

STATE OF MAINE MAINE DEPARTMENT OF AGRICULTURE, FOOD & RURAL RESOURCES BOARD OF PESTICIDES CONTROL 28 STATE HOUSE STATION AUGUSTA MAINE 04333-0028

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2006 Ground Water Monitoring of Hexazinone

The following is a summary of the results of ground water sampling activities conducted in blueberry growing regions of the state in 2006, compared with 1994, 1998, and 2002 results.

I. Goal

The goal of this project is to assess the quality of drinking water from private domestic wells in blueberry growing areas of Maine to determine if measures -- voluntary and regulatory -- implemented by blueberry growers are mitigating the impact of hexazinone on water quality.

II. Background

In the early 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 targeted a variety of agricultural and nonagricultural pesticide use sites. The most frequently detected pesticide was hexazinone, an herbicide 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 sites down gradient and within one-quarter 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 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.

As described in Section VII of the plan, the Board of Pesticides Control is committed to conducting an assessment of private domestic wells in hexazinone-use areas every four years. The 1994 study is used as the benchmark. Four years was selected as the time interval to allow for two full cycles of blueberry production and hexazinone use.

III. Program Design

A. Site Selection

Fifty-three sites sampled in 1994 near blueberry growing areas were targeted for resampling in 1998, 2002, and 2006. Twenty of these sites were originally selected using stratified-random-sampling criteria; the remaining sites were selected using the triple-point sampling principle, whereby sites with hexazinone detections in the first round of sampling were evaluated by sampling two other sites in the same local watershed with similar geological and pesticide use characteristics as the first site.

Generally, all sites that were sampled have the following characteristics:

- the site contains a private domestic well, currently used for drinking water;
- the site is within one-quarter mile of an active blueberry field; and
- the site is down gradient or of equal elevation with the blueberry field.

B. Sample Collection and Protocol

The BPC field staff collected 46 samples during the months of January and February, 2006. The time period was selected to coincide with the time of year sampling was done in 1994, 1998, and 2002, and to attempt sampling while water tables were at their lowest before the spring recharge.

Field staff collected samples from as many previously sampled domestic plumbing systems as possible after ensuring the water supply was not filtered. At most sites, water was collected from the tap that was allowed to run for at least ten minutes. In 2002, 8 of the 49 samples were from new sites chosen when existing sites proved difficult or impossible to sample due to various reasons such as lack of electricity to power the well or fire damage to the home housing the well. The new sites followed the old criteria of being within one-quarter of a mile from an active blueberry field and at an elevation equal to or less than the field. New sites were as close to the site that didn't work as possible. In 2006, 18 of 46 samples were from new sites. In some cases a well changed ownership and the new owner did not want to participate. In other cases new filters had been set up on the water system.

Well water was collected in 950 ml amber glass jars (one jar per sample, unless QA/QC required) and placed immediately in iced coolers. This was done to preserve the samples by maintaining the cool temperatures and preventing exposure to sunlight. Samples were delivered weekdays, except Fridays, to the University of Maine, Department of Food Science Laboratory, within three days of collection. Chain-of-custody procedures were observed throughout the sampling program.

C. Data Collection

The BPC staff updated their preprinted sample information sheets for well and site characteristics. The BPC staff also gathered longitude and latitude data, where needed, using portable, hand held global positioning system (GPS) units.

D. <u>Analytic Methodology</u>

The University of Maine, Food Chemical Safety Laboratory performed the sample analyses. Samples were analyzed for hexazinone and one of its primary metabolites using solid phase extraction and gas chromatography with a mass spectrometer (GCMS). The limit of quantification (LOQ) was 0.1 parts per billion (ppb), as it was in 2002 (also with GCMS). In 1998 the LOQ was 0.2 ppb (GCMS), and in 1994 it was 0.05 ppb obtained with high performance liquid chromatography (HPLC). The 2006 samples were also analyzed for captan, terbacil, azinphos-methyl, phosmet, propiconazole, methoxychlor, chlorothalonil, and malathion although none of these active ingredients were detected.

E. Quality Assurance/Quality Control Procedures

The University of Maine, Food Chemical Safety Laboratory maintains a QA/QC plan 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. Three field blanks and duplicates of three of the 46 samples were run.

IV. Sample Results

In 2006, 32 of 46 samples (or 69.6%) showed detectable levels of hexazinone. Table 1 compares this percentage to the percentages in 1994, 1998, and 2002. Table 1 also displays mean and median concentrations of all of the samples analyzed per year, and the highest reading per year.

Table 1.							
Hexazinone Detection Rate, Mean and Median Concentration, and Highest Reading per Sampling Period							
Reading per Sampir	Spring 1994	Spring 1998	Spring 2002	Spring 2006			
Total Number of Samples Collected	20	42	49	46			
Number of Positive Detections	15	18	29	32			
Percentage with Positive Detections	75%	42.8%	59.2%	69.6%			
Mean Concentration*(ppb)	1.07	0.44	1.45	0.98			
Median Concentration (ppb)	0.31	ND	0.43	0.34			
Highest Reading (ppb)	5.97	2.15	11.41	8.43			

*For statistical purposes only, mean concentration was calculated assuming that non detections (ND) were equal to half of the limit of quantification (LOQ).

Data collected in 1994, 1998, 2002, and 2006 is displayed below in Table 2.

TABLE 2. Maine BPC Hexazinone Detections							
in Private Wells (ppb)							
Well Parameters			Т	Year (spring sampling)			
TD.	D 41	Distance to	1004	1000	2002	2007	
ID	Depth	Hexazinone	1994	1998	2002	2006	
02DDCC012	(ft)	Use Site (ft)	NID.	NID	B.T.A. www	NT A	
03BPCG012	unknown	400	ND*	ND ND	NA**	NA 1.49	
05BPCG005	unknown	150	2.57	ND	2.27	1.48	
05BPCG006	80	240	4.78	NA ND	7.86	NA 2.25	
05BPCG007	unknown	240	NA	ND	11.41	3.35	
05BPCG008	unknown	300	NA	0.34	0.55	NA	
05BPCG009	212	200	NA	NA	0.15	NA	
05BPCG010	300	125	NA	NA	1.05	1.11	
05BPCG023	unknown	100	NA	NA	NA	ND	
05BPCG024	unknown	100	NA	NA	NA	0.37	
05BPCG025	65	50	NA	NA	NA	3.55	
05BPCG026	100	75	NA	NA	NA	ND	
05BPCG027	unknown	50	NA	NA	NA	ND	
05BPCG028	unknown	100	NA	NA	NA	0.75	
05BPCG029	4	0	NA	NA	NA	3.08	
06BPCG026	75	75	0.09	0.30	1.68	1.21	
06BPCG027	unknown	1000	ND	NA	NA	NA	
06BPCG028	16	400	0.55	0.30	ND	ND	
06BPCG030	16	125	NA	1.16	1.50	NA	
06BPCG031	100	125	NA	ND	0.16	0.34	
06BPCG032	300	800	NA	NA	0.29	0.24	
06BPCG033	200	800	NA	NA	NA	0.43	
06BPCG047	110	0	NA	NA	3.62	NA	
06BPCG049	125	200	NA	NA	NA	0.52	
06BPCG058	dug	800	NA	NA	NA	2.26	
08BPCG008	5	240	1.50	1.66	3.81	8.43	
08BPCG009	200	350	0.30	0.14	0.74	0.57	
08BPCG010	115	200	NA	2.10	1.73	1.39	
08BPCG011	unknown	1000	NA	0.33	ND	1.01	
08BPCG012	350	250	NA	ND	1.18	ND	
08BPCG013	500	250	NA	ND	ND	NA	
08BPCG021	deep	600	NA	NA NA	NA NA	ND	

O9BPCG020	00DDCC019	40	50	5.07	2.15	2.57	1.05
09BPCG021 50	09BPCG018	40	50	5.97	2.15	2.57	1.95
14BPCG005							
14BPCG005							
14BPCG007							
14BPCG007							
14BPCG008							
14BPCG010 365 35 0.25 ND ND ND ND 14BPCG011 140 300 2.53 0.45 5.75 2.42 14BPCG012 132 300 NA 1.52 9.24 3.35 14BPCG013 120 180 NA ND ND NA 14BPCG014 unknown 100 NA ND NA NA ND NA NA ND NA NA							
14BPCG011							
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15BPCG032 25 100 NA NA NA ND 15BPCG033 325 150 NA NA NA NA 2.54							
15BPCG033 325 150 NA NA NA 2.54							
	16BPCG016	25	1000	ND	ND	NA	NA

^{*} ND=Not Detected

^{**}NA=Not Analyzed

Of the 49 samples collected in 2002, the primary metabolite of hexazinone (hexazinone metabolite B) was detected 17 times, all below 1.71 ppb. In 2006 hexazinone metabolite B was detected 15 times, all below 2.12 ppb. This data was not included in Table 2 since the BPC does not have metabolite data from 1994 and 1998 for comparison. Specific hexazinone metabolite B data can be obtained by contacting the BPC at 287-2731.

V. Conclusions and Discussion

The 2006 ground water sampling results show an increased frequency of hexazinone detections compared to 1998 and 2002 results. Overall concentrations of hexazinone in 2006 samples were not higher than in 2002, however. All results continue to be well below the EPA Health Advisory of 400 ppb.

A probable explanation for the apparent difference in 1998 results is that the laboratory LOQ was 0.2 ppb in 1998 compared to 0.1 ppb in 2002 and 2006. In addition, the LOQ for hexazinone in 1994 was 0.05 ppb, which could explain the difference in data that year. Also noteworthy is that the State Climatologist has declared 2001 the driest year on record, and 2005 the wettest in about 100 years of data.