

LEVELS OF SELECTED PESTICIDES IN FARM DITCHES
LEADING TO RIVERS IN THE LOWER MAINLAND OF
BRITISH COLUMBIA

Keywords: azinphosmethyl, diazinon, dinoseb,
endosulfan, fensulfothion, farm ditches,
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Michael T. Wan

Environment Canada,
Conservation and Protection, Environmental Protection,
Pacific & Yukon Region, Kapilano 100, Park Royal, West
Vancouver, British Columbia, CANADA V7T 1A2

ABSTRACT

A monitoring survey was conducted from 1985 to 1987 to determine the levels of agricultural pesticides azinphosmethyl, diazinon, dinoseb, endosulfan, and fensulfothion in selected farm ditches leading to the Lower Fraser, Nicomekl, and Sumas rivers in British Columbia, Canada. In ditch water, azinphosmethyl, diazinon, endosulfan, and fensulfothion were not detected (limit of detection, 1 µg/L). However, dinoseb was consistently found in ditch water for one year after the spray season at levels varying from 0.3 - 18.6 µg/L, averaging 4.9 µg/L. The endosulfan level in ditch water of one farm

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reached 1530 $\mu\text{g/L}$ shortly after a spray application, even though it was not found at other times of the year. In ditch sediments, low levels, i.e., 2.7, 4.0, 22.9 and 10.3 $\mu\text{g/kg}$ respectively of azinphosmethyl, diazinon, dinoseb, and fensulfothion were sporadically found. Endosulfan was, however, consistently found in sediments at all study sites at levels varying from 2 - 150 $\mu\text{g/kg}$, averaging 18.8 $\mu\text{g/kg}$.

INTRODUCTION

Pesticides may enter the aquatic environment via direct and indirect depositions, runoff, and leaching (Frank and Sirons, 1979; Grover et al., 1985b). Although studies on the movement of pesticides from agricultural land to streams have been conducted extensively in other parts of Canada, e.g., Ontario (Harris and Miles, 1975; Frank et al., 1982), Quebec (Muir et al., 1978) and Manitoba (Muir and Grift, 1987), this problem received little attention in British Columbia until recently.

In 1985, Environment Canada initiated a 3-year survey to determine the residue levels of the more commonly used agricultural pesticides in selected farm ditches leading to the fishery sensitive Fraser, Nicomekl, and Sumas rivers. The main objective of this study is to evaluate the potential impact to aquatic invertebrates

and Pacific salmonids of pesticide residues in ditches which provide nursery areas important in fish food production and as seasonal fish habitat areas.

The selection of pesticides for this study was based on a 1983/1984 post-registration use pattern survey of domestic and commercial pesticides in British Columbia (Wilson, 1985). The five commonly used farm pesticides adjacent the Lower Fraser, Nicomekl, and Sumas rivers were: azinphosmethyl, diazinon, dinoseb, endosulfan, and fensulfothion. These pesticides were used annually to protect a number of crops from pest infestations and weeds.

MATERIALS AND METHODS

Sampling sites

The following criteria were used for the selection of sampling sites, i.e., areas where:

(1) a similar mixture of crops was grown, e.g., beans, broccoli, cabbage, corn, onions, peas, potatoes, strawberry;

(2) dinoseb was used as a top killer in early May and mid June, and azinphosmethyl, diazinon, endosulfan, and fensulfothion as insecticides in one part of the farm or another in July/August;

(3) farm ditches were leading either singly or collectively to the Fraser, Nicomekl, and Sumas rivers;

(4) crop setbacks from ditches were 3 m or less;

(5) ditches with water averaging about 1.5 m in width, and 0.5 m in depth.

Based on the above considerations, ditches from 7 sampling sites were selected for this study (Figure 1): (1) Farm A, (2) Pump stations B (2 sites), (3) Farm C, (4) 168th Street, (5) Farm D, (6) Dixon Street, and (7) Sumas Lake Canal.

Farm A, a 100-ha farm, is located on the SE corner of Westham Island, about 32 km south of Vancouver, B.C. (Figure 1). Pump stations B and Farm C (110 ha) are situated about 20 km south of Vancouver. Pump stations B regulate the water levels of Crescent Slough by discharging excess water to the Fraser River. Crescent Slough receives ditch runoff from 12,000 ha of farmland.

Farm D, Dixon Street, and ditches draining to Sumas Lake Canal are located about 65 km east of Vancouver. Sumas Lake Canal receives drainage from 10,000 ha of farmland. Water flows via the canal to the Sumas River, a tributary of the Fraser River.

The 168th Street ditches are located in Cloverdale, 45 km east of Vancouver. The ditches on both sides of this highway (south of Nicomekl River) receive runoff from 200 ha of farmland and discharge into the Nicomekl River.

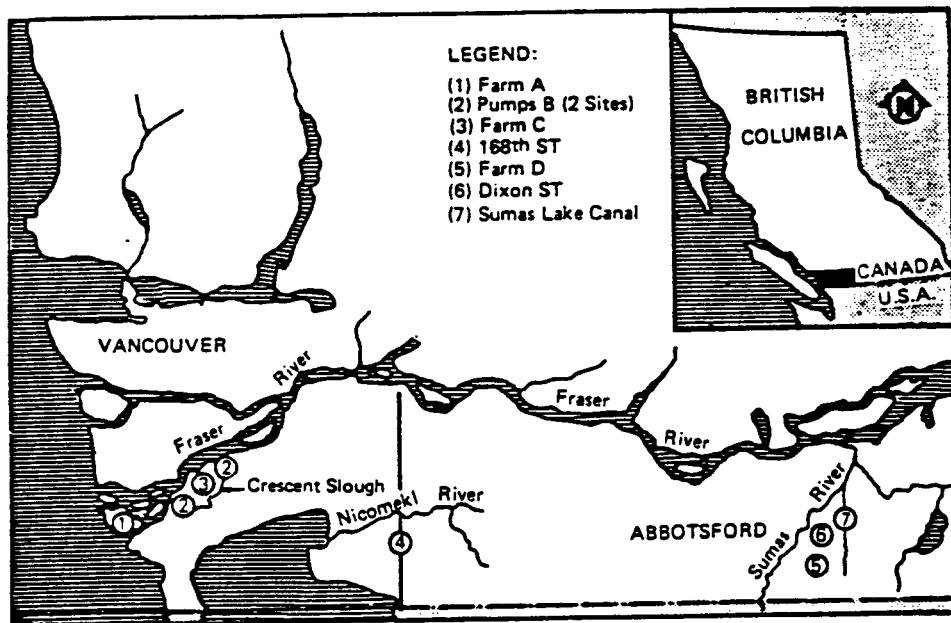


FIGURE 1. LOCATION of Survey and Sampling Sites

Sampling procedure

Sample bottles and jars were prewashed in pesticide grade acetone and petroleum ether and preheated to 300°C for 12 hours before use. Solvent washed and heated aluminium foils were used for the lining of all water bottles and glass jars to prevent contamination. Water and sediment samples were taken from ditches at random within the same general area of each study site.

Water samples were collected in 4.5 L amber bottles by holding the bottle just below the water surface. Ten 400-ml composite samples were pooled to make up a 4-L

sample per site during each sampling occasion. Ten 45-g composite sediment samples were collected at each site and were stored in 500 g widemouth amber glass jars. The samples were obtained with a circular (15 cm diameter) steel trowel fitted to a 3.5 m wooden handle. Another steel trowel was used to transfer the required portion of sediment to the storage jars.

Both the sediment and water samples were stored at 4°C and shipped to the laboratory the same day. Water samples were extracted with solvents before storage in the laboratory, while the sediment samples were frozen immediately for subsequent analysis.

Sampling regime

The sampling regime was designed to fulfill the following survey objectives:

(1) 1985 - to determine the occurrence and levels of azinphosmethyl, diazinon, dinoseb, endosulfan, fen-sulfothion in ditch water and sediments of Farm A, Pump stations B, Farm C, Farm D, and ditches leading to the Sumas Lake Canal.

(2) 1986 - to monitor more intensively the residue levels of dinoseb and endosulfan in ditch sediments of farm A, including an assessment of endosulfan residue levels in soil with crops before and after insecticide application.

(3) 1987 - to determine the occurrence and levels of dinoseb and endosulfan in the ditch sediments of two

other farm areas, i.e., 168th Street (Cloverdale) and Dixon Street (Sumas).

Water and ditch sediment samples were taken in early spring in the first week of May each year starting in 1985, prior to any pesticide application. Subsequent samples were taken in July, shortly after treatment. Further samples were obtained during the rainy and wet season, i.e., in October, December, and February of the following year.

Residue analysis

Residue analyses were conducted by the British Columbia Ministry of Environment & Parks Laboratory, Vancouver, British Columbia. A 1,800-mL sample was transferred to a 2 L separatory flask and extracted 3 x 50 mL with dichloromethane (CH_2Cl_2). The CH_2Cl_2 extract was drained through a plug of heat treated sodium sulfate (Na_2SO_4) and combined in a 250 mL round bottom evaporating flask. The extract was rotary evaporated and transferred to 5 mL iso-octane. The extract was then analyzed on a Hewlett Packard 5880 gas liquid chromatograph (GLC) equipped with both an electron capture detector (ECD) and a nitrogen phosphorus specific detector (NPD) using a splitless injection system and BD-5 30 m x 0.32 mm id. capillary column. The endosulfans were detected on the GLC-ECD and diazinon, fensulfothion and azinphosmethyl were detected on the GLC-NPD. The

extract was cleaned up on a carbon/cellulose column if needed.

To analyze for dinoseb, a second 1,800 mL aliquot of the sample was transferred to a 2 L separatory flask and acidified with H_2SO_4 prior to extracting 3 x 50 mL CH_2Cl_2 . The CH_2Cl_2 extract was drained through a plug of acidified and heated Na_2SO_4 . The extract was then rotary evaporated to 15 - 20 mL and methylated with diazomethane. The derivatized extract was then transferred to 5 mL of iso-octane and analyzed on the GLC-ECD system previously described. The extract was cleaned up on a Florisil^R column if needed.

A quality control programme was implemented to check the recovery rates of the five pesticides. Fortified water and sediment samples were submitted to the laboratory along with the regular samples at least twice a year.

RESULTS AND DISCUSSION

Quality control programme

Recoveries of the five pesticides in fortified water and sediment samples are presented in Table 1. The recovery rates for water were generally satisfactory. However, the recovery from sediment was unsatisfactory for diazinon, dinoseb and fensulfothion. The cause of low recovery for these pesticides is presently not

TABLE 1

Recoveries of Pesticides from Sediment and Water

| Pesticide | Level of fortification | N | Percent Recovery (%) Mean + S.E. | Detection Limit |
|-----------------|---|---|-------------------------------------|---|
| <u>Sediment</u> | <u>($\mu\text{g}/\text{kg}$)</u> | | | <u>($\mu\text{g}/\text{kg}$)</u> |
| Azinphos methyl | 50 | 4 | 118.8 \pm 9.5 | 2 |
| Dinoseb | 100 | 4 | 39.0 \pm 7.2 | 1 |
| Diazinon | 100 | 4 | 68.3 \pm 32.9 | 2 |
| Endosulfan* | 50 | 5 | 104.4 \pm 5.8 | 1 |
| Fensulfothion | 200 | 3 | 47.7 \pm 13.2 | 2 |
| <u>Water</u> | <u>($\mu\text{g}/\text{L}$)</u> | | | <u>($\mu\text{g}/\text{L}$)</u> |
| Azinphos methyl | 25 | 5 | 92.6 \pm 11.4 | 1 |
| Dinoseb | 20 | 6 | 70.0 \pm 10.2 | 0.1 |
| Diazinon | 10 | 5 | 105.0 \pm 5.8 | 1 |
| Endosulfan* | 10 | 6 | 84.0 \pm 7.3 | 1 |
| Fensulfothion | 25 | 5 | 87.0 \pm 6.0 | 1 |

* (endosulfan I + endosulfan II + endosulfan sulfate)

known. A correction factor based on the mean recovery efficiency was applied in the calculation of concentrations of these pesticides.

Pesticide residues in ditch water

In 1985, azinphosmethyl, diazinon, endosulfan, and fensulfothion, were not found at a detection limit of 1

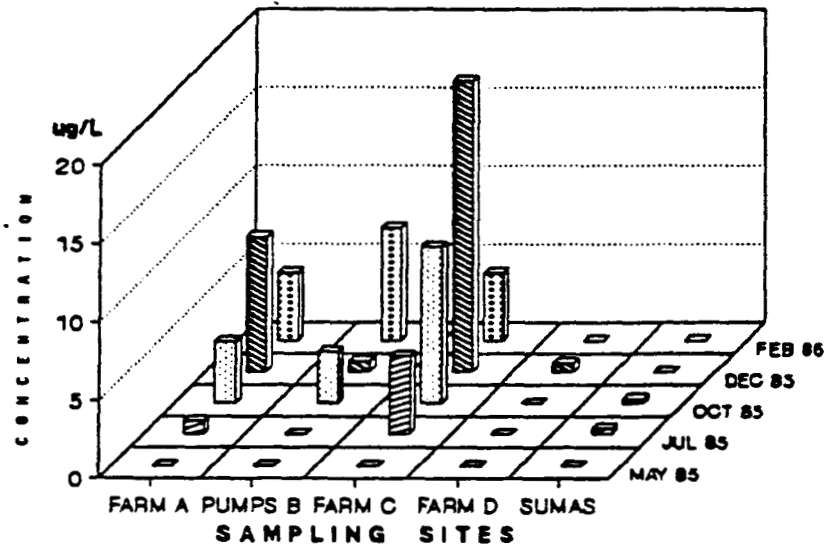


Figure 2. Dinoseb residue levels in ditch water leading to the Fraser and Sumas rivers

$\mu\text{g/L}$ in the ditch water at any of the study sites. Dinoseb was, however, consistently found in ditch water of Farm A, pump station B (Pumps B), Farm C, Farm D and also in ditches leading to Sumas Lake Canal (Figure 2).

Although dinoseb was not detected in the May sample (before the spraying season), low levels of this herbicide were detected at all study sites after the May spray application. The mean level found in ditch water averaged $4.9 \mu\text{g/L}$ (range, $0.3 - 18.6 \mu\text{g/L}$). As shown in Figure 2, elevated levels of dinoseb occurred in ditches from October 1985 to February 1986 at three sampling locations: Farm A, Pumps station B, and Farm C. In

Farm D, however, dinoseb was found only once at 0.6 $\mu\text{g/L}$ in December 1985, while in ditches leading to the Sumas Lake Canal, this herbicide was detected twice, in July 1985 and October 1985 at 0.4 and 0.3 $\mu\text{g/L}$ respectively.

Dinoseb was detected only once at 5.0 $\mu\text{g/L}$ (range, 5 - 7 $\mu\text{g/L}$) at Farm A in October 1986, despite a more intensive sampling effort (i.e., $n = 5$; each sample contained 10 pooled subsamples). The higher than normal rainfall shortly after treatment in May and July 1986 when compared to the same months in 1985 (Figure 3) may have removed the dinoseb residues in water before the first post-spray sample was taken.

While endosulfan residues were not detected in water in 1985, this insecticide was detected once in July 1986, when the water samples were collected shortly (i.e., 0.5 h) after treatment in the ditches of Farm A. The level was $1530 \pm 476 \mu\text{g/kg}$ (mean \pm S.E., $n = 5$). This insecticide was not detected in the next three post-spray sampling occasions.

Pesticide residues in ditch sediments

Low levels of azinphosmethyl, diazinon, dinoseb, endosulfan, and fensulfothion residues were found in ditch sediments. Azinphosmethyl was found at two sites (Farm A and Pumps B) in July 1985 with a mean level of 2.7 $\mu\text{g/kg}$. Both diazinon and fensulfothion were

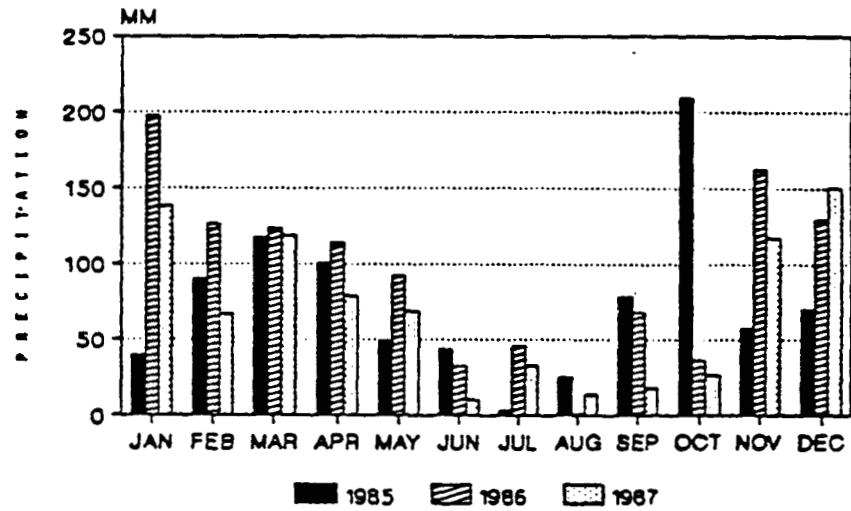


Figure 3. Monthly precipitation and snow equivalent of Delta/Ladner station (near Farm A & Pump stations B)

detected once at two sites (Pumps B and Farm D) in the July 1985 sample with a respective average level of 4.0 and 10.3 $\mu\text{g}/\text{kg}$. Dinoseb was found only once at 22.9 $\mu\text{g}/\text{kg}$ in the ditch sediment of Farm D in July 1985.

However, in 1985 endosulfan residues was more frequently found in the ditch sediments of Farm A, Pumps B, Farm C and Farm D but was only detected once in the ditches leading to Sumas drainage canal (Figure 4). The mean concentration was 18.8 $\mu\text{g}/\text{kg}$ (range, 2 - 150 $\mu\text{g}/\text{kg}$), with the highest concentration detected in the December 1985 sample at Farm A.

In 1986, despite a more intensive monitoring effort, dinoseb was not detected in the ditch sediments of

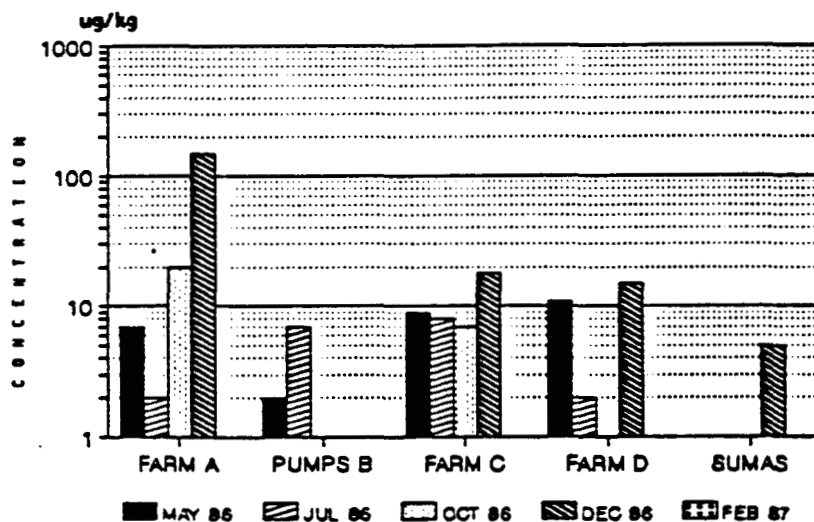


Figure 4. Endosulfan residue levels in sediments of farm ditches leading to the Fraser and Sumas rivers

Farm A during the five sampling occasions. The higher than normal rainfall post-treatment in May and July when compared to same period in 1985 (Figure 3), may have removed dinoseb residues in sediments.

Residues of endosulfan were found in the cropped area of Farm A, 2 m and 3 m (inside ditch) outside the treated area at different times post-treatment in 1986 (Figure 5). There is evidence to suggest that endosulfan residues were carried over from previous years in the top soil (to 5 cm depth) and in the adjacent ditch sediments (i.e., the prespray May 1986 samples). While

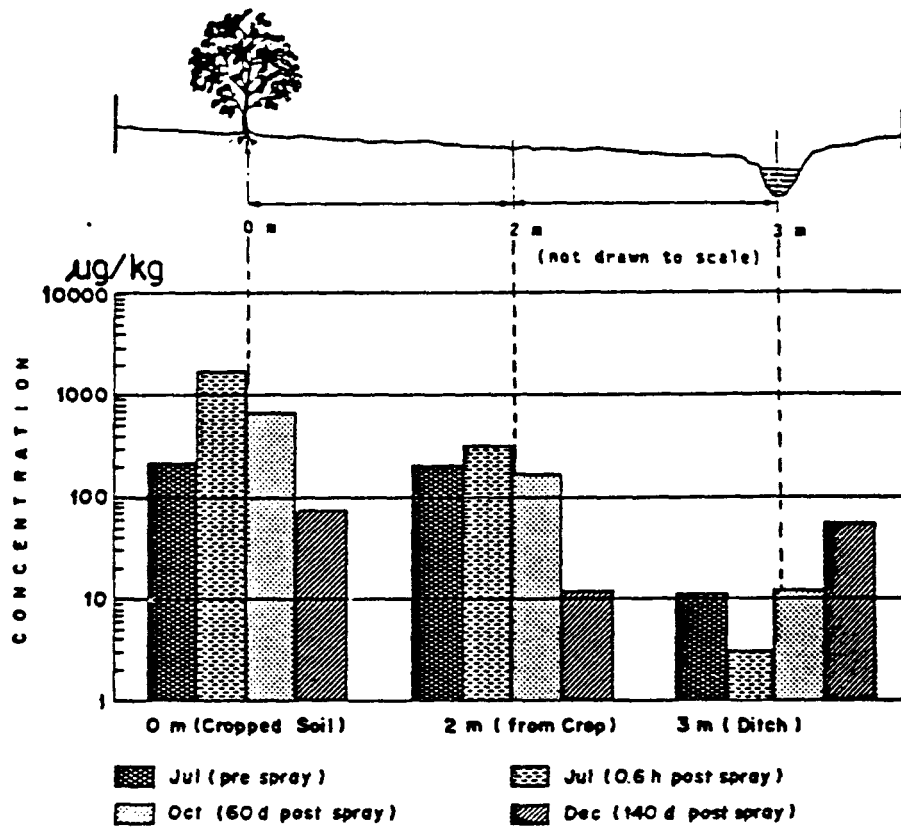


Figure 5. Endosulfan residue levels in soil and ditch sediments of farm A

the mean level in the top soil was $219 \mu\text{g}/\text{kg}$, the concentration in ditch sediments was about 20 times lower at $11 \mu\text{g}/\text{kg}$.

Shortly after the July 1986 treatment (i.e., 0.5 h; tractor mounted sprayer; at 0.568 kg a.i./ha), endosulfan level in the top 5 cm of soil in Farm A increased to

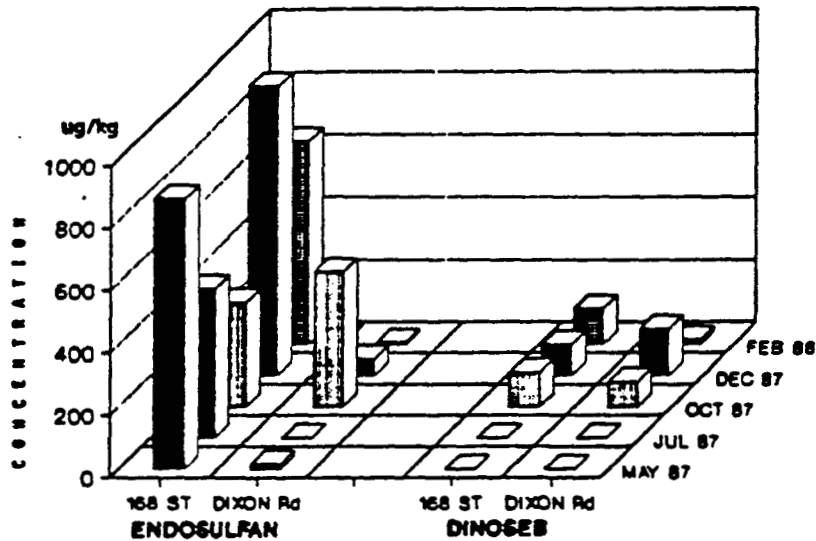


Figure 6. Endosulfan and dinoseb residue levels in ditch sediments in 1986/1987

1712 $\mu\text{g}/\text{kg}$ within the sprayed area. This level decreased to 674 $\mu\text{g}/\text{kg}$ 60 days post-spray, and to 73 $\mu\text{g}/\text{kg}$ after 140 days post-spray. In contrast, endosulfan levels in ditch sediments were 11.0 and 3.0 $\mu\text{g}/\text{kg}$ before and shortly after spray application respectively. This level increased to a mean of 54 $\mu\text{g}/\text{kg}$ in the December 1986 samples.

In 1987, both dinoseb and endosulfan residues were found in the ditch sediments of 168th Street (Cloverdale) and Dixon Road (Sumas) (Figure 6). The mean level of dinoseb in 168th Street and Dixon Road was 81.2 and 108.6 $\mu\text{g}/\text{kg}$ respectively. For endosulfan, a much higher

level was found in 168th Street than in Dixon Road ditches, with a respective mean \pm S.E. of $652 \pm 126 \mu\text{g}/\text{kg}$ (range, 334 - 926, n = 5) and $135 \pm 127 \mu\text{g}/\text{kg}$ (range, 7 - 465, n = 5). Elevated levels of both pesticides in ditch sediments were detected during the wet season of the year (December 1987 and February 1988 samples), an indication that they were transported from the treated areas to the ditches via surface runoff.

Implications on aquatic organisms

The potential impact of agricultural pesticides on non target aquatic invertebrates and fish in farm ditches and streams could be determined on the basis of the 1986 observations of a tractor mounted endosulfan spray application at 0.568 kg a.i./ha with a setback (buffer zone) of 3 m from ditches in Farm A.

Although not detected in the water before treatment, endosulfan residues in ditch water reached a mean of $1530 \mu\text{g}/\text{L}$ (range, 500 - 2,700 $\mu\text{g}/\text{L}$; n = 5) one half hour after treatment. This level of endosulfan exceeds the 96 h LC₅₀ value for rainbow trout, daphnia, and stonefly by about 1100, 6, and 670 times respectively (Table 2). Mortality of these organisms would likely occur if they were present in the ditch soon after endosulfan application. Moreover, this observation indicates that pesticide levels in ditch water with a setback of less than 3 m were more likely to exceed the

TABLE 2

Toxicity to Aquatic Invertebrates and Salmonids of Technical Azinphosmethyl, Diazinon, Dinoseb, Endosulfan, and Fensulfothion

| Pesticide | 96-h LC ₅₀ (µg/L) ^a | | |
|------------------|---|---------|----------|
| | Mean value | | |
| | Rainbow trout | Daphnia | Stonefly |
| Azinphos. methyl | 4.3 | 1.7 | 1.9 |
| Diazinon | 90 | 0.9 | 25 |
| Dinoseb | 67** | 680 | - |
| Endosulfan | 1.4 | 240 | 2.3 |
| Fensulfothion | 8,600 | 0.9 | - |

^a (Pimentel, 1971; Kenaga, 1979; Johnson & Finley, 1980)

** Cutthroat trout

96-h LC₅₀ values of aquatic invertebrates and fish shortly after spray application than at other times. Nevertheless, any deleterious effects to stream invertebrates and fish occurring downstream would depend on the volume and flow rate of the water body, and the type and degradation rate of the pesticide.

The 96-h LC₅₀ values in Table 2 represent the toxicity values to aquatic organisms of the technical materials of the five pesticides. Studies have shown that emulsifiers used in formulating pesticide may increase or decrease the toxicity of the products (Man et

al. 1987a, 1987b, 1988). Presently, little information is available on the toxicity to aquatic invertebrates and salmonid fish of the formulated products of azinphosmethyl, diazinon, dinoseb, endosulfan, and fensulfothion.

The potential impact to aquatic invertebrates and fish of low levels of azinphosmethyl, diazinon, dinoseb, and fensulfothion that were sporadically found in ditch sediments is difficult to assess, as little is presently known on the effects of sublethal effects of pesticides to non-target organisms. However, for the more persistent pesticide such as endosulfan and its transformation products, with a half life in laboratory soils at 20°C varying from 3 - 6 months or more (Martens, 1977, Miles and Moy, 1979), the potential for bioconcentration and sub-lethal impacts probably exists. On many farms in the Fraser Valley, endosulfan is used annually and the conditions exist for continual transport of this chemical to the non-target aquatic environment via surface runoff during the wet season of the year.

CONCLUSIONS

Azinphosmethyl, diazinon, dinoseb, endosulfan, and fensulfothion residues were detected in ditches leading to the Lower Fraser, Nicomekl, and Sumas rivers of Bri-

tish Columbia. The levels of these pesticides in water and sediments varied but appeared to be elevated during the high seasonal rainfall periods. There was evidence that the levels of pesticides in ditch water shortly after application exceed, (e.g., endosulfan) the 96-h LC50 values of fish and aquatic invertebrates. The impact to salmonids and aquatic invertebrates of low levels of pesticides in sediments is presently not known. A setback greater than 3 m from ditches for tractor mounted spray operations may be necessary to minimize the level of pesticide contamination in farm ditches.

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