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Transport of the Fungicide Chlorothalonil from Its Operational Use on a Pond Ecosystem

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Chlorothalonil (tetrachloroisophthalonitrile) is a fungicide used extensively in the Maritime Provinces of Eastern Canada to combat potato blight. In 1982, 5120 kg of active ingredient were used in New Brunswick while 1150 L and 23,530 L were used in Nova Scotia and Prince Edward Island respectively (Monenco 1984). Gillis and Walker (1986) placed chlorothalonil on a regional Priority II pesticide list due to its high usage and soil persistence. Chlorothalonil has an estimated LC50 of 0.39 mg/L, 0.25 mg/L and 0.43 mg/L for bluegill (*Lepomis macrochirus*), rainbow trout (*Salmo gairdneri*), and channel catfish (*Ictalurus punctatus*) respectively (British Crop Protection Council 1979). Davies and White (1985) reported chlorothalonil to be highly toxic to fish with a 96 hr LC 50 in the range of 10-30 µg/L, for rainbow trout (*Salmo gairdneri*), common jollytail (*Galaxias maculatus*), spotted galaxias (*G. trutaceus*) and golden galaxias (*G. auratus*). Recent evidence (Krawchuk 1987) has shown that chlorothalonil will migrate in irrigated soil as observed in tile drainage effluent and ground water. Concentrations were observed at 0.02 to 3.66 µg/L in tile effluent and 272 µg/L in ground water. It was also reported that there was indication of carry over from one growing season to the next in the soil matrix with subsequent leaching to ground water. Davies (1988) reported that chlorothalonil was associated with suspended material in field stream studies and that volatilization and stripping by adsorption are apt to be dominant pathways in fast flowing streams. No aquatic field studies have been carried out in Atlantic Canada to ascertain the aquatic effects or transport of chlorothalonil.

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MATERIALS AND METHODS

A small water course on Prince Edward Island, known locally as the Cape Traverse River, was selected in the spring of 1988 as an appropriate location for concurrent field studies into the transport and aquatic effects of chlorothalonil. The terrain and croppage (potato) was typical of PEI and conducive to aerial applications which are frequently employed. The study site was along a 1 km section of the stream and centred upon a small pond (0.2 ha) that would be oversprayed at operational concentrations. The stream had generally good cover with alders at the outlet and alders and coniferous growth upstream. The stream width and depth averaged approximately 1 m and 0.5 m along the stretch of stream studied. Sampling stations were established 0.75 km upstream of the pond, at the pond inlet, and 30 m downstream from the pond outlet. Sediment traps constructed from 5.5 cm (id) x 60 cm glass tubes inserted in stainless steel sleeves were installed in the stream at each site a month in advance of spray operations. At each site water, bottom sediments and sediment trap materials were collected three times prior to the commencement of operational spraying. On two occasions after over spraying, intensive water sampling took place to describe the transport of chlorothalonil from the pond.

To verify the work of Davies (1988), in an Atlantic Canadian setting, an Aqueous Phase Liquid Extractor, APLE, similar to that of Fox (1985) was employed after one overspray to separate the water column into suspended solids and aqueous phases. Filters were changed frequently to permit as free a flow of water as possible through the APLE. One litre whole water samples were also collected after a second overspray. All water samples were collected using glass bottles with teflon liners, while bottom sediments were placed in Mason(R) jars with foil covered caps. All sample containers were detergent washed and rinsed with distilled water, acetone and hexane under laboratory conditions.

All water samples were field preserved with the addition of hexane and kept in coolers while all sediment samples were kept in coolers and frozen upon receipt by the laboratory.

All pesticide analyses were performed under contract by a private-sector laboratory. A quality control program using blind blanks, spikes, duplicates, triplicates and time delayed samples was implemented to monitor the contractor's performance. Water samples were extracted with hexane (3 x 100 mL) while bottom sediments and suspended sediments were extracted with dichloromethane (3 x 100 mL). All sediment extracts were clean-up using a 2.5 g Florisil column prior to quantification. Chlorothalonil residues were quantified using a Perkin Elmer 8500 gas chromatograph with a Ni^{63} electron capture detector on a 30m DB-1701 column. Identification was based on the relative retention time of the compound versus an internal standard of hexachlorobenzene and using an external chlorothalonil standard. Gas chromatographic/mass selective techniques were used to confirm some of the analytical results.

RESULTS AND DISCUSSION

Data from the field sampling following a morning over spray on July 13, 1988 are presented in Figures 1 and 2. Both water and suspended material were collected in duplicate using the APLE. Figure 1 presents the persistence curve for chlorothalonil mean concentration in µg/L in the filtered aqueous phase while Figure 2 illustrates the mean mass in µg total of chlorothalonil retained on filter papers. Concentrations diminished over time as would be expected in a flowing system. Ten hours post-spray the concentration of chlorothalonil in whole water was observed to be 1.9 µg/L. Stream flow was 0.033 m^3/s during the period of sampling. However, one distinguishing feature of the suspended sediment plot (Figure 2) indicates that for a period of up to 1.5 hrs post-spray the mass of chlorothalonil on the suspended fraction remained above 10 µg. Two processes could account for this observation. The work of Davies (1988) would imply saturation of the suspended material in the water column. A more likely explanation lies with activities associated with a concurrent study into aquatic effects in the pond which could have resulted in bottom disturbance and increased availability of sediment.

The second overspray occurred on the evening of July 27, 1988 when streamflow was 0.015 m^3/s. The sampling period was of two hour duration in order to describe any differences in the concentrations observed at the outlet of the pond and at the sampling site 30 m downstream. One litre whole water samples were collected starting at 15 minutes post-spray. Figure 3 presents the observations from both sites. A maximum concentration of 365 µg/L was observed at the outlet at t=30 min. post-spray while a maximum of 452 µg/L was recorded at t=25 min. at the downstream location. A secondary peak was observed at time 60 minutes most likely due to disturbance caused by concurrent monitoring activities in the pond. Three samples from the pond were also

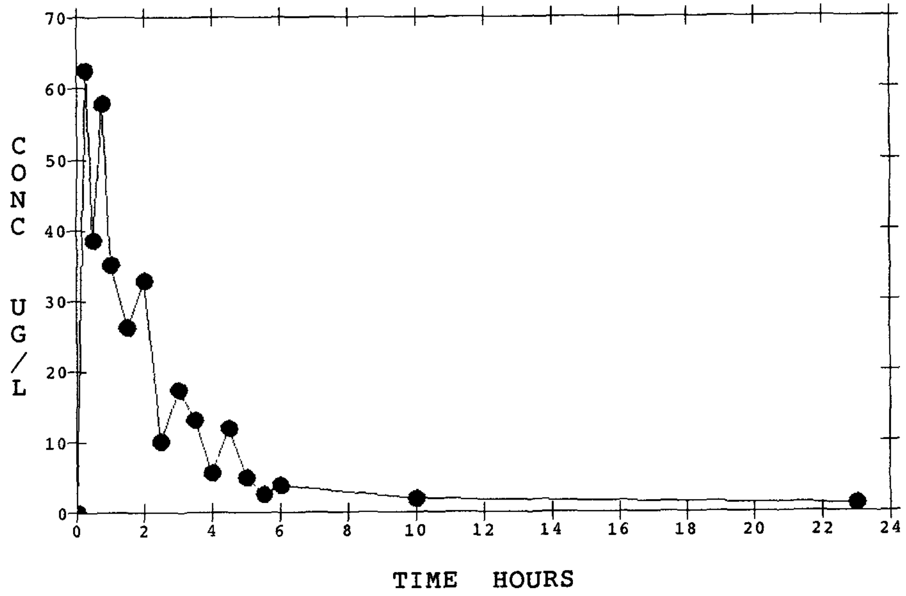

FIGURE 1. Chlorothalonil in aqueous phase, July 13, 1988

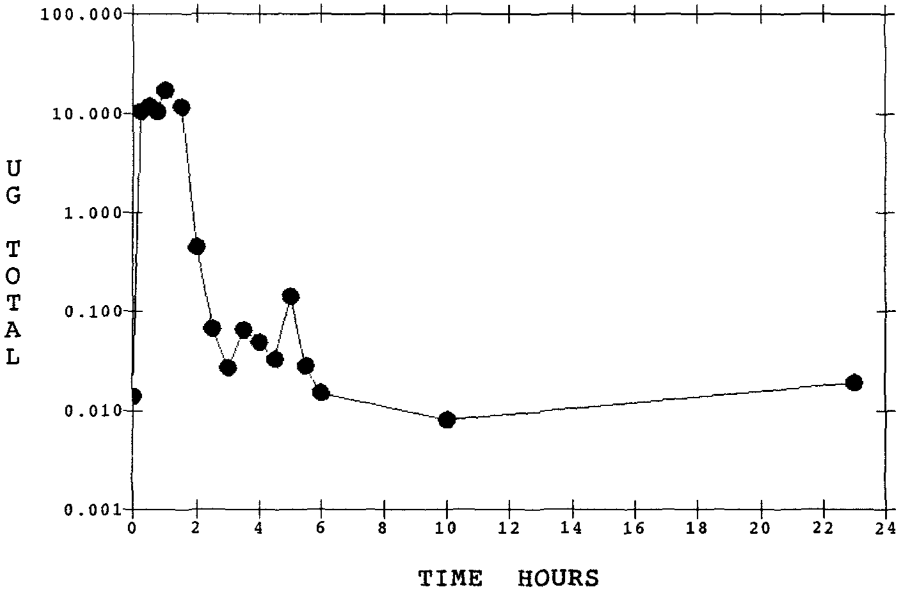

FIGURE 2. Chlorothalonil in suspended material, July 13, 1988

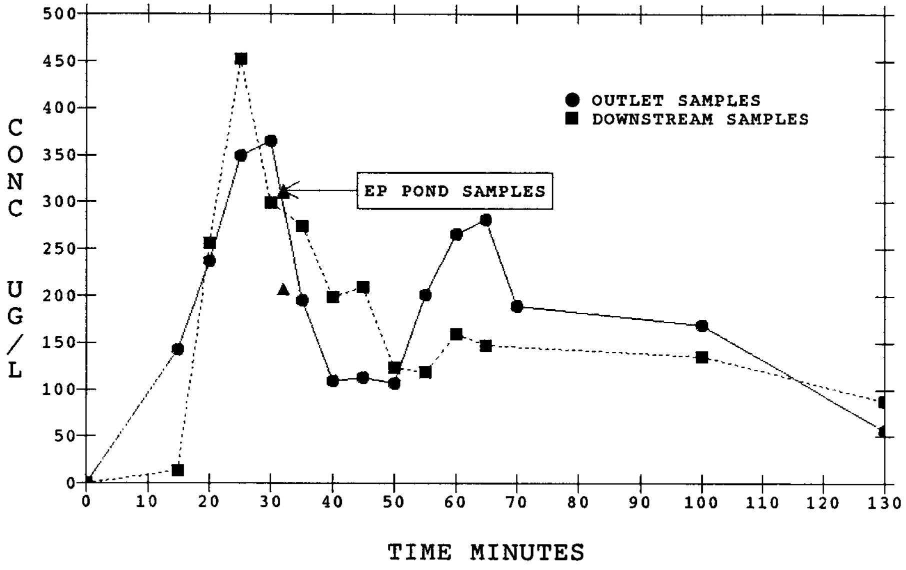

FIGURE 3. Chlorothalonil in whole water at the outlet and downstream sites July 27, 1988

collected at t=30 min. to provide a QA/QC function. Concentrations were 207 μg/L, 313 μg/L and 310 μg/L which is in good agreement with the outlet observations for t=30 min, and t=35 min. Additionally, the concentrations are in agreement with mean concentrations reported from 10 sampling locations on the pond surface monitored by Environmental Protection Service personnel who were concurrently investigating direct aquatic effects of chlorothalonil (W.R. Ernst, personal communication). A mass transport comparison between the two sites indicated a 12% difference with the outlet being greater. The outlet was sampled in triplicate the following morning 12 hours post spray and a mean concentration of 6.3 μg/L was observed.

Sediment trap materials and bottom sediments collected pre- and post-spray at the upstream, inlet and downstream sites were all less than the analytical detection limit (0.004 mg/kg). The composition of bottom sediment ranged from 63% to 91% sand which has reduced adsorption capabilities in comparison to clay and silt. However results from the APLE do indicate that the suspended component of the water column plays a major role in chlorothalonil transport. GC/Mass Selective Detector techniques were used to verify qualitatively the less than detection observations on 2 bottom sediment, and 2 sediment trap samples, and to confirm the presence of chlorothalonil in 2 suspended phase extracts.

The maximum observed post-spray concentration of 452 µg/L was above the estimated LC_{50} of 390,250 and 430 µg/L for bluegill, rainbow trout and channel catfish (British Crop Protection Council 1979) and an order of magnitude above the LC_{50} values of Davies and White (1985). Concentrations greater than 250 µg/L would have been sustained for 1.5 to 2 hours, under the operational conditions and stream flows encountered. Data from the first over-spray indicate that chlorothalonil concentrations would have exceeded the LC_{50} of Davies and White (1985) for approximately 4.5 hrs. Within 12 hours on both spray occasions, the aqueous concentration was below the 10-30 µg/L 96 hr LC_{50} reported by Davies and White (1985).

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