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DIOXIN MONITORING PROGRAM

STATE OF MAINE

2000

BY

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Acknowledgements

Successful collection of the samples was accomplished directly by DEP staff, the Penobscot Indian Nation assisted by Acheron Inc. on behalf of Lincoln Pulp and Paper Co and Ft James Inc.. The Department of Marine Resources and Department of Inland Fisheries and Wildlife also assisted in collecting samples and providing nets. Heather Shoven, a graduate student at the University of Maine, conducted the SPMD studies. Close cooperation with the Water Research Institute (now the Environmental Chemistry Laboratory) also at the University made the analytical results much better. Assistance of Friends of Merrymeeting Bay and a consultant, Applied Biomonitoring, made the caged mussel study possible.

EXECUTIVE SUMMARY

The goal of Maine's Dioxin Monitoring Program, established in 1988, is "to determine the nature of dioxin contamination in the waters and fisheries of the State". Charged with administration of the program, the Department of Environmental Protection (DEP) is required to sample fish once a year below no more than 12 bleached pulp mills, municipal wastewater treatment plants, or other known or likely sources of dioxin. DEP is required to incorporate the results of all studies into a report to the Joint Standing Committee on Natural Resources by March 31 of the following year. Costs of sample collection and analysis are assessed to the selected facilities. DEP is advised by the Surface Water Ambient

Toxic (SWAT) Monitoring Program Technical Advisory Group in implementation of the program.

The primary objective of the Dioxin Monitoring Program is to monitor dioxin in fish for assessment of ecological and human health. A second objective is to measure trends, progress toward reduction in environmental concentrations, and effectiveness and need for further controls. A third objective is to determine if bleached kraft pulp mills are discharging dioxin into Maine rivers, which is prohibited as of December 31, 2002 by the dioxin law of 1997 [38 MRSA section 420(2)(I)] The final test is that fish (or surrogate) downstream have no more dioxin than fish (or surrogate) upstream of a mill's discharge, the 'above/below' test.

In 2000, the Dioxin Monitoring Program continued development of a suitable 'above/below' fish test. Intensive monitoring of bass and suckers on the Kennebec River and the Penobscot River, as in 1999, was repeated to gather similar data for a second year. Changes from 1999 included use of 1. small bass instead of small suckers and 2. composite samples of livers on the Kennebec River. In addition, as part of DEP's SWAT monitoring program, semi-permeable membrane devices (SPMDs) and caged mussel studies were conducted as potential surrogates for the fish test.

Fish Consumption Advisories
Based on data through 1999, the Maine Bureau of Health revised the fish consumption advisories in August 2000 (Appendix 1). There is a 'General Consumption Advisory for All Inland Surface Waters due to Mercury Contamination'. Also there are more restrictive 'Specific Freshwater Fish Consumption Advisories' for the Androscoggin River, Kennebec River below Madison, the Penobscot River below Lincoln, Salmon Falls River below Berwick, and Sebasticook River (including East and West branches) due to PCBs and dioxins. An advisory on lobster tomalley was continued from 1994 along the entire coast of Maine due to dioxins and PCBs.

Findings of the 2000 Program

1. **Concentrations of dioxin toxic equivalents (DTEh) were much lower than in past years at many stations, some of which are below pulp and paper mills showing significant reductions in their discharges of dioxin,**

while other stations are below industrial/municipal facilities that have done less or nothing to reduce their discharges of dioxin. These results are interesting and results of the future years will be necessary to interpret any trends.

2. **Concentrations of DTEH exceeded the Bureau of Health's Fish Tissue Action Level for cancer (FTALc=1.5 ppt) only in eels from the Penobscot River below Brewer.**

3. **The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in higher levels of total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level at other locations as well. Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition.**

4. **Concentrations of 2378-TCDD (TCDD) and DTEh in all fish samples collected below bleached kraft mill discharges to the Androscoggin River, Kennebec River, and Penobscot River, were significantly greater than those at reference stations unimpacted by point sources, except for TCDD in bass at Riley on the Androscoggin River.**

5. **Concentrations of TCDD in white perch and DTEh in white perch and suckers from Androscoggin Lake were significantly greater than in any species from all other lakes (n=8) or river reference stations that have been sampled. For the first time, however, concentrations of both TCDD and DTEh in bass were similar to reference stations. Concentrations of both TCDD and DTEh in bass and suckers are lower than those found in those species from the Androscoggin River, the most likely the source, but concentrations in white perch are similar to those in bass from the river.**

6. **There was no significant difference in TCDD or DTEh in bass from above and below SAPPI Westbrook's paper mill, now that the pulp mill has closed, but traces of furan remain elevated below the mill.**

7. **Since the development of the Above/Below test began in 1997, over 78 tests have been conducted for different dioxins, species, tissue types, and other surrogates in an attempt to develop a test powerful enough to**

accurately measure any differences above and below a mill. Bass and semi-permeable membrane devices show the most promise and will be tested again in the 2001 program.

INTRODUCTION

Maine's Dioxin Monitoring Program (DMP), established in 1988, has been amended and reauthorized through 2002 by the Maine legislature. The goal of the program is "to determine the nature of dioxin contamination in the waters and fisheries of the State". Charged with administration of the program, the Department of Environmental Protection (DEP) is required to sample fish once a year below no more than 12 bleached pulp mills, municipal wastewater treatment plants, or other known or likely sources of dioxin. The Department is also required to sample sludge once a quarter from the same facilities.

The primary objective of the DMP is to monitor dioxin in fish for assessment of ecological health and of human health. The data are used by the Maine Bureau of Health (BOH) to determine the need for any Fish Consumption Advisories to protect human consumers of fish from certain Maine rivers. The data are also used by DEP and other state and federal agencies in determining impacts of discharge of dioxin on wildlife species.

A second objective is to continue monitoring at some historical stations to measure trends. Trends are followed to measure progress toward reduction in environmental concentrations and effectiveness and need for further controls.

A third objective, to identify sources and magnitude of dioxin discharges, received new emphasis in 1997 when the Maine legislature enacted LD 1633 "An Act to Make Fish in Maine Rivers Safe to Eat and Reduce Color Pollution". The key requirement is that ‘a (bleach kraft pulp) mill may not discharge dioxin into its receiving waters’ [38 MRSA section 420(2)(I)]. Interim tests that concentrations of TCDD in effluent from the bleach plant must be below EPA’s method 1613 nominal detection limit (10 ppq) by July 31, 1998 and TCDF must be below the same detection limit by December 31, 1999 have been achieved. As the final test, by December 31, 2002 fish below a bleached kraft pulp mill have no more dioxin than fish above the mill, the so-called "above/below (A/B) fish

test". Although the DMP has successfully detected differences above and below discharges in past years, as the amount of dioxin discharged is reduced, the DMP needs to be modified to allow an enhanced ability to detect smaller differences with known statistical confidence.

The monitoring program is coordinated with other ongoing programs conducted by the Department, US Environmental Protection Agency (EPA), or dischargers of wastewater. The proposed annual monitoring plan must be submitted to the Surface Water Ambient Toxic (SWAT) monitoring program Technical Advisory Group (TAG), created under 38 MRSA section 420-B, for review and advice. The selected facilities must be notified of their inclusion in the proposed program at least 30 days prior to submittal to the TAG. The Department must incorporate the results of all studies into a report due the Natural Resources Committee by March 31 of the following year. A draft of the report is reviewed by the TAG before completion of the final report. Costs of sample collection and analysis are assessed as a fee to the selected facilities. Payment of the fees is a condition of the waste discharge license granted by the state for continued operation and discharge of wastewater to waters of the State. However, if the selected facility is a publicly owned treatment works (POTW), then the fees may be assessed to the known or likely industrial generator of dioxin and payment will not be a condition of the waste discharge license of the POTW.

Due to continuing controversy over the effects of dioxin on human and ecological health, the US Environmental Protection Agency (EPA) announced that in 1991 it would begin a thorough scientific reassessment of dioxin. EPA proposed that the process would be open to the public and consequently held several meetings to share information and receive comments. A draft report was issued in 1994 and subsequent review in 1995 by EPA’s Science Advisory Board called for revisions of some chapters. Revised drafts published in 2000 indicate that dioxin may exhibit reproductive and developmental effects, immuno-toxic effects, neuro-toxic effects, and cancer. In addition, the reports find that concentrations of dioxin in the environment have decreased since the 1970S. Also ‘EPA currently estimates that the amount of dioxin in tissues of the general human population closely approaches within a factor of 10, the levels at which adverse effects might be expected to occur’. In March 2001 EPA's Scientific

Advisory Board published its draft review of EPA's new revisions and is divided on whether or not dioxin is a carcinogen, but does believe EPA has underestimated non-cancer effects. The SAB also does not agree that there is enough evidence to support EPA's statement about current body burdens and probable adverse health impacts.

DEP has determined, from fish collected since 1984, that concentrations of dioxins in fish from locations unaffected by certain industrial discharges are less than 0.15 ppt, while concentrations in fish below those sources of dioxin are consistently greater than that. Consequently, as one method of determining known or likely sources of dioxin, a Fish Monitoring Threshold (FMT=0.15 ppt) is used by DEP as a monitoring threshold to determine stations that will be retained in the annual program.

For informing the public about potential risk from consuming fish contaminated with dioxin and dioxin-like compounds, the BOH publishes fish consumption advisories. These advisories are based on a comparison of a Fish Tissue Action Level (FTAL) for dioxin toxic equivalent (DTE) concentrations with the 95^{th} percentile upper confidence limit on the mean DTE in fish tissue. Should a tissue concentration exceed an FTAL, a fish consumption rate (e.g., #meals per month) which is unlikely to result in deleterious effects is determined. Two FTALs have been derived for evaluating potential deleterious effects from exposure to dioxins and dioxin-like compounds. Both FTALs were developed using standard USEPA risk assessment methods (EPA 1997). For potential carcinogenic effects associated with long-term exposure, BOH has developed a FTALc of 1.5 ppt, while for reproductive and developmental effects potentially arising from shorter exposure durations, BOH has developed a FTALr of 1.8 ppt (Frakes, 1990). The FTALr for reproductive and developmental effects is relevant to women of child bearing age, pregnant women, and lactating women. The FTALs are compared to the concentration of DTE in edible portions of the fish, skinless filet data. Where whole fish data are reported, the DTE concentration is divided by a factor of 3.5, determined from previous studies with white suckers, to estimate skinless filet concentration. In this report all comparisons with DTE in fish are made with FTALc, since that is the lower of the two and protective of both effects.

PROGRAM DESIGN

The primary emphasis of the 2000 program was to collect fish samples from the appropriate stations and species from each river such that accurate, complete, and current data are available to assess impact to wildlife and human consumers. The program design included sampling at least one station below each major source to document trends and sampling of historic stations that showed dioxin above the FMT, whether or not any fish consumption advisories were issued. Finally the program was modified to evaluate the ability to detect minimum significant differences of the appropriate magnitude for the above/below fish test.

The 2000 program was initially drafted by DEP according to the objectives listed above and sent to participating facilities for comment in early May and to the SWAT TAG later in the month. The workplan was discussed finalized at the SWAT TAG meeting on June 22, 2000.

In 2000 all stations were monitored for ecological and human health assessment and trends (Table 1). At least 5 game fish (bass or other important species) were collected from each station and analyzed individually as skinless fillets.

In order for DEP to accurately determine whether or not there is a discharge of dioxin from a mill, for the Above/Below Fish Test the minimum significant difference (MSD) that can be determined with acceptable statistical probability needs to be relatively small and relevant to background concentrations. Ideally the MSD should be established before the test at some absolute value or fraction of the background concentration. During debate in the legislature, a MSD of 10 % of the background concentration was proposed as a goal by DEP. This would work for TCDF and DTE, where measurable quantities are determined, but not for TCDD, where background concentrations are generally below detection. For TCDD, the detection level (0.05-0.1 ppt wet weight) itself was proposed to serve as the goal, an MSD of 100%. Although initially thought to be achievable, results from the 1997-1998 program with whole suckers showed MSDs to be much higher. In 1999 MSDs for both bass and sucker

filets were lower than in previous years, approaching the target in some samples.

Therefore, in 2000 parts of the DMP was repeated to gather data for a second year to see if MSDs from 1999 could be repeated or improved. At the Kennebec River in Norridgewock and Fairfield, filets from 10 legal sized smallmouth bass and 50 male white suckers were collected to be analyzed as individuals for the bass and as 10 composites of 5 each for the suckers. At Rumford Point and Rumford on the Androscoggin River and at Woodville and South Lincoln on the Penobscot River, filets from 10 smallmouth bass were also collected, and from the two Penobscot stations filets of 10 suckers were also collected. At all other Above/Below stations, ten white suckers were captured and combined into 2 composites of 5 fish each. Trout were analyzed as individuals at all stations, except that brown trout from Gilead on the Androscoggin River were analyzed as a composite of all five fish.

In addition, the DMP was modified in a number of ways. Ten small smallmouth bass, instead of 10 small white suckers that were collected in 1999, were collected at the two Kennebec River stations. To increase the tissue sample size in order to lower detection limits, livers from 50 male white suckers were combined into 10 composites of 5 livers at each of the two Kennebec River stations. As part of DEP's SWAT monitoring program, semi-permeable membrane devices (SPMDs) were deployed in 4 experiments in the Androscoggin River and Kennebec River (described in a later section). Also as part of the SWAT program, caged mussels were deployed at the two Kennebec River stations for the same time as the SPMDs (described in a later section).

All samples were analyzed for all 2378-substituted dioxins and furans. Station locations along with specified fish species are shown in Table 1. Station location maps show exact locations of collections (Appendix 6).

At stations affected by a single discharger, sampling will continue yearly until there are at least two consecutive cycles for each species where dioxin is below the FMT and is not increasing. At stations affected by more than one discharger where fish concentrations are not below the FMT, each discharger will continue to be

included in the annual sampling program until enough evidence has been gathered to demonstrate that dioxin is no longer present in the discharge in significant quantities. Such evidence must be at least 8 consecutive sludge analyses, equally distributed over all seasons for a minimum of two years, that show no 2378-TCDD (TCDD) detected at a suitably low detection level, (2) full congener analysis of sludge for all 2378 substituted dioxins and furans, (3) other pertinent information such as process changes, changes in hook-ups that show reductions in the level of dioxins and furans being discharged to insignificant levels.

The preferred sampling time is late in the summer when fish are likely to be most contaminated after being exposed to higher concentrations of dioxin during low river flows and after significant growth has occurred. At some locations there has been a problem collecting enough fish later in the summer. Here sampling began in mid-May to try to insure that a suitable sample was collected. These stations were also visited after the beginning of July. If fish were captured during the later period, those samples were submitted for analyses. Otherwise, the fish collected during the early period were used. Sampling at other stations began in July (Appendix 8).

SAMPLING PROCEDURES

Fish were collected by DEP with assistance of state agencies and the Penobscot Indian Nation. Upon capture, fish were immediately killed, weighed and measured, rinsed in river water, wrapped in aluminum foil with the shiny side out, labeled, and placed in a cooler on ice for transport to the DEP lab. Chain-of-custody forms were used to record all field information and document all transfers. In the lab, all fish samples were frozen and later transported whole to the Senator George J. Mitchell Center for Environmental and Watershed Research (formerly the Water Research Institute) at the University of Maine for analysis. All other procedures generally followed EPA's Sampling Guidance Manual for the National Dioxin Study (July 1984). A laboratory log was kept for an inventory of samples in the lab at any time and final disposition.

Table 1. 2000 Dioxin Monitoring Program- Stations, facilities, and species

STATION	FACILITY	SPECIES
Androscoggin R		
Gilead	Mead	bass, sucker, trout
Rumford	Mead	bass, sucker
Riley	IP	bass
Liv Fls(Otis imp)	IP	bass
Turner (GIP)	Mead & IP	bass
Lisbon Falls	Mead & IP	bass
Androscoggin Lake	Mead & IP	bass, sucker,w perch
Kennebec R		
Norridgewock	SAPPI Somerset	bass, sucker
Fairfield	SAPPI Somerset	bass, sucker
Sidney	KSTD	bass, sucker
Penobscot R		
Woodville	Lincoln P&P	bass, sucker
S Lincoln	Lincoln P&P	bass, sucker
Milford	Fort James Co	bass, sucker
Veazie	Fort James Co	bass, sucker
Orrington	Brewer	eel
Salmon Falls R		
S Berwick	Berwick Sewer Dist.	bass
Sebasticook R		
W Br Palmyra	Town of Hartland	bass

Most of the facilities in the program already sample sludge or effluent as part of their Maine Sludge Spreading Permit or Waste Discharge License or Federal NPDES permit. Data from those programs provide adequate information about sources of dioxin. Therefore, no additional sludge samples were collected as part of this program. Effluent data are also used when available to indicate sources and any trends.

CALCULATIONS

In this report, DTE are shown as a range with non-detects calculated at zero (DTEo) and at the detection limit (DTEd) as a mean for all samples of a given species at each station (Table 2). For comparison with the FMT and FTALc, and comparison between years and stations, DTEh were used as calculated using non-detects at 1/2 the detection limit. The upper 95th percentile confidence limit (UCL) was used for these comparisons, consistent with the policy of the BOH. In some cases (reference stations) DTEo were also discussed since those were below the FMT while DTEh exceeded the FMT, which shows the importance of low detection limits and the treatment of non-detects. For the other stations both DTEo and DTEh were above the FMT, and DTEo were not discussed.

A related issue is that of EMPCs, estimated maximum possible concentrations. Some compounds, particularly hydroxydiphenyl ethers (DPEs), are coextracted with furans. Various steps have successfully been taken to minimize these interferences, but some DPEs remain. In this report, EMPCs were treated as non-detects.

Statistical analyses of differences in TCDD and DTEh between stations were performed using the non-parametric Mann-Whitney test. Trends were determined using Kendall's tau, a rank-order correlation statistic, for the period 1990-1999. In this report only differences that are statistically significant at p=0.05 will be reported as significant.

RESULTS AND DISCUSSION

Most of the samples of fish targeted in the initial workplan were collected (Appendix 2). Mean concentrations of TCDD and DTEh for each species and station for the last 5 years are shown in Table 2 while earlier data are in Appendix 12. A description of fish collected and results for each sample location with respect to the objectives of the program is discussed below. For each station there are (1) a comparison of DTEh to the Fish Tissue Action Level cancer endpoint (FTALc=1.5 ppt in filets, 5.25 in whole suckers), (2) a comparison of TCDD and DTEh with those at reference stations, (3) a discussion of trends in TCDD and DTEh in fish and (4) a discussion of TCDD and TCDF in sludge or wastewater as an indicator of trends in discharges.

Following discussion of each station is one of the Above/Below test comparing the efficacy of many different tests.

TCDD in fish have normally been below detection (0.1 ppt) in river reference stations (except the Presumpscot at Windham) and lakes (except Androscoggin Lake) tested. Trace amounts of DTEh (0.2-0.3 ppt, less than 10% of the FTALc) at these reference stations are likely due to the ubiquitous atmospheric depostion. Reference stations in 2000 are discussed below.

Since the initial results indicated that TCDD, TCDF, and DTEo were much lower at many stations, some of which are below facilities that have done more or less than others or nothing to reduce discharges of dioxin, in 1999 than in 2000, some samples were rerun. As an objective criterion for selection of which samples to rerun, those samples with results that were greater than 30% different, DEP's data quality objective for duplicates, from 1999, were rerun. As both the initial 2000 data set and reruns all met their QA data quality objectives, in this report values from both sets were averaged for each sample where there was enough tissue left to duplicate the initial sample weight. One exception was bass at Norridgewock on the Kennebec which will be discussed below.

Androscoggin River

Gilead Five rainbow trout and five brown trout were collected near Peabody Island in Gilead, while ten bass and the ten suckers were caught further downsteam at Rumford Point (Appendix 7). As both stations are downstream of the American Pulp and Paper Co's bleached kraft mill in Berlin, New Hampshire, they are therefore not true reference stations unimpacted by direct discharge of dioxin. Both stations are upstream of all Maine mills on the river and are considered the same station relative to point sources.
DTEh in rainbow trout, brown trout, bass and suckers were 90%, 44%, 80% and 43% of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in higher levels of total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely

include long-range transport and atmospheric deposition. Every year measured, TCDD and DTEh in fish have been significantly higher at this station than in fish from reference stations in Maine.

Rumford Ten smallmouth bass and ten white suckers were collected from the river reach from just below the discharge from Mead's bleached kraft pulp and paper mill in Rumford downstream about 4 miles to Dixfield (Appendix 7).
Concentrations of DTEh in the bass and in the suckers were 63% and 45% of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP’s SWAT program, to DTEh may result in higher levels of total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in the suckers as well (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. TCDD and DTEh concentrations were significantly greater than reference stations on other Maine rivers. Concentrations of DTEh in bass were lower than those upstream at Rumford Point, but TCDD levels were not different between the two stations for either species. No sludge data have been reported since 1989. Concentrations of both TCDD and TCDF have been reported below variable detection levels in final effluent since 1993 and below a 10 ppq detection limit in bleach plant effluent since 1998 (Appendix 4).
Table 2

Table 2

Riley Five smallmouth bass were collected from the river above the Riley Dam, about 19 miles downstream of Mead Paper Company and upstream of International Paper Company's discharge (Appendix 7). Concentrations of DTEh in the bass were 31% of the FTALc (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. DTEh were significantly greater than reference stations on other Maine rivers but appear to be slowly declining in recent years (Table 2). TCDD concentrations were all below detection for the first time.

Livermore Falls Five smallmouth bass were captured in the Otis Impoundment, approximately 2 miles downstream of the discharge from International Paper Company's Jay mill (Appendix 7). Concentrations of DTEh in the bass were 62% of the FTALc (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. TCDD and DTEh were significantly greater than reference stations on other Maine rivers. There has been a significant decline of TCDD in both bass and suckers and of DTEh in suckers since 1990. There are no new sludge data since 1996, but concentrations of TCDD and TCDF in bleach plant effluent and final effluent are well below EPA's reporting level (Appendix 4).

Auburn-GIP Five smallmouth bass were collected in Gulf Island Pond (GIP) near the deep hole at Seagull Island, approximately 30 miles downstream of International Paper Company (Appendix 7). Concentrations of DTEh in the bass were 49% of the FTALc (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in higher levels of total toxic equivalents (TTEh) in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. TCDD and DTEh were significantly greater than reference stations on other Maine rivers. There was a significant decline in TCDD in

the early 1990s, and in 2000 DTEh were for the first time lower than in recent years.

Lisbon Falls Five smallmouth bass were captured in the Pejepscot Impoundment, approximately 45 miles below International Paper Company (Appendix 7). This station showed the largest decline in TCDD and DTEh from 1999 of all the stations in the initial 2000 dataset, and although the reruns were higher, they were still much lower than those of 1999 (Table 2). Concentrations of DTEh were 66%of the FTALc (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in higher concentrations of total toxic equivalents (TTEh) in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. TCDD and DTEh were significantly greater than reference stations on other Maine rivers.

Androscoggin Lake

Wayne Androscoggin Lake in Wayne and Leeds is a 4000 acre 38 foot deep meso-trophic lake with a unique reverse delta at the outlet formed by centuries of periodic backflow from the Androscoggin River via the Dead River into the lake. There is a dam on the Dead River that reduces but does not prevent the backflow into the lake, which usually occurs once or twice every year. Significant amounts of dioxin were found in fish from the lake in 1996, 1998, and 1999. In 2000, ten smallmouth bass, ten white perch, and ten white suckers were collected from the lake and analyzed as 2 composites of 5 fish each.

DTEh were 64, 37%,% and 13% of the FTALc for bass, white perch, and suckers respectively, (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD in white perch and DTEh in white perch and suckers were significantly greater than in any species from all other lakes (n=8) that have been sampled and significantly higher than in fish from all river reference stations, but, for the first, time concentrations of both in bass were similar to reference stations. Concentrations of both in bass and

suckers are lower than those found those species from Livermore Falls on the Androscoggin River, which is most likely the source, but concentrations in white perch are similar to those in bass in the river. Concentrations of TCDD and DTEh in suckers appear lower than in previous years.

Kennebec River

Norridgewock Ten smallmouth bass, and fifty male white suckers were collected from the river at Norridgewock (Appendix 7). Five brown trout were also collected from below the dam in Madison. Although these locations are downstream of the discharge from Madison Paper Industries discharge in Madison, comparison of dioxin in fish from this station in 1998 and 1999 with that from fish caught at the Kennebec River reference station above Madison previously, showed no significant difference between the two locations. These locations therefore serve both as a reference for the river and the upstream station for the SAPPI Somerset mill.

DTEh in all three species were 26-27% FTALc, but this was an artifact of relatively high detection limits as shown by DTEo at 3% of the FTALc for all three species (Appendix 2). In fact, TCDD and most other congeners that add significantly to the DTE were below detection and therefore the FMT for all samples. TCDF was present in all samples in trace amounts. The differences between DTEh and DTEo are much larger at these stations than at any station downstream of point sources on the river, and document the problem of the impact of high detection limits and treatment of non-detects. The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. TCDD and DTEo were similar to those from previous years for this and the Madison station. DTEh vary among years due to different detection limits. The trace amount of DTE measured in these fish is likely due to long-range transport and atmospheric deposition from remote sources. This station was also used for additional development of the above/below fish test described in a later section of this report.

Fairfield Ten smallmouth bass, five brown trout and fifty male white suckers were collected from the river between the Shawmut Dam and the I-95 bridge, approximately 7-8 miles below SAPPI Somerset's bleached kraft pulp and paper mill in Skowhegan (Appendix 7). Concentrations of DTEh in bass, brown trout, and suckers were 61%, 39% and 57% of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2000). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD and DTEh were significantly greater than those at the reference station at Norridgewock for all three species. There was no significant trend in concentrations in bass during the 1990s, but there appears a slight reduction in both TCDD and DTEh since 1994. There was, however, a significant reduction in TCDD and DTEh in suckers during the longer period. Effluent data (Appendix 4) and sludge data (Appendix 3) document decreases in discharges over the years especially since early 1997. Concentrations of TCDD and TCDF are well below the limits of the new law (<10ppq in the bleach plant). This station was also used for additional development of the above/below fish test described in a later section of this report.

Sidney

This station is downstream of Lockwood Dam in Waterville/Winslow which is about 10 miles downstream of the current discharges from SAPPI Somerset in Skowhegan. The Kennebec Sanitary Treatment District discharges about 2 miles downstream of the dam. Five brown trout were captured just below the dam and five smallmouth bass were collected about 10 miles below the dam in Sidney. Both of these fish samples are considered to be from the Sidney station since the fish have free movement within this river reach. Concentrations of DTEh in bass and trout were 41% and 48% of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2000). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of

TCDD and DTEh in bass were significantly greater than those at the reference station at Norridgewock. There has been no trend in bass during the 1990s, which have been more variable over the years, but concentrations since 1997 were slightly lower than all but one previous year. Sludge data from KSTD in recent years show that TCDD is below 1 ppt, but TCDF and DTEh are usually detected at a few ppt documenting the discharge of small amounts of dioxin to the river.

Penobscot River

Woodville Although this station is downstream of Great Northern's pulp and paper mills in Millinocket and East Millinocket, fish collected at this station in 1997 and 1998, had similarly low concentrations of dioxin as the historical reference station at Grindstone on the East Branch, uninfluenced by these mills. Therefore, this station may serve as a reference station for the Penobscot River and the upstream station for Lincoln Pulp and Paper. In 2000 ten smallmouth bass and ten white suckers were collected from this station.

Concentrations of DTEh in bass and suckers were 32% and 8% of the FTALc respectively (Appendix 2), but this was an artifact of detection levels and the impact of treatment of non-detects. Concentrations of all congeners that add significantly to DTE were below detection and therefore the FMT, except for trace amounts of TCDF in suckers and somewhat higher levels than previously in bass. As a result concentrations of DTEo were only 9% and 2% of the FTALc for both species. The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002).

Winn As in 1999, at the request of Lincoln Pulp and Paper Company in Lincoln, bass (8) and suckers (10) were captured from the river at Winn, approximately 4 miles below the confluence with the Mattawamkeag River and about 8 miles upstream of the Company's bleached kraft mill in Lincoln. The Mattawamkeag River is thought by the Company to potentially be a source of dioxin downstream of the Woodville station and the Winn station is believed by the Company to be a more appropriate station for the above/below test. Funding for this work

was provided by the Company above and beyond the DMP. TCDD was not detected in any sample for either year. DTEh were 10% and 29% for bass and 11% and 9% for suckers of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Concentrations of all congeners that add significantly to DTE were below detection and therefore the FMT, except for TCDF. As a result concentrations of DTEo were an even smaller percentage of the FTALc for both species. TCDF in bass and TCDF and DTEo in suckers were higher than usually found at the Woodville reference station for 1999 but not 2000. Since these results are variable from year to year, they do not support the idea that there is a significant source between the Woodville station and mill. Since the results and other fish and sediment data collected by the Penobscot Indian Nation are not conclusive and there is no barrier to prevent fish from moving up from below the mill, this station may not be a good reference for the Above/Below fish test.

South Lincoln Ten smallmouth bass and ten white suckers (Appendix 7) were collected from the river near the boat ramp in South Lincoln, approximately 4 miles downstream of Lincoln Pulp and Paper Company's bleached kraft mill in Lincoln. Concentrations of DTEh in bass and suckers were 44% and 27% of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD and DTEh were significantly greater than those at the Woodville reference station. There has been, however, a significant decrease in TCDD and DTE in both bass and suckers during the 1990s, although less so with bass since 1996. This decline is likely a result of decreased discharges from the mill as documented by decreased concentrations of TCDD and TCDF in sludge (Appendix 3) and in effluent, which shows compliance with the limits of the new law (Appendix 4), since 1997. A change in the mill's bleaching process from chlorine based bleaching to primarily oxygen based bleaching in 1999 may account for the slightly lower TCDD and DTEh

concentrations in 2000, but full benefit will likely take longer to discern.

Milford Located at Freese Island near the boat ramp in Costigan, this station is approximately 34 miles downstream of Lincoln Pulp and Paper Company's bleached kraft mill in Lincoln and is the upstream station for the above/below test for the Fort James mill about 5 miles downstream. Five smallmouth bass and ten white suckers were captured from this station. Concentrations of DTEh in bass and suckers were 47% and 29% of the FTAlc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD and DTEh were significantly greater than those at the Woodville reference station. Like the South Lincoln station, at this station there has been a significant decrease in TCDD and DTEh in both suckers and bass during the 1990s, although less so for bass since 1996, likely due to decreased discharges from Lincoln Pulp and Paper Company during that time.

Veazie Five smallmouth bass and ten white suckers (Appendix 7) were collected from the Veazie Impoundment about 7-8 miles below Fort James' bleached kraft mill in Old Town.
Concentrations of DTEh in bass and suckers were 60% and 28% of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD and DTEh were significantly greater than those at the Woodville reference station both years. At this station there has been a significant decrease in TCDD and DTEh in bass and DTEh in suckers since the early 1990s, although not much since 1996, likely a result of decreased discharges from both upstream mills as documented by effluent (Appendix 4) and sludge (Appendix 3) data. TCDD and TCDF bleach plant effluent concentrations at the Fort James mill have continued to decline since early 1998 and have met the limits of the new law.

Orrington Ten eels were collected from an eel fisherman from the river in Orrington, downstream of the Town of Brewer's sewage treatment plant outfall and combined into 2 composites of 5 fish each. The Brewer treatment plant treats wastewater from the Eastern Fine Paper mill which uses pulp made at Lincoln Pulp and Paper Co in Lincoln. Concentrations of DTEh exceeded the FTALc (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD and DTEh were significantly greater than those for bass, another top predator, at the Woodville reference station or any other station. Concentrations were significantly greater than those in eels from this same location in 1996. The reason for this is unknown, since concentrations in discharges, as documented by lower concentrations in Brewer's sludge and effluent or sludge from Lincoln Pulp and Paper and Fort James, have decreased since that time (Appendix 3, 4).

Presumpscot River

Windham Five smallmouth bass (Appendix 7) were collected from the river below North Gorham Pond in Windham. Concentrations of DTEh in bass and suckers were 30% of the FTALc but DTEo were only 7%, documenting the impact of treatment of non-detects (Appendix 2). Concentrations of all congeners that add significantly to DTE were below detection and therefore the FMT, except for trace amounts of TCDF. The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. This station has been used as a reference station for the Presumpscot River since 1993 since there are no known point sources of dioxin upstream. However, concentrations of TCDD, TCDF, PeCDD, PeCDF and DTEh from this station have been significantly higher than all other reference stations in the program every year through 1998. These results suggest that there are other local sources of dioxin which have not yet been discovered. These concentrations must represent a combination of background from local

sources and long range transport and atmospheric deposition from remote sources. The data for 2000, however, look more like those from other reference stations have for all years monitored.

Westbrook Five smallmouth bass (Appendix 7) were collected from the river near the US Route 302 bridge about 1.5 miles downstream of the discharge from SAPPI Westbrook's bleached kraft pulp and paper mill. In 1999 the pulp mill ceased operation and the paper mill now purchases its pulp. This is the first year since then that fish have been monitored.
Concentrations of DTEh in bass were 35% of the FTALc although DTE0 was only 11%, documenting the impact of treatment of non-detects (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD and DTEh were similar but concentrations of TCDF were significantly greater than the Windham reference station, showing both improvement with some residual from past discharges remaining in the river. The latest data, taken within a few months of the cessation of the pulp mill document reduced discharges from the mill (Appendix 3, 4), but there are no new data since.

Salmon Falls River

South Berwick Five smallmouth bass (Appendix 7) were collected from the Rollinsford Impoundment about 2 miles below the discharge from the Berwick Sewer District's municipal wastewater treatment plant in Berwick, whose discharge is 85% effluent from Prime Tanning Company.

DTEh were 39% of the FTALc all bass combined (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD (marginally) and DTEh were significantly greater

than in fish from previous years at an upstream reference station at Acton, which had concentrations similar to other reference stations in Maine. There was no significant trend for TCDD or DTEh in bass during the 1990s. There are no new sludge or effluent data from the treatment plant to show any changes in discharges. These results document a local source of dioxin to this reach of the river most likely the Prime Tanning discharge.

Sebasticook River

West Branch at Palmyra Ten smallmouth bass were collected from the river near the US Route 2 bridge about 3-4 miles below the discharge from the Town of Hartland, whose effluent is about 85% effluent from Irving Tanning Company, and combined into two samples of five fish each.

Concentrations of DTEh were 103% of the FTALc, but DTEo were much less, documenting the impact of the treatment of non-detects, especially for this station (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2000). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD and DTEh were significantly greater than in fish from the reference site upstream of the discharge in Great Moose Lake in years past. There are no significant trends for TCDD or DTEh during the 1990s. These results document a local source of dioxin to this reach of the river most likely the Irving Tanning discharge. Although the only sample result reported (1996) showed no detectable amount of dioxin in effluent (Appendix 4), low solubility and high bioconcentration of dioxin make effluent data less meaningful than sludge data. Sludge data from 1989 show measurable levels of TCDF (Appendix 3), but there are no newer sludge data to aid interpretation of current levels of discharge.

Sebasticook Lake

Newport Eight smallmouth bass and ten white perch were collected from Sebasticook Lake, about 4 miles downstream of the Corinna Sewer District's discharge. This facility treated the waste from the Eastland Woolen Mill in Corinna until 1996, when the mill ceased operation. Since then groundwater and river sediments have been found to be contaminated with a number of pollutants from

the mill. The site was placed on the National Priorities List of Superfund sites in 1999, and cleanup has begun. This work was funded by Maine's SWAT monitoring program. Concentrations of DTEh in bass and white perch were 50% and 64% of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of DTEh in bass and both TCDD and DTEh in white perch were significantly greater than in fish from the reference site upstream of the discharge in Corinna in years past (Table 2, Appendix 12). Concentrations of DTEh were significantly lower than when last measured (1996,1997) at the East Branch of the Sebasticook River at the inlet to the lake.

Above/Below Test

The goal in development of a suitably sensitive Above/Below test, is to be able to detect a minimum significant difference (MSD) in dioxin and/or furan concentrations above and below a mill as small as a target value of 10% of that above the mill or as small as possible. MSDs are normalized to mean concentrations above the discharge to provide a relative measure, since units and scales are different for different congeners, test types, species, and tissues. Where the concentrations above the mill are below the detection limit, as is the case for TCDD in muscle tissue, the MSD target is an absolute value (0.05-0.1 ppt) rather than a relative one.

Since the development of the Above/Below test began in 1997, tests of TCDD, TCDF, and DTEo on both a wet and lipid weight basis have been conducted in small bass, single and composite large bass filets, bass livers, large and small whole suckers, single and composite sucker filets, single and composite sucker livers, single and 2 composites of SPMDs, and caged mussels, for a total of 78 tests. Some tests continue to show promise while others do not and have been discarded. The modifications in the 2000 DMP resulted in further progress towards determination of the most sensitive test. Each modification is discussed separately.

<u>Bass</u>

Ten large bass were captured at one pair of stations on each of the Androscoggin (ARP at Rumford Point above and ARF at Dixfield below the Mead mill in Rumford), Kennebec (KNW at Norridgewock above and KFF at Fairfield below the SAPPI Somerset mill), and Penobscot (PBW at Woodville above and PBL at S Lincoln below Lincoln Pulp and Paper in Lincoln) rivers, essentially repeating studies conducted in 1999. All bass were to be within a 25 mm length range within and between paired stations, which was achieved for most of the the Kennebec and Penobscot but less so for the Androscoggin Due to difficulty in collecting fish (Appendix 7). All bass were analyzed as individuals.

Concentrations of TCDF on a wet weight basis and both TCDF and DTEo on a lipid weight basis were significantly lower at Rumford than at Rumford Point, but there was no difference in TCDD between the two stations (Appendix 2). MSDs were normalized to the mean concentrations of Norridgewock and Woodville since Rumford Point is downstream of American Tissue mill in Berlin New Hampshire. MSDs were lower than in 1999, except for TCDF and DTEo which were higher on a lipid weight basis (Table 3). MSDs were lower for lipid weights than for wet weights, but none were close to the target values. Considerable variation in concentrations at Rumford Point were primarily responsible for the relatively high MSDs. Concentrations of TCDD, TCDF, and DTEo were significantly higher at Fairfield than at Norridgewock on both wet and lipid weight basis as in all previous years (Appendix 2). MSDs were generally similar to those in 1999 (Table 3). MSDs were closest to targets for TCDF followed by TCDD and then DTEo, and lipid weight based MSDs were lower than wet weight MSDs. MSDs were lower than those from the Androscoggin. None of the MSDs met target values, however.

Concentrations of TCDD, TCDF, and DTEo were significantly higher at South Lincoln than at Woodville for both wet and lipid weights except for DTEo based on lipid (Appendix 2). MSDs were generally lower than in 1999 except for TCDF on a lipid basis (Table 3). Lipid weight MSDs were slightly lower than wet weight MSDs except for TCDF which was the only one that came close to meeting the target value. MSDs here were the lowest of those from all three rivers.

Small Bass

Since small fish of a given species at a station are younger than much larger fish, they generally have lower body burdens of contaminants such as dioxin. In addition, younger fish generally have higher growth rates and uptake of contaminants that may more reflect current ambient contaminant levels better than older fish which may have residues from years past. And small fish tend to have smaller home ranges, therefore may be more representative of local conditions than larger fish which may move to different areas within the year. All of these may result in less variation in concentrations and decrease MSDs.

To examine this idea, in 1999 we collected small suckers from the Kennebec River at Norridgewock (KNW)and Fairfield (KFF). Interestingly, MSDs were higher for the small suckers than for the larger suckers for TCDD, TCDF, and DTEo both on a wet and lipid weight basis. Since, in studies conducted beginning in 1997, MSDs were often lower for large bass than for large suckers, in 2000, small bass, rather than small suckers, were collected from these same stations (Appendix 7).

Concentrations of TCDD, TCDF, and DTEo were significantly higher at Fairfield than at Norridgewock. On a wet weight basis, small bass MSDs were quite a bit lower than those for large bass for TCDD and DTEo, and similar for TCDF (Table 3). And lipid normalized MSDs were even lower relative to background concentrations than the wet weight MSDs. MSDs were lower for large bass for DTEo, however. Small bass MSDs were also lower than large sucker MSDs on both a wet and lipid weight basis. Nevertheless, MSDs were still much higher than the targets.

Table 3

Suckers

The 10 composites of 5 fish each of sucker filets showed significantly higher concentrations of TCDD, TCDF, and DTEo at Fairfield (KFF) below the SAPPI Somerset mill on the Kennebec River than Norridgewock (KNW) above the mill (Appendix 2). MSDs were lowest for TCDF, followed by TCDD, and then DTEo in order (Table 3). Lipid weight based MSDs were lower than wet weight MSDs. MSDs were higher for TCDD and similar for TCDF and DTEo compared to individual filets in 1999 (Table 3). MSDs for these composites of sucker filets were much greater than the targets. MSDs were higher than those for both large and small bass for TCDF and DTEo, but slightly lower for TCDD, quite similar to that of 1999. It appears that suckers may not be as good a test species as bass.

Ten large suckers were captured from the Penobscot River at Woodville (PBW) above and at S Lincoln (PBL) below Lincoln Pulp and Paper in Lincoln. All suckers were within a 30 mm length range within and between stations (Appendix 7). All were analyzed as whole fish. Concentrations of TCDD, TCDF, and DTEo were significantly higher at South Lincoln than at Woodville. MSDs were higher for some measurements and lower for others than suckers from the Kennebec. Lipid based MSDs were lower than wet weight based MSDs as with most other species and stations. MSDs were higher than those for the bass at this station, also similar to most other stations. MSDs were not close to the target values.

Livers

Previous monitoring of lobsters in Maine has shown higher levels of dioxin and furans in the hepatopancreas or liver than muscle tissues. Other studies elsewhere have similarly shown higher concentrations of these compounds in the livers of fish and shellfish. Because higher levels might make it easier to detect differences between stations, in 1999, livers were collected from bass and suckers from the Norridgewock (KNW) and Fairfield (KFF) stations and analyzed individually. It was uncertain if individual livers would be large enough to analyze and contain enough dioxin and furan to measure.

Initial extractions of the fish livers resulted in a large amount of diphenyl ether interferences for the furans, especially the TCDF. The methods currently used

for separation of these compounds from fish tissue are not adequate for the liver samples. The analytical method was modified to minimize this interference.

Due to low tissue sample size and resulting relatively high detection levels, no detectable amounts of any congeners were measured in either bass or suckers from the reference station Norridgewock, except for a few samples where HpCDF was detected (Appendix 10). Therefore, calculation of MSDs was not meaningful. At Fairfield, detectable amounts of TCDD and TCDF were measured in most samples and other congeners were detected in many samples.

In order to increase the tissue sample size and lower minimum detection limits to be able to measure TCDD or TCDF at the reference station, in 2000 we collected 50 male suckers to be combined into 10 samples of 5 livers each at the same stations, Norridgewock and Fairfield. Results showed that detectable levels of TCDD and TCDF were measured in all (but one at each station for TCDD) samples (Appendix 10). Detectable levels of most other congeners were measured in many samples as well. Concentrations of TCDD, TCDF, and DTEo were significantly higher at Fairfield than at Norridgewock. This occurred even though the MSDs were much higher than the 10% target value making the test relatively insensitive (Table 3). There was not much difference in wet weight MSDs and lipid weight MSDs.

Concentrations of TCDD, TCDF, and DTEo in one composite of 10 liver samples from female suckers at Fairfield were well within the ranges of those for the 10 samples of males, although well below the mean. Mature females would be expected to have lower levels due to annual purging of lipiophilic contaminants with eggs.

SPMDs

Semipermeable membrane devices (SPMDs) are 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). SPMDs have some features that give them some 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. There are, however, a number of conditions, such as temperature, DOC, solids which can effect the efficiency of these devices. 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.

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. Laboratory handling of the SPMDs after field deployment involves the removal of biofouling, which is exterior debris and periphyton, before extraction. After this initial cleanup, the devices are then spiked with a cocktail of surrogates consisting of C-13 labeled analogs of the toxic native dioxin congeners in order to monitor recovery. After surrogate addition, individual SPMDs are dialyzed and the collected dialysates are cleaned by gel permeation chromatography followed by Florisil solid phase extraction. The extracts from the three SPMDs in each deployment site canister are then combined to enhance detection and each resulting sample is concentrated to ten microliters for HR GC/MS analysis.

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, four studies or deployments were conducted as described below (Tables 4 and 5)and in more detail by Shoven (2001).

TABLE 4. Objectives of the 2000 Field Season Deployments

Objective	#	# of SPMDs
➢ Deployment Time Study: To determine SPMD uptake rates and biofouling over the 28-day deployment period. **Location: Androscoggin R. at Dixfield (10A,B)**	1, 2	20 SPMDs per deployment with 5 retrieved each week for 4 weeks
➢ Androscoggin Above/Below Study: To test the ability of SPMDs to detect differences in dioxin in the river Above/Below a mill. **Locations: Rumford Point (13) and Dixfield (10)**	4	20 SPMDs per site with all retrieved after 28 days
➢ Kennebec Above/Below Study: To test the ability of SPMDs to detect differences in the river Above/Below a mill. **Locations: Norridgewock (11) and Fairfield (12)**	3	10 SPMDs per site with all retrieved after the 54 days

TABLE 5. Descriptions of the 2000 Field Season Deployments

Deployment #	Deployed	Retrived	Time (days)	Site	SPMDs per site	#SPMDs / sample	# Reps
1	6/2/00	6/9/00	7	10-A	5	5	1
		6/16/00	14	10-B	5	5	1
		6/23/00	21	10-A	5	5	1
		6/30/00	28	10-B	5	1	5
2	7/7/00	7/14/00	7	10-A	5	5	1
	6/30/00	7/14/00	14	10-B	5	5	1
	7/7/00	7/28/00	21	10-A	5	5	1
	6/30/00	7/28/00	28	10-B	5	1	5
3	8/3/00	9/26/00	54	11	10	2	5
				12	10	2	5
4	9/19/00	10/17/00	28	10	20	2	10
				13	20	2	10

Results were as follows.

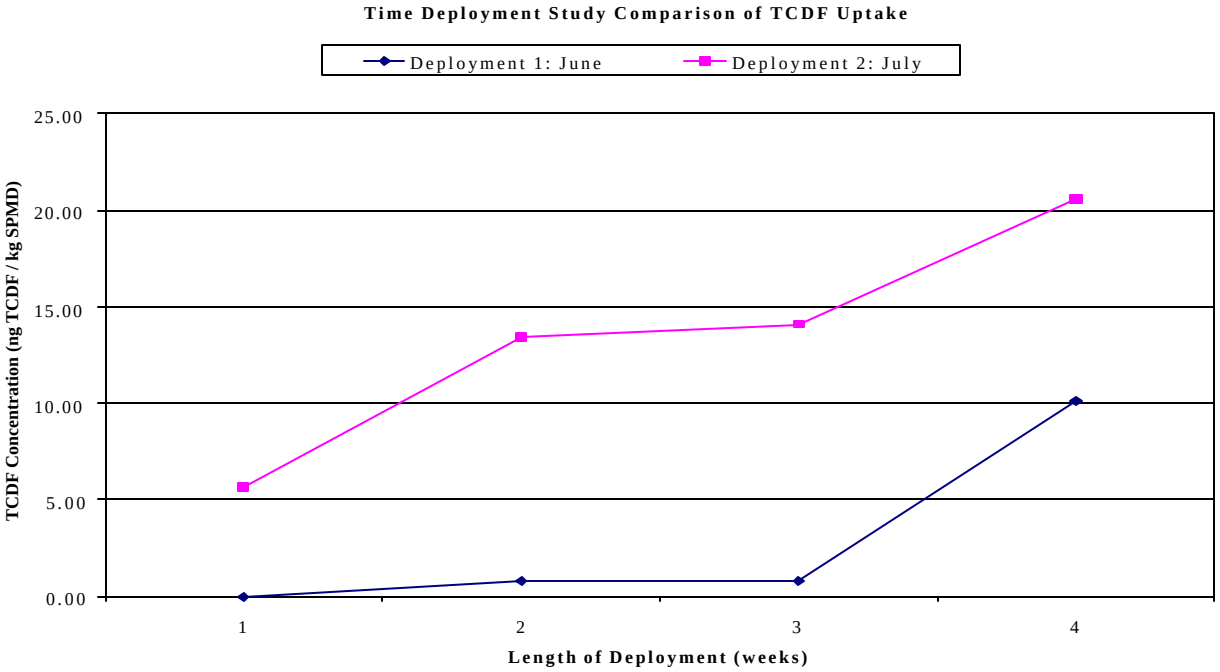
Deployment Time Study, Deployments 1 and 2

One objective was to determine differences in uptake in colder water (June) than in warmer water (July). Another objective was to determine if uptake rates were constant over time or if biofouling with growths of algae and accumulation of other materials would change the uptake rates. This is critical to know to help determine the optimum length of deployment time. Longer deployment times should result in more uptake of dioxin unless biofouling or other processes reduce or eventually stop further uptake. For these and all deployments, SPMDs were suspended from floats so as to be approximately 1 meter below the water surface in all water levels at a location that was at least 4 m deep.

Results showed that uptake of TCDF continued over the 4 weeks in each month (Figure 1), as did uptake of many other furans as well (Table 6). No TCDD or PeCDD and only a few other dioxins were detected. The two curves show that uptake rates were considerably higher in warmer water (July) than in colder water (June)(Figure 1). The different slopes documented different uptake rates for each week for each deployment. In June uptake rates were relatively low for the first three weeks also likely reflecting lower temperatures during that period. Differences for all weeks may also be due to other factors including river velocities, dilution of dioxin levels in the river due to changes in river flow volume, suspended sediment load, dissolved organic carbon, and measurement error, among others.

Qualitatively, the biofouling on the membrane increased in coverage and changed characteristics over the four-week period progressing from tiny tan specs to larger army green, rod-like shapes. Each week the deployment canisters had more growth collected on the surfaces. Since uptake rates during week 4 was not diminished from earlier weeks in either month, biofouling did not seem to be an important factor in these 30 day exposures during June and July.

Figure 1.

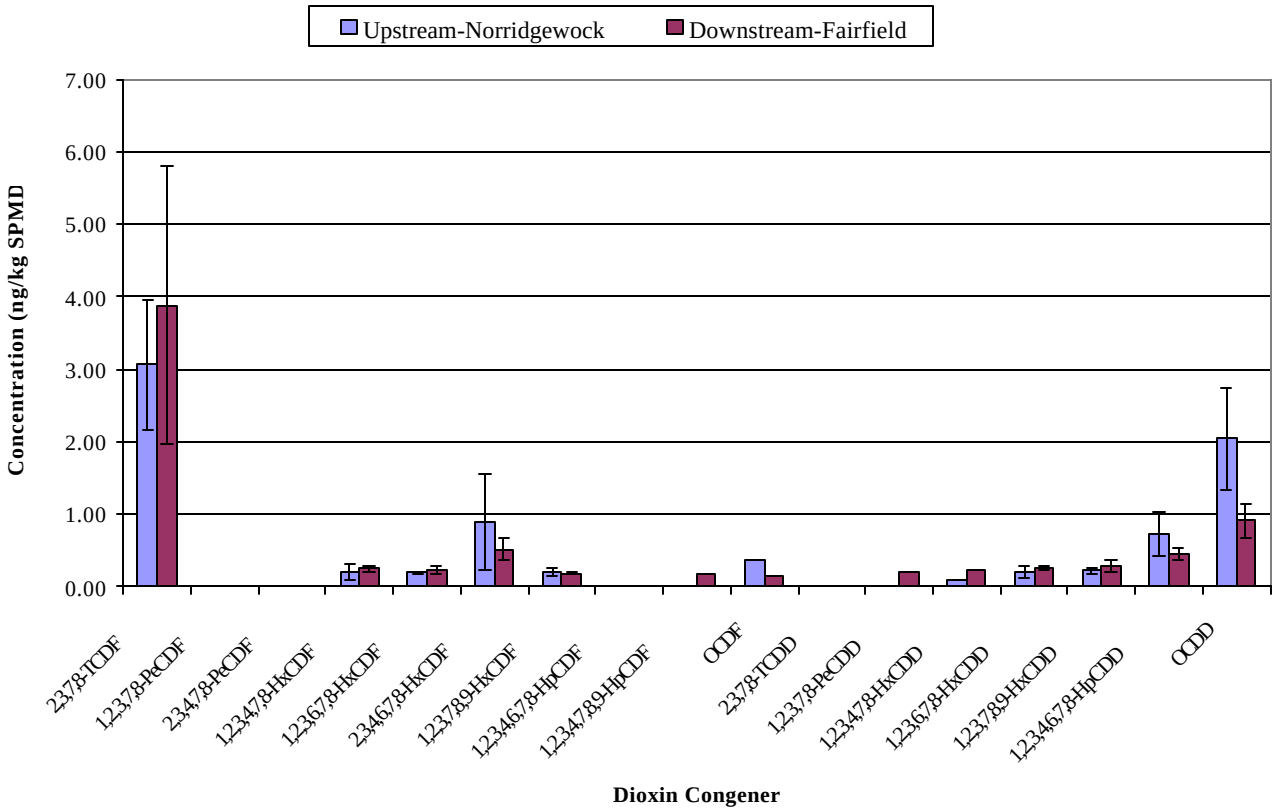


Kennebec Above/Below Study, Deployment 3

This study was conducted in conjunction with fish collections and caged mussel studies at the same two stations in order to be able to compare performance of all the studies in terms of MSDs for the above/below stations. This was a longer deployment than any of the others (Table 5). Results of deployment 3 show that TCDF was the most abundant congener detected (Figure 2). No TCDD nor any PeCDD or PeCDF were detected, but small amounts of other dioxins and furans were detected. Although TCDF appeared increased at Fairfield, the station below the SAPPI Somerset mill, the difference was not significant (error bars are 95% confidence limits). There were no significant differences in above/below concentrations for any other congener with the exception of OCDD, which was higher at the station above the mill. However, relatively small sample size (n=5) and considerable variation at each site (TCDF CV=24-40%, DTEo CV=26-29%) resulted in MSDs (105% for TCDF and 78% for DTEo) well above the target of 10% (Table ?).

Androscoggin Above/Below Study, Deployment 4

Figure 2. Kennebec River Upstream-Downstream Deployment

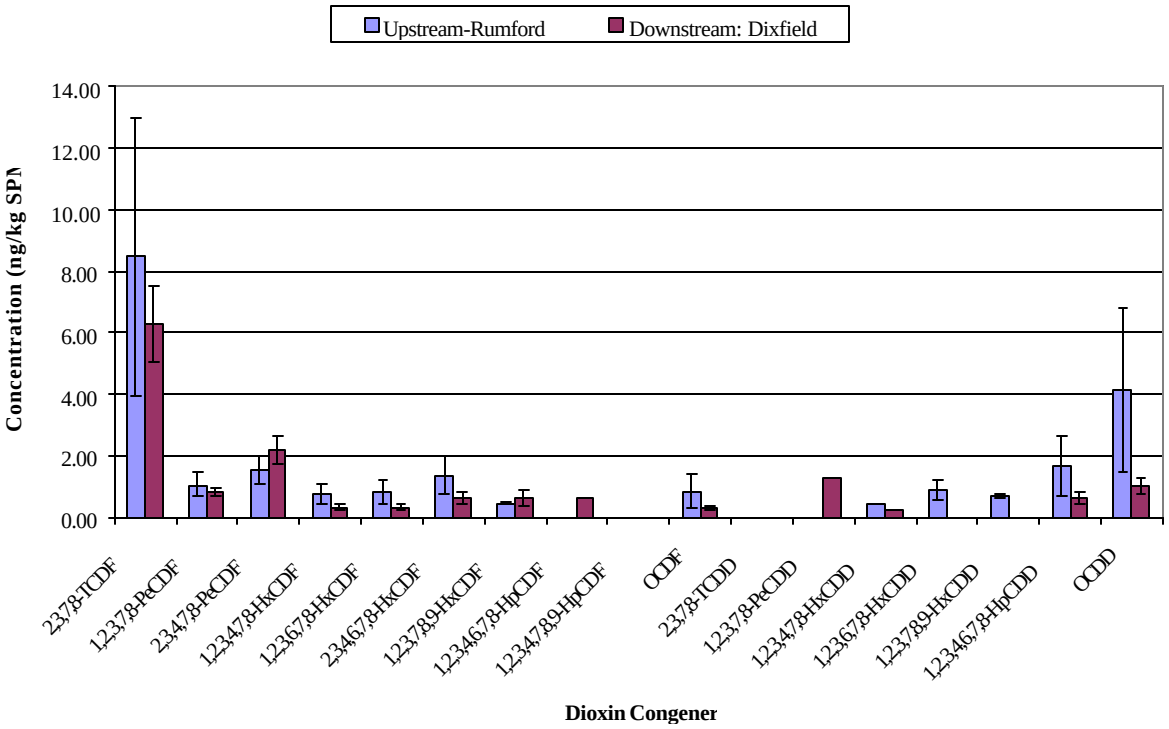


Like the Kennebec study, TCDF was most abundant, but appeared slightly higher upstream of the mill, although the difference was not significant. No TCDD was detected but most other congeners were at one or both stations. There were no significant differences between the two stations for any congener with the exception of OCDD which was significantly higher upstream. Although sample sizes were higher (n=10) than for the Kennebec study (n=5), so was the variance (TCDF CV=28-75%, DTEo CV=45-79%) resulting in MSDs (77% and 129% for TCDF and DTEo respectively) that were similar to those from the Kennebec, also well above the target of 10%.

Conclusions

Comparison of deployments 1,2 and 4 showed uptake of TCDF (mean=8.66+-6.33 ng/kg) in mid September-mid October deployment were lower, similar to those of June (mean=10.08+-0.62 ng/kg), than those of July (mean=20.6+-7.09 ng/kg) likely resulting from temperature differences. Therefore, for maximum uptake, July and August would be better months for use of SPMDs. Uptake rates were not

Figure 3. Androscoggin River Upstream-Downstream Deployment 4



constant probably due to a number of factors, but bio-fouling did not seem to be the problem in 30 day exposures. Deployment 3, a 54 day exposure on the Kennebec River resulted in lower uptake than the other deployments, which is most likely due to lower levels of dioxins and furans in the Kennebec compared to the Androscoggin.

Caged Mussels

This project was a cooperative one with the Maine Department of Inland Fisheries and Wildlife (DIFW) and Friends of Merrymeeting Bay (FOMB) assisted by a consultant, Applied Biomonitoring of Kirkland, Washington. Caged bivalves have been used to monitor pulp and paper mill effluents in Finland for over 20 years. Environment Canada is currently considering caged bivalves as an alternative to the required adult fish survey in their Environmental Effects Monitoring after several successful pilot studies. Caged bivalves are a potentially powerful tool because of their ability to quantify exposure and effects over space and time. Caged bivalves offer an advantage of increased sample size over fish that are often difficult to collect in desired numbers. The initial size range can be also be standardized. This should limit dioxin variability in mussel tissues thereby allowing smaller MSDs

to be detected. Caged mussels anchored in place represent exposure at a fixed point in space unlike fish which may move around.

The approach was to measure survival, growth, and bioaccumulation of dioxins and furans in caged freshwater mussels at the same time and locations above and below the SAPPI Somerset bleached kraft pulp and paper mill on the Kennebec River, Norridgewock and FAIRFIELD, as the fish collections and SPMD studies, in order to compare uptake of contaminants and MSDs among all these Above/Below tests. Freshwater mussels, *Elliptio complanata*, were collected by SCUBA divers from DIFW and FOMB from Nequasset Lake, an undeveloped lake in Woolwich serving as Bath's water supply. The mussels were weighed, sorted by length, and then randomly distributed by length to nylon mesh bags that were then attached to PVC frames and enclosed with polypropylene mesh predator guards according to the methods of Salazar and Salazar (2000). An initial sample of 5 composites of 35 mussels was collected and subsequently analyzed for all 2378- substituted dioxins and furans, percent lipid and percent solids. Individual identities were noted by position within each mesh bag and cages enabling calculation of survival and growth for each individual.

Ten cages of 35 mussels each were placed at both Norridgewock and Fairfield on August 3, 2000 and retrieved on September 26, 2000, giving a 54 day exposure. Upon retrieval mussels were measured for length and weight, and then shucked. Shell and soft tissues were then weighed. Tissues of mussels from each cage were composited into one sample for analysis for all 2378- substituted dioxins and furans, percent lipid and percent solids. Individual mussels were also monitored for survival and growth.

Results of the initial 5 composite samples from Nequasset Lake showed no detectable dioxins or furans (Appendix 11). This was interesting because feral fish from a number of other relatively undeveloped and somewhat developed lakes and ponds as well as rivers have always been found to contain measurable levels of TCDF and some other dioxins and furans. Nor at the end of the exposure did the mussels contain any measurable TCDD either. Measurable concentrations of TCDF, however, were found in all samples at both stations, and many other dioxins and furans were found as well in most samples. Concentrations were similar to those in bass at Norridgewock but 2-3 x lower than those in bass at Fairfield on a wet weight basis, and similar to those in large bass but higher than in small bass on a lipid weight basis at both stations. Concentrations were higher than those in suckers, sucker livers, and SPMDs on a lipid weight basis at both stations. MSDs were similar for TCDF and lower for DTEo to those of fish, but lower for

TCDF and higher for DTEo than SPMDs (Table 3). There was no significant difference in TCDD, TCDF, or DTEo between the two stations, unlike the results for fish.

Conclusions

Of all the test types (large and small bass, large sucker filets and whole fish, sucker liver composites, freshwater mussels, and SPMDs) tested in 2000, only the fish and livers were able to detect significant differences between stations above and below some bleached kraft pulp and paper mills. Freshwater mussels and SPMDs did not detect any differences. SPMDs were tested again in 2001 with an enhanced sample design that may lead to improved capability to detect differences. Freshwater mussels did not appear to be a useful monitoring device, perhaps because they are at a lower trophic level than fish. MSDs were generally lower for bass than for suckers or livers. Neither liver nor mussel studies were repeated, but studies with fish were repeated in 2001.

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APPENDIX 1

MAINE BUREAU OF HEALTH

FISH CONSUMPTION ADVISORY, AUGUST 2000

LOBSTER TOMALLEY CONSUMPTION ADVISORY, 2 FEBRUARY 1994

APPENDIX 2

DIOXIN AND FURAN CONCENTRATIONS IN FISH

2000

CODES	STATIONS
AGL	ANDROSCOGGIN RIVER AT GILEAD
ARP	ANDROSCOGGIN RIVER BELOW GILEAD AT RUMFORD POINT
ARF	ANDROSCOGGIN RIVER BELOW RUMFORD
ARY	ANDROSCOGGIN RIVER AT RILEY
ALV	ANDROSCOGGIN RIVER AT LIVERMORE FALLS
AGI	ANDROSCOGGIN RIVER AT GULF ISLAND POND, AUBURN
ALS	ANDROSCOGGIN RIVER AT LISBON FALLS
ALW	ANDROSCOGGIN LAKE AT WAYNE
KMD	KENNEBEC RIVER AT MADISON
KNK	KENNEBEC RIVER AT NORRIDGEWOCK
KFF	KENNEBEC RIVER AT SHAWMUT, FAIRFIELD
KSD	KENNEBEC RIVER AT SIDNEY
KAG	KENNEBEC RIVER AT AUGUSTA
PBG	PENOBSCOT RIVER AT GRINDSTONE
PBR	PENOBSCOT RIVER W BR AT EAST MILLINOCKET
PBW	PENOBSCOT RIVER AT WOODVILLE
PBM(PBN)	PENOBSCOT RIVER AT WINN
PBL	PENOBSCOT RIVER AT SOUTH LINCOLN
PBC	PENOBSCOT RIVER AT MILFORD
PBV	PENOBSCOT RIVER AT VEAZIE
PBB	PENOBSCOT RIVER BELOW BANGOR AT ORRINGTON
PWD	PRESUMPSCOT RIVER AT WINDHAM
PWB	PRESUMPSCOT RIVER AT WESTBROOK
SFA	SALMON FALLS RIVER AT ACTON
SFS	SALMON FALLS RIVER AT SOUTH BERWICK
SEC	SEBASTICOOK RIVER E BR AT CORINNA
SEN	SEBASTICOOK RIVER E BR AT NEWPORT
SLN	SEBASTICOOK RIVER AT NEWPORT
SWH	SEBASTICOOK RIVER W BR AT HARTLAND
SWP	SEBASTICOOK RIVER W BR AT PALMYRA
SCW	ST CROIX RIVER AT WOODLAND
SCB	ST CROIX RIVER AT BARING

SPECIES

BNT	BROWN TROUT
CHP	CHAIN PICKEREL
LMB	LARGEMOUTH BASS
SMB	SMALLMOUTH BASS
WHP	WHITE PERCH
WHS	WHITE SUCKER

APPENDIX 3

TCDD AND TCDF IN SLUDGE FROM

MAINE WASTEWATER TREATMENT PLANTS

APPENDIX 4

TCDD AND TCDF IN EFFLUENT FROM MAINE WASTEWATER TREATMENT PLANTS

APPENDIX 5

2378-TCDD AND 2378-TCDF IN SEDIMENTS

FROM VARIOUS STATIONS ON THE ANDROSCOGGIN RIVER

APPENDIX 6

SAMPLE LOCATION MAPS

APPENDIX 7

LENGTHS AND WEIGHTS

IN 2000 FISH SAMPLES

APPENDIX 8

SAMPLING SCHEDULE FOR THE 2000 DIOXIN MONITORING PROGRAM

Sampling schedule for the Dioxin Monitoring Program

May (early stations)

Androscoggin R at Lisbon Falls for brown trout
Kennebec R above Madison for brown trout
Kennebec R at Augusta for brown trout
Kennebec R at Fairfield for brown trout
E Br Sebasticook R at County Rd, Newport for bass/wh perch
W Br Sebasticook R at Rt 2 Palmyra for bass

JULY-AUGUST (all rivers in order, beginning at upstream stations)

Androscoggin R - July
Kennebec R - July
Penobscot R - August
Presumpscot R - August
Salmon Falls R - August
Sebasticook R (East and West Branches) - August

APPENDIX 9

TOXIC EQUIVALENCY FACTORS FOR PCDDS AND PCDFS

Appendix 9. Toxicity Equivalency Factors for PCDDs AND PCDFs

(Van den Berg et al, 1998)

Congener	Toxic Equivalency Factor (TEF)		
	Humans/ Mammals	Fish	Birds
Dioxins			
2,3,7,8-TCDD	1	1	1
1,2,3,7,8-PeCDD	1	1	1
1,2,3,4,7,8-HxCDD	0.1	0.5	0.05
1,2,3,6,7,8-HxCDD	0.1	0.01	0.01
1,2,3,7,8,9-HxCDD	0.1	0.01	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.001	<0.001
OCDD	0.0001	<0.0001	0.0001
Furans			
2,3,7,8-TCDF	0.1	0.05	1
1,2,3,7,8-PeCDF	0.05	0.05	0.1
2,3,4,7,8-PeCDF	0.5	0.5	1
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
OCDF	0.0001	<0.0001	0.0001
PCBs			
3,4,4',5-TCB (81)	0.0001	0.0005	0.1
3,3',4,4'-TCB (77)	0.0001	0.0001	0.05
3,3',4,4',5-PeCB (126)	0.1	0.005	0.1
3,3',4,4',5,5'-HxCB (169)	0.01	0.00005	0.001
2,3,3',4,4'-PeCB (105)	0.0001	<0.000005	0.0001
2,3,4,4',5-PeCB (114)	0.0005	<0.000005	0.0001
2,3',4,4',5-PeCB (118)	0.0001	<0.000005	0.00001
2',3,4,4',5-PeCB (123)	0.0001	<0.000005	0.00001
2,3,3',4,4',5-HxCB (156)	0.0005	<0.000005	0.0001
2,3,3',4,4',5'-HxCB (157)	0.0005	<0.000005	0.0001
2,3',4,4',5,5'-HxCB (167)	0.00001	<0.000005	0.00001
2,3,3',4,4',5,5'-HpCB (189)	0.0001	<0.000005	0.00001

APPENDIX 10

DIOXIN AND FURAN IN 1999 AND 2000 FISH LIVERS

APPENDIX 11

DIOXIN AND FURAN IN CAGED FRESHWATER MUSSELS

APPENDIX 12

DIOXIN AND FURAN IN FISH AND SHELLFISH 1984-1995