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## Pleasant River Time Series Study

The following is a summary of the Pleasant River Time Series Study, conducted by the Maine Board of Pesticides Control (BPC) from 1998 to 2002.

### I. Goal

The goal of this project was to determine the amount of hexazinone present at one sampling site on the Pleasant River during the course of a year. The BPC wanted to determine whether hexazinone was present in the river all year and determine the variations of concentrations in relation to time of pesticide application. Hexazinone is generally applied in the spring of a non-bearing year.

### II. Background

In the spring of 1994 the Board of Pesticides Control conducted a statewide assessment to determine the impact of highly leachable pesticides on ground water in Maine. This assessment crossed a variety of agricultural and nonagricultural pesticide use sites. The most frequently detected pesticide was hexazinone, the active ingredient in the herbicides Velpar and Pronone used in the production of blueberries. Fifteen of twenty sites sampled in blueberry growing areas had detectable levels of the herbicide. Follow-up and expanded sampling of wells down gradient and within ¼ mile of active blueberry fields was conducted in the late summer of that year. Those results found detectable levels of hexazinone in 35 of 48 sites sampled.

Simultaneously that spring, a citizen petition drive was underway to cancel the state registration of hexazinone. Following public hearings and lengthy discussions, the Board of Pesticides Control chose to allow continued use of the pesticide, yet directed the formation of a pesticide-specific state management plan (SMP) advisory committee to look at management options for hexazinone. The advisory committee, working closely with the Board, created the *Hexazinone State Management Plan for the Protection of Ground Water*. This pesticide-specific SMP, the only one of its kind to date in Maine, was adopted by the Board in July 1996.

In Section VII, "Monitoring" of the Hexazinone SMP, the Board of Pesticides Control is committed to conducting an assessment of private domestic wells in hexazinone use areas every four years, using the 1994 study as the benchmark. Four years was selected as the time interval to allow two, full cycles of blueberry production and hexazinone use. This assessment is ongoing.



In order to support the Maine Atlantic Salmon Conservation Plan, the BPC established a surface water monitoring program in 1997. Sixty-four surface water samples were collected from the seven designated Atlantic salmon rivers or tributaries and 19 of these samples had positive detections of hexazinone. The surface water time series project was then initiated in 1998 for the Pleasant River because of the large expanse of blueberries in the watershed and the frequency of samples with positive detections of hexazinone in that area.

### **III. Program Design**

#### **A. Site Selection**

There are extensive blueberry fields in both bearing and non-bearing rotations in the Pleasant River watershed each year. Three sites along the Pleasant River were monitored during 1998: a site in Beddington south of the dam, a site on Colonel Brook before its confluence with the Pleasant River, and a site at a boat landing in Columbia. Highest concentrations of hexazinone were found in Columbia, so that is where sampling continued to occur for the rest of the study.

#### **B. Sample Collection and Protocol**

The original sampling plan was for BPC staff to collect surface water grab samples once per month during the non-spray season (November through March), then twice per month during the spray season (April through October). Due to unforeseen field staffing issues, samples were occasionally not collected during a given month in a particular year, or were collected more than twice in a given month.

Water was collected in two-950 ml amber glass jars (one jar used as a backup) and placed immediately in iced coolers. This was done to preserve the samples by maintaining cool temperatures and preventing exposure to sunlight. Samples were delivered weekdays, except Fridays, to the University of Maine, Department of Food Science Laboratory within 96 hours of collection. Chain-of-custody procedures were observed throughout the sampling program.

#### **C. Analytic Methodology**

The University of Maine, Department of Food Science Laboratory performed the sample analyses. Samples were analyzed for hexazinone using high-performance liquid chromatography (HPLC) with a photodiode array, with the exception of 2002 samples that were analyzed with gas chromatography/mass spec (GC/MS). The limit of quantification (LOQ) was 0.1 parts per billion (ppb) for all years of this study except for 1998 when the LOQ was 0.2 ppb. The lab's GC/MS instrument had trouble meeting the lab's quality assurance/ quality control (QA/QC) protocols for hexazinone metabolite B, and as a result hexazinone metabolite B was not reported. However, the lab has noticed that in looking at samples from past years that were analyzed by HPLC/PDA, there has been far less hexazinone metabolite B in surface water as compared to ground water. It is possible that this metabolite is more susceptible to breakdown from the sun, microbes, etc. than its parent. The samples were also analyzed for the following active ingredients, which have been recommended for use on blueberries by

University of Maine Cooperative Extension Wild Blueberry Fact Sheets: captan, chlorothalonil, propiconazole, diuron, terbacil, azinphos-methyl, phosmet, diazinon, malathion, and methoxychlor, although none of these active ingredients were detected. Results from these sampling activities indicate that hexazinone continues to be the only active ingredient consistently detected at this site.

#### D. Quality Assurance/Quality Control Procedures

The University of Maine, Department of Food Science Laboratory maintains a quality assurance project plan (QAPP) with QA/QC protocols for the Board of Pesticides Control and the United States Environmental Protection Agency for the analysis of samples used in the enforcement of state and federal pesticide regulations. This plan is updated biennially.

#### IV. Sample Results

Results from this study show that it is possible for hexazinone to be found in the Pleasant River during every month of the year. Concentrations of hexazinone are low compared to EPA's Health Advisory for drinking water of 400 parts per billion (ppb). There is no established guideline for surface water. Figure 1 shows sample results varying from ND (non detect) to 1.98 ppb over the course of the five-year study. Figure 2 allows for a different comparison of results per year. Discontinuous portions of the graphs indicate missed samples. See Appendix A for a table containing the raw data.

Figure 1.

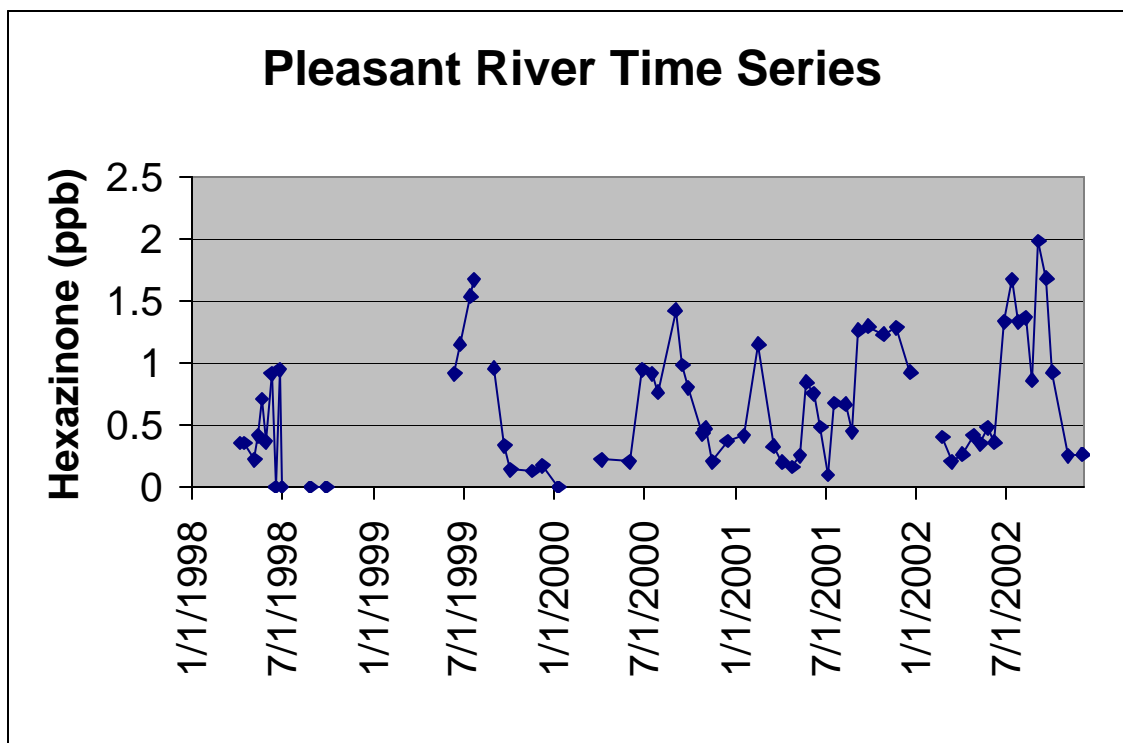
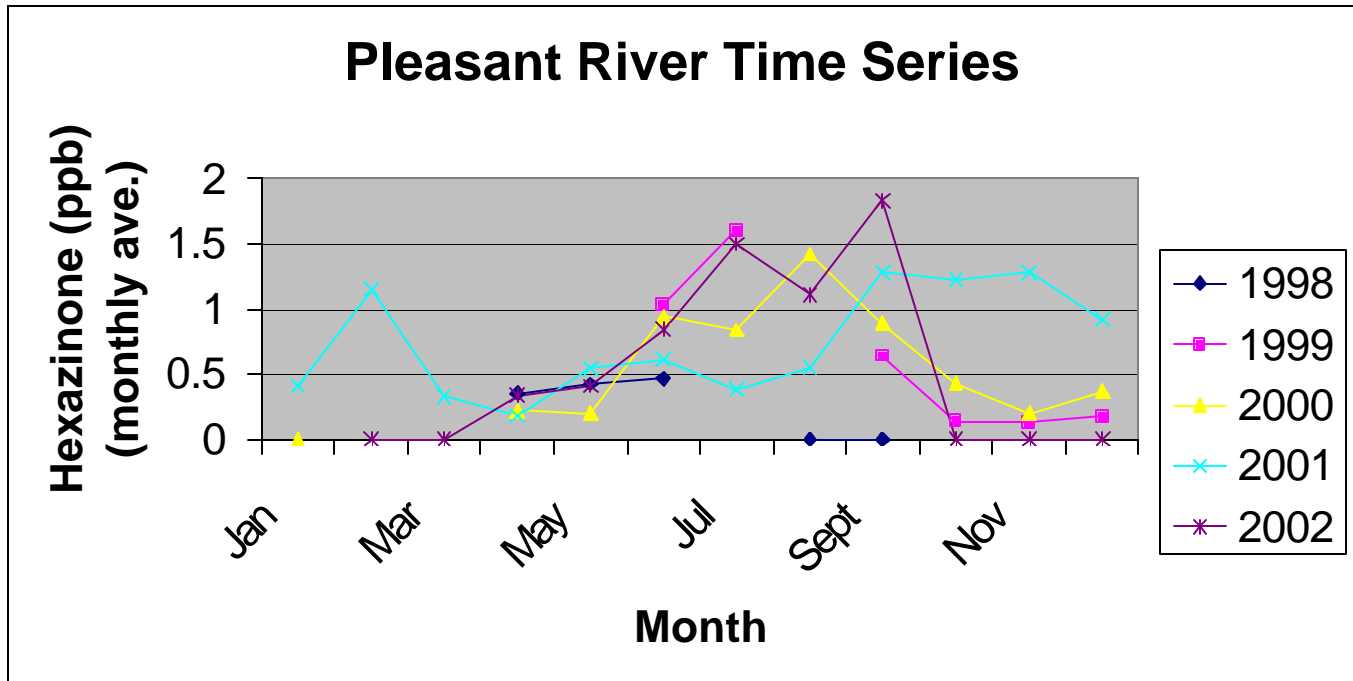


Figure 2.



## V. Conclusions and Discussion

While hexazinone has been detected in the Pleasant River at least once during every month of the year, concentrations are well below the EPA Health Advisory for drinking water of 400 ppb. From one year to the next the data does not seem to show an obvious increase or decrease in hexazinone concentrations. There appears to be slightly higher concentrations of hexazinone during the summer and early fall of most years. This is most likely correlated with the time of application and fall rains.

When looking at the data generated from this study, it is important to consider all of the variables associated with surface water sampling. Weather differences from month to month and year to year have the ability to affect results. In addition, while hexazinone was applied to non-bearing fields one year, the next year a new set of fields were non-bearing and thus, received an application of hexazinone. The new set of fields may have had more or less buffers, or different geologic conditions.

It is unknown what proportion of hexazinone getting into the Pleasant River is from surface runoff during rain events, and what proportion is from ground water base flow into the river. However, it is clear that at least some of the hexazinone in the Pleasant River is contributed by ground water discharge. A study looking

at hexazinone concentrations in ground water (springs or seeps) discharging to surface water was conducted by the BPC within the Pleasant River watershed in 2000. A list of known ground water discharge locations was obtained from the United States Fish and Wildlife Service and samples were collected from eight of those locations. Results showed positive detections of hexazinone at six of those sites ranging in concentrations from 0.17 ppb to 3.08 ppb.

### Appendix A. Pleasant River Time Series Hexazinone Data (ppb)

	1998	1999	2000	2001	2002
Jan			ND (1/10/00)	0.41 (1/17/01)	missing (1/18/02)
Feb				1.2 (2/16/01)	0.40(2/22/02)
Mar				0.33 (3/17/01)	0.20 (3/12/02)
Apr	0.35 (4/6/98)		0.22 (4/4/00)	0.20 (4/5/01)	0.26 (4/4/02)
Apr	0.35 (4/15/98)			0.16 (4/25/01)	0.41 (4/25/02)
May	0.22 (5/6/98)		0.20 (5/30/00)	0.25 (5/10/01)	0.35 (5/9/02)
May	0.41 (5/13/98)			0.84 (5/24/01)	0.47 (5/23/02)
May	0.71 (5/20/98)			lab error (5/24/01 duplicate)	
May	0.36 (5/27/98)				
Jun	0.91 (6/9/98)	0.91 (6/14/99)	0.94 (6/27/00)	0.75 (6/7/01)	0.36 (6/7/02)
Jun	ND (6/17/98)	1.2 (6/24/99)		0.48 (6/21/01)	1.3 (6/27/02)
Jun	0.94 (6/24/98)				
Jun	ND (6/30/98)				
Jul		1.5 (7/15/99)	0.91 (7/15/00)	0.10 (7/5/01)	1.7 (7/12/02)
Jul		1.7 (7/22/99)	0.76 (7/28/00)	0.68 (7/19/01)	1.3 (7/25/02)
Aug	ND (8/26/98)		1.4 (8/31/00)	0.66 (8/9/01)	1.4 (8/8/02)
Aug				0.45 (8/23/01)	0.86 (8/22/02)
Sept	ND (9/28/98)	0.95 (9/1/99)	0.98 (9/15/00)	1.3 (9/6/01)	2.0 (9/4/02)
Sept		0.33 (9/22/99)	0.80 (9/27/00)	1.3 (9/26/01)	1.7 (9/19/02)
Oct		0.14 (10/4/99)	0.43 (10/25/00)	1.2 (10/25/01)	0.92 (10/9/02)
Oct			0.47 (10/31/00)		
Nov		0.13 (11/17/99)	0.20 (11/15/00)	1.3(11/21/01)	0.25 (11/15/02)
Dec		0.17 (12/8/99)	0.37 (12/15/00)	0.92 (12/20/01)	0.26 (12/19/02)

ND = Not detected