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A Survey of Azinphos Methyl and Azinphos Methyl Oxon in Water and Blueberry Samples from Hancock and Washington Counties of Maine

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In Maine the organophosphate pesticide, azinphos methyl (Guthion), is used extensively to protect lowbush blueberries from insects such as the thrip, spanworm, and maggot (Rhagoletis mendax). Azinphos methyl is applied on more than 20,000 acres of blueberries with most of the spraying occurring in Washington (15,000 acres) and Hancock (4,000 acres) Counties (WERTAM 1980). Both counties contain many streams and rivers and are bordered by the ocean. The importance of this pesticide to the blueberry industry cannot be denied, but there are areas of concern in using any pesticide as to its effect on the ecosystem.

Much of the blueberry acreage is located on what are known as the "barrens", which, according to BORNS (1976), are classical examples of glaciomarine deltas. These deltas are large areas of sand and gravel which were left behind by the last glacier to cover Maine. Due to the composition of these barrens, water falling on them moves through the top and forest layers, eventually emerging as springs at the bases of these deltas. This outflow is incorporated into rivers in the area. Thus pesticides applied on the barrens can potentially move through the system and end up in the rivers and ocean. An example of such an incident was observed when calcium arsenate was used in the barrens years ago (BORNS 1976).

Even though azinphos methyl is an organophosphate pesticide, it has been shown to persist in water and soil under certain conditions (WERTAM 1980). One possible result of the presence of azinphos methyl in the estuaries of this area is its effect on clams. The Maine clam (Mya arenaria) is the second most important commercial seafood produced in the state at a value of 7.8 million dollars per year (WERTAM 1980). The spraying of azinphos methyl and the spawning of clams may not be well separated in time every year. Although no research has been performed on the effects of azinphos methyl on the clam (Mya arenaria) found in Maine, there has been a study of the hard clam (Mercenaria mercenaria) performed by DAVIS (1961), who

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demonstrated that 1 ppm azinphos methyl was quite toxic to clam eggs whereas 0.50 and 0.25 ppm had no toxic effect and in fact may slightly increase survival rates under hatchery conditions. When clam larvae were used, a concentration of 1 ppm had no effect while 5 ppm azinphos methyl caused 100 percent mortality.

Besides possible water contamination and clam toxcity, there is much concern as to the amount of azinphos methyl that remains on the blueberry when harvested. The average yearly harvest of lowbush blueberries in Maine is approximately 19 million pounds. Most of this is canned or frozen. The major concern with contaminated blueberries would involve fruit entering the fresh or frozen market, since canning should degrade much of the pesticide.

Because of the susceptibility of this area in Maine to extensive water drainage and since extensive spraying of azinphos methyl has occurred during the last several years, a study was undertaken to ascertain if azinphos methyl and/or its more toxic metabolite, azinphos methyl oxon, may be present in the water or fruit at levels to be a potential hazard to the ecosystem.

METHODS AND MATERIALS

Sampling was done at a blueberry processing plant near Ellsworth and in the Franklin, Gouldsboro, Cherryfield, and Deblois localities at sites chosen in relation to clam flats and sprayed blueberry fields (Figure 1). Site 1 is at the outlet of Lower West Bay Pond. Site 2 is midway along a stream flowing out of the pond into West Bay, a well-protected arm of the deeply convoluted coast of the Gulf of Maine. Site 3 is a highly productive clam flat area on the west side of West Bay about 2 km south of the mouth of the stream. Since a crop is not produced on a blueberry field in pruning years (usually alternate years), a substantial but unknown portion of the blueberry acreage above these sites may not have been sprayed. Site 4 is a sprayed blueberry field near Cherryfield in which a household well is located. Site 5 is the processing plant. Site 6 comprises two sprayed blueberry fields in the barrens and a small brook draining the fields. Site 7 is a tidal flat bordering a sprayed blueberry field.

Water samples, collected in 1-quart solvent-cleaned Mason jars with aluminum foil lined lids, were taken (grab samples) from all sites. The site 3 water samples were scooped at midpoint of ebb tide in a manner to include some visible particulate matter. Blueberry samples were collected using aluminum foil as

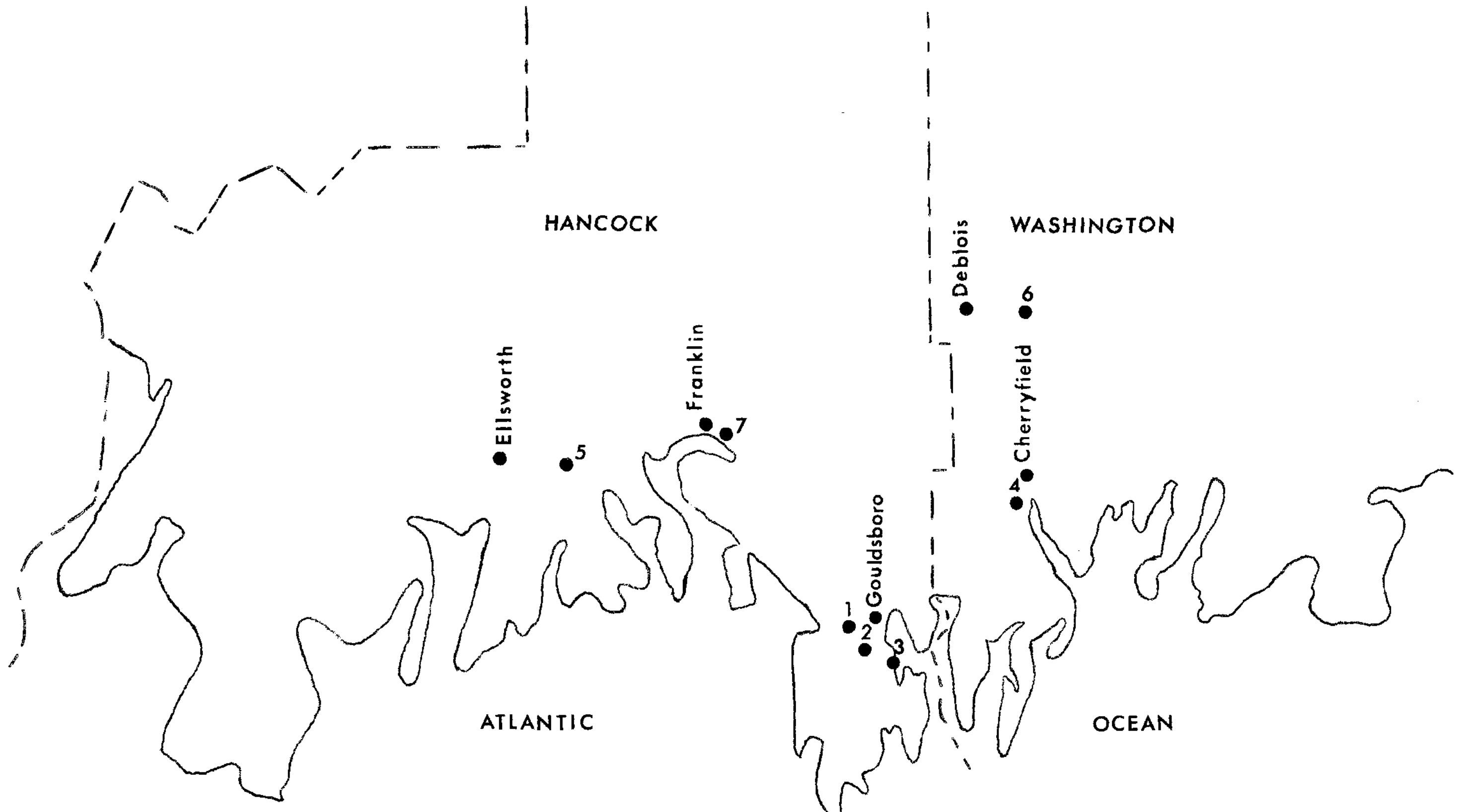

Figure 1. The sampling sites (1-7) in Hancock and Washington Counties of Maine

the container from locations 4, 6, and 7. Sampling began June 29th and ended August 11th, 1981. Analyses were completed within 24 h from the time they were obtained, and all samples were refrigerated until analyzed.

All solvents used in this study were high-performance liquid chromatographic (HPLC) grade (Fisher Scientific Co., Fairlawn, N.J.). Azinphos methyl and azinphos methyl oxon were obtained from Mobay Chemical Company (Kansas City, MO.).

The procedure used for the water analyses was that of BUSHWAY (1981). For the blueberries the method of WILSON & BUSHWAY (1981) was employed. Azinphos methyl was confirmed by concentrating the extracts and spotting the entire sample on a thin-layer chromatography plate using the procedure of LAING & LICHTENSTEIN (1972).

RESULTS AND DISCUSSION

The results of the analyses of water samples for azinphos methyl and its oxon from sites in Washington and Hancock Counties are presented in Table 1. Azinphos methyl was detected in water at two of seven locations (detection limit 230 ppt (ng/L) for both compounds). Azinphos methyl oxon was not observed at any of the sites. One of the two places where azinphos methyl was found is a well located in a blueberry field which had been sprayed twice -- July 5th and July 20th. The first sample taken on July 9th contained 1,900 ng azinphos methyl/L of water. During a two week interval which included much rain in the area (Table 2) and another application of pesticide, the amount of azinphos methyl increased to 24,000 ng/L. However by August 11th, the level of pesticide had decreased to below the limit of detection. Such a decline in the concentration of azinphos methyl would indicate that it was undergoing some type of degradation and/or was being diluted with fresh ground water. The latter seems most likely, since a stability test performed on these well samples demonstrated that azinphos methyl was stable under similar conditions for a period of more than 19 days.

The process water from a blueberry plant near Ellsworth was the only other water sample that was shown to contain azinphos methyl at or above the detection limit. The pesticide was found at a concentration of 12,700 ng/L (Table 1). This observation would not be unexpected since the blueberries entering the plant were all from sprayed areas, according to the plant management. Azinphos methyl has a water solubility of

TABLE 1. Concentration of azinphos methyl and azinphos methyl oxon in water from Hancock and Washington Counties, Maine.

Site	Date Collected	pH	Temperature (C)	Azinphos Methyl (ng/L)	Azinphos Methyl Oxon (ng/L)
2	6/29	5.7	21.5	ND*	ND*
3	6/29	7.2	20.0	ND	ND
2	7/7	6.0	23.5	ND	ND
3	7/7	7.0	27.0	ND	ND
2	7/9	5.5	24.0	ND	ND
3	7/9	6.5	18.0	ND	ND
4	7/9	-	-	1,900	ND
2	7/10	5.5	25.0	ND	ND
3	7/10	7.0	22.0	ND	ND
2	7/14	5.5	26.0	ND	ND
3	7/14	7.0	20.0	ND	ND
4	7/14	5.5	16.0	11,200	ND
1	7/23	5.5	24.0	ND	ND
2	7/23	5.0	22.0	ND	ND
3	7/23	6.5	28.0	ND	ND
4	7/23	5.3	18.0	24,000	ND
7	7/23	-	-	ND	ND
5	8/5	-	-	12,700	ND
4	8/11	5.0	14.0	ND	ND
6	8/11	5.0	12.0	ND	ND

*ND= none detected at a detection limit of 230 ppt (ng/L)

29 ppm at 25 C (WERTAM 1980). Of course discharging the process water into receiving bodies could be of concern, but the dilution effect should be sufficient to protect the ecosystem.

TABLE 2. Amount of rainfall in the 3 sites around Gouldsboro.

Rainfall Date	Volume of Rainfall (inches)
6/4	0.05
6/9	0.75
6/16	0.10
6/22	1.50
6/26	1.77
7/5	0.90
7/9	1.10
7/14	0.75
7/21	2.45
7/27	1.30
7/29	0.40
7/30	0.10
8/7	1.13

Water analyzed from sites 1, 2, 3, 6, and 7 contained no detectable amounts of azinphos methyl or azinphos methyl oxon (Table 1). These sites were chosen to represent locations containing blueberry fields near water systems that have been (several years) and are being sprayed with azinphos methyl. Therefore, if azinphos methyl is being translocated by water to any appreciable extent during spraying or through a sediment-water equilibrium, it could be determined. Since no detectable amount of azinphos methyl or oxon was observed in any of the five samples, this indicates that if either is present it must be at a concentration less than 230 ng/L, which is low. Furthermore if azinphos methyl or azinphos methyl oxon are being trapped by the sediment, the water-sediment equilibrium is such that very little is leaching out.

The concentration range observed for azinphos methyl on blueberries from three locations ranged from none detected (detection limit 50 ng/g) to 120 ng/g. The oxon was not shown to be present on any blueberry samples at or above the detection limit of 0.4 ug/g (Table 3). Two of the three locations sampled had blueberries with a measurable amount of azinphos methyl. However, these values are low when one compares them to the EPA tolerance of 5 ppm for azinphos methyl on blueberries.

TABLE 3. Concentration of azinphos methyl and azinphos methyl oxon in blueberries from Hancock and Washington Counties, Maine.

Site	Date Collected	Azinphos Methyl (ng/g)	Azinphos Methyl Oxon (ng/g)
4	7/23	75-93*	ND**
6	7/23	110-120	ND
7	7/23	ND***	ND

*Ranges from three samples
**ND= none detected at a detection limit of 0.4 ppm
***ND= none detected at a detection limit of 50 ppb

In summary, this investigation has found no azinphos methyl above or at 230 ng/L in the water at the sites and times sampled, except from a well in a sprayed blueberry field and in recycled wash water at a blueberry processing plant. We have found no evidence of conversion to the oxon within the detection limits, either in water or blueberries. According to the study by DAVIS (1961) of eggs and larvae of another clam species a few days old, this would not suggest a toxic effect on populations of the Maine clam. Moreover, the applicability of that study is further affected by our failure to find any clams on July 28th in spawning condition at the site sampled. Elsewhere along the Maine coast it had been noted that the clam populations had finished spawning by July 1. The possibility has not been totally ruled out that sediment accumulation of the two toxic compounds near the flats could affect the clam populations at some time. Ingestion of azinphos methyl by consumers of sprayed blueberries that have passed through the processing plants would appear minimal in view of the levels we found in berries not yet washed. As we have shown, some of the azinphos methyl is removed during washing.

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