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Potential for Agricultural Pesticide Runoff to a Puget Sound Estuary: Padilla Bay, Washington

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Eelgrass meadows, worldwide, are major contributors to estuarine primary productivity (Thayer et al. 1978). The highly productive eelgrasses that lie submerged in parts of Puget Sound serve as nursery grounds and habitat for many species of fish, sea mammals, and birds (Thayer and Phillips 1977). For this reason the potential for chemical contamination of the eelgrass ecosystem is of great concern.

To date the known chemical contaminants associated with eelgrass meadows and bottom sediments in Puget Sound are petroleum, heavy metals, polychlorinated biphenyls (PCBs), and wood preservatives (NOAA 1986). Malins et al. (1984) found that in Puget Sound urban embayments of Seattle, Tacoma, and Everett there appears to be a significant correlation between chemically contaminated sediments and liver tumors in bottom-dwelling fish such as English sole (Parophrus vetulus), rock sole (Lepidopsetta bilineata) and starry flounder (Platichythus stellatus). This finding has prompted additional water quality studies in Puget Sound.

Padilla Bay (Figure 1), an estuary of Puget Sound, possesses one of the three most extensive eelgrass communities in the Pacific Northwest (Phillips 1984). The estuary is comprised of 4,500 ha (11,000 A) of intertidal channelized mudflats which serve as substrate for the eelgrasses Zostera marina and Zostera japonica which occupy 3,097 ha (7,651 A) within the Padilla Bay National Estuarine Research Reserve (Webber et al. 1987). The Bay's importance is reflected in the fact that 57 species of fish have been identified in Padilla Bay including five species of Pacific salmon, steelhead, trout, smelt, herring, sole, flounder, and sculpins (NOAA 1980).

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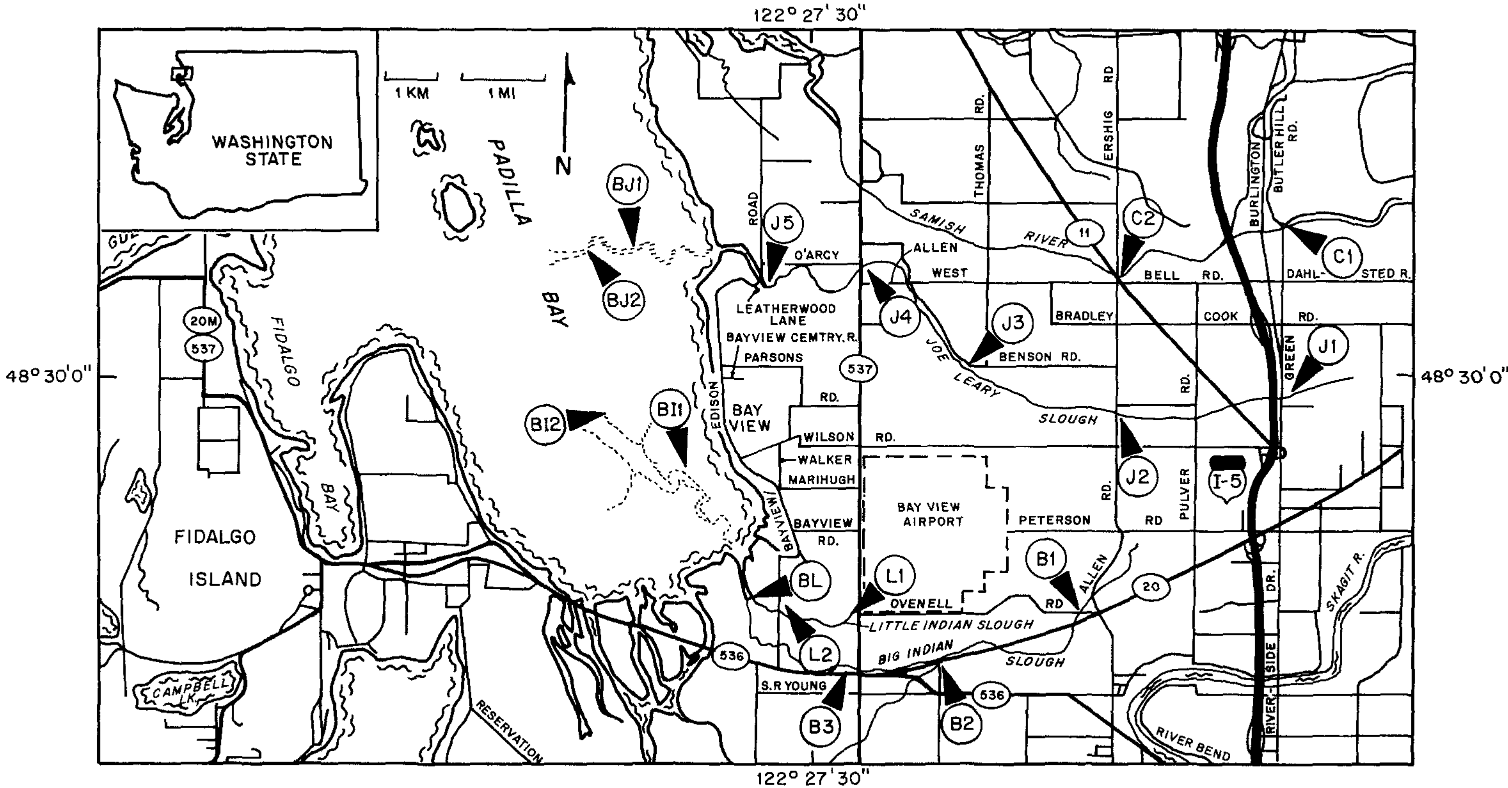

Figure 1. Sampling Stations on Padilla Bay and Joe Leary, Big Indian and Little Indian Sloughs

Recently the potential for pesticide contamination of Padilla Bay has received attention due to intensively managed agricultural areas immediately to the east of the Bay. Pesticide runoff could pose a threat not only to the eelgrasses per se but also to the complex epiphytic community associated with eelgrass meadows (USEPA 1982). The purposes of this 2-yr investigation were (1) to identify and quantify pesticide runoff in this agricultural environment and (2) to assess the ecological significance of pesticide runoff to Padilla Bay given the knowledge that fourteen pesticides are applied each summer at known rates.

MATERIALS AND METHODS

The predominant land uses in the Padilla Bay watershed include pasture and croplands 72%, forest 20%, and small urban areas 8%; watershed soils are clay (69%) and sandy/clay (29%) reflecting slow infiltration rates and a high potential for direct runoff (Entranco Engineers 1989). The croplands are intensively farmed and are noted for the production of snow peas, wheat, carrots, potatoes, sweet corn, cucumbers, cauliflower, strawberries, vegetable/grass seed, raspberries, blueberries, barley, oats, corn silage, hay, tulip bulbs, flowers, and Christmas trees.

Watershed runoff to Padilla Bay is transported primarily by three sloughs: Joe Leary Slough drains a 4,695 ha (11,600 A) subbasin; Big Indian Slough drains a 1914 ha (4730 A) subbasin; and Little Indian Slough drains a 249 ha (615 A) subbasin. Annual rainfall averages 83.95 cm (33.05 in). Total annual runoff through these three sloughs is estimated to be 2.10 E7 m^3 or 17,059 acre-feet (DOE 1989).

Early each summer (mid-June) 14 chemical pesticides (Table 1) are applied to watershed farm lands to control weeds, insects, and fungi (R. Hawkins pers. commun. 1987). Seventeen sampling stations were established to assess pesticide levels in runoff water and sediments: 11 stations on the three sloughs; 4 stations in the Bay itself; and 2 control stations, C-1 and C-2 (Figure 1).

Four sampling expeditions were carried out. The first was during the spring of 1987 (May 19, 25, and June 16) before any pesticide applications that year. The second was during the summer of 1987 (June 22, 29, and July 7) after pesticide applications were completed. The third was during the spring of 1988 (April 13) before any pesticide application that year. The fourth was during the summer of 1988 (August 7 and 9) after pesticide applications were completed.

Table 1. Principal pesticides applied to farmlands in the Padilla Bay watershed each summer: application rate and analytical detection limits in this study.

Pesticide	Application Rate kg ai/ha (lb ai/A)[a]	Detection Limits Water[b]	Sediment[c]
Atrazine	2.24-4.48 (2.0-4.0)	0.49	0.049
Chlorthalonil	0.58-3.50 (0.52-3.13)	0.15	0.015
Diazinon	15.7-23.5 (14-21)	0.18	0.018
Dicamba	0.067-0.280 (0.06-0.25)	6.10	0.610
Dinoseb	0.84-13.4 (0.75-12.0)	0.11	0.113
Methamidophos	0.22-2.24 (0.2-2.0)	10.8	0.108
Methyl parathion	0.28-1.68 (0.25-1.50)	0.03	0.003
Metribuzin	0.3-1.1 (0.25-1.0)	0.01	0.001
Parathion	0.63 (0.56)	0.06	0.006
PCNB	1.12-20.2 (1.0-18.0)	0.01	0.001
Simazine	2.2-4.4 (2.0-4.0)	0.63	0.063
Terbutryn	1.34-2.46 (1.2-2.2)	5.76	0.576
Trifluralin	0.6-1.1 (0.5-1.0)	0.02	0.002
2,4-D	0.28-2.2 (0.25-2.0)	0.10	0.001

[a]R. Hawkins, pers. commun.
[b]ug/L (ppb)
[c]g/kg (ppm)

Sampling and analytical protocols were based on EPA Method 508 (1988a). Briefly, sampling was carried out following significant rain events to maximize the discovery of pesticide runoff in water and sediment samples. Duplicate surface water samples were collected using a clean metal pail and stored in pre-labeled 1-L amber glass bottles with aluminum foil-lined screw caps. Duplicate sediment samples were scooped from the upper 3 cm benthic environment and stored in pre-labeled glass jars with aluminum foil-lined screw caps. Samples were cooled in the field using "blue ice" in an insulated sample carrier and then transferred to a lab refrigerator within three hours.

Water samples were extracted with ether: 3 times at pH 2; 3 times at pH 7; and 3 times at pH 10. (It was found necessary to use ether to extract 2,4-D, dicamba, and dinoseb from spiked samples.) Sediment samples (about 20 g) were sonified with about 100 mL of 50/50 acetone/methylene chloride and centrifuged. Water and sediment sample extracts were concentrated and solvent-exchanged with hexane to 10 mL. Sulfur-containing contaminants were removed by vigorously shaking each hexane concentrate with approximately 1 gram of metallic mercury in a ground-glass stoppered centrifuge tube for one minute followed by centrifuging to remove insoluble mercury sulfides.

Clean hexane concentrates from water and sediment samples were treated with diazomethane (EPA 1988b) to methylate any 2,4-D, dicamba, and dinoseb that might be present. The other 11 pesticides were shown to be unaffected by this procedure.

Gas chromatography of the final hexane sample was carried out on an HP 5890A gas chromatograph (Hewlett Packard, North Hollywood, California) fitted with a ^{63}Ni electron capture detector, 30 m 0.53 mm id SPB-5 (Supelco) megabore capillary column, and on-column injector. 2.0 uL of sample was chromatographed isothermally at 180°C and 30 kPa head pressure. Confirmation chromatography and quantitation was conducted isothermally using a 30 m 0.53 mm id Supelcowax-10 (Supelco) megabore capillary column at 200°C and 40 kPa head pressure.

Pesticide standards were obtained from the USEPA Research Triangle Park, NC. 2,4-D, dicamba, and dinoseb were diazomethane methylated (EPA 1988b) prior to their use as standards.

RESULTS AND DISCUSSION

In both the spring of 1987 and the spring of 1988, periods preceding annual pesticide applications, none of the fourteen pesticides under study were detected in the water or sediments of the three sloughs or the Bay itself. This was not surprising because any pesticide residues from the previous summer would most likely have experienced runoff and/or weathering during the wet, rainy winter of western Washington. The pesticides studied are known to have relatively short half-lives of six to ten weeks.

Sampling during the summer of 1987, on June 22 (slough sites), June 29, and July 7 (Bay sites), followed a major rain event: 1.14 cm (0.45 in) on June 21. This was the only time during the study that positive findings for pesticides were observed (Table 2).

Following the June 21, 1987 rain event, dicamba was found in all slough and Bay water samples ranging from 10 to 160 ug/L (ppb). Dicamba was also found in three slough sediment samples ranging from 5.8 - 17.1 ug/g (ppm). No dicamba was found in any of the Bay sediments. 2,4-D was found in nine slough water samples and one Bay water sample ranging from 0.1 - 1.1 ug/L (ppb). No 2,4-D was found associated with slough or Bay sediments. None of the other 11 pesticides under study was found in water or sediment samples.

The sampling expedition carried out in the summer of

Table 2. Pesticide residues found in water and sediment samples collected from watershed and Padilla Bay sampling stations on June 22, 29, and July 7, 1987.

Sampling Stations (Fig 1)	Dicamba Water[a] ug/L	Dicamba Sediment[b] ug/g	2,4-D Water ug/L	2,4-D Sediment ug/g	Other Pesticides Water ug/L	Other Pesticides Sediment ug/g
J-1	160	U[c]	1.1	U	U	U
J-2	10	U	U	U	U	U
J-3	110	U	0.3	U	U	U
J-4	140	U	0.5	U	U	U
J-5	120	U	0.2	U	U	U
BJ-1	50	U	U	U	U	U
BJ-2	80	U	0.1	U	U	U
B-1	130	5.8	0.7	U	U	U
B-2	70	5.8	0.3	U	U	U
B-3	60	U	0.2	U	U	U
L-1	150	U	0.2	U	U	U
L-2	130	17.1	U	U	U	U
BL	50	U	0.2	U	U	U
BI-1	90	U	U	U	U	U
BI-2	80	U	U	U	U	U
C-2	U	U	U	U	U	U

[a]Means from two sets of water samples: less than 20% variation between each set.
[b]Means from two sets of sediment samples: less than 20% variation between each set.
[c]"U" signifies that a pesticide was undetected (below the detection limit).

1988 on August 7 (slough sites) and August 9 (Bay sites) followed two relatively minor rain events: 0.030 cm (0.12 in) on August 5 and 0.08 cm (0.03 in) on August 6. The summer of 1988 proved to be very dry, and these were the only rain events that occurred close to pesticide applications. No detectable levels of any of the pesticides under study were demonstrated in any water or sediment samples that year.

Of the fourteen pesticides studied during the 2-yr Padilla Bay region investigation, only two were found in water or sediment samples: dicamba and 2,4-D, both of which are known to migrate across land surfaces (runoff) following precipitation events (Wauchope 1978; Trichell et al. 1968).

Dicamba, like 2,4-D, is selectively toxic toward perennial and annual broad-leaf weeds and brush. No literature was found dealing with the toxic effects of dicamba on eelgrass species. Algal species, however, showed reduced growth rates when exposed to 10 ppm dicamba (Cullimore 1975). This level of exposure is about 100 times the level of dicamba found in Padilla Bay waters.

Eelgrasses are sensitive to 2,4-D (Thomas 1968) and can be eradicated using Aqua Kleen (a product of Amchem Products Inc. containing 20% 2,4-D). Eelgrass, at his experimental site (Prince Edward Island, Nova Scotia) was shown to be most sensitive to 2,4-D in late June. Assuming that the amounts of 2,4-D applied to the submerged eelgrass beds were dispersed in a water column averaging 10 to 100 cm deep, the concentration of 2,4-D would be between 2.24 ppm and 22.4 ppm. Therefore the toxic level of 2,4-D to eelgrass was from 1,700 to 17,000 times the highest level of 2,4-D we observed in Padilla Bay sloughs.

The result of this project is that no ecologically significant levels of any of the fourteen pesticides studied were found in the water or sediments associated with Padilla Bay sloughs or the Bay itself during this 2-yr investigation. The very low levels of dicamba and 2,4-D found in some water and sediment samples supports the view that they are subject to runoff following significant rain events. These findings parallel those of Wauchope (1978) whose review on pesticide drainage showed that in general less than 0.5% of commercial pesticides applied to agricultural fields was lost in runoff.

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