MODULE 4 SPECIAL STUDIES

4.1

SEMI-PERMEABLE MEMBRANE DEVICES

SEMI-PERMEABLE MEMBRANE DEVICES (SPMDS)

SPMDs (SEMI-PERMEABLE MEMBRANE DEVICES)

Semipermeable membrane devices (SPMDs) are passive integrative sampling devices which combine membrane diffusion and liquid-liquid partitioning to concentrate low to moderate molecular mass hydrophobic compounds from water (Huckins et al, 1996). Made of low-density polyethylene lay-flat tubing (2.5 cm wide by 91.4 cm long), containing a thin film of neutral triolein and placed inside stainless steel canisters, SPMDs are deployed in the waterbody where they accumulate contaminants until retrieved.

SPMDs have some features that give them advantages over monitoring contaminants in fish. SPMDs can be deployed in water to accumulate single, pulsed, or continuous contaminant releases over time. SPMDs are anchored to sample at specific locations, thereby avoiding any question of origin of contaminants caused by fish movement. SPMDs do not change function under stress, unlike gills of fish. There are no biotransformations or elimination like that in fish. And accumulation of contaminants does not occur by the same process of uptake in fish, thereby potentially limiting their use to accumulation in a relative sense.When deployed in Maine Rivers for approximately a month, SPMDs are able to sequester enough dioxin/furans for quantification by HRGC/HRMS (Shoven, 2001). SPMD uptake rates have been determined for dioxin/furans in order to calculate dissolved water concentrations (Rantalainen et al, 2000).

There are, however, a number of environmental factors, such as water temperature, biofouling, dissolved organic carbon (DOC), suspended solids, and flow velocity that affect the uptake kinetics of SPMDs.Assuming isotropic exchange kinetics, permeability reference compounds (PRCs) can be added to the SPMD prior to deployment to calibrate the rate change of dioxin/furan uptake caused by environmental conditions (Huckins et al., 2002)

In order to assess the potential of SPMDs to determine if mills are discharging dioxin, DEP has funded studies at the University of Maine Environmental Chemistry Laboratory (formerly the Water Research Institute) since 1999 through the Surface Water Ambient Toxics (SWAT) program. In 1999, the focus was development and refinement of field and laboratory techniques by deploying the SPMDs in the nearby Penobscot River for 3 one-month trials and then retrieving them for laboratory analysis. In 2000, two deployments were made in the Androscoggin River to investigate the effect of time and duration of deployment on biofouling. An above/below trial was also made in both the Androscoggin and Kennebec rivers.

2001

In 2001 the goals were as follows:

1. Validate the deployment scheme and analytical method developed in 2000.
2. Increase the sample size for more statistical power.
3. Decrease the variability between samples to lower the minimal statistical difference and improve the sensitivity of the A/B test.
4. Compare the results from 2000 with 2001.

Site Location

The SPMD field deployments for 2001 were above and below the MeadWestvaco Mill in Rumford from 7/13/01 to 8/10/01 and the International Paper Mill in Jay from 9/22/01 to 10/20/01 on the Androscoggin River. The GPS determined latitude-longitudes for the sites were:

Site	Latitude (DegMinSec)	Longitude (DegMinSec)
Upstream Rumford	N44*31'04"	W70*33'05"
Downstream Rumford	N44*30'10.5"	W70*23'53.3"
Upstream Jay	N44*28'42.4"	W70*16'18.7"
Downstream Jay	N44*29'06.2"	W70*12'13.8"

The Rumford site was chosen to compare the SPMD results from 2001 with those from 2000 at that site. Originally, both 2001 deployments were going to be at the Rumford site. However, due to a shutdown of the MeadWestvaco mill in September, the second deployment was downstream above and below the International Paper mill at Jay. The below sites were a sufficient distance below the mills to ensure proper mixing of the effluent so the dioxin/furans river concentrations were assumed to be at equilibrium.

Deployment Scheme

The Rumford deployment scheme used an elaborate system of surface buoys, ropes and anchors to submerge the SPMD-filled canisters (Shoven, 2001). The system was developed so the canisters would remain approximately 3 feet under the water surface regardless of the water level making sure the canisters avoided contact with the sediment. The deployment consisted of 40 SPMDs in 8 canisters submerged by two buoy systems at each site. Upon retrieval of the SPMDs, one buoy system at the upstream site had been vandalized by one of the buoys being punctured. Those 20 SPMDs had been resting on the bottom for an unknown amount of time. Due to the difficulties at Rumford, the deployment scheme was changed for Jay. In an effort to avoid vandalism, submerged milk jugs were used as floats to keep the canisters upright at ~10 feet above the sediment with a water depth of ~15 feet. There were four sets of submerged milk jugs with two canisters and 10 SPMDs at each site. No vandalism occurred. However, at the upstream site, 3 sets of milk jugs lost buoyancy and six canisters with 30 SPMDs were found near the sediment. The sediment at this site was

sand and gravel; therefore, there was probably no contamination of dioxin from the sediments. For each site, appropriate measures were taken to ensure no contamination during transport, deployment, and retrieval. Also, attached to one canister at each site was a HOBO temperature logger to monitor the hourly water temperature throughout the deployment.

Laboratory Methods

All SPMDs and deployment canisters are purchased from Environmental Sampling Technologies, St. Joseph, MO. All standards are purchased from Cambridge Isotope Laboratories, Andover, MA. All solvents are GC-resolve grade.

The Rumford samples were analyzed according to the 2000 procedural method (Shoven, 2001). The procedure consisted of external washing of the SPMD to remove any periphytic growth followed by an injection of carbon-labeled dioxin/furan and PCB standards to accurately quantify the congeners using the isotope dilution method outlined in EPA Method 1613 (Telliard, 1994). After spiking and drying, the samples underwent a two-stage 24 hour dialysis with 150 ml of hexane at sub-ambient temperatures (~18 C?The dialysates of two SPMDs were then combined into one composite sample to make an N=20 composite samples for each site. The samples were cleaned up using acidified silica gel slurry to hydrolyze any remaining lipid after dialysis. Gel permeation chromatography (GPC) was then used as a further clean up before quantification by HRGC/HRMS. Quality control samples consisted of a trip blank for each site, a lab dialysis blank, a lab matrix spike, and a lab procedural blank. Water samples were collected at the beginning and end of each deployment to measure total organic carbon (TOC), dissolved organic carbon (DOC), and specific conductivity.

Due to preliminary results from Rumford, the Jay samples were analyzed differently. The chromatograms for the Rumford deployment had numerous interferents causing quantification problems such as concentration over-estimation or, conversely, non-detection. The physical clean up and the two-stage 24 hour dialysis remained the same. However, the dialysates were combined into composite samples of 5 SPMDs each resulting in an N=8 for each site. Also, the PCB standards were not injected because PCBs are a known interferent during dioxin/furan quantification. The same acidified silica gel slurry and GPC method were performed on the samples, but a fractionation with ENVI-carb reversible tubes from Supelco, Bellafonte, PA was utilized to ensure a better clean up of the samples. The same quality control was performed for the Jay samples.

Results

The results from the 2001 field season were calculated as nanogram of dioxin/furan per kilogram of SPMD. Estimated dissolved dioxin/furan concentrations in the river have yet to be determined for each of the sites. The coefficient of variation (CV) for the

Rumford deployment ranged from 29 to 368% with an average of 92% for all the congeners. The Rumford data are not yet completed (12 of the 40 still have not been quantified). Most of the variation from Rumford originates from an ineffective clean up procedure and laboratory inexperience. The CV for the Jay deployment ranged from 9 to 115% with an average of 42%. However, after removing one statistical outlier (> 2 standard deviations from the mean) from the upstream data and two downstream samples that didn't satisfy EPA Method 1613 quality assurance, the CV ranged from 6% to 38% with an average of 18%. Both data sets have a co-eluting peak with 2,3,7,8-TCDD leading to quantification problems for that congener. The toxic equivalency values (DTE) were determined using the World Health Organization's toxic equivalency factors for mammals.

Concentrations of most congeners were lower below the mills than above (Figures 1 and 2). The comparison between the 2000 and 2001 Rumford deployments show distinct similarities in congener profile for the population of samples with the exception of less non-detections in the 2001 data. However, with the amount of variability present in each set of samples, more validation is needed for that site.

Objectives for 2002

1. Reduce the variability between replicates to facilitate development of a more sensitive A/B test. A coefficient of variation of ~20% is expected.

2. Use PRCs as an *in situ* calibration for varying environmental conditions such as water velocity, temperature, and biofouling.

3. Develop a deployment scheme to eliminate possible vandalism and other logistical problems.

4. Perform a method detection limit study with composites of 4 SPMDs.

Conclusions

Of all the test types (large and small bass, large sucker filets and whole fish, sucker liver composites, freshwater mussels, and SPMDs) tested since 1997, only the fish and livers were able to detect significant differences between stations above and below some bleached kraft pulp and paper mills. MSDs were generally lower for mature or juvenile bass or for suckers depending on station, contaminant and year, but none have attained or consistently approached the goal of an MSD of 10% of background concentrations. SPMDs have not performed as well as fish, but new sampling design and cleanup techniques promise better results. These devices will be tested again along with fish in 2002.

Figure 1. DTE values for 2001 deployments.

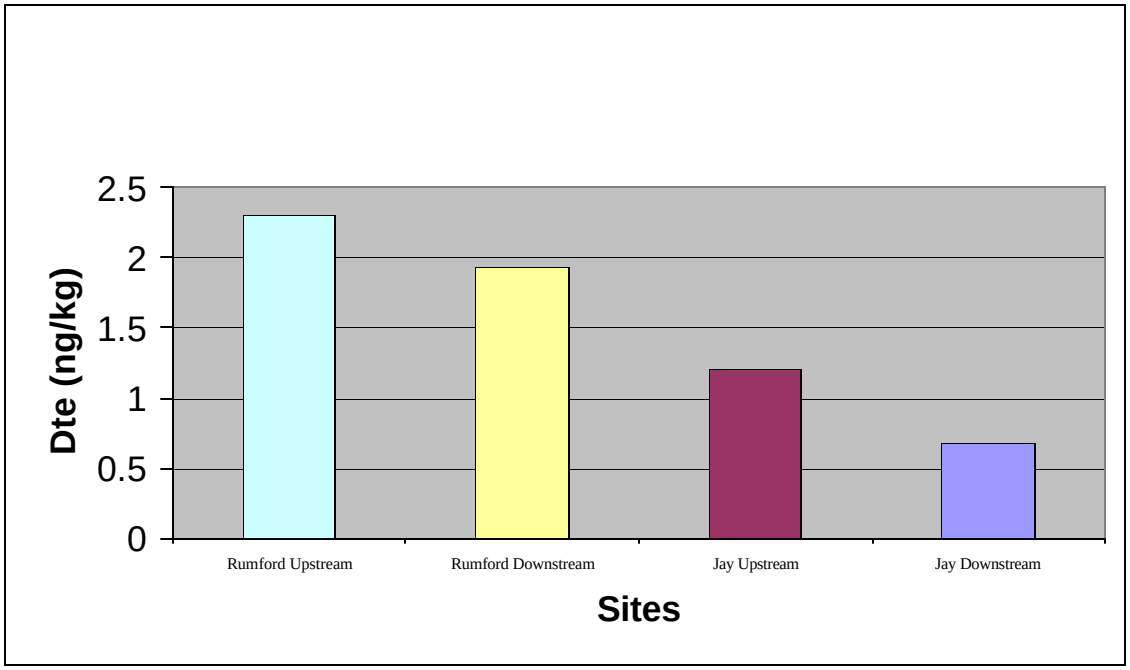
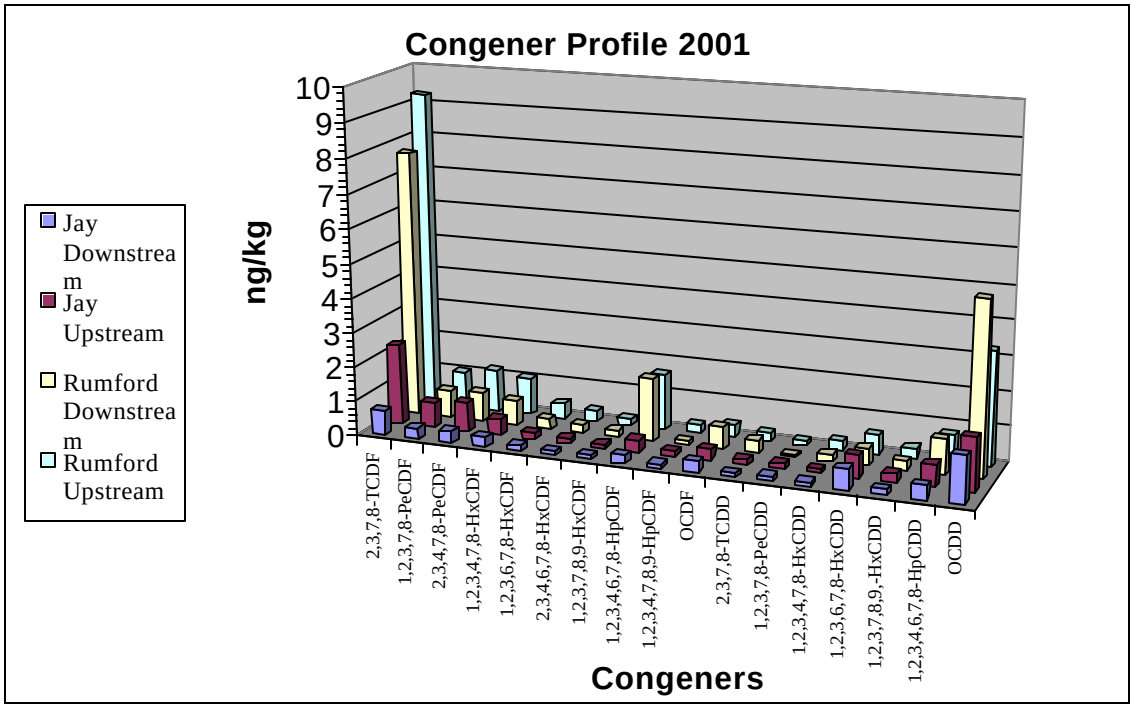


Figure 2. Congener Profile for the 2001 deployments.



Rumford Upstream Data July 2001 N=20 2 SPMDs per sample <DL=0 Average Temperature 19.34 DOC 8/10 4.6

Congener	MDL*	SPMD 21	SPMD 22	SPMD 23	SPMD 24	SPMD 25	SPMD 26	SPMD 33
2,3,7,8-TCDF	0.8		11.815	7.814	11.072	8.941		
1,2,3,7,8-PeCDF	2.08		0.626	0.838	1.363	0.612		
2,3,4,7,8-PeCDF	3.13		1.069	1.229	1.148	1.036		
1,2,3,4,7,8-HxCDF	2.59		1.228	0.990	0.934	1.064		
1,2,3,6,7,8-HxCDF	2.46		0.340	0.306	0.557	0.427		
2,3,4,6,7,8-HxCDF	2.88		0.201	0.386	0.342	0.286		
1,2,3,7,8,9-HxCDF	1.68		0.130	0.183	0.135	0.221		
1,2,3,4,6,7,8-HpCDF	2.65		0.390	1.173	0.164	2.896		
1,2,3,4,7,8,9-HpCDF	1.56		0.000	0.108	0.000	0.200		
OCDF	7.18		0.000	0.401	0.000	0.704		
2,3,7,8-TCDD	2.1		0.219	0.243	0.198	0.222		
1,2,3,7,8-PeCDD	2.14		0.166	0.000	0.163	0.088		
1,2,3,4,7,8-HxCDD	3.08		0.195	0.277	0.288	0.287		
1,2,3,6,7,8-HxCDD	1.22		0.611	0.573	0.930	0.506		
1,2,3,7,8,9,-HxCDD	2.84		0.000	0.247	0.355	0.362		
1,2,3,4,6,7,8-HpCDD	2.31		1.077	0.825	0.757	0.876		
OCDD	6.7		3.938	2.056	5.764	3.944		
TEQ			2.418	1.998	2.474	2.108		

			DOC 7/17	TOC 7/17	Sp. Cond.	Flow 7/13		
			4.5042	4.5066	55.57	1.8		
Congener	MDL*	SPMD 27	SPMD 28	SPMD 29	SPMD 30	SPMD 31	SPMD 32	SPMD 39
2,3,7,8-TCDF	0.8			0.000		11.079	10.818	12.083
1,2,3,7,8-PeCDF	2.08			1.741		1.159	0.793	2.765
2,3,4,7,8-PeCDF	3.13			1.539		1.381	0.764	2.789
1,2,3,4,7,8-HxCDF	2.59			1.077		0.987	0.964	2.163
1,2,3,6,7,8-HxCDF	2.46			0.430		0.287	0.277	1.316
2,3,4,6,7,8-HxCDF	2.88			0.308		0.240	0.168	1.126
1,2,3,7,8,9-HxCDF	1.68			0.046		0.124	0.060	1.220
1,2,3,4,6,7,8-HpCDF	2.65			3.051		1.377	1.770	2.398
1,2,3,4,7,8,9-HpCDF	1.56			0.000		0.127	0.126	1.028
OCDF	7.18			0.000		0.000	0.000	1.979
2,3,7,8-TCDD	2.1			0.344		0.263	0.305	0.419
1,2,3,7,8-PeCDD	2.14			0.077		0.029	0.016	0.629
1,2,3,4,7,8-HxCDD	3.08			0.000		0.216	0.029	1.227
1,2,3,6,7,8-HxCDD	1.22			0.190		0.367	0.204	1.484
1,2,3,7,8,9,-HxCDD	2.84			0.048		0.270	0.136	1.324
1,2,3,4,6,7,8-HpCDD	2.31			0.000		0.694	0.535	1.461
OCDD	6.7			2.291		2.135	2.472	3.766
TEQ		0	0	1.518		2.420	2.033	4.824

M/z ion ratio data flags, DPE,co-elution etc.
Surrogate recovery data flags
Both M/z ratio and Surrogate Recovery data flags
* MDL from Heather's work
# Major problems with pentachlorinated dioxin/furans

Rumford Upstream Data July 20		TOC 8/10	Sp. Cond.	Flow 8/10		
		4.5	61.8	0.5		
Congener	MDL*	SPMD 34	SPMD 35	SPMD 36	SPMD 37	SPMD 38
2,3,7,8-TCDF	0.8				12.816	13.735
1,2,3,7,8-PeCDF	2.08				0.153	1.205
2,3,4,7,8-PeCDF	3.13				0.440	1.621
1,2,3,4,7,8-HxCDF	2.59				1.004	1.155
1,2,3,6,7,8-HxCDF	2.46				0.279	0.236
2,3,4,6,7,8-HxCDF	2.88				0.261	0.158
1,2,3,7,8,9-HxCDF	1.68				0.096	0.026
1,2,3,4,6,7,8-HpCDF	2.65				1.480	1.853
1,2,3,4,7,8,9-HpCDF	1.56				0.208	0.898
OCDF	7.18				0.283	0.223
2,3,7,8-TCDD	2.1				0.241	0.241
1,2,3,7,8-PeCDD	2.14				0.000	0.009
1,2,3,4,7,8-HxCDD	3.08				0.110	0.051
1,2,3,6,7,8-HxCDD	1.22				0.488	0.486
1,2,3,7,8,9,-HxCDD	2.84				0.134	0.066
1,2,3,4,6,7,8-HpCDD	2.31				0.881	0.842
OCDD	6.7				3.309	2.501
TEQ		0	0	0	2.013	2.749

Congener	MDL*	SPMD 40	Mean	Std. Dev.	%RSD
2,3,7,8-TCDF	0.8	1.623	9.254	4.500	48.621
1,2,3,7,8-PeCDF	2.08	0.176	1.039	0.748	72.002
2,3,4,7,8-PeCDF	3.13	0.351	1.215	0.662	54.474
1,2,3,4,7,8-HxCDF	2.59	0.445	1.092	0.407	37.313
1,2,3,6,7,8-HxCDF	2.46	0.314	0.434	0.307	70.795
2,3,4,6,7,8-HxCDF	2.88	0.254	0.339	0.270	79.676
1,2,3,7,8,9-HxCDF	1.68	0.147	0.217	0.338	155.455
1,2,3,4,6,7,8-HpCDF	2.65	1.307	1.624	0.915	56.330
1,2,3,4,7,8,9-HpCDF	1.56	0.120	0.256	0.358	140.042
OCDF	7.18	0.504	0.372	0.586	157.355
2,3,7,8-TCDD	2.1	0.130	0.257	0.077	29.938
1,2,3,7,8-PeCDD	2.14	0.206	0.126	0.182	145.091
1,2,3,4,7,8-HxCDD	3.08	0.162	0.258	0.338	130.647
1,2,3,6,7,8-HxCDD	1.22	0.194	0.549	0.380	69.201
1,2,3,7,8,9,-HxCDD	2.84	0.224	0.288	0.364	126.607
1,2,3,4,6,7,8-HpCDD	2.31	0.686	0.785	0.355	45.264
OCDD	6.7	4.270	3.313	1.153	34.803
TEQ		0.878	2.312	0.977	42.251

M/z ion ratio data flags, DPE,co-elution etc.
Surrogate recovery data flags
Both M/z ratio and Surrogate Recovery data flags
* MDL from Heather's work
# Major problems with pentachlorinated dioxin/furans

Rumford Downstream Data July 2001 N=20 2 SPMDs per sample <DL=0 Average Temperature 23.7909 DOC 8/10 6.2

Congener	MDL*	SPMD 1	SPMD 2	SPMD 3	SPMD 4	SPMD 5	SPMD 6	SPMD 13
2,3,7,8-TCDF	0.8			7.110	11.622	10.874	2.113	4.733
1,2,3,7,8-PeCDF	2.08			0.873	1.573	0.490	0.261	0.160
2,3,4,7,8-PeCDF	3.13			0.466	0.630	1.025	0.278	1.782
1,2,3,4,7,8-HxCDF	2.59			0.734	0.690	0.495	0.220	0.611
1,2,3,6,7,8-HxCDF	2.46			0.254	0.471	0.187	0.260	0.164
2,3,4,6,7,8-HxCDF	2.88			0.150	0.415	0.175	0.316	0.146
1,2,3,7,8,9-HxCDF	1.68			0.094	0.183	0.035	0.209	0.040
1,2,3,4,6,7,8-HpCDF	2.65			1.765	0.388	1.896	1.022	2.218
1,2,3,4,7,8,9-HpCDF	1.56			0.134	0.067	0.000	0.000	0.023
OCDF	7.18			0.650	0.000	0.000	0.547	0.569
2,3,7,8-TCDD	2.1			0.341	0.343	0.296	0.040	0.503
1,2,3,7,8-PeCDD	2.14			0.000	0.000	0.084	0.000	0.000
1,2,3,4,7,8-HxCDD	3.08			0.076	0.175	0.150	0.318	0.063
1,2,3,6,7,8-HxCDD	1.22			0.193	0.660	0.554	0.522	0.209
1,2,3,7,8,9,-HxCDD	2.84			0.239	0.314	0.318	0.237	0.226
1,2,3,4,6,7,8-HpCDD	2.31			0.948	1.537	0.872	0.522	0.938
OCDD	6.7			5.193	8.310	4.864	3.756	6.087
TEQ		0	0	1.532	2.211	2.224	0.627	2.054

			DOC 7/17	TOC 7/17	Sp. Cond.	Flow 7/13		
			6.0332	6.2299	95.26	2.6		
Congener	MDL*	SPMD 7	SPMD 8	SPMD 9	SPMD 10	SPMD 11	SPMD 12	SPMD 19
2,3,7,8-TCDF	0.8	12.966	9.503	7.640	9.915	7.505	6.803	
1,2,3,7,8-PeCDF	2.08	1.422	1.060	0.606	0.988	0.603	0.145	
2,3,4,7,8-PeCDF	3.13	1.367	0.331	0.924	1.151	2.554	0.000	
1,2,3,4,7,8-HxCDF	2.59	1.068	1.428	0.649	0.703	0.933	0.514	
1,2,3,6,7,8-HxCDF	2.46	0.177	0.342	0.186	0.179	0.245	0.186	
2,3,4,6,7,8-HxCDF	2.88	0.147	0.279	0.102	0.189	0.199	0.156	
1,2,3,7,8,9-HxCDF	1.68	0.038	0.141	0.027	0.115	0.143	0.031	
1,2,3,4,6,7,8-HpCDF	2.65	3.068	2.247	1.408	1.573	2.114	1.707	
1,2,3,4,7,8,9-HpCDF	1.56	0.124	0.250	0.000	0.099	0.000	0.039	
OCDF	7.18	0.000	0.679	0.366	4.036	0.000	0.531	
2,3,7,8-TCDD	2.1	0.253	0.397	0.266	0.390	0.200	0.406	
1,2,3,7,8-PeCDD	2.14	0.000	0.000	0.000	0.000	0.000	0.000	
1,2,3,4,7,8-HxCDD	3.08	0.164	0.161	0.071	0.134	0.287	0.071	
1,2,3,6,7,8-HxCDD	1.22	0.599	0.472	0.167	0.144	0.548	0.259	
1,2,3,7,8,9,-HxCDD	2.84	0.140	0.288	0.057	0.286	0.314	0.176	
1,2,3,4,6,7,8-HpCDD	2.31	0.914	0.957	0.706	0.794	1.453	0.746	
OCDD	6.7	3.014	3.675	4.653	0.414	6.152	4.575	
TEQ		2.579	1.911	1.670	2.207	2.561	1.258	0.000

M/z ion ratio data flags, DPE,co-elution etc.
Surrogate recovery data flags
Both M/z ratio and Surrogate Recovery data flags

Rumford Downstream Data July		TOC 8/10	Sp. Cond.	Flow 8/10		
		6.3	115.3	1.3		
Congener	MDL*	SPMD 14	SPMD 15	SPMD 16	SPMD 17	SPMD 18
2,3,7,8-TCDF	0.8	4.529	7.177	6.874	9.484	8.823
1,2,3,7,8-PeCDF	2.08	0.150	1.234	0.527	0.753	2.429
2,3,4,7,8-PeCDF	3.13	0.000	0.432	0.000	1.322	2.166
1,2,3,4,7,8-HxCDF	2.59	0.505	0.628	0.499	0.847	1.421
1,2,3,6,7,8-HxCDF	2.46	0.169	0.184	0.344	0.266	1.176
2,3,4,6,7,8-HxCDF	2.88	0.138	0.210	0.264	0.194	0.857
1,2,3,7,8,9-HxCDF	1.68	0.055	0.000	0.197	0.092	1.453
1,2,3,4,6,7,8-HpCDF	2.65	2.628	3.448	1.351	1.584	0.708
1,2,3,4,7,8,9-HpCDF	1.56	0.074	0.000	0.189	0.119	0.681
OCDF	7.18	0.415	0.461	0.592	0.363	0.000
2,3,7,8-TCDD	2.1	0.443	0.289	0.372	0.566	0.825
1,2,3,7,8-PeCDD	2.14	0.000	0.000	0.000	0.017	0.864
1,2,3,4,7,8-HxCDD	3.08	0.051	0.220	0.166	0.128	1.207
1,2,3,6,7,8-HxCDD	1.22	0.226	0.508	0.473	0.446	2.083
1,2,3,7,8,9,-HxCDD	2.84	0.167	0.000	0.333	0.246	0.795
1,2,3,4,6,7,8-HpCDD	2.31	0.850	1.323	0.848	0.964	1.208
OCDD	6.7	3.690	6.114	3.790	3.001	3.806
TEQ		1.070	1.507	1.338	2.479	4.701

Congener	MDL*	SPMD 20	Mean	Std. Dev.	%RSD
2,3,7,8-TCDF	0.8	3.987	7.745	2.870	37.057
1,2,3,7,8-PeCDF	2.08	0.187	0.792	0.618	78.062
2,3,4,7,8-PeCDF	3.13	0.000	0.849	0.790	93.039
1,2,3,4,7,8-HxCDF	2.59	0.500	0.732	0.325	44.334
1,2,3,6,7,8-HxCDF	2.46	0.266	0.297	0.241	80.910
2,3,4,6,7,8-HxCDF	2.88	0.235	0.245	0.175	71.453
1,2,3,7,8,9-HxCDF	1.68	0.136	0.189	0.332	176.171
1,2,3,4,6,7,8-HpCDF	2.65	1.863	1.823	0.780	42.814
1,2,3,4,7,8,9-HpCDF	1.56	0.160	0.115	0.164	142.436
OCDF	7.18	1.633	0.638	0.963	150.963
2,3,7,8-TCDD	2.1	0.249	0.363	0.170	46.704
1,2,3,7,8-PeCDD	2.14	0.000	0.057	0.209	368.147
1,2,3,4,7,8-HxCDD	3.08	0.112	0.209	0.268	128.186
1,2,3,6,7,8-HxCDD	1.22	0.504	0.504	0.440	87.316
1,2,3,7,8,9,-HxCDD	2.84	0.302	0.261	0.167	63.886
1,2,3,4,6,7,8-HpCDD	2.31	1.606	1.011	0.307	30.357
OCDD	6.7	14.044	5.008	2.891	57.729
TEQ		0.900	1.931	0.927	48.023

M/z ion ratio data flags, DPE,co-elution etc.
Surrogate recovery data flags
Both M/z ratio and Surrogate Recovery data flags

Jay Upstream Data July 2001 N=8 5 SPMDs per sample <DL=0 (ng/kg) | Temp | DOC 7/17 N/A

Congener	SPMD 49^	SPMD 50^	SPMD 51*	SPMD 52	SPMD 53^	SPMD 54^	SPMD 55^	SPMD 56^
2,3,7,8-TCDF	2.319	2.374	2.849	2.522	2.238	2.124	2.228	2.187
1,2,3,7,8-PeCDF	0.606	1.000	0.941	0.683	0.709	0.610	0.675	0.683
2,3,4,7,8-PeCDF	0.772	1.120	1.027	0.847	0.739	0.732	0.860	0.724
1,2,3,4,7,8-HxCDF	0.399	0.838	0.548	0.459	0.376	0.384	0.455	0.398
1,2,3,6,7,8-HxCDF	0.145	0.469	0.182	0.144	0.156	0.101	0.130	0.146
2,3,4,6,7,8-HxCDF	0.126	0.373	0.225	0.146	0.125	0.094	0.097	0.088
1,2,3,7,8,9-HxCDF	0.057	0.390	0.128	0.043	0.071	0.048	0.045	0.043
1,2,3,4,6,7,8-HpCDF	0.273	0.819	0.363	0.262	0.230	0.184	0.399	0.240
1,2,3,4,7,8,9-HpCDF	0.080	0.422	0.175	0.107	0.134	0.058	0.103	0.066
OCDF	0.206	0.887	0.358	0.256	0.271	0.186	0.255	0.207
2,3,7,8-TCDD	0.115	0.238	0.158	0.141	0.095	0.127	0.131	0.190
1,2,3,7,8-PeCDD	0.098	0.447	0.186	0.079	0.135	0.069	0.113	0.074
1,2,3,4,7,8-HxCDD	0.076	0.368	0.103	0.061	0.109	0.076	0.105	0.071
1,2,3,6,7,8-HxCDD	0.626	1.058	0.321	0.655	0.655	0.472	0.853	0.547
1,2,3,7,8,9,-HxCDD	0.137	0.562	0.310	0.191	0.270	0.172	0.200	0.165
1,2,3,4,6,7,8-HpCDD	0.603	0.921	0.687	0.582	0.553	0.555	0.658	0.522
OCDD	1.444	2.205	1.754	1.528	1.253	1.305	1.446	1.275
TEQ	1.028	1.960	1.384	1.110	1.044	0.947	1.130	1.033

Jay Downstream Data July 2001 N=8 5 SPMDs per sample <DL=0 (ng/kg) | Average Temperature | DOC 9/22 N/A

Congener	SPMD 41	SPMD 42	SPMD 43	SPMD 44	SPMD 45	SPMD 46	SPMD 47	SPMD 48
2,3,7,8-TCDF	0.759	0.711	0.781	0.770	0.640	0.656	0.612	0.613
1,2,3,7,8-PeCDF	0.547	0.350	0.312	0.324	0.265	0.264	0.258	0.201
2,3,4,7,8-PeCDF	0.519	0.304	0.293	0.359	0.297	0.262	0.262	0.266
1,2,3,4,7,8-HxCDF	0.450	0.287	0.241	0.263	0.263	0.231	0.221	0.223
1,2,3,6,7,8-HxCDF	0.276	0.170	0.152	0.125	0.119	0.160	0.100	0.082
2,3,4,6,7,8-HxCDF	0.253	0.104	0.144	0.134	0.088	0.118	0.061	0.055
1,2,3,7,8,9-HxCDF	0.255	0.091	0.104	0.117	0.088	0.101	0.074	0.052
1,2,3,4,6,7,8-HpCDF	0.301	0.293	0.317	0.255	0.229	0.241	0.188	0.165
1,2,3,4,7,8,9-HpCDF	0.232	0.157	0.103	0.114	0.060	0.128	0.060	0.068
OCDF	0.405	0.371	0.344	0.333	0.287	0.368	0.304	0.228
2,3,7,8-TCDD	0.213	0.174	0.116	0.093	0.083	0.086	0.086	0.102
1,2,3,7,8-PeCDD	0.351	0.158	0.142	0.115	0.101	0.148	0.100	0.097
1,2,3,4,7,8-HxCDD	0.193	0.096	0.100	0.097	0.101	0.087	0.074	0.082
1,2,3,6,7,8-HxCDD	0.890	0.499	0.482	0.731	0.535	0.723	0.483	0.541
1,2,3,7,8,9,-HxCDD	0.354	0.198	0.154	0.157	0.152	0.156	0.131	0.099
1,2,3,4,6,7,8-HpCDD	0.453	0.461	0.504	0.415	0.386	0.368	0.343	0.303
OCDD	1.786	1.503	1.602	1.471	1.175	1.137	1.211	0.975
TEQ	1.205	0.726	0.646	0.651	0.552	0.609	0.512	0.522

FLAGS

- M/z ion ratio
- Surrogate recovery
- Both M/z ratio and Surrogate Recovery
- Retention Time

* Loss from GPC Clean Up Run

^ Deployed for 37 days

All TCDD concentrations should be viewed with trepidation due to existing furan interference

Jay Upstream Data July 2	TOC 7/17	Sp. Cond.	Flow 7/13	Flow 8/10	DOC 8/10	TOC 8/10	Sp. Cond.
	N/A	45.03	0.8	1.4	5.9275	6.3892	95.22
					Without SPMD 50 & 51		
Congener	Mean	Std. Dev.	%RSD		Mean	Std. Dev.	%RSD
2,3,7,8-TCDF	2.355	0.234	9.954		2.270	0.139	6.133
1,2,3,7,8-PeCDF	0.739	0.148	20.099		0.661	0.043	6.451
2,3,4,7,8-PeCDF	0.853	0.148	17.319		0.779	0.060	7.727
1,2,3,4,7,8-HxCDF	0.482	0.155	32.085		0.412	0.036	8.782
1,2,3,6,7,8-HxCDF	0.184	0.117	63.780		0.137	0.020	14.349
2,3,4,6,7,8-HxCDF	0.159	0.097	60.859		0.113	0.023	20.349
1,2,3,7,8,9-HxCDF	0.103	0.119	115.608		0.051	0.011	21.543
1,2,3,4,6,7,8-HpCDF	0.346	0.204	58.801		0.265	0.073	27.513
1,2,3,4,7,8,9-HpCDF	0.143	0.119	83.098		0.091	0.028	31.167
OCDF	0.328	0.232	70.627		0.230	0.035	15.063
2,3,7,8-TCDD	0.149	0.046	30.638		0.133	0.032	24.111
1,2,3,7,8-PeCDD	0.150	0.126	83.997		0.095	0.026	27.239
1,2,3,4,7,8-HxCDD	0.121	0.101	83.577		0.083	0.019	23.283
1,2,3,6,7,8-HxCDD	0.648	0.226	34.925		0.635	0.129	20.262
1,2,3,7,8,9,-HxCDD	0.251	0.138	54.936		0.189	0.045	23.895
1,2,3,4,6,7,8-HpCDD	0.635	0.128	20.158		0.579	0.048	8.249
OCDD	1.526	0.319	20.912		1.375	0.113	8.185
TEQ	1.205	0.332	27.539		1.049	0.065	6.233

Jay Downstream Data Jul	TOC 9/22	Sp. Cond.	Flow 9/27	Flow 10/20	DOC 10/20	TOC 10/20	Sp. Cond.
	N/A	76.94	0.75	0.67	7.7361	7.8293	134.6
					Without SPMD 41		
Congener	Mean	Std. Dev.	%RSD		Mean	Std. Dev.	%RSD
2,3,7,8-TCDF	0.693	0.071	10.289		0.683	0.071	10.439
1,2,3,7,8-PeCDF	0.315	0.105	33.179		0.282	0.050	17.755
2,3,4,7,8-PeCDF	0.320	0.087	27.015		0.292	0.034	11.779
1,2,3,4,7,8-HxCDF	0.273	0.075	27.558		0.247	0.025	9.913
1,2,3,6,7,8-HxCDF	0.148	0.060	40.369		0.130	0.032	25.005
2,3,4,6,7,8-HxCDF	0.119	0.062	52.298		0.100	0.034	34.149
1,2,3,7,8,9-HxCDF	0.110	0.062	55.956		0.090	0.021	23.910
1,2,3,4,6,7,8-HpCDF	0.249	0.054	21.712		0.241	0.054	22.250
1,2,3,4,7,8,9-HpCDF	0.115	0.058	50.768		0.099	0.037	37.993
OCDF	0.330	0.056	16.946		0.319	0.051	15.906
2,3,7,8-TCDD	0.119	0.048	40.459		0.106	0.032	30.446
1,2,3,7,8-PeCDD	0.152	0.084	55.561		0.123	0.026	20.774
1,2,3,4,7,8-HxCDD	0.104	0.037	35.749		0.091	0.010	11.058
1,2,3,6,7,8-HxCDD	0.611	0.151	24.810		0.571	0.109	19.147
1,2,3,7,8,9,-HxCDD	0.175	0.077	44.214		0.150	0.030	19.886
1,2,3,4,6,7,8-HpCDD	0.404	0.067	16.522		0.397	0.069	17.340
OCDD	1.358	0.274	20.218		1.296	0.230	17.739
TEQ	0.678	0.225	33.178		0.603	0.078	12.996

FLAGS

M/z ion ratio

Surrogate recovery

Both M/z ratio and Surrogate Recovery

Retention Time

* Loss from GPC Clean Up Run

^ Deployed for 37 days

All TCDD concentrations should be viewed with trepidation due to existing furan interference

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4.2

EEL STUDY

EEL STUDY

There are two principle fisheries for adult eels in Maine, a river fishery and a lake fishery. Most of the eels are sold outside Maine in US and international markets, although some are consumed in Maine. People fishing eels need permits from either DMR or DIFW. DMR also funds several eel research projects at the University of Maine. Limited data from previous years show that eels from rivers are often among the species most highly contaminated with a number of contaminants. Contaminant levels in eels from lakes are unknown. In 1998 eels were captured from 3 lakes. Since then we have tried to get eels from 3 rivers as well, but were successful only in collecting eels from the Penobscot River in 2000. Therefore, in 2001, we attempted to collecte 20 eels from each of three rivers to be analyzed as four composites of five fish each for dioxins, coplanar PCBs, total PCBs, and mercury. We were able to collect eels from only the Penobscot River at Orrington which were analyzed for dioxins and coplanar PCBs. Concentrations of both were among the highest of all species and exceeded the Maine Bureau of Health’s Fish Tissue Action Level as can be seen in section 3.1 in the Rivers module of this report. Samples of eels have already been collected from the Kennebec River and Penobscot River in 2002 to be analyzed for mercury and total PCBs.

4.3

MINK AND OTTER MERCURY STUDY

Investigation of Mercury Exposure in Maine's Mink and River Otter

(BRI 2002-10)

Submitted to:

Barry Mower, Maine Department of Environmental Protection
&
Wally Jakubas, Maine Inland Fisheries and Wildlife

Submitted by:

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19 April 2002

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Abstract

Anthropogenic releases of mercury into the environment for the past several decades have collected in aquatic ecosystems. The impact of this mercury build-up is of concern to regulators and policy makers. Maine and much of New England are especially at high risk because of local and regional emission sources, prevailing wind patterns, and certain hydrological and biogeochemical features. This study helps establish an exposure profile for mercury in mink and river otter populations in Maine. Although a total of 26 otter and 47 mink carcasses have been collected, parametric statistical analysis of covariables is not yet possible. Mercury levels do tend to be greater in mink vs. otter, interior vs. coastal populations, and females vs. males. Respective mean mercury levels in otter and mink fur, 19.6 and 21.8 ppm, were near concentrations considered to have adverse effects in other studies. The proportion of sampled populations exceeding 20 ppm in the fur was 61% for otter and 47% for mink. Mink fur Hg levels ranged up to 68.5 ppm. Brain and liver Hg levels were well below published lethal levels. The strong relationship among brain, liver, and fur Hg levels indicates great flexibility in using one compartment for determining mercury exposure. Otter and mink mercury levels from western and northern Maine indicate greatest risk. Continued collection of carcasses through our established trapper network will increase sample size and geographic scope. Soon, we will have a suitable mercury exposure profile that can be used to model a wildlife criterion value protective of Maine's mink and river otter population.

The full report is available as a separate file with the 2001 SWAT report at http://www.state.me.us/dep/blwq/monitoring.htm

4.4

MERCURY METHODS STUDY

Optimization of the Methyl Mercury in Ambient Water Method (Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS) for Detection Limits Below 0.05 ng/L.

T. Haines and C. Devoy

Final Report – December 12, 2002

Summary

The analytical method has been improved dramatically resulting in peaks that are taller, sharper, and more reproducible. The system is now composed of a greater number of standard, readily available consumable components, rather than relying on custom-made components. This makes maintenance and repair easier and cheaper.

Some components of the project have not been developed completely, due to resource limitations. Design changes to the gas chromatography and pyrolysis components have been successful. Development of the sparging and distillation components has been partially successful, but further work is required. The ethylation procedure was evaluated and found to be acceptable. An alternate detector was evaluated and found to be more stable and is recommended as a future improvement.

The lowest standard that can be included in a calibration curve has declined from 0.05 to 0.02 ng/L. The calculated method detection limit (MDL) is 0.0397 ng/L, which is higher than expected. Refinement of the distillation method in particular is expected to lower this value.

Part I - Methyl Mercury Detection

Ethylation Efficiency

Ethylation performance was tested, using a range of ethylating agent concentrations (0.25, 0.5, 1.0 and 2.0%), within a completely randomized design. Each concentration was used to produce a standard curve, which could be evaluated in terms of mean calibration factor (CF) size, percent relative standard deviation (%RSD), and low-standard percent recovery. The CF for a standard is the peak height divided by the mass of methyl mercury injected. Percent RSD is the standard deviation of the CF values for the standards, relative to the mean CF.

It is important to note that 24 hours after production of the ethylating agents, all the vials containing the 1% solution had a yellow tinge. This indicates that reaction with air had occurred, most likely in the original vial of sodium tetraethyl borate ($NaBEt_4$). The experimental results support this conclusion, based on reduced response across the entire standard curve.

Ethylating agents contain trace amounts of methyl-, ethyl-mercury that contribute to the response produced by each standard. Small additions may actually be helpful because a quantified value for the blank (rather than a "noise" value) is crucial to the success of the calibration. However, as the size of the blank response increases, it can mask the lower standards. In cases where the blank value is 2 or 3 times the value of the blank-subtracted lowest standard, the validity of blank subtraction may be questioned. However, omitting blank subtraction at the lowest levels of detection prevents successful calibrations because the calibration factors of the lower standards are inflated relative to those of the higher standards.

An addition of 40 μL of 0.5% $NaBEt_4$ is currently used for methyl mercury analysis. Results from this experiment support this choice because the concentration is sufficient to produce a large Mean CF, while yielding a small enough blank response. Low standard recovery consistently lies within the 65-135% range specified in the draft EPA Method.

Sparging system

The initial sparger design is shown in Appendix A and was fabricated by Popper & Sons. Testing confirmed that it was able to sparge multiple sealed samples, and could be connected tightly to the gas lines. However, the machined holes proved to be too large to allow even vertical distribution of gas bubbles. A flow rate of 500-1000 mL/min was required to produce bubbles from each row of holes. This flow rate is too high, driving methyl mercury too far into the trapping material and increasing the risk of thermal decomposition during desorption. During testing, the use of this assembly produced peak heights approximately 0.9 times as large as those from the original glass bubblers. However, the ease of connection, use and cleaning of this system were a significant improvement over the original design. In order to solve this problem, the tip of the original assembly was replaced with a section of porous stainless steel (by Applied Porous Technologies), which resulted in finer bubble formation. While the new design can successfully generate bubbles in a sample at a flow rate of approximately 100-200 mL/min, bubble production is still not vertically uniform. Further development is needed to satisfy the design requirements.

A second aspect of the sparging setup is the ability to stir the sample during the ethylation phase. A miniature stirring assembly was purchased and modified to provide enough power to drive a 3 mm x 12 mm stirbar. During a dye test, complete mixing was achieved within 45 seconds. This indicates that distribution of ethylating agent within the bottle would be uniform during the 15 minute ethylation step.

Chromatography

The original stationary phase of the gas chromatography (GC) column (15% OV-3 on Chromasorb W) is not available in a capillary format. The closest match is 5% phenyl, 95% methylpolysiloxane in a 10 m, 0.53 mm ID column. An Alltech AT-5 column was purchased and installed in a modified HP 5890 Series II gas chromatograph. The modification (Appendix B) involved replumbing the gas flow and sample introduction mechanism. The new design uses a column flow rate of 15 mL/min (at 35 °C and 4.5 psi head pressure), and has operated successfully since installation.

An advantage of switching from packed column to capillary GC is the ability to better control temperatures during the analysis. It was necessary to develop a multistage temperature program (Figure 1) in order to successfully separate the mercury species Hg(0), methyl-, ethyl-mercury and diethyl-mercury. The initial 35 °C is ideal for separation and the first rise is needed to reduce the retention time of the diethyl mercury peak. The temperature is then increased quickly to 115 °C in order to remove residual water from the column. Typical retention times are approximately 1-1.5, 2.25-2.75, and 3.75-4.25 minutes for the three peaks.

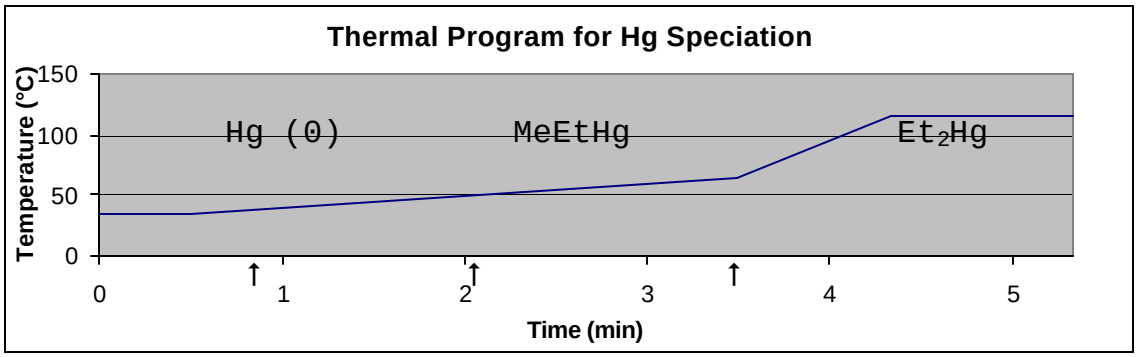


Figure 1. Thermal program and peak elution order.

Thermal Decomposition Furnace and Column

A new pyrolysis furnace has been constructed (Appendix C). Briefly, a ceramic fiber tube heater is connected to a

programmable power controller, which monitors temperature via a thermocouple (Omega). Temperature control is very accurate and stable, allowing settings to be maintained over long periods of time. The design of the furnace will allow for the use of a variety of different pyrolytic columns, in order to allow for future development. During testing, the furnace operated well at 500, 700, 800 and 850 °C and maximum variation was ± 0.3 °C (± 0.1 °C typical). An example of the thermal stability of the furnace is given in Figure 2.

The new pyrolytic column design has a reduced internal diameter and a longer, coiled flow path. The quartz wool packing has been eliminated, in order to reduce peak spreading. This column was fabricated by Chemglass. Calibration was very successful during testing, indicating that the coil design is an effective replacement for the packed, wide bore column.

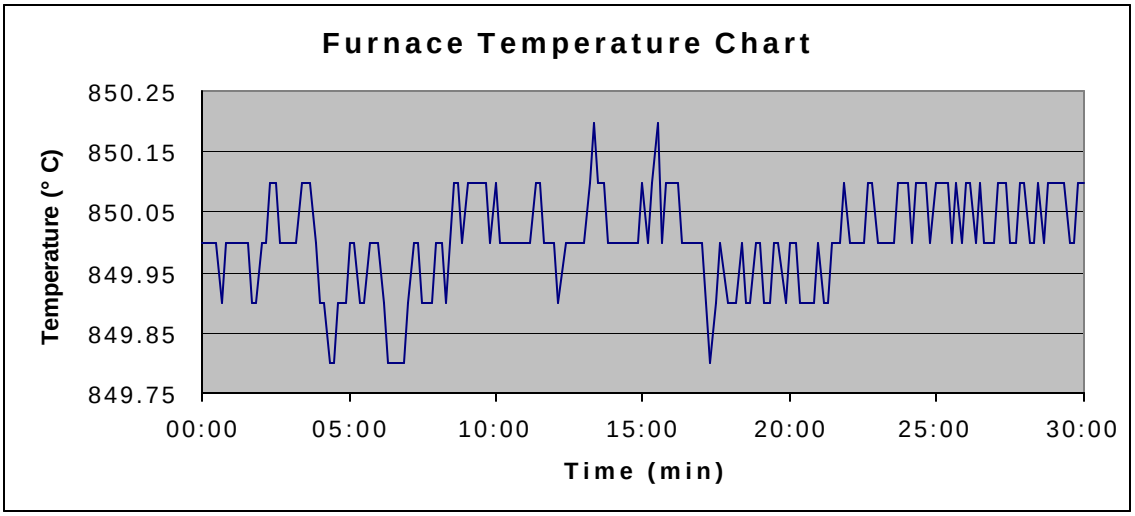


Figure 2. Thermal stability of pyrolysis furnace.

Fluorescence Detector

A comparison of two detector designs (Brooks Rand Model III and Tekran 2600) has been made and example chromatograms are shown in Appendix D. Successful calibration was performed with both detectors, defined as one having a percent RSD <15 % and the low standard having a percent recovery between 65 and 135 %. The Tekran detector yielded the lowest %RSD (8.6 vs 14.1) and a low standard percent recovery closer to 100% (104.2, 94.3 vs 115.4, 111.7).

The limit of detection appears to be controlled by different factors for each of these detectors. The Brooks Rand detector suffers from baseline noise of sufficient magnitude to interfere

with peak integration below 0.02 ng/L. The Tekran detector does not exhibit this phenomenon and so the limit of detection could be controlled by factors such as system gas leaks, flow and temperature control, and trap dryness. These factors may yet be improved and so this detector offers the best opportunity for future method improvement.

Part II - Methyl Mercury Distillation Procedure

The new system is composed of a pair of wide-mouth Teflon® 120 mL vessels connected by a 90° elbow. The diameter of the vessels and elbow is 4.7 cm (1.85”), as compared to the 1/16” ID of the transfer tubing in the old system. The results of the initial testing were encouraging, but further work needs to be done before final evaluation. The “hot” side (containing the sample) reached 103 °C on the outside, but only 77 °C on the inside (determined after disassembly). The “cold” side was chilled to 10 °C and the internal temperature reached 15 °C. These conditions resulted in a ΔT of 62 °C and a distillation of approximately 25 mL (of 100 mL) in 4.5 hours. The internal temperatures need to be brought closer to 95 °C and 2 °C respectively, in order to maximize ΔT while preserving the methyl mercury.

Part III - Method Evaluation

Some components of this project could not be fully developed due to resource limitations. These include the sparging components and the distillation system. There are still several ideas which will be explored as time and funding becomes available. The MDL calculation was performed on data produced from the existing distillation method, and the improved analytical equipment. Seven replicates of a 0.02 ng/L standard were distilled and analyzed.

MDL = $s(t \bullet 99)$ for n replicates

where: n = number of replicates analyzed
s = standard deviation of the values
$t \bullet 99$ = students t value for a one-tailed test at the 99% confidence level with n-1 degrees of freedom

MDL = 0.0126 x 3.143 = 0.0397 ng/L

The calculated MDL is not as low as expected, despite several key improvements in the method, which have increased precision and instrument sensitivity. New components have been designed with standard, easily replaceable fittings. The thermal decomposition furnace is very well controlled and the addition of the GC has improved control of the remaining flow and temperature settings. The peak height of a 0.02 ng/L standard is approximately that of a 0.05 ng/L standard one year ago. The system has been successfully calibrated to 0.02 ng/L, with acceptable RSD (<15%) of the standards.

This work has resulted in an improved analytical system, including sparging, trapping/desorption, chromatography and pyrolysis. However, it also highlights the need for the use of a more stable detector, such as a Tekran 2600 and the development of an improved distillation system. Increased detector stability is expected to reduce %RSD in low concentration calibrations. Improvements to the distillation system should focus on precision (consistent distillation conditions) and ease of cleaning. Contamination is extremely hard to control below 0.02 ng/L. A combination of these improvements should lead to a lower calculated MDL, and therefore a lower limit of quantization.

This work has additionally laid the groundwork for automation of the analytical system. Although there are several issues to be resolved, automation could increase both data quality and quantity. In particular, automation could eliminate the need to connect and disconnect traps repeatedly throughout the analysis. This would result in traps being exposed to less air, and enable trap fittings to be more permanent (resulting in fewer leaks). A major component of this development would be to continue and finish development of a sparging probe that can be used in an autosampler. The probe developed in this work suffered from weakness at the tip, and non-uniform bubble production. Resolution of these issues, together with detector – GC – computer interfacing would clear the way for analytical automation.

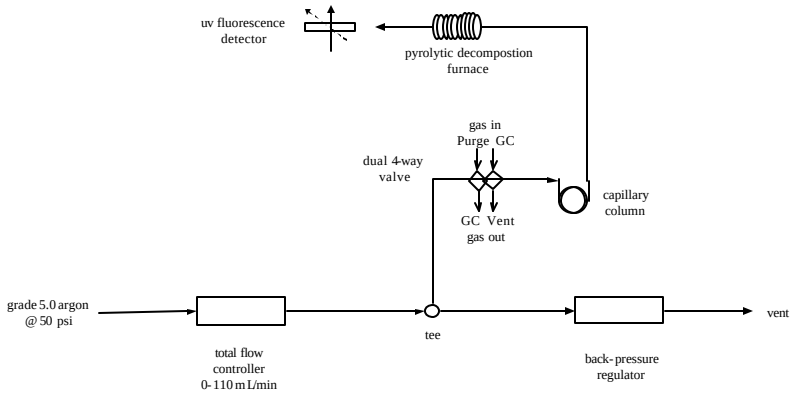
Appendix A – Sparge Assembly

Notes: [a] Gas line in [b] Sparge holes [c] Return holes [d] Gas line out [e] Luer-lok connector

Once the sparger has pierced the septum, the section from about 0-95 mm is within the bottle. Gas return holes are above liquid level. Gas flows down the center tube, bubbles out of the tip section and returns through the outer tube and out of the side arm due to the pressure in the sealed bottle.

Appendix B – Chromatograph Plumbing

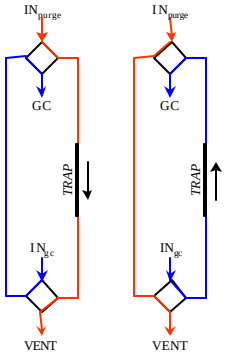
Plumbing Diagram for Methyl Mercury Analysis using Series 5890 GC



Dual 4-way switching valve shown in this figure is given in detail below. Detector flow rate is 15 mL/minute.

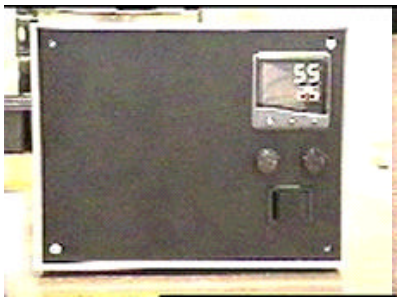
Valve arrangement allows loading of trap in one direction and purging in reverse. Gas flow to GC is maintained from the same source.

Plumbing Diagram for Dual 4-way Valve

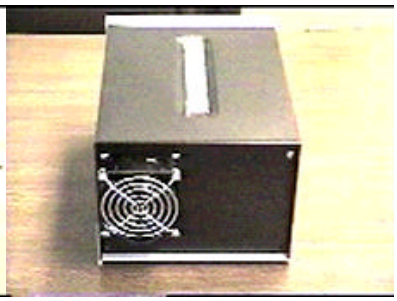


Trap Purge Trap Inject

Appendix C – Pyrolytic Furnace Assembly

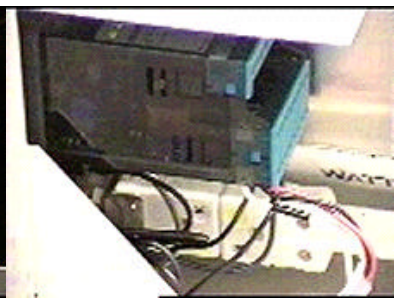


a. Front panel



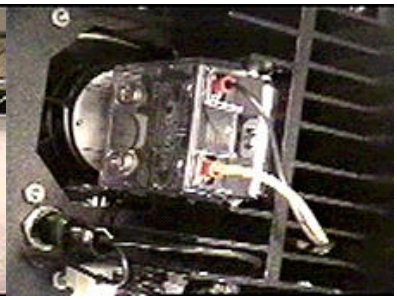
b. Rear panel / cooling fan

c. Internal organization



d. Temperature control module

e. Furnace and connections



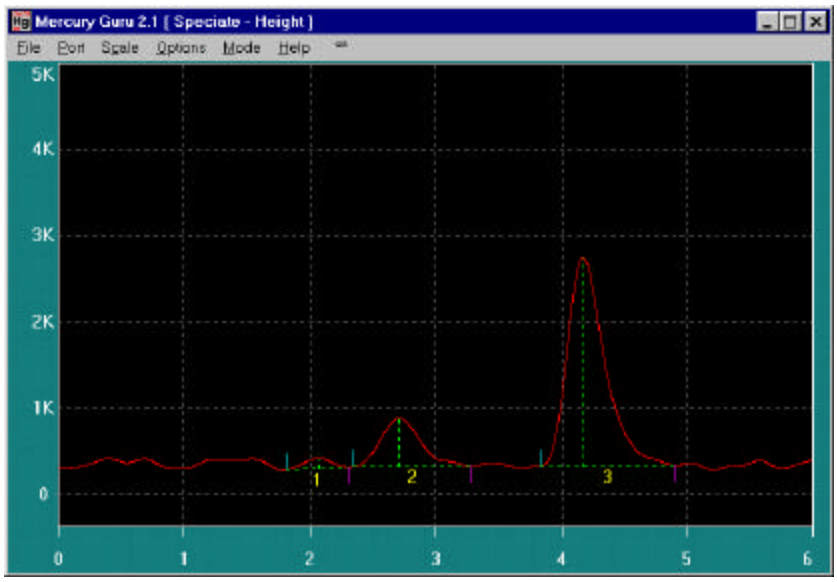
f. Solid state relay and heatsink

The cooling fan draws cool air in over the solid state relay (SSR) heatsink, maintaining a suitable operating temperature for the switching apparatus. This air also flows around the outer surface of the tube furnace before exiting the enclosure via a row of holes along the top of the left side. The temperature control module is also shielded from radiant heat, while obtaining a temperature signal from a stainless steel thermocouple located in the center of the furnace. Argon gas is fed into the cavity of

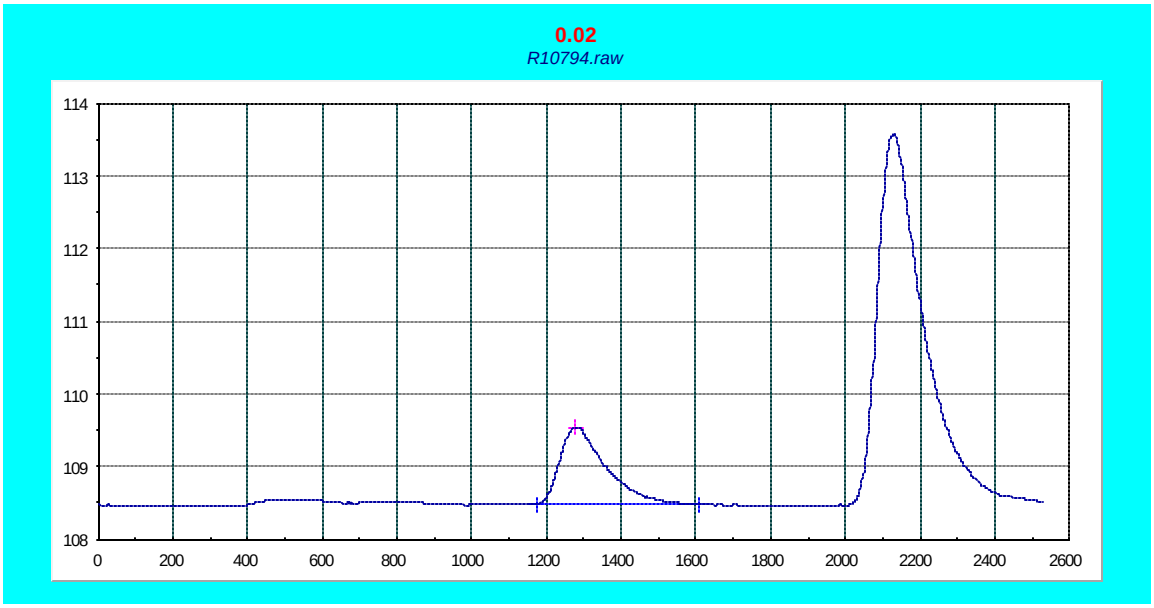
the tube heater, in order to reduce aging and oxidation of the heater coils and quartz coil.

The furnace is programmable from ambient temperature to 850 °C and will maintain the desired temperature to within ±0.3 °C. The temperature control module operates on a 1 second cycle time during which the SSR is switched on for long enough to maintain the desired temperature. Control is constantly adjusted in order to minimize variations.

Appendix D – Peak Comparison for Two Detectors



Graph of Response vs Time for 0.02 ng/L standard (100 mL), using a Brooks Rand Model III detector. Peak 2 is MeEtHg, derived from MeHg. Peak 3 is Et_2Hg, derived from inorganic Hg. Note symmetrical peak shape, and good spacing of peak 2 and 3. Note also, noisy baseline (approximately 20% of standard) which can influence peak height calculation.



Graph of Response vs Time for 0.02 ng/L standard (100 mL), using a Tekran 2600 CVAFS detector. Peak 1 (centered on 500) is elemental Hg. Peak 2 (centered on 1275) is MeEtHg, derived from MeHg. Peak 3 (centered on 2125) is Et_2Hg, derived from inorganic Hg. Note excellent signal to noise ratio, reasonable peak shape and good spacing of peaks. Note also, very stable baseline.

4.5

BROMINATED ORGANICS
(from 2000)

BROMINATED ORGANICS
SCREENING FOR POLYBROMINATED DIPHENYL ETHERS (PBDE) IN MAINE RIVERS

By Therese Anderson, University of Maine

Polybrominated diphenyl ethers (PBDEs) are a group of 209 congeners that are found as components in flame retardants and plastics. Their structure is similar to dioxins, furans, and PCBs, with bromines substituted instead of chlorines. Because of this similarity, they are named in the same manner. These compounds have been found in increasing concentrations in the environment and initial studies have shown evidence of toxicity.

This project involved an initial screening of fish from Maine rivers by utilizing past dioxin extracts and analyzing them for the presenxe of PBDEs. Since the extraction process is the same for both the dioxins and the PBDEs, these compounds should have been extracted along with the target compounds. The samples analyzed were from the 2000 dioxin project and included original and re-extracted samples. The sample extracts from each site were composited to provide enough sample to analyze. The composites ranged from 3 to 5 extracts per sample. PBDE standards were purchased from Cambridge Isotope Labs and run prior to the analysis of the samples. Since the samples were not originally extracted for PBDEs, surrogates were not added at the beginning of the extraction and the results are not corrected for surrogate recovery.

The results are, therefore, considered qualitative and are used to indicate only the presence or absence of these compounds. The estimated concentrations of the PBDEs ranged from <0.1 to 100s ppb. Station and species codes are shown below. Table 4.5.1 shows estimated average amounts of one of the compounds in each homologue group. These concentrations indicate that PBDEs are present in these watersheds. In order to develop quantitative results, additional fish samples will be collected in the future and extracted and analyzed by a method specific to PBDEs.

SPECIES CODES

BNT	brown trout
EEL	eel
LMB	largemouth bass
RBT	rainbow trout
SMB	smallmouth bass
WHP	white perch
WHS	white sucker

STATION CODES

AGL	Androscoggin R at Gilead
ARP	Androscoggin R at Rumford Point
ARF	Androscoggin R at Rumford
ARY	Androscoggin R at Riley
AGI	Androscoggin R at GIP, Auburn
ALV	Androscoggin R at Livermore Falls
ALS	Androscoggin R at Lisbon Falls
ALW	Androscoggin Lake at Wayne
KRM	Kennebec R at Madison
KNW	Kennebec R at Norridgewock
KFF	Kennebec R at Shawmut, Fairfield
KRS	Kennebec R at Sidney
PBW	Penobscot R at Woodville
PBM	Penobscot R at Winn
PBL	Penobscot R at S Lincoln
PBV	Penobscot R at Veazie
PBO	Penobscot R at Orrington
PWD	Presumpscot R at Windham
PWB	Presumpscot R at Westbrook
SFS	Salmon Falls R at S. Berwick
SEN	E Br Sebasticook at Newport
SED	E Br Sebasticook at Detroit
SWP	W Br Sebasticook at Palmyra

Table 4.5.1 PBDEs in fish samples from Maine Rivers, 2000 (ppb)

STATION	SPECIES	N	P1BDE	P2BDE	P3BDE	P4BDE	P5BDE	P6BDE	P7BDE
AGL	RBT	1	<0.1	1.13	19	1.23	0.63	<0.1	<0.1
ARP	SMB	2	<0.1	1.28	14	4.48	1.15	<0.1	<0.1
ARP	WHS	1	<0.1	0.28	0.51	1.8	1.21	<0.1	<0.1
ARF	SMB	1	0.12	0.57	0.25	6.12	0.41	<0.1	<0.1
ARY	SMB	1	<0.1	2.65	2.2	0.34	1.45	0.1	<0.1
ARY	WHS	1	0.58	9.48	16	0.85	0.63	<0.1	<0.1
ALV	SMB	1	<0.1	26	7.95	3.9	1.44	0.1	<0.1
AGI	SMB	1	<0.1	0.094	5.79	1.89	0.88	<0.1	<0.1
ALS	SMB	1	<0.1	7.24	23	2.19	6.83	0.1	<0.1
KNW		1	<0.1	1.01	<0.1	2.44	1.73	<0.1	<0.1
KNW	SMB	1	<0.1	0.011	<0.1	0.33	<0.1	<0.1	<0.1
KFF	SMB	2	<0.1	0.016	<0.1	0.53	<0.1	<0.1	<0.1
KSD	BNT	1	<0.1	0.64	0.1	0.42	5.73	0.15	<0.1
KSD	SMB	1	<0.1	<0.1	0.38	0.14	0.41	<0.1	<0.1
PBM	SMB	2	<0.1	3.12	1.05	1.05	0.42	<0.1	<0.1
PBM	WHS	1	<0.1	9.62	0.11	2.7	0.3	<0.1	<0.1
PBL	SMB	2	<0.1	1.02	<0.1	0.46	<0.1	<0.1	<0.1
PBL	WHS	1	<0.1	58	4.83	3.36	<0.1	<0.1	<0.1
PBC	SMB	1	<0.1	0.1	<0.1	0.18	<0.1	0.17	<0.1
PBC	WHS	1	<0.1	65	<0.1	0.61	0.49	0.66	<0.1
PBV	SMB	1	<0.1	1.57	0.11	1.92	8.54	0.17	<0.1
PBV	WHS	1	0.1	2.68	1.58	1.74	4.86	0.2	<0.1
PBB	EEL	1	0.13	6.77	13	3.22	17	0.1	<0.1

N= number of samples