factor with regards to dioxin concentration in the water column. Numerous consultants and interested parties have questioned the existing upstream and downstream locations. In future research, a gradient scheme is recommended. Two to three more sites downstream from the mill should be monitored to investigate the possibility of dilution. For example, the Rumford site has points of confluence in Rumford (Swifts River) and near Dixfield (Webber River) where SPMD exposures would be recommended to investigate the dilution effect of those tributaries. Collection of more hydrological data would be beneficial as well.
- Now, that the assessor can adjust for differing environmental factors using PRCs, there are fewer complications with deploying in the mill effluent. With several

years of data from the 'end of the pipe' to the 'point of mixing' in the river, investigators should be able to model the fate of dioxin from elemental chlorine free bleaching pulp and paper mills in Maine rivers.

- Future researchers should be concerned about the levels of particulate and dissolved organic matter in the water column at the exposure sites, especially at the 'end of the pipe'. TOC and DOC represent a obstacle for accurate total dioxin concentrations in the water column. K_{OC} values for dioxin at the average temperature should be investigated to better estimate the total dioxin concentration in the water. There are no K_{OC} values for the seventeen toxic congeners. However, there are some estimated K_{OC} values for lower chlorinated dioxin/furans in Lodge (2001) and Barring et al (2002) which could be used for total dioxin concentration estimations. Dissolved dioxin concentrations should be greater at sites with more contamination, if the TOC values of the different sites are relatively equal (i.e. within an order of magnitude). This assumption needs to be investigated.
- The analytical procedure has been the biggest obstacle to the progress of the SPMD project. Two of the difficulties that remain are improvement of the detection limit of the HRGC/HRMS and the validation of the current method. The standard operating procedure for SPMD sample analysis at the University of Maine should follow these steps:

  1. Exterior clean up of the membrane

  2. Either a two-stage 24 hour 200 ml hexane dialysis or a one-stage 48 hour 500 ml hexane dialysis

3. Gel Permeation Chromatography (Size Exclusion Chromatography)

4. A Power Prep™ automated clean up using an acid/base/neutral silica column, a basic alumina column and a carbon/celite column

5. Quantification on HRGC/HRMS

- Permeability reference compounds (PRCs) should be researched further using different compounds of the same class as dioxins (or non-toxic dioxins). For example, chlorinated compounds should be used with a range of log K_{OW} from 4.4 to 5.5 to determine if the halogenation affects the elimination rate. The hypothesis that compounds of different classes can correct for each other should be tested. A range of log K_{OW} compounds should be utilized to investigate how compounds of different hydrophobicity perform as PRCs.
- If the levels of dioxin contamination in Maine rivers continue to decrease, manipulation of the SPMD matrix should be investigated. For example, as long as the lipid to membrane surface area is 0.2, SPMDs could be made or special ordered to avoid having to combine more than 4 SPMDs in a composite sample. This would mean a new deployment canister would have to be made as well.

Chapter 5

CONCLUSION

The SPMD project is in its fifth year. Over that period of time, progress in the field and analytical methods has been made, with each step bringing the procedure closer to a robust upstream/downstream test for the Maine Dioxin Monitoring Program. The continual refinement of the SOP during this project has removed many complications arising from the field and analytical protocols and lowered the method detection limit. With the improvements, it is now possible to investigate the fate and transport of dioxin in Maine rivers using SPMD technology, discover any inherent complications with the use of PRCs, and decipher any concentration differences for the U/D test.

The biggest accomplishment of this study was demonstrating the ability of PRCs to correct for environmental factors affecting uptake rates. With regards to the upstream/downstream test, PRCs have eliminated the need to have any laboratory derived calibration data. The dioxin concentration in water (C_W) is not a real value but rather an estimate using calibration data. When using SPMD technology, the real values are the dioxin/furan concentrations in the SPMD after chemical analysis. The injected PRCs in the upstream samples can be used as the reference (like the calibration data obtained in the laboratory when calculating dioxin water concentrations). Regardless of the temperature, flow velocity, or the biofouling at any of the sites (unless the biofouling is so extreme that no uptake at all occurs during the exposure), the downstream sites can be compared to the upstream sites (the reference) by the elimination rates of the PRCs. By measuring the difference in PRC elimination rates from the two sites, an exposure

adjustment factor (EAF) can be calculated. This EAF ratio can alter the dioxin concentrations (pg-dioxin/g-SPMD) in the downstream samples to reflect the actual concentration as compared to the upstream site (the reference). If there is no difference in PRC elimination (i.e. the results in this study), then the EAF does not need to be calculated and the upstream and downstream sites can be compared as is, since the uptake rates are the same. This provides the Maine DEP a strong U/D test determining mill compliance for the 1997 dioxin law.

Now that the coefficients of variation among samples are between 10-20% for detected congeners using the revised analytical procedure, smaller sample sizes can be used to obtain a significant difference in mean concentrations between upstream and downstream sites. However, in order to use the robust, parametric statistical tests instead of the non-parametric tests, a larger sample size is required than what was used in this study. The results from this project determined that in order to obtain a normal distribution and thereby use parametric statistics, more samples than eight are needed. Therefore, if the Maine DEP is to utilize SPMD technology for U/D compliance test, it is recommended that more than 10 samples per site are collected to more likely ensure the data fits a normal distribution, unless further reduction of the variability is achieved. This reduction is highly unlikely to occur knowing the inherent variability in this type of chemical analysis.

The results from this study conclude that the concentrations at the downstream site are lower than the upstream site. More than likely, this is explained by the distance the downstream site is from the mill. Two phenomena are occurring as a result of this distance. One is a dilution factor from the five tributaries entering the Androscoggin

River upstream from the downstream site. The second explanation is the role of particulate and dissolved organic matter in the transport of dioxin. Dioxin has an extremely high affinity for sorbing to organic matter. This means by the time the dioxin reaches the present downstream site, most of it has either precipitated to the sediment or sorbed to water soluble DOC which cannot be sequestered by the SPMD. Either explanation can possibly confound the other. Further research should examine this issue.

In this study, tetra and penta chlorinated congeners were the most consistently quantified of the seventeen toxic congeners. The other congeners displayed higher coefficients of variation or were not detected at all. Therefore, in the future, chemical analysis by high resolution gas chromatography/ high resolution mass spectrometry should only include the tetra and penta chlorinated furan and dioxin spectral windows when quantifying for the upstream/downstream test. By concentrating on those congeners only, further reduction of the method detection limit is possible creating a more sensitive test. This is accomplished by better separation of congeners and interferents using an altered gas chromatograph procedure. Also, the clean-up procedure can be changed to better refine the samples for those congeners. However, the U.S. EPA has not released the dioxin reassessment which should be considered before removal of the more chlorinated congeners from the quantification process for toxicological purposes.

Toxic equivalencies (TEQs) should not be calculated for the U/D test compliance. Other than tetra and penta furans, most of the toxic congeners are inconsistently quantified. Therefore the TEQ is a value with high variability decreasing the sensitivity of the U/D test. Since this compliance test is not directly related to toxicity, using a toxic

equivalency is not needed. For congeners that are not consistently quantified (i.e. TCDD), presence/absence of those pollutants is be a better way to investigate mill compliance.

In conclusion, SPMD technology is a viable option for the Maine DEP to use in the upstream/downstream compliance testing. SPMDs will not provide toxicological data other than estimates of the dioxin water concentration. For this reason, fish sampling should continue for toxicological reference, with SPMDs replacing fish for temporal and spatial trend analysis at most sampling locations. SPMDs eliminate many of the problems with monitoring dioxin levels with fish for the U/D test. These are: (1) SPMDs are not mobile, (2) SPMDs do not metabolize or depurate dioxin, (3) SPMDs are uniform samplers, and (4) SPMDs do not sequester historical dioxin when properly deployed. Therefore, SPMDs are recommended for monitoring dioxin levels in Maine rivers.

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