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Distribution of 1,3-Dichloropropene and 1,2-Dichloropropane in Big Creek Watershed

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Big Creek is situated in prime agricultural land in southwestern Ontario. The basin has an area of 728 km^2, while the Creek runs for the most part in a north-south direction for a length of 56 km and empties into Lake Erie at Long Point Bay. A large portion of the watershed is dominated by the Norfolk sand plain with thicknesses of 5 to 15 m not uncommon (Chapman and Putnam, 1973). Some of Ontario's best tobacco producing areas lie within the Big Creek watershed where soil fumigants are used extensively for the control of nematodes and black root rot which result in the stunting of tobacco.

The compounds of interest in this study are 1,3-dichloropropene (1,3-D) and 1,2-dichloropropane (1,2-D). The former is the active ingredient that is presently used in nematocides and is found in formulations ranging from 34 to 94% by volume. The latter (1,2-D) is present in small quantities, around 2% by volume as a manufcturing by-product of 1,3-D. In previous years when 1,2-D was the active ingredient, it was present at concentrations as high as 25%. Because of its persistence in the environment, nematocides with 1,2-D were discontinued in favour of formulations with 1,3-D as the major active ingredient.

The major active ingredient, 1,3-D is comprised of a cis- and a trans- isomer. It is highly volatile with vapour pressures of 43 mm at 25°C for the cis- isomer and 34 mm at 25°C for the trans- isomer (Verschueren, 1977). Water solubility ranges from 2700 mg/L for the cis- and 2800 mg/L for trans- isomer (Dilling, 1977). 1,3-dichloropropene is hydrolyzed in soil to cis- and trans-3-chloroallyl alcohol (Maddy et al., 1982). Studies have shown varying dissipation rates in soil which are

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dependent on moisture conditons, soil temperature and clay content (Van Dijk, 1980). Half-lives tend to be higher in sandy soils compared to those having a higher clay content.

Both 1,3-D and 1,2-D are considered to be moderately toxic to aquatic life, with 1,3-D being significantly more toxic than 1,2-D (U.S. EPA, 1980). Acute toxicity of 1,3-D to freshwater aquatic life occurs at concentrations of 6,060 ug/L based on 96 hr LC_{50} tests on bluegill (Lepomis macrochirus) and chronic toxicity occurs at 244 ug/L based on embroyo-larval tests on fathead minnows (Pimephales promelas). Similar acute and chronic tests for 1,2-D resulted in concentrations of 300,000 ug/L and 8,100 ug/L respectively (U.S. EPA, 1980). Krijgsheld and van der Gen (1986) have reported that 1,3-D exhibits strong mutagenic activity with the Ames test.

The ambient water quality criterion set by EPA for 1,3-D in surface water is 87 ug/L, while their drinking water equivalent level is 11 ug/L. The California Department of Health Services has set an informal suggested no adverse response level (SNARL) advisory of 10 ug/L for 1,2-D in drinking water when the water is consumed for a period of greater than 10 days (Cohen et al., 1983). Massachusetts has set interim drinking water guidelines of 1 ug/L for both 1,2-D and 1,3-D (Hallberg 1989).

In 1989, the Water Quality Branch of Environment Canada undertook a study to determine the presence/absence of 1,3-D and 1,2-D in the Big Creek watershed. To date, most monitoring of these fumigants has been restricted to groundwater. It has been estimated, that almost 48% of Big Creek flow is from groundwater recharge (Yakutchik and Lammers, 1970). The objective of this study was to determine ambient concentrations and their spatial distribution in surface and well water.

MATERIALS AND METHODS

Seven locations comprised of 4 surface and 3 well water sites were selected for monitoring (Figure 1). With the exception of the two sites located at the downstream end of the basin, all sites were chosen to reflect tobacco growing areas where there was extensive use of soil fumigants.

Weekly sampling commenced in April before application of soil fumigants in early May. This sampling frequency was increased to twice weekly during the application period, then reverted back to weekly sampling until the middle of June and then one final survey was carried out towards

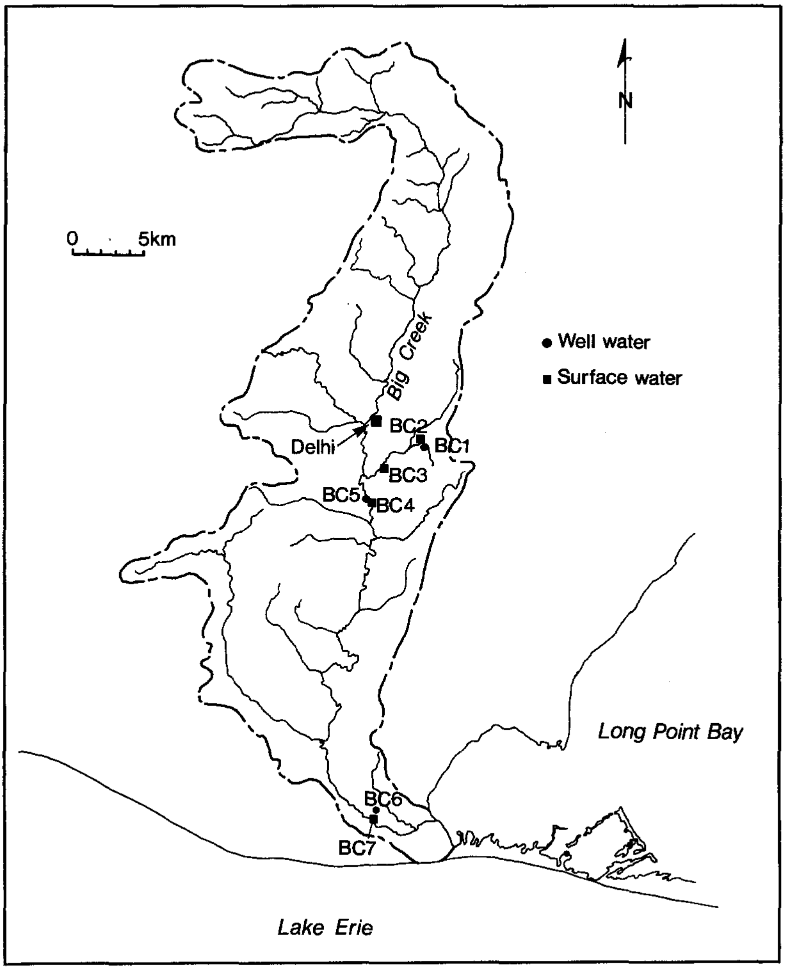

Figure 1. Sampling locations in Big Creek watershed.

the end of July. There were a total of 11 sets of samples collected over the study period.

Samples were collected in 40 ml glass bottles with Teflon septa. All bottles were washed with soap and water, rinsed in hot water and then drained. The bottles were then rinsed twice with acetone and hexane and then dried using nitrogen. Septa underwent the same washing protocol.

In the field, sample bottles were rinsed twice with sample water. When groundwater samples were collected, lines were thoroughly flushed before sampling. Bottles were filled to overflowing, then the septum seal placed on the convex miniscus and sealed by screwing down the cap. Absence of trapped air in the sample indicated a successful seal. If bubbles were present the procedure

was repeated. Samples were kept on ice in the field until returned to the laboratory for analysis.
In the laboratory, 1,3-dichloropropene and 1,2-dichloropropane were analysed using a purge and trap technique. Sample water was transferred into a Tekmar LSC-2 purge and trap unit. Volatiles were purged from the water sample and concentrated on a trap containing Tenax sorbent resins. The retained organic compounds were then desorbed and reconcentrated in a liquid nitrogen trap. This system resulted in the effective purging and trapping of the analytes from water and concentration of the volatiles in a manner that is designed for efficient transfer of analytes to the analytical capillary column.

Subsequent to the purge and trap sequence, the liquid nitrogen trap assembly was rapidly heated and the analytes were desorbed directly into a capillary column connected to a Finnigan Ion Trap Detector for mass spectral identification of the analyte structure and determination of the concentration of each analyte.

RESULTS AND DISCUSSION

Results of all surveys are presented in Table 1. Throughout the sampling period, 1,2-dichloropropane was not found above the detection limit of 0.16 ug/L in any sample. This compound is a manufacturing by-product of 1,3-dichloropropene, and is present only in very small quantities in the soil fumigants; thus, it is not likely that it would be found above the detection limit.

Cis- and trans- 1,3-D were detected at least once at all the surface water stations sampled. The frequency of detection over the study period varied from one detection at stations BC2 and BC3, while, stations BC4 and BC7 had two samples each with 1,3-dichloropropene above the detection limit (Table 1). There were no detections of 1,3-dichloropropene in well water.

Concentrations of 1,3-dichloropropene, which includes the total of the cis and trans isomer, ranged from 0.18 to 4.12 ug/L. The lowest detected amount, 0.18 ug/L is only slightly above the detection limit of 0.14 ug/L for trans- 1,3-dichloropropene. For this particular sample, only the trans- isomer was detected, whereas, in all other samples that were above the detection limit, both the cis- and trans- were found. The analytical detection limit for the cis- isomer is 0.12 ug/L.

In total there were six surface water samples with detectable quantities of 1,3-dichloropropene. Three of the samples collected on May 9th showed the cis- isomer to have higher concentrations than the trans-. The remaining three positive detections that occurred on the

Table 1. Concentrations of 1,3-D and 1,2-D in surface and well water.

Cis- 1,3-dichloropropene (ug/L)

Date	BC 1	BC 2	BC 3	BC 4	BC 5	BC 6	BC 7
25 April	LD	LD	LD	LD	LD	LD	LD
2 May	LD	LD	LD	LD	LD	LD	LD
9 May	LD	2.45	2.01	2.18	LD	LD	LD
11 May	LD	LD	LD	LD	LD	LD	LD
15 May	LD	LD	LD	LD	LD	NS	LD
18 May	LD	LD	LD	0.84	LD	LD	0.37
24 May	LD	LD	LD	LD	LD	LD	LD
30 May	LD	LD	LD	LD	LD	LD	LD
6 June	LD	LD	LD	LD	LD	LD	LD
15 June	LD	LD	LD	LD	LD	LD	LD
26 July	LD	LD	LD	LD	LD	LD	LD

Trans- 1,3-dichloropropene (ug/L)

Date	BC 1	BC 2	BC 3	BC 4	BC 5	BC 6	BC 7
25 April	LD	LD	LD	LD	LD	LD	LD
2 May	LD	LD	LD	LD	LD	LD	LD
9 May	LD	1.00	1.01	1.94	LD	LD	LD
11 May	LD	LD	LD	LD	LD	LD	0.18
15 May	LD	LD	LD	LD	LD	NS	LD
18 May	LD	LD	LD	2.59	LD	LD	0.73
24 May	LD	LD	LD	LD	LD	LD	LD
30 May	LD	LD	LD	LD	LD	LD	LD
6 June	LD	LD	LD	LD	LD	LD	LD
15 June	LD	LD	LD	LD	LD	LD	LD
26 July	LD	LD	LD	LD	LD	LD	LD

1,2-dichloropropane (ug/L)

Date	BC 1	BC 2	BC 3	BC 4	BC 5	BC 6	BC 7
25 April	LD	LD	LD	LD	LD	LD	LD
2 May	LD	LD	LD	LD	LD	LD	LD
9 May	LD	LD	LD	LD	LD	LD	LD
11 May	LD	LD	LD	LD	LD	LD	LD
15 May	LD	LD	LD	LD	LD	NS	LD
18 May	LD	LD	LD	LD	LD	LD	LD
24 May	LD	LD	LD	LD	LD	LD	LD
30 May	LD	LD	LD	LD	LD	LD	LD
6 June	LD	LD	LD	LD	LD	LD	LD
15 June	LD	LD	LD	LD	LD	LD	LD
26 July	LD	LD	LD	LD	LD	LD	LD

NS - No sample
LD - Less than detection

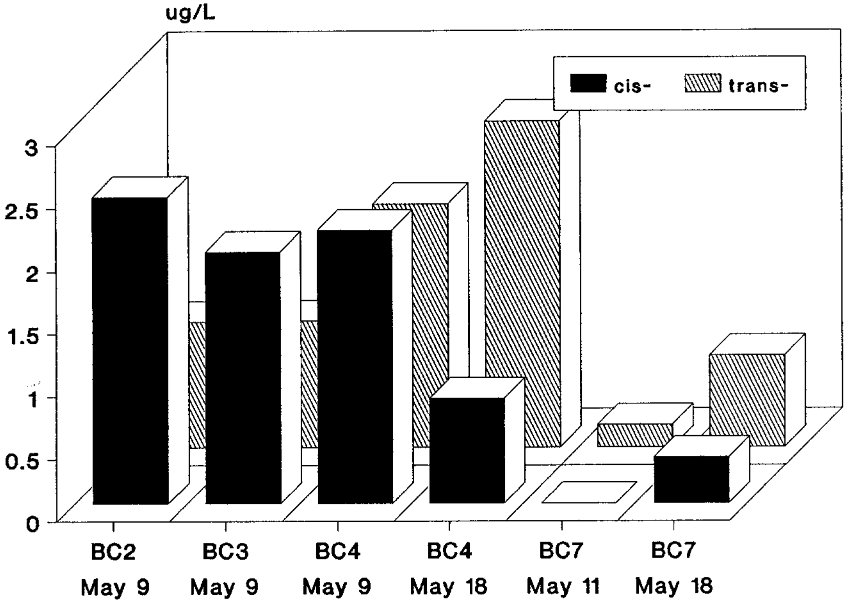

Figure 2. Distribution of 1,3-dichloropropene isomers.

11th and 18th of May showed the opposite distribution between the isomers, in that the trans- isomer was greater in concentration than the cis- (Figure 2). The change in distribution between cis- and trans- 1,3-dichloropropene is not likely due to different rates in hydrolysis, since both isomers are reported to have similar rates (Castro and Belser, 1966). Volatilization rates are higher for cis-1,3-D compared to trans- 1,3-D. It appears that the difference in isomer distribution may be related to the amount of time the isomers are present in the aquatic environment. The longer they persist, the more likely the trans- isomer will have higher concentrations because its vapour pressure is less than that of cis- 1,3-D.

All detectable levels of 1,3-dichloropropene were found during or just after application. As would be expected, not all farmers apply the soil fumigants at the same time, due to personal preferences, but from field observations, it appeared that most of the fumigants had been applied during the first two weeks of May. There were 7 sample collection periods during May. The surveys conducted on May 9, 11 and 18 were the only surveys which produced detectable quantities of 1,3-dichloropropene, which suggests that the compound is not very stable, but is present in surface waters for short periods both during and after soil fumigant application.

Spatial distributions of 1,3-D concentrations were evident, in that higher concentrations were found at the upstream sites. The highest concentrations were recorded at stations BC2, BC3 and BC4, while concentrations at the downstream station, BC7 showed levels of one third or less than those found upstream. Station BC7 is not situated in the tobacco growing region of the basin, thus it is not unexpected to find lower concentrations at this site, primarily due to the dilution effect of being further downstream and not receiving any direct inputs of 1,3-dichloropropene.

Although there were no positive detections of 1,3-dichloropropene in any of the well water samples, this may be a function of environmental conditions around the time of fumigant application. Work carried out by Kotcon and Loria (1987) on fall fumigation of potato fields with 1,3-dichloropropene indicated there was no groundwater contamination from the compound but suggested that the potential for groundwater contamination was somewhat decreased because of low levels of precipitation immediately after fumigation. Precipitation data from the Atmospheric Environment Service of Environment Canada for their station at Delhi Ontario, which is situated close to the upstream stations showed that after May 11 there were only 3 minor precipitation events until May 25. This may in fact have been a contributing factor in not detecting 1,3-dichloropropene in any of the well water samples.

Once in the aquatic environment, 1,3-D is not expected to be persistent and is unlikely to bioaccumulate because of its low octanol water partition coefficient. Volatilization is the most likely mode of disappearance from surface water, while hydrolysis may play a significant role, it is secondary to volatilization. Concentrations of 1,3-D found in surface waters in the Big Creek watershed do exceed the 1 ug/L interim drinking water guideline established by the State of Massachusetts, but do approach the 11 ug/L drinking water equivalent criterion set by the U.S. EPA and are well below those considered toxic to aquatic life. Because the compound is present in surface waters for a limited timeframe around the application period, adverse effects are not expected at the concentrations found.

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