Diazinon and Its Degradation Products in Agricultural Water Courses in British Columbia, Canada

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Diazinon (O,O'-diethyl O-[4-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate) is an organophosphorus insecticide. It was first commercially introduced in 1952, and it is still commonly used in Canada and elsewhere for insect control. The insecticide inhibits an enzyme, acetylcholinesterase (AChE), in insects that breaks down the neurotransmitter, acetylcholine (ACh). Without the functioning enzyme, ACh builds up in the synaptic junction, causing incoordination, convulsions and, ultimately, death of insects. However, it has been established by US Environmental Protection Agency (EPA) that a diazinon concentration of 350 ng/L may be toxic to aquatic organisms (Amato et al. 1992). Toxicity of diazinon to humans has also been reported (Chapman & Hall 1996; Cox 1992). For instance, fatal human dose was reported to be about 90-444 mg/kg (Chapman & Hall 1996), and two EPA surveys found that diazinon was the 6th most frequent cause of accidental death due to pesticides (USEPA 1988). While diazinon is considered as moderately toxic, a more toxic impurity, O,O,O,O-tetraethyl dithiopyrophosphate (sulfotepp), has been found in the pesticide formulations of diazinon (Meier et al. 1979). Sulfotepp, which is 1000 times more toxic than diazinon (Sovocool et al. 1981), may exist either as an impurity in the manufacture of diazinon or as a breakdown product in the presence of trace water in the pesticide formulation. But, in the presence of large amount of water, sulfotepp was not formed (Ruzicka et al. 1967; Karr 1985). This is probably due to hydrolytic degradation of diazinon into harmless products.

Additional studies on the degradation of diazinon have identified that 2-isopropyl-6-methyl-4-hydroxypyrimidine (IMHP) is a major degradation product when low concentration of diazinion was studied in compost (Sumner et al. 1987), soil (Michel et al. 1997) and water (Ku et al. 1998). Although IMHP is found to be potentially leachable, it is less toxic than diazinon (Sumner et al. 1987). Moreover, diazinon-O-analog (or diazoxon), which can be produced by the action of certain enzymes—commonly found in insects, fish, birds and mammals—on diazinon, is a much more potent inhibitor of AChE than diazinon is (Cremlyn Year). Diazoxon can also be produced by aqueous chlorine in wastewater treatment plant (Zhang and Pehkonen 1999).
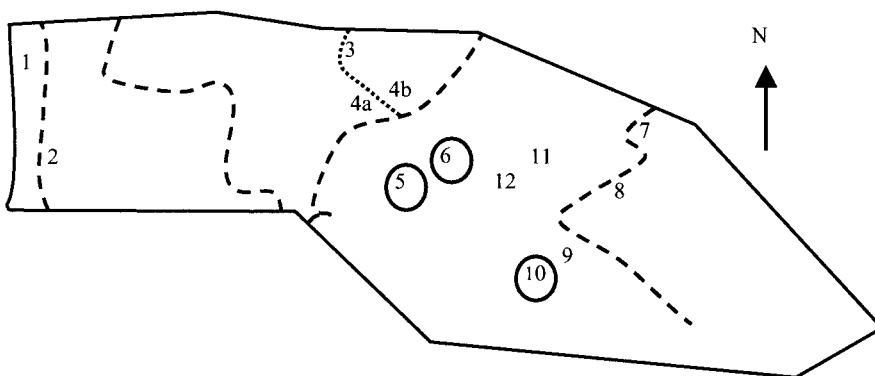

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Figure 1. Sample site locations for diazinon study (dotted lines represent creeks; circled numbers represent locations where diazinon has been detected)

About 1 L of ditch water from each of the 13 sites was collected into glass bottles. Distilled water was added into a glass bottle and considered the field blank. These 14 samples were collected on June 6, August 14 and October 15 of 2000 in an attempt to match with different phases of diazinon application during the growing season (i.e. before, immediately after and well after application). The weather was cloudy during the three sampling dates. On each sampling day, a field blank was prepared during sampling by filling a glass bottle with distilled water.

A standard method for analysis of organophosphorus pesticides developed by Environment Canada (Environment Canada 1999) was followed for sample handling, preservation and extraction. Gas chromatography (GC) was employed for chemical separation. Regarding detection method, a mass-selective detector (in the electron ionization or EI mode), instead of a nitrogen-phosphorus detector (NPD), was used because NPD is not applicable to detect the degradation products of diazinon that do not contain phosphorus, such as IMHP. EI was selected because of adequacy in sensitivity and ease of operation.

Each water sample, including the field blank, was quantitatively transferred into a 1-L separatory funnel for sample extraction. To prepare the laboratory blank, 1-L distilled water was added to another separatory funnel. To prepare the spike, a second 1-L distilled water was added into another separatory funnel, with 100 µl of a method spike solution (containing 20-µg/mL of each of the 4 standard compounds) added. Then, 20 µL of a 100-µg/mL surrogate standard (triphenylphosphate) was added into each of the samples, field blank, laboratory blank and spike. This spike was included in order to determine recovery and to validate the extraction procedure.

The sample extracts are all prepared in hexane, with the internal standard (1,3-dimethyl-2-nitrobenzene) added. The extracts were subsequently analyzed of the

Chemical analysis of diazinon in environmental samples has been undertaken in various countries, including Canada (Wan 1989), Japan (Tsuda et al. 1992; Kawata and Yasuhara 1994), and US (Domagalski 1996) to monitor the aqueous concentration of diazinon. Surveys on breakdown products in diazinon formulations have also been undertaken in various countries, such as Australia (Allender and Britt 1994), and US (Sovocool et al. 1981), but these studies did not involve environmental samples. It is the objective of this study to determine the presence of diazinon and diazinon degradation products, (i.e. sulfotepp, IMHP, and diazinon-O-analog) in water from ditches near fields where diazinon was reported to be applied. As far as we know, this is the first study to monitor concentrations of diazinon and its degradation products in ambient water samples. In this study, we report the selection of sampling sites, sample collection method and simultaneous chemical analysis of diazinon and its three degradation products in thirteen farm ditch sites at the Big Bend area in the city of Burnaby of British Columbia.

MATERIALS AND METHODS

Standards of diazinon, sulfotepp, triphenylphosphate (surrogate standard), and 1,3-dimethyl-2-nitrobenzene (internal standard), and pesticide-grade of hexane, isooctane, and methanol were purchased from Supeclo (Oakville, ON). Pesticide-grade acetone and dichloromethane (DCM) were obtained from Anachemia Science (Richmond, BC). 2-isopropyl-6-methyl-4-hydroxypyrimidine (IMHP) and diazinon-O-analog was purchased from Ultra Scientific (North Kingstown, RI, USA). Anhydrous sodium sulfate was obtained from Sigma-Aldrich (Oakville, ON).

All glassware, aluminium foil and sampling equipment that came in contact with the sample were washed with laboratory-grade detergent. Subsequently, they were rinsed first with distilled water, and then with acetone, and heated at 200 °C for a minimum of 12 h. Water samples were collected in 1-L heat-treated amber-coloured glass bottles, sealed with Teflon-lined caps. Samples were stored on ice in a cooler before extraction was carried out. The water samples were extracted within 2 days after sampling.

After interviews with farm operators to confirm diazinon application, thirteen sites of farm ditches located at the Big Bend area in the city of Burnaby of British Columbia (Figure 1) were selected for water sampling. The ditch water all leads to the North Arm of Fraser River. These sampling sites were selected based on the farms that have applied diazinon for insect control and were considered possible sources of diazinon runoffs. We collected water samples from upstream and downstream sites of 5 possible sources (i.e. 1 and 2, 3 and 4b, 7 and 8, 9 and 10, 11 and 12 in Figure 1). However, sites 4a, 5 and 6, which are downstream of 3 additional sources, do not have the upstream counterparts.

amount of diazinon and its degradation products using the instrument: GC Electron Ionization Detector (Hewlett-Packard, HP1800A, Palo Alto, CA, USA). Splitless injection of a volume of 1 μL was employed. The GC column used was HP-5MS cross-linked 5% PH ME-siloxane 30 m x 0.25 mm x 0.25 μm film thickness. Helium gas flow rate was 0.7 mL/min. A solvent delay of 3.5 min. was used to avoid overloading the electron ionization detector. The inlet and detector temperatures were 230 °C and 300 °C, respectively. A temperature program: (1) from 60 to 185 at 20 °C/min (2) increase to 209 °C at 3 °C/min (3) increase to 300 at 20 °C/min, was used to enhance chemical separation.

RESULTS AND DISCUSSION

Identification of diazinon and its degradation products was based on the GC retention times as well as the presence of selected ions which are specific to the compounds. This mode of mass spectrometric detection is called selected ion monitoring (SIM). For instance, in the chromatogram (Figure 2), diazinon (compound E) was eluted at 12.10 min. Compound E was confirmed to be diazinon by the molecular ion (m/z = 273) and selected fragment ions (m/z = 137 and 179). Similarly, ions selected for detection of other compounds are given in parenthesis as follows: diazinon-O-analog (137, 273), IMHP (84, 137) and sulfotepp (202, 322).

The recovery of diazinon ranged from 101 to 110%. The recoveries of sulfotepp and diazinon-O-analog ranged between 98-110%, and 111-145%, respectively. This confirmed that the extracted procedure was successful in recovering the compounds from water.

The limit of detection (LOD) of diazinon was estimated to be 2 μg/L, based on 3 times of the signal/noise ratio. With about 500 times preconcentration by solvent extraction, the method detection limit (MDL) was 4 ng/L. This MDL is comparable to the value in one study 5 ng/L (Tsuda et al. 1992), and is lower than 38 ng/L of another one (Domagalski 1996). Our MDL of diazinon is higher than the value obtained in a study using online preconcentration, with the detection limit of diazinon estimated to be 2 ng/L (Lacorte and Barcelo 1996). With solid-phase microextraction, another report estimated a lower detection limit of diazinon, i.e. 1 ng/L (Boyd-Boland et al. 1996). The MDL values for sulfotepp, IMHP, and diazinon-O-analog were determined to be 10, 1000, and 30 ng/L, respectively.

Diazinon was found to range from not detected (i.e. below 4 ng/L) to a maximum level of 259 ng/L. The standard deviation of diazinon concentration as determined from the calibration line ($r^2 = 0.999$) was 4-6 ng/L. Although all values are below the value (350 ng/L) which may be toxic to aquatic organisms (Amato et al. 1992), we did obtain one value (259 ng/L) that is quite high. Accordingly, the significance of our finding is that this provides a clearer picture than a previous report that diazinon was not found to be above the detection limit of 1 μg/L in

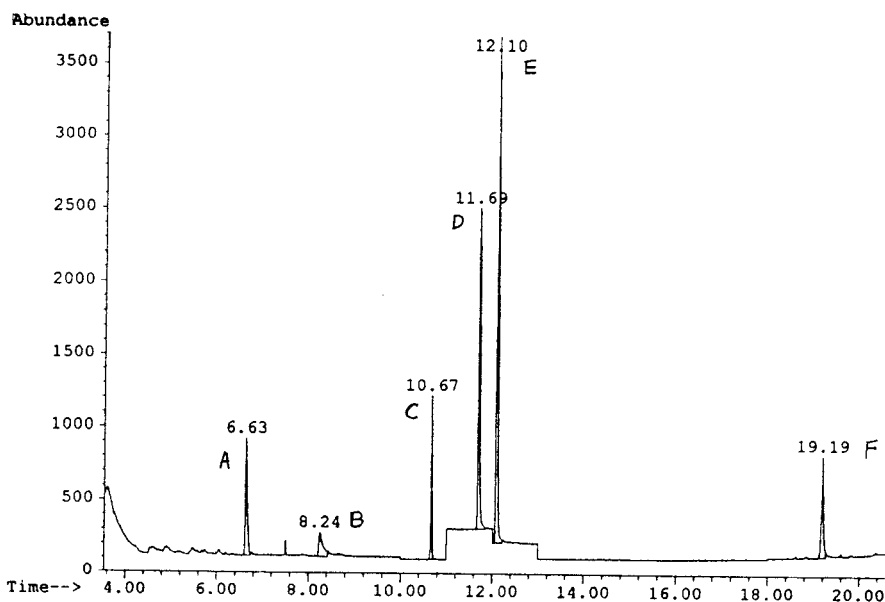**Figure 2.** Gas chromatogram of 6 standards (500 µg/L, except otherwise stated): A: 1,3-dimethyl-2-nitrobenzene (internal standard, 100 µg/L), B: 2-isopropyl-6-methyl-4-hydroxypyrimidine (IMHP), C: sulfotepp, D: diazinon-O-analog E: diazinon, F: triphenylphosphate (surrogate standard)

ditch water (Wan 1989). It is because we have achieved a lower detection limit of 4 ng/L.

Sulfotepp, IMHP, and diazinon-O-analog were not detected above their respective MDL values. Nevertheless, these species have been detected in environmental samples (Domagalski 1996; Boyd-Boland et al. 1996). For instance, sulfotepp has been found in Russian Arctic samples) to range from 2.1 to 5.7 ng/L (Boyd-Boland et al. 1996). Therefore, it is likely that our method was not sensitive enough to detect sulfotepp.

The observation that diazinon could not be detected in the majority of the farm ditches investigated in this study indicates that, after application, either only a small amount of the applied diazinon was released into the waterways or diazinon is flushed away quickly after entering the farm ditches. Diazinon is a relatively water soluble substance with a water solubility of 40 mg/L at 25 °C (Mackay et al. 1992). Its sediment-water partition coefficient is small, indicating that the sediments do not have a large capacity to retain the substance. After a release of diazinon in running water, diazinon can be expected to be quickly removed because of the presence of water currents. It is possible that diazinon could have been discharged in the tested waterways at some time point prior to sampling, and therefore, no detectable concentrations were found at the time of sampling.

The high diazinon concentrations, i.e. up to 259 ng/L, likely reflect a recent release, perhaps associated with an application. This indicates that at certain times of application or use, high diazinon concentrations can be reached in local waterways. These concentrations may be of ecological relevance given that concentrations of 350 ng/L have been associated with toxic effects in aquatic organisms (Amato et al. 1992).

Diazinon applications can therefore in some cases be associated with significant risks to aquatic life in nearby streams or waterways. Given the environmental fate characteristics of diazinon, relatively high concentrations in water can be expected immediately after release. After termination of a release, diazinon levels can be expected to fall quickly. Therefore, in order to monitor for the occurrence of elevated diazinon levels in water, a water sampling strategy requires a fairly high sampling frequency. Considering that it is possible that high and potentially "toxic" diazinon levels in water can be associated with the application of this substance, it is important to further explore the relationship between diazinon application and resulting water concentrations.

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