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Monitoring Dioxin in Maine Overview, Update, Next Steps

March 31, 2003



MONITORING DIOXIN IN MAINE
OVERVIEW, UPDATE, NEXT STEPS
March 31, 2003

OVERVIEW

This report provides an update on the dioxin monitoring program in Maine and an outline of recommended next steps. The report concludes that testing using various mediums should continue this summer, after which the Department will issue its final proposal for dioxin monitoring. Extending the testing this year will enable the Department to provide a more meaningful and scientific-based platform for state policy on dioxin.

BACKGROUND

In the 1980s, the U.S. Environmental Protection Agency was studying the extent to which a family of chemical compounds collectively referred to as "dioxins" was detectable in the environment. Impetus for the study lay in concerns for the potential ecological and human health impacts linked to the chemicals. (For basic information on dioxin, see Appendix 1.) Sampling was conducted in the proximity of bleached kraft paper mills, where dioxin was produced as an unwanted by-product of the chlorine bleaching process. Maine's Androscoggin River was used as a reference station in the study.

In 1985, results of an analysis of fish collected from the Androscoggin during the previous year unexpectedly documented significant concentrations of dioxin. Consequently, the Maine Bureau of Health issued Maine's first fish consumption advisory in 1987. Additional sampling in 1985 and 1986 found similar levels in fish from other rivers below bleached kraft pulp and paper mills, leading to inclusion of parts of the Kennebec, Presumpscot, Sebasticook, and Penobscot Rivers in a revised fish consumption advisory in 1990.¹

In 1988, a bill was presented to the Maine legislature instituting a ban on the discharge of dioxin. The bill was amended to establish a monitoring program instead. Maine's Dioxin Monitoring Program ("DMP") was created (38 MRSA section 420-A) with a provision for it to sunset in 1990.

¹ Note that Advisories for several pollutants have been issued or modified several times over the years. Currently 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. See Appendix 2.

Discovery of continuing significant concentrations in fish from these and other rivers resulted in the DMP being re-authorized in 1990, 1995, 1997, and most recently in 2002. This continuing program has provided data documenting dioxin contamination in fish over the last 15 years.

Based on that data and the known health risks associated with dioxin, the Maine legislature enacted LD 1633, "An Act to Make Fish in Maine Rivers Safe to Eat and Reduce Color Pollution" (38 MRSA section 420(2)(I)- the "Dioxin/Color Law") in 1997. The key requirement is that "After December 31, 2002, a (bleach kraft pulp) mill may not discharge dioxin into its receiving waters".

Two interim requirements were established to track progress toward the goal of no discharge. These involved sampling the effluent from a mill's bleach plant, presumably the place where concentrations would be highest if dioxins were present. The law required that mills may not have a detectable quantity of dioxin (TCDD) after July 31, 1998, and may not have a detectable quantity of furans (TCDF) after December 31, 1999. A detection limit of 10 parts per quadrillion (10 ppq) was specified in the law. All mills passed these interim tests for by having dioxins and furans below the detection limit in the bleach plant effluent².

For the ultimate requirement – no discharge of dioxin after December 31, 2002 – a mill is considered to have discharged dioxin if:

- Dioxin or furan in bleach plant effluent is above 10 ppq (or picograms per liter), unless the Department adopts a lower detection limit by rule, or by incorporating a method in use by US EPA; or,
- Levels of dioxins and furans in fish tissue sampled below the mill's wastewater outfall are higher than levels of fish tissue sampled at an upstream reference site not affected by the mill's discharge. Differences between average concentrations upstream and downstream must be measured with at least 95% statistical confidence. (This measure has become known as the "above/below" test or A/B test); or,
- As determined through a comparable surrogate procedure acceptable to the commissioner.

The 1997 lawmakers recognized that this test would need to be interpreted in the broader context of implications for public health, Maine's environment, and Maine's industry. Therefore, they required the commissioner to consult with the Technical Advisory Group ("TAG") established to guide the Dioxin Monitoring Program in establishing the tests or surrogate procedures.

² The results can be found in Appendix 4 of the annual DMP reports beginning with the 1998 report. The 2000 and 2001 reports can be seen at <http://www.state.me.us/dep/blwq/docmonitoring/dioxin/index.htm>

The 11 member TAG advises the Department on its dioxin monitoring activities and consists of representatives of business, municipal, conservation, public health and academic interests. (See Appendix 3 for a list of current members).

Thus, the goal of Maine's Dioxin Monitoring Program is "to determine the nature of dioxin contamination in the waters and fisheries of the State". The Dioxin Monitoring Program now has three main objectives. Two were established when the Program was authorized in 1988: to monitor dioxin in fish for assessment of human health and ecological impact; and to measure trends, progress toward reduction in environmental concentrations, and effectiveness and need for further controls. A third objective comes from the Dioxin/Color law enacted in 1997. It is to identify the sources and magnitude of dioxin discharges and to develop and apply a suitably sensitive test for the "above/below ("A/B") fish test," with the end result to be no discharge of dioxin.

This document presents a preliminary report of a comprehensive assessment of the Dioxin Monitoring Program. The comprehensive assessment is required to address five points:

1. Dioxin concentrations in fish above and below mills and the health implications of those concentrations;
2. Any evidence that dioxin is being discharged from any mill;
3. Current technology that achieves no discharge of dioxin;
4. The need for continuing the dioxin monitoring program;
5. Other known sources of dioxin polluting rivers in this State.

CURRENT STATUS

1. Dioxin concentrations in fish above and below mills and the health implications of those concentrations

The Department's Dioxin Monitoring Program Report for 2001, issued last summer, shows the latest data. The Table in Appendix 4 provides illustrative data for the 2001 season. The table shows some samples higher below the mills than above, and some samples higher above the mills than below. However, due to the small number of fish sampled, these raw score differences may not be "statistically significant". In other words, you cannot be confident that a few tests are representative of the entire fish population in the area. Successfully completing the assessment of dioxin is directly linked to developing a valid Above/Below ("A/B") test. To be "valid", the test must be able to measure small differences, in a way that is statistically representative. Since this effort began in 1997, DEP has conducted a total of 78 different types of tests. Of these tests, those using fish filets³ have most consistently demonstrated the ability to measure the smallest differences.

³ Tests have been conducted in juvenile bass, single and composite mature bass filets, bass livers, juvenile and mature whole suckers, single and composite sucker filets, single and composite sucker livers, single and 2 composites of semi-permeable membrane devices ("SPMDs"), and caged mussels. For a description of the alternatives, see Appendix 5.

During testimony in 1997, DEP stated that it would try to develop a test sensitive enough to detect a difference between concentrations in fish above and below a discharge of no more than 10% of background or as low as possible in order to signal virtual elimination of discharges.

The fish tests conducted to date are done with samples of up to 10 fish above, and 10 fish below. These samples are *not* able to determine differences as low as 10% of background concentrations. Even after trying to standardize for age, tissues, species, type or congeners of dioxins and furans, there is simply too much variation in the fish samples collected both above and below the mills to “see” differences that small amid the variation in the data. Even doubling the number of fish sampled would not substantially improve the ability to see small differences that would be representative of the whole population. The fish tests conducted to date *are* sufficient to detect relatively large differences in fish concentrations above and below outfalls, differences as much as 50 to 400% of the background amount. Appendix 7 includes a discussion of the TAG’s recommended above/below testing methodology.⁴

Evaluating the health implications of dioxin concentrations is the responsibility of experts within the Maine Bureau of Health. The difficulty of the task is compounded by the fact that the fish also contain concentrations of certain polychlorinated biphenyl (“PCBs”) that act similarly in the cells of animals to the 17 toxic dioxin and furan compounds. The Bureau of Health evaluates the *total* toxicity of samples in determining the need for fish consumption advisories.

2. Any evidence that dioxin is being discharged from any mill

As previously discussed, even though none of the tests are very sensitive, they do demonstrate that some of the mills were continuing to discharge as of 2001.

Every year of testing (2001 is the latest data⁵) showed significantly more dioxin in fish caught below two mills than in fish caught above them. Those two mills are the only ones that have no other mill above them, namely Lincoln Pulp and Paper on the Penobscot River and SAPPI-Somerset on the Kennebec. The absence of the most toxic dioxin congener, TCDD, in any samples of fish above these mills and the presence in all samples of fish below these mills by itself strongly suggests continuing discharges. Ironically, concentrations in fish below these mills were not any higher and in some cases lower than in fish below mills on other rivers where concentrations in fish upstream make differences harder to see.

⁴ In December 2002 a report entitled “Evaluation of Maine’s Dioxin Monitoring Program (2000)” (the “Geisy Report”) was prepared for the Maine Pulp and Paper Association. The report was presented to the TAG and included several useful recommendations. See Appendix 6 for the Executive Summary of this report.

⁵ The most recent sampling data (Summer 2002) will be incorporated in the final assessment due May 1, 2003. A final determination for compliance with the 12/31/2002 deadline for no discharge will be made using data to be collected in the summer 2003.

For the mills that have other mills upstream (MeadWestvaco⁶ and International Paper Company on the Androscoggin River, and Fort James on the Penobscot River), it was impossible to determine whether or not there was a continuing discharge. Some samples indicated that there was a discharge and other samples indicated there was none. This is because the A/B test could not detect any differences in fish concentrations above/below smaller than 50-400% of the background amount, which does not seem to be low enough to say whether or not there is (virtually) no discharge. While they do not "fail" the current tests which only show large differences, we cannot tell with statistical confidence whether there is *no* difference or simply a smaller but still indicative difference.

Appendix 4 includes a brief summary of other methodologies considered for measuring dioxin in the environment upstream and downstream of a mill outfall, including Semi-permeable membrane devices (SPMDs), caged mussels, and High Volume Water Sampling (HVWS).

3. Current technology that achieves no discharge of dioxin

The Department recently retained N. McCubbin Consultants, Inc. of Quebec, Canada to present current information on technologies available to the pulp and paper industry to reduce or eliminate dioxin from their wastewater effluent. Mr. McCubbin is an internationally recognized expert in pulp and paper technology and related pollution control technologies.

The McCubbin report (see executive summary attached as Appendix 8) describes several technologies available that would reduce dioxin discharges by significant fractions. Some of these technologies, such as ozone bleaching and improved process control, could increase mill profitability. Other technologies could have a negative impact on mill profitability. While some technologies are relatively expensive investments, they could offer other environmental benefits such as reduction in biological oxygen demand (BOD), color and phosphorous in mill effluent. Actual reductions in dioxin and the economic impact on mill profitability would depend on individual mill circumstances.

⁶ On December 30, 2002, MeadWestvaco Corporation sent a report prepared by AMEC Earth and Environmental consultants of Westford, Massachusetts, to Governor King announcing their compliance with the Dioxin/ Color law. The basic approach was different than that EPA and DEP use in the water programs and raised a number of issues that were discussed with the Technical Advisory Group of the Surface Water Ambient Toxics Program (SWAT TAG). The consensus is that the approach proposed by MeadWestvaco could lead to an inaccurate conclusion. Therefore, DEP will use a different approach applied to data collected in 2003 in evaluating whether any of the mills are still discharging dioxin.

Mr. McCubbin concludes that while it would be technically possible to eliminate dioxin formation and discharges from Maine mills by converting to Totally Chlorine Free (TCF) bleaching processes, the capital costs would not likely be offset by reductions in operating costs sufficient to support such an investment.

4. The need for continuing the dioxin monitoring program

The Department believes there are sound reasons for continuing the Dioxin Monitoring Program. (It is now authorized through 2007.) There are still fish consumption advisories on several rivers due to dioxins and PCBs. Consequently, there is a need for ongoing assessment of the health risk to humans of eating contaminated fish, which is a critical goal of the Dioxin Monitoring Program. It will be even more important to continue monitoring if the level of concern for human health is heightened based on information in the as yet unreleased scientific reassessment of dioxin conducted by US EPA⁷.

In addition, there is insufficient evidence that any of the mills pass the requirements of the Dioxin/Color law. Although the fish test is not very sensitive, it does identify some mills that continue to discharge dioxins, and leaves the question open for the other mills. Furthermore, more than one year of sampling should be done to check for changes in production processes, process controls, raw materials, or product requirements.

5. Other known sources of dioxin polluting rivers in Maine

While it is known that some of the dioxin in our rivers is the result of runoff and air deposition, since its inception in 1988, the DMP has sampled fish below facilities with 'known or likely dioxin contamination' in their discharged effluent. Finding dioxins in wastewater or sludge from the wastewater treatment plants has provided one way to identify these facilities.

Facilities other than bleach kraft pulp mills that have been found to discharge dioxins include: paper mills that procure pulp from somewhere else, mills producing recycled paper, textile mills, and tanneries. These included: Scott Paper Mill in Winslow, American Tissue (formerly Statler Tissue) in Augusta, and Eastland Woolen Mill in Corinna, all of which have gone out of business.

Currently, Prime Tanning in Berwick, Irving Tanning in Hartland, and Huhtamaki in Waterville, all of which discharge to a local Publicly Owned Treatment Works ("POTW") are also considered potential sources⁸.

⁷ EPA's website regarding the dioxin reassessment includes a wealth of information about dioxin: <http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid+55264>

⁸ In November 2002, Huhtamaki became certified by the Chlorine Free Products Association as the first food service manufacturer to offer processed chlorine free (PCF) packaging. PCF means that, among a number of other requirements, no chlorine is added during processing. But there is a requirement that there is at least 30% post-consumer fiber used in the paper products--fiber that may have been previously bleached with chlorine.

The SAPPI Westbrook mill ceased its pulping and bleaching operation in 1999, but still procures pulp for its paper mill and may also be considered a possible source.

The Domtar mill (formerly Georgia Pacific) in Woodland does not show detectable levels of dioxin in fish downstream from the mill, for reasons that are not well understood.

The Great Northern Paper mills in Millinocket and East Millinocket do not use the kraft process, and do not appear to discharge dioxin.

There is some argument that concentrations in fish may represent historical rather than recent discharges. There are two mechanisms by which this could theoretically occur. First, dioxins in fish tissue could simply be residual accumulations from past years. The half-life of dioxin in fish has ranged from months to a few years in various reports, but the most report that it is less than 1 year. The DMP collects fish of a standard size, and hence likely the same age, at each location.

For mature bass, fish of a legal size (>12 inches in length) are collected and these are probably 3-4 years old. Assuming a half-life of dioxin in fish of 1 year, then 3-4 years after cessation of the discharge of dioxin, any residual concentrations would have been significantly reduced. Mature suckers commonly caught are 6-8 years old and will take longer to purge the dioxins from their tissue and come to a new lower equilibrium with the new discharges. Yearling bass and suckers, however, do show current concentrations in the river. Comparative tests with yearling fish from 1999 to 2001 showed similar results to those of mature fish. Consequently it appears that mature fish do represent current river concentrations.

Whether current river concentrations represent current or historical discharges may be influenced by a second mechanism. Historically-contaminated sediments may be the cause of current concentrations in water and/or food resulting in contaminated fish. Fine-grained organic sediments are necessary for accumulation of organic contaminants like dioxin. Recent studies on these rivers have failed to find these sediments to any great extent. The reasons include: improved wastewater treatment has resulted in a lower discharge of organic solids; the rivers have more oxygen, which hastens breakdown of accumulating organic solids; and spring floods, which move the fine grained solids downstream. Because the areal extent of fine grained sediments is such a small proportion of the total amount of sediments in the river, it is unlikely that sediments are contributing all the dioxins that are being measured in fish.

NEXT STEPS

To date, the Dioxin Monitoring Program has documented a notable decline in dioxin concentrations in Maine fish. However to interpret those trends in a broader context and to track progress toward all three goals of the DMP, there are several key "next steps."

- We need to analyze the 2002 DMP data.
- Based on the data, we will work with the legislature and interested parties to establish procedures for the 2003 round of sampling. We anticipate using the fish test as the primary test, supplementing it with SPMDs, high volume water and mussels.
- Report back the results of the 2003 sampling and a final proposal for dioxin testing at mills, and a comprehensive review of other sources of dioxins in Maine rivers.

[DEP > Dioxin](#)

Tuesday, April 1, 2003

Dioxin

A serious concern for Maine

Dioxin is a serious concern for Maine and the world. It is found everywhere, and we all have some in our bodies. While there is scientific debate about exactly how much of a health hazard it poses, many health scientists agree that it is significant, and that dioxin reduction and elimination is essential to protect human health.

[Exposure](#)[Concerns](#)[What's been done?](#)[What's happening now?](#)

What is dioxin? Where does it come from?

When we talk about "dioxin", we're really talking about a family of chemical compounds. These are formed through combustion, chlorine bleaching and manufacturing processes. The critical ingredients are heat and chlorine.

Since chlorine is commonly found in our environment, natural events such as a volcano or a forest fire can lead to dioxin formation. However the greatest source of dioxin is human activity.

Dioxin is created by individual activity like backyard burning of trash and by wood stoves. Industrial processes, like using chlorine to bleach paper or burning municipal trash in an incinerator, produce dioxin as well.

How are we exposed to dioxin?

Particles released by combustion eventually fall to earth. The dioxin they contain clings to dirt and organic matter, and is only slowly broken down. Through a process called "bioaccumulation", very small amounts of dioxin can be taken up by plants; animals that eat those plants accumulate dioxin in their fatty tissues. A similar bioaccumulation process occurs in waters when dioxin builds up in the fatty tissue of fish. At the federal level, there is an effort underway to better understand how we are exposed to dioxin once it is created.

Nearly all of the dioxin that we take into our bodies comes from eating meat, poultry and dairy products in the regular food supply. One reason that **Maine** has a fish consumption advisory is to limit the amount of dioxin we get from fish in our own rivers.

What concerns us about dioxin?

- **Its persistence:**
Unlike many compounds, dioxin does not quickly break down and can exist for many years after it is formed.
- **Its health impacts:**
At extremely low levels, dioxin can alter the way cells grow and develop. Scientists agree that one form of dioxin causes cancer in humans; some chemical forms of dioxin are considered likely to cause cancer. Other known

human health effects range from a severe acne-like condition to reproductive problems and birth defects.

What has been done to limit our exposure to dioxin?

- Efforts to reduce air pollutants have cut dioxin emissions **nationally** by an estimated 80% between 1987 and 1995. These efforts continue.
- **In Maine**, dioxin concentrations as measured in the fish in our rivers has declined significantly since 1990 (see the most recent [Dioxin Monitoring Program Report](#))--more than 75% in the Penobscot River alone. Initiatives contributing to this continuing decline include:
 - new emission standards for municipal and medical waste incinerators;
 - the toughest [dioxin wastewater discharge law](#) in the country;
 - a groundbreaking [agreement with the Maine Hospital Association](#) to reduce the use of plastics that create dioxin when burned; and
 - a [new law to limit backyard burning](#) of those same plastics.

What's happening now to better understand and deal with dioxin?

- At the **federal** level, a scientific advisory has completed its review of a [comprehensive reassessment of dioxin](#) and its effect on human health. Once finalized, it will provide new insights into the dangers posed by dioxin and how best to address them.
- **Maine's** Department of Environmental Protection has undertaken to [inventory the sources of dioxin in our state](#) in order to be in a position to make the best use of EPA's reassessment. The data and models tell us that about 15.5 grams of dioxin are emitted into our air each year. Nearly half of that comes from commonplace activities, such as back yard burning of trash and wood stoves. Wood fired commercial boilers, municipal waste incinerators and medical waste incinerators make up most of the rest. Almost 100 percent of the solid waste materials with dioxin (e.g., ash, paper mill sludge) are landfilled, effectively preventing the estimated 35.4 grams of dioxin in them from escaping to the environment. Finally, of the 2.5 grams estimated to be discharged directly in wastewater, most is believed to be from pulp and paper mill discharges.

The discouraging news is the pervasive dioxin already present in our environment is not going away soon. However, the good news is that the amount of new dioxin being created is steadily decreasing, and dioxin concentrations in our fish, in our bodies and in our environment are by all measures decreasing. With diligent efforts to keep reducing sources of new dioxin and the passage of time, this potent toxin will become less of a health threat, and more of a cautionary legacy of the industrial revolution.

WARNING ABOUT EATING FRESHWATER FISH

Warning: Mercury in Maine freshwater fish may harm the babies of pregnant and nursing mothers, and young children.

SAFE EATING GUIDELINES

- **Pregnant and nursing women, women who may get pregnant, and children under age 8 SHOULD NOT EAT** any freshwater fish from Maine's inland waters. Except, for brook trout and landlocked salmon, 1 meal per month is safe.
- **All other adults and children older than 8 CAN EAT 2** freshwater fish meals per month. For brook trout and landlocked salmon, the limit is 1 meal per week.

It's hard to believe that fish that looks, smells, and tastes fine may not be safe to eat. But the truth is that fish in Maine lakes, ponds, and rivers have mercury in them. Other states have this problem too. Mercury in the air settles into the waters. It then builds up in fish. For this reason, older fish have higher levels of mercury than younger fish. Fish (like pickerel and bass) that eat other fish have the highest mercury levels.

Small amounts of mercury can harm a brain starting to form or grow. That is why unborn and nursing babies, and young children are most at risk. Too much mercury can affect behavior and learning. Mercury can harm older children and adults, but it takes larger amounts. It may cause numbness in hands and feet or changes in vision. The Safe Eating Guidelines identify limits to protect everyone.

Warning: Some Maine waters are polluted, requiring additional limits to eating fish.

Fish caught in some Maine waters have high levels of PCBs, Dioxins or DDT in them. These chemicals can cause cancer and other health effects. The Bureau of Health recommends additional fish consumption limits on the waters listed below. Remember to check the mercury guidelines. If the water you are fishing is listed below, check the mercury guideline above and follow the most limiting guidelines.

SAFE EATING GUIDELINES

Androscoggin River Gilead to Merrymeeting Bay:----- 6-12 fish meals a year.
Dennys River Meddybemps Lake to Dead Stream:----- 1-2 fish meals a month.
Green Pond, Chapman Pit, & Greenlaw Brook
 (Limestone):-----Do not eat any fish from these waters.
Little Madawaska River & tributaries
 (Madwaska Dam to Grimes Mill Road):-----Do not eat any fish from these waters.
Kennebec River Augusta to the Chops:-----Do not eat any fish from these waters.
 Shawmut Dam in Fairfield to Augusta:----- 5 trout meals a year, 1-2 bass meals a month.
 Madison to Fairfield: ----- 1-2 fish meals a month.
Meduxnekeag River: ----- 2 fish meals a month.
North Branch Presque Isle River----- 2 fish meals a month.
Penobscot River below Lincoln:----- 1-2 fish meals a month
Prestile Stream:----- 1 fish meal a month.
Red Brook in Scarborough: ----- 6 fish meals a year.
Salmon Falls River below Berwick: ----- 6-12 fish meals a year.
Sebasticook River (East Branch, West Branch & Main Stem)
 (Corinna/Hartland to Winslow):-----2 fish meals a month.

For more details, including warnings on striped bass, bluefish and lobster tomalley call (207)-287-6455 or visit our web site at janus.state.me.us/dhs/bohftp/index.html



Revised August 29, 2000
 Environmental Toxicology
 Program
 Maine Bureau of Health

WARNING ABOUT EATING SALTWATER FISH AND LOBSTER TOMALLEY

Warning: Chemicals in some Maine saltwater fish and lobster tomalley may harm people who eat them. Women who are or may become pregnant and children should carefully follow the Safe Eating Guidelines.

It's hard to believe that fish that looks, smells, and tastes fine may not be safe to eat. But the truth is that some saltwater fish have mercury, PCBs and Dioxins in them.

All these chemicals settle into the ocean from the air. PCBs and Dioxins also flow into the ocean through our rivers. These chemicals then build up in fish.

Small amounts of mercury can damage a brain starting to form or grow. That's why babies in the womb, nursing babies, and young children are at most risk. Mercury can also harm older children and adults, but it takes larger amounts.

PCBs and Dioxins can cause cancer and other health problems if too much builds up in your body. Since some saltwater fish contain several chemicals, we ask that all consumers of the following saltwater species follow the safe eating guidelines.

Revised February 20, 2001



Environmental Toxicology Program
Maine Bureau of Health

SAFE EATING GUIDELINES

- **Striped Bass and Bluefish:** Eat no more than 2 meals per month.
- **Shark, Swordfish, King Mackerel, and Tilefish:** Pregnant and nursing women, women who may get pregnant and children under 8 years of age are advised to not eat any swordfish or shark. All other individuals should eat no more than 2 meals per month.
- **Canned Tuna:** Pregnant and nursing women, women who may get pregnant and children under 8 years of age can eat no more than 1 can of "white" tuna or 2 cans of "light" tuna per week.
- **All other ocean fish and shellfish, including canned fish and shellfish:** Pregnant and nursing women, women who may get pregnant and children under 8 years of age can eat no more than 2 meals per week.
- **Lobster Tomalley: No Consumption.** While there is no known safety considerations when it comes to eating lobster meat, consumers are advised to refrain from eating the tomalley. The tomalley is the soft, green substance found in the body cavity of the lobster. It functions as the liver and pancreas, and test results have shown the tomalley can accumulate contaminants found in the environment.

For more information, including warnings on freshwater fish call (886)-292-3474 or visit our web site
janus.state.me.us/dhs/bohetp/index.html

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DIOXIN AND FURAN (Dioxin Toxic Equivalents) CONCENTRATIONS IN MAINE
FISH AT STATION ABOVE AND BELOW KRAFT PULP MILLS - 2001 Samples

Source: Table 3. 2001 Dioxin Monitoring Program Report, Maine DEP, August 2002

MILL (Location) River	FISH SPECIES	Dioxin (TCDD) ppt		Dioxin Toxic Equiv. (DTE) ppt	
		Bass	Sucker	Bass	Sucker
MeadWestvaco (Rumford) Androscoggin River	Above - Gilead	0.3	0.1	1.0-1.4	0.7-1.1
	Below - Rumford	0.2	0.3	0.5-1.0	2.0-2.4
International Paper (Jay) Androscoggin River	Above - Riley	0.2	0.3	0.8-1.0	1.9-2.1
	Below - Livrmr Falls	0.3	0.3	0.9-1.4	1.6-1.7
SAPPI - Somerset Kennebec River	Above - Norridgewk	<0.1	<0.1	0.1-0.8	<0.1-0.7
	Below - Fairfield	0.3	0.3	0.4-1.0	0.5-1.1
Lincoln Pulp & Paper Penobscot River	Above - Woodville	<0.1	<0.1	0.1-0.7	0.1-0.7
	Below - S Lincoln	0.4	0.3	0.5-1.1	0.5-1.1
Georgia Pacific (Old Town) Penobscot River	Above - Milford	0.3	0.4	0.5-1.1	0.5-1.1
	Below - Veazie	0.2	1.3	0.3-0.8	1.7-2.2

1. All figures are in parts per trillion (ppt).

2. **Dioxin Toxic Equivalents (DTE) for both dioxins and furans are shown as a range of values with the lower figure showing non-detects at zero (DTEo), and the higher figure showing non-detects at the detection limit (DTEd) as a mean for all samples if a given species at each station.**

3. For reference: Fish Tissue Action Level, cancer (FTALc) = 1.5 ppt
Fish Tissue Action Level, reproductive
and development, (FTALr) = 1.8 ppt



ALTERNATIVE TECHNOLOGIES CONSIDERED FOR MEASURING DIOXIN IN ENVIRONMENT

SPMDs

Semi-permeable membrane devices (SPMDs) hold promise to be more sensitive than fish since the SPMDs are manufactured and should theoretically have less variability than fish. And variability is the most important and uncontrollable determinant of sensitivity of any test. Beginning in 1999, annual testing with SPMDs by the University of Maine Environmental Chemistry Lab has not shown any less variability than have fish tests. In fact, some early SPMDs tests have failed to show the large differences seen in the fish tests, while more recent tests sometimes, but not always, show more similar results to those from the fish tests. The results of the 2002 tests may shed more light on their efficacy. A more detailed discussion may be seen in the annual DMP report (August 2002).

HIGH VOLUME WATER SAMPLING

Given the low solubility of dioxin, it has always been non-detectable in river water and now, with the recent reductions made by the mills, is usually non-detectable in effluents as well using standard methods. It was always found in the sludge from the mill wastewater treatment plants but is now much reduced and often non-detectable there also. Nevertheless, with the high bioaccumulation factor, it is always found in fish downstream of the mills.

New methods for high volume water sampling (HVWS) allow about 10,000 times lower detection limits in river water than EPA's nominal detection limit. Even so, there may still be a need to compare concentrations above and below a mill due to variability in the necessary multiple measurements at each location. The variability should be lower with HVWS than with fish since there is no biological process involved. SPMDs also involve no biological process and offer the same promise of lower variability, but the results have so far been no better, and sometimes worse, than those for fish. A potential advantage of HVWS is that fingerprinting, or matching either presence/absence or relative abundances of specific congeners, could be used to distinguish differences above and below and determine if there is a discharge. Specific congeners are typically discharged by the mills and not so much by other sources that would be impacting waters above the mills. While fingerprinting can theoretically be used for fish and SPMDs, interpretation is more difficult. Fish metabolize congeners differently and SPMD uptake may vary for different congeners.

HVWS was recommended by Maine Pulp and Paper Association's consultant, Dr. John Giesy, at the SWAT meeting December 13, 2002. The method has been used by other states and agencies with reasonably useful results. The state of North Carolina, US Environmental Protection Agency, and US Geological Survey (USGS) have successfully used this method for the past 7 years to do exactly what Maine law

requires--determine if a facility is discharging dioxin. USGS has offered to assist Maine in a trial of this methodology this summer.

MUSSELS

In 2000, the DEP conducted studies in cooperation with the Friends of Merrymeeting Bay and Dr. Michael Salazar, a consultant who has used caged mussels for similar purposes around the country. Mussels hold some promise as a test organism since source and movement is more controlled. However, they are at a lower trophic level (i.e. lower in the food chain) which reduces the amount of "biomagnification" (accumulation). Other concerns remain about effects of environmental variables, such as effluent temperature and suspended solids. Further study would be needed before this method could be employed as a surrogate to the above/below fish test.

**EVALUATION OF MAINE'S
DIOXIN MONITORING PROGRAM (2000)**

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1.0 Executive Summary

The Maine Dioxin Monitoring Program (DMP) was established in 1988 and reauthorized in 1997 and again in 2002 to evaluate the extent and magnitude of dioxin contamination in the waters and fisheries of Maine [38 MRSA section 420 (2) (I)]. The primary purpose of this report is to review the monitoring data and statistical approaches that have been utilized by the Maine DMP and to suggest necessary improvements to the program. The scope of this report includes an evaluation of available data, statistical methods, selection of fish species, congeners, TEFs, and a discussion of the utility of SPMD data. While a comprehensive and critical evaluation of the DMP is beyond the intended scope of this report, comments and recommendations are included to provide decision-makers with information on the appropriateness of various approaches and conclusions contained in the DMP reports. Overall, the Dioxin Monitoring Program (DMP) can be critiqued on both a programmatic and reporting basis. On a programmatic basis, the goals of the DMP are clearly stated. For example, it is clear that one of the primary goals of the DMP is to ensure that Maine's Kraft pulp mills are in compliance with a key provision of the State's 1997 dioxin law, whereby the mills must demonstrate that dioxin is not being discharged to receiving waters as determined by levels of dioxin measured in fish tissue from above and below the mills, the so called "above/below fish test". In this way, the laws relative to the DMP represent enabling legislation. However, the methodology to accomplish this goal is not clearly stated. Here, we present our understanding of the intent of the pertinent dioxin legislation related to the DMP along with a critique of the methods currently used in the DMP. Finally, we present our recommendations for how the DMP in future years can be made more streamlined, transparent, and technically defensible.

1.1 Upstream/downstream locations

The locations of the upstream and downstream sampling areas have been adequately established in the current DMP. However, the current report could be much improved by providing one or more clear tables and maps that list the paired locations (full name and 3-letter abbreviation) that were evaluated in any given year. More importantly, the purpose and method for calculating the background reference concentrations used in the above/below fish test has not been fully defined in the report. The legislation states that fish from downstream of a mill be compared to "an upstream reference site not affected by the mill's discharge or on the basis of a comparable surrogate procedure acceptable to the commissioner" (38 MRSA section 420, subsection 2I(3)). Thus, the appropriate comparison should be between locations immediately upstream and downstream of a mill and not be based on background reference location that is a significant distance from the mill. In addition, locations selected for the evaluation of fish surrogates (SPMDs and caged mussels) were not appropriate in that their placement was based on the current fish site locations. This type of placement lessens the ability of these methods to identify specific sources to the river.

1.2 Fish species, tissues, size, and surrogates

In each sampling season conducted for the DMP, several different fish species and tissue types have been analyzed for dioxins and furans (PCDD/Fs). Species include smallmouth bass, white suckers, rainbow trout, white perch, and brown trout while tissues include whole body, fillets and livers. In addition, surrogates such as SPMDs and caged mussels have also been evaluated for use in the monitoring program. While it is recognized that there are different uses of the data including the assessment of human health and ecological health, the experimental design and

species selection should focus on the above/below fish test. With sample sizes that range from as few as 1 or 2 to 15, it is impossible to perform meaningful statistical tests to determine the statistical significance of differences in the above/below tests. In order to minimize variability and uncertainty of PCDD/F concentrations associated with differing fish species, sizes of fish, and tissue type, it is recommended that a single tissue type and fish species of standard size be used in the above/below fish test. The concentration data should be lipid normalized prior to statistical analysis to reduce the influence of confounding factors such as size and lipid content that influence fish PCDD/F concentrations. To date, the data collected suggest that smallmouth bass fillets have the most promise because historical data are available for trend analysis, sampling is relatively straightforward, smallmouth bass are relatively abundant at each of the sampling locations, and sufficient sample mass is available to allow for low detection limits. If additional fish species, tissue types, and appropriate surrogates continue to be collected, they should be considered as secondary or tertiary information to be used as a weight-of-evidence approach for determining compliance.

1.3 Pre-determined sample size to achieve desired statistical power

In each sampling season of the DMP, sample sizes have been variable, ranging from 1 to 15. Ideally, the DMP report should include a power analysis to determine the necessary sample size to achieve the desired power to detect a statistically significant difference. As discussed previously, a sample size of 1 or 2 precludes any meaningful comparison among locations. A related concern is the issue of minimum significant difference (MSD). Currently, the DMP report presents calculated MSDs for each location and each sample type. Nowhere in the report is there a description of how these calculated MSDs are used relative to evaluating the significance of potential differences between sites. Furthermore, the DMP legislation does not discuss the issue of MSDs. In spite of this, the DMP report states that a MSD of 10% of background concentrations for TEQs has been proposed as a goal by DEP to evaluate differences. However, there is no justification for how or why this value was selected. As currently presented in any DMP report, it is not transparent how the MSDs are used in the analysis for the above and below tests. The crux of the issue should not be whether MSDs are achieved but whether or not there is a statistically significant difference in the above/below fish test and whether the sample size provides sufficient statistical power to detect any potential difference in concentration.

It is also recommended that a further consideration be made relative to biological significance since artifacts can occur due to sample sizes and detection limits in which small, biologically insignificant differences may be discerned. Over the past several years, the TEQ concentrations have substantially decreased at both upstream and downstream locations for all mills. From a review of the scientific literature, concentration trends for dioxins and related chemicals such as PCBs have been shown to decrease at a relatively constant rate once sources have been abated. Thus, it is possible to show differences in the above/below fish test *ad infinitum* given sufficiently low detection limits, large enough sample sizes, and through the use of a MSD that is based on a relative difference. However, at what point should considerations be made for biological significance? It is recommended here that if TEQ concentrations downstream of a mill are less than threshold values for effects in humans, fish, or animals that consume fish, the mill could be deemed in compliance. The actual threshold values for effects in humans, fish, or animals should be based on the most scientifically defensible toxicological data to be protective of human and ecological health. Furthermore, it is recommended that when differences between the upstream and downstream sites are less than the threshold for effects or a regulatory guideline, the

downstream site must be two-fold greater than the upstream site for a mill to be out of compliance.

1.4 Endpoint Selection

Currently, the DMP reports a number of endpoints including concentrations of 17 individual PCDD and PCDF congeners as well as TEQ concentrations. Each of these endpoints are reported on a wet weight and a lipid weight basis. Moreover, in cases where a congener was not detected, three different approaches were followed that replaced the non-detected value with either zero, one-half of the detection limit, or the full detection limit. The text of the DMP report is inconsistent in how differences among several of these endpoints are evaluated and discussed relative to the primary objectives of the program. Currently, the lack of focus on a single endpoint results in convoluted discussions of the various endpoints. Furthermore, some endpoints followed the same general trends when above and below fish were compared, while in other situations the trends went in different directions. Thus, concentrations measured in downstream fish could be greater or less than that measured in upstream fish depending on the endpoint selected. Whatever significance may or may not exist is lost in such a discussion since all endpoints seemingly are given equal weight in evaluating differences between the sites for the measured endpoints. To minimize unnecessary confusion over multiple endpoints, it is recommended that one endpoint be selected as the primary endpoint that is the most meaningful and biologically significant (e.g., TEQ_h on a wet weight, normalized for lipid basis), with other endpoints as secondary endpoints as necessary for confirmation or for source evaluation. Such an approach is consistent with DMP legislation that defines dioxin in the above/below fish test as any PCDDs and PCDFs.

1.5 Statistical approach and decision rules

Currently, the DMP utilizes non-parametric Mann-Whitney test and reports statistically significant differences at $p \leq 0.05$. While correct, this approach tends to be statistically conservative and may not adequately evaluate potential concentration differences between locations. It is preferable to utilize parametric statistics that tend to be statistically more powerful than non-parametric tests. As a first step in determining the appropriate statistical approach (e.g., parametric versus non-parametric statistics), it is recommended that an evaluation be made to determine if data are normally distributed and that the variances to be used in the above/below tests are homogeneous. If a parametric approach is determined to be the most appropriate approach, then a "t-test" is recommended. If a non-parametric approach is the most appropriate approach, then a Mann-Whitney U test is recommended. For either parametric or non-parametric approaches, a one-way test for statistical difference should be conducted to test the following hypothesis: $H_0: [TEQ]_{\text{downstream}} > [TEQ]_{\text{upstream}}$. In addition, a power analysis should be conducted such that the significance of the statistical result can be evaluated in terms of Type II errors.

DISCUSSION OF THE TECHNICAL ADVISORY GROUP'S RECOMMENDED ABOVE/BELOW TESTING METHODOLOGY

Following the recommendations of the SWAT TAG meeting March 5, 2003, DEP will use fish filets as the primary method in the above/below test at this time. Both bass and suckers will be analyzed for dioxin (TCDD), furan (TCDF), and DTEo (weighted average of dioxin "toxic equivalents" with non-detect set at zero). However, the TAG recommended further analysis of the existing data, including the 2002 data, to determine if the test might be reduced to a single fish species, and to determine the number of fish sampled above and below.

Comparisons between above/below stations will be based on either wet or lipid weight, whichever is most appropriate following a proper analysis of the relationship between dioxin and lipids (fat) in the samples used. Following EPA's principle of Independent Applicability, detection of a significant difference above and below with *any* of the tests will be considered evidence of a continuing discharge. Determination that there is a discharge will require at least two consecutive years where one or more test documents a significant difference above/below. Even if the test does not indicate a significant difference (and thus a discharge), periodic monitoring shall continue through at least 2007 to ensure conditions do not change such that a discharge reappears. The t-test (a standard statistical test) shall be used to determine differences where appropriate; otherwise the Mann-Whitney test (another standard statistical test) will be used.

Because the fish test is relatively insensitive, it can detect only large differences. While differences were large enough to be detected at some mills in the last set of data (2001), smaller differences above/below, if there are any, could not be detected by the fish test. Therefore, DEP will continue to develop more sensitive tests that may be applied in future years. Results of the 2002 SPMD study will be available by end of April and will determine whether or not they may be useful for the test. DEP will propose to the SWAT TAG a collaborative project with the UM Environmental Chemistry Lab and USGS to evaluate the efficacy of High Volume Water Sampling. The SWAT TAG will also consider study designs that include mussels.



**Review of
Current Technology for
Control of Dioxin Discharge in
Effluents from Kraft Pulp Mills**

prepared for

State of Maine

Department of Environmental Protection

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1. Summary

1.1 Overview

Technology available from worldwide sources to reduce or eliminate discharge of dioxins¹ is reviewed, in the context of the pulp and paper industry in the State of Maine.

Discharges of dioxin by Maine mills have been reduced dramatically over the past 15 years, principally due to the conversion of all mills to Elemental Chlorine Free (ECF) bleaching technology. Dioxins are generally no longer measurable in mill effluents, but their presence in mill effluents is inferred by some observers from the noticeable increase in the concentrations in fish flesh downstream of several of the mills in Maine.

There are several technologies available that would reduce dioxin discharges, and hence probably the body burden in fish to a fraction of today's values. Some of these technologies (such as ozone bleaching and improved process control) would increase mill profitability. Others would have much less impact on mill profitability than the normal swings in pulp and paper sales prices. Some of the available dioxin control technologies are expensive, relative to the normal pulp mill's revenues, but offer environmental advantages beyond dioxin control, such as reductions in Biological Oxygen Demand (BOD), color and phosphorus discharges.

The various dioxin discharge control techniques discussed in the body of the report are summarized in Table 3, along with indicative costs for application in Maine conditions.

Table 1 Summary of dioxin control techniques potentially applicable in Maine

Control measure	Capital cost \$million	Operating cost \$/year	% reduction of discharge
Control precursor use	-----	Very low	Modest
Process control optimization	< \$1 MM	Save up to \$1MM	Up to 25%
Oxygen delignification	\$20MM	Save \$1MM to \$4MM	One half ???
Oxygen assisted extraction	\$1	Save \$1MM	40%
Hydrogen peroxide in extraction	\$0.2MM	Save \$0.6MM	50%
Pressurized peroxide	Several million	Roughly a million	70%
Ozone / ClO ₂ (ZD)	\$1 to \$2	Save \$0.4 to \$1.5MM	Up to 90% for hardwood
Enzyme pretreatment of pulp	\$0.05MM	Save up to \$0.5MM	Up to 60% for softwood
Alkaline filtrate recovery	Several \$MM	Modest	25%
Bleach filtrate Recovery (BFR [®])	\$25 MM	\$2MM	80% to 100%
Totally Chlorine Free (TCF)	\$80MM	Modest saving	100%
Optimize effluent treatment	\$0.1	Up to \$1MM	Unknown

This table presents a simplified summary. Costs refer to an average Maine fiberline with 600 t/day capacity.

The degrees of reduction shown for individual control techniques are not simply additive

Maine mills have already implemented some of the techniques listed

Refer to the body of report for caveats and basis for data

¹ The popular terms "dioxin" is used herein to refer to 2378 tetrachloro-dibenzo-p-dioxin (TCDD) and 2378 tetrachlorofuran (TCDF). Where other congeners of dioxin and furan are mentioned, they are clearly identified as such.

It is technically feasible to eliminate dioxin formation and discharge by converting mills to use Totally Chlorine Free (TCF) bleaching processes. The total capital cost for the mills in Maine would be in the order of \$500 million, and the associated reductions in operating costs would be insufficient to support such an investment. Any such conversions would probably require restructuring of the industry to consolidate production in a smaller number of mills than operate at the time of writing.

1.2 Dioxin control techniques

It was established in the early 1990s that dioxin discharges could be substantially reduced by replacing all chlorine used in bleaching pulp with chlorine dioxide², and by avoiding the use of defoaming chemicals containing dioxin precursors. Maine mills adopted these technical features³ progressively through the 1990s.

Measures which are proven in commercial operation, and could further reduce discharges of dioxins are discussed below. The most appropriate technology for each mill will depend on the local situation. In some cases, the implementation of one measure would interfere with the use of another, so the attainable reductions in dioxin mentioned are not all additive.

1.2.1 Low cost and profitable dioxin reduction measures

Enzyme treatment of the pulp before bleaching can reduce chlorine dioxide requirements, by up to 25%, thus reducing dioxin formation by about 60%. Capital costs are very low, and a saving of up to a few dollars per ton⁴ pulp can be realized. Enzymes are most effective when applied to softwood⁵ pulp that has not been oxygen delignified.

The use of ozone quasi-simultaneously with chlorine dioxide has been developed in the past few years, and is becoming widespread. It offers the potential to reduce dioxin discharges at modest capital cost, and with a net positive effect on mill profitability, particularly when processing hardwood pulps.

Rigorous control of defoamer quality, chip quality, pulp screening and washing can reduce dioxin formation, but there is insufficient information available to quantify the necessary process changes and benefits.

State-of-the-art control of bleaching process conditions, including the mixing of chemicals, the use of modern instrumentation, and optimal operator training will minimize dioxin formation in any

² The practice of bleaching where chlorine dioxide is the only chlorine based chemical used is known as "Elemental Chlorine Free" or "ECF".

³ The one exception to the complete adoption of ECF bleaching was the SAPPi mill at Westbrook, where the bleach plant was permanently decommissioned.

⁴ Unless otherwise indicated, "ton" refers to the SI ton = 1000 kg, = 2205 lbs. Pulp is mostly sold by the SI ton, and EPA effluent guidelines are defined in terms of SI tons. Paper mills use mostly US tons.

⁵ Maine mills process roughly equal quantities of hardwood and softwood. Generally any one fiberline concentrated on one or other type of wood.

given system. There is insufficient information available to quantify the necessary process changes and benefits. The kappa factor in an ECF bleach plant is a useful indicator of minimizing dioxin discharges.

Reinforcement of the first extraction stage of the bleach plant with hydrogen peroxide, at atmospheric pressure, is normally profitable, and can reduce dioxin formation in the bleach plant by about 70%, in mills that have not already implemented the upgrade.

There is probably an opportunity to reduce dioxin discharges by up to about 50% by optimizing the control of suspended solids losses in the effluent treatment plants.

1.2.2 High capital cost dioxin reduction measures

Implementation of oxygen delignification (OD) will probably reduce formation and discharge of dioxins. There is insufficient information available to quantify the extent of reduction attainable. Capital costs of retrofitting in Maine mills would be relatively high, but there would be reductions in mill operating costs of approximately \$10/ton pulp, and other environmental benefits, such as reduction of BOD and phosphorus discharges. OD is generally profitable in large softwood fiberlines, but not in hardwood lines.

Recovery of the bleach alkaline filtrate is technically feasible, and could reduce dioxin discharges by up to about 40%. Capital costs would probably be several million dollars. The operating costs would be small, if any.

The BFR® process operating in the kraft mill in Canton, NC successfully recovers and incinerates 80% of the filtrates from a softwood ECF bleach plant, so it can therefore be expected to reduce dioxin discharges by a similar proportion. The process has the potential to recover all bleach plant filtrates, and hence eliminate dioxin discharge with effluents. Costs are relatively high, and operating experience is limited to this one mill.

Despite considerable research, and several attempts at complete process closure in kraft mills (popularly known as "zero-effluent"), the only successful systems rely on a tropical "wet season – dry-season" climate and irrigation of effluents. These conditions do not prevail in the US. While perhaps desirable as a long-term goal, zero-effluent kraft mill operation is not likely to be technically feasible in the foreseeable future in Maine.

1.2.3 TCF bleaching

Totally Chlorine Free (TCF) bleaching offers the possibility of reducing dioxin discharges to the point that no effect on the body burden of fish would be detected. TCF bleaching is proven in several full-scale mill operations, with over ten years operating experience. The capital cost of converting Maine mills to TCF operation would be in the order of \$80 million for a single line mill, and almost double that for the two Maine mills with two fiberlines. Significant operating cost savings would result, but less than would be required to make the conversion of existing mills economically attractive.

Although a few large profitable, mills in Scandinavia use TCF processes, it is noticeable that when building new mills, the owners of these TCF mills have selected "ECF-light" technology⁶.

⁶ "EFC light" refers to the use of TCF process for part of the bleaching, with final bleaching using less than 10 kg/t chlorine dioxide/ton pulp. It can be considered as a compromise between TCF and conventional ECF bleaching.