Dissipation and Persistence of Chlorpyrifos within Littoral Enclosures

Michael L. Knuth* and Larry J. Heinis

Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, Minnesota 55804, and Lake Superior Research Institute, University of Wisconsin—Superior, Superior, Wisconsin 54880

This study was performed to characterize the distribution, persistence, and mass balance of chlorpyrifos in pond water and sediment and to investigate the feasibility of an enclosure design for environmental chemistry studies. The organophosphorus insecticide chlorpyrifos was applied once to the surface of 12 littoral enclosures (5 × 10 m) constructed in a 2-ha pond near Duluth, MN. The insecticide was applied as Dursban 2E at nominal concentrations of 0.0, 0.5, 5.0, and 20.0 μg/L active ingredient. Maximum concentrations in the water were measured 1 h after application, and the half-life ranged from 4.7 h in the 20.0 μg/L enclosure to 8.0 h in the 0.5 μg/L enclosure. In the 20.0 μg/L treatment, 95% had dissipated by 7 days. The bulk of the pesticide was initially in the aqueous phase but, after quickly dissipating from the water, trace amounts remaining were primarily associated with the sediment phase. The mass balance at 1 day was 22.5% aqueous and 3.2% sediment, by 64 days it was 0.17% and 0.95%, respectively, and by 420 days there was an estimated 0.04% and a measured 0.5%, respectively. The littoral enclosure design proved to be a feasible means of studying the environmental chemistry of chlorpyrifos.

INTRODUCTION

Chlorpyrifos [*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate] is an organophosphorus insecticide available in a variety of formulations under the trade names Dursban and Lorsban for control of a broad spectrum of agricultural and other insect pests. Laboratory and field tests have shown chlorpyrifos to be toxic to aquatic life and to exhibit moderate persistence in natural systems (Marshall and Roberts, 1978; U.S. Environmental Protection Agency, 1986; Odenkirchen and Eisler, 1988).

The U.S. Environmental Protection Agency, Environmental Research Laboratory at Duluth, MN, in cooperation with the Lake Superior Research Institute, University of Wisconsin—Superior, Superior, WI, has developed a natural aquatic system testing protocol that utilizes littoral enclosures to assess the environmental impact of toxic chemicals and pesticides (Siefert et al., 1989). Small ponds, enclosures, and limnocorrals have been used by others for this purpose (Hurlbert et al., 1970; Stephenson and Kane, 1984; Crossland and Wolff, 1985; Solomon et al., 1985, 1986). Littoral enclosures incorporate the natural shoreline into the test structure, contain an undisturbed natural bottom, allow for replication, are versatile, and allow investigation of the persistence and distribution of chemicals in a cost effective manner.

This study was part of a larger multidisciplinary project utilizing the littoral enclosures to estimate the acute and secondary or ecological effects of pesticides on the structure and function of a lentic ecosystem and to determine the persistence and distribution of pesticides in this environment. Chlorpyrifos was chosen because of prior experience gained in testing chlorpyrifos in laboratory and outdoor systems (Holcombe et al., 1982; Jarvinen et al., 1983, 1988; Eaton et al., 1985) and the high priority given chlorpyrifos by the Agency's Office of Pesticide Programs. The experimental design, test concentrations, and application frequency were chosen to fulfill several broad objectives including biological and ecological effects studies. The specific objective of the study reported here was to characterize the dissipation and persistence of chlorpyrifos in water and sediment following a surface application to littoral enclosures and to investigate the feasibility of the littoral enclosure design to perform environmental chemistry studies.

MATERIALS AND METHODS

Experimental Design. Twelve enclosures (5 × 10 m) were constructed on the north side of a 2-ha pond near Duluth, MN. Each enclosure included 5 m of shoreline and three walls made from an inert polyolefin plastic (888 H UV Clear Scrimweve, Sto-Cote Products Inc., Richmond, IL). Portable aluminum walkways were placed horizontally over the enclosures to facilitate sampling procedures. Since the enclosures included natural shoreline, littoral zone, and undisturbed sediments, all components of the habitat and forage base for endemic pond organisms were available. The enclosures had an average water depth of 0.6 m, contained 15–32 m^3 of water, and enclosed an average surface area of 45 m^2. The littoral areas were well developed with cattails, pond grasses, and aquatic macrophytes growing in highly organic sediments. Details of the design and construction of these systems have been described (Brazner et al., 1989).

The enclosures were built in two blocks of six each, with blocks separated by approximately 30 m of shoreline. Block locations were selected to maximize habitat similarity within and between blocks. Twelve enclosures were constructed and three concentrations of chlorpyrifos were chosen to provide exposures likely to generate a range of toxic effects on aquatic biota. Within this experimental framework the environmental chemistry of chlorpyrifos was investigated.

Pesticide Application. A single application of chlorpyrifos as emulsifiable concentrate Dursban 2E (240 g/L active ingredient) was performed on June 16, 1986, at 10:00 a.m. (CDT). A measured volume of the concentrate was mixed thoroughly with 6 L of distilled deionized water in an 8-L stainless steel hand sprayer and applied evenly over the enclosure water surface with a 2.4-m wand to obtain three nominal treatment concentrations and a control (Table I). The surface application took approximately 10 min for each enclosure. Care was taken during the application procedure to avoid spray drift and uneven surface distribution.

Sample Collection. Grab water samples were collected weekly in prewashed 1-L linear polyethylene bottles for the analysis of pH, conductivity, alkalinity, color, turbidity, and dissolved organic carbon (DOC). DOC samples were filtered through a prewashed Gelman type A-E 47 mm 1.6-μm glass fiber filter prior to analysis. Composite water samples for chlorpyrifos analysis were collected by taking four 1-L subsamples at middepth from each of four locations within each enclosure and

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Table I. Littoral Enclosure Treatment

treatment level	no. of replicate enclosures	application rate,[a] kg/ha	mass applied,[a] mg	EEC,[b] μg/L
control	2	0.0	0.0	0.0
low	2	0.0023	10.3	0.5
medium	4	0.034	144	5.0
high	4	0.10	568	20.0

[a] The application rate and mass applied are reported as averages of all replicate enclosures at the specified treatment level. [b] EEC, estimated environmental concentration (mass applied, kg/mass of water, kg).

combining them in a 4-L brown glass solvent bottle. The samples were collected at 1 day pretreatment and at 1, 2, 4, 8, and 12 h and 1, 2, 4, 8, 16, 32, 64, and 128 days posttreatment. Additional samples from the low-treatment enclosure were taken on days 3 and 5 to better define the dissipation curve.

The vertical mixing rate of chlorpyrifos after application was investigated in one of the 20.0 μg/L enclosures. Water samples were taken simultaneously at 20-min intervals for 2 h starting at a depth of 7.6 cm and at 15-cm depth intervals thereafter to the maximum depth of 99 cm. Samples were taken at a single location at the deepest end of the enclosure.

Sediment samples were collected from one enclosure of each treatment level and analyzed to determine changes in chlorpyrifos concentration over time. A 150-L composite sediment sample was collected from outside the enclosure area with a 15 × 15 cm Ekman dredge 16 days before pesticide application. The sample was sieved through a 6-mm screen to remove rocks, sticks, and aquatic vegetation. The sediment was stored overnight at 4 °C, and the water was siphoned off the top. Fourteen days before pesticide application, 10 × 10 × 6 cm plastic containers were filled to the top with sieved sediment, covered with a plexiglass plate, and set into the sediment. Sixteen sediment containers each were set into four enclosures. When the container top was even with the surrounding sediment, the plexiglass plate was removed. A wooden dowel was attached at the center of each container before the containers were filled with sediment to act as a removal device and location marker. Two sample containers were removed from each enclosure on days 1, 2, 4, 8, 16, and 32 posttreatment; one sample container was removed on days 64, 128, 338, and 420 posttreatment. The samples were collected by sliding a plexiglass plate over the dowel onto the in-situ sample containers to prevent disturbance of the top layer of sediment and using the dowel to remove the sample from the enclosure bottom. The plexiglass plate and dowel were removed, a tight fitting cover was put on the sample, and the sample was bagged and frozen (−10 °C) until analysis.

Sample Extraction. Unfiltered water samples were extracted in 250-mL volumetric flasks containing 25 mL of 2,2,4-trimethylpentane (isooctane). Each water sample was shaken to resuspend particulates, and a 25–225 mL aliquot was transferred to the volumetric flask. Flasks containing sample volumes less than 225 mL were filled to the mark with distilled water. The flasks were shaken by hand for 2–3 min and then allowed to separate prior to removal of the solvent for gas–liquid chromatographic (GLC) analysis.

Sediment samples were thawed overnight, allowing the pore water to drain into a receiving flask. The sediment was removed from the container by inverting it onto a sheet of solvent-washed aluminum foil and then set upright. The sample was wrapped with aluminum foil; the top 1 cm was left exposed. By using the top of the foil as a guide, 50 g of the top 1 cm of sediment was transferred to a tared 1-L boiling flask. An additional subsample was taken for total moisture analysis.

The sediment was combined with 250 mL of deionized water and 25 g of anhydrous sodium sulfate, and the chlorpyrifos was extracted by exhaustive steam distillation (Veith and Kiwas, 1977). The extract was concentrated to 2 mL, and interfering sulfur material was removed by shaking with tetrabutylammonium hydrogen sulfate saturated with sodium sulfite (Jensen et al., 1977).

Sample Analysis. Alkalinity titrations were performed using a Radiometer DTS 800 series digital titration system. DOC was determined using an Ionics Model 1270M oxidative combustion total carbon analyzer (U.S. Environmental Protection Agency, 1983). Analyses of all other physical and chemical properties were performed according to standard techniques (U.S. Environmental Protection Agency, 1983).

Water sample extracts were analyzed for chlorpyrifos on Hewlett-Packard Model 5700 and 5710 gas–liquid chromatographs equipped with ^{63}Ni electron capture detectors. Both instruments were equipped with 1.85 m × 2 mm i.d. glass columns packed with 1.95% SP 2401/1.5% SP 2250 on 100/120-mesh Supelcoport. The carrier gas was $ArCH_4$ (95:5 v/v) at a flow rate of 30 mL/min. Injector and detector temperatures were 200 and 300 °C, respectively. The column oven was operated isothermally at 200 °C. The retention time of chlorpyrifos was 5.2 min.

Sediment sample extracts were analyzed on a Hewlett-Packard Model 5890 capillary gas–liquid chromatograph equipped with a ^{63}Ni electron capture detector. The instrument was operated in the splitless mode using 1-μL injections of isooctane solutions. The injector and detector were operated at 250 and 300 °C, respectively. A 30 m × 0.25 mm i.d. DB-1 0.25-μm film thickness column (J&W Scientific, Inc., Folsom, CA) was operated at an initial temperature of 80 °C for 1 min with a 4 °C/min ramp to 210 °C, a 30 °C/min ramp to 280 °C, and a 5-min hold. Hydrogen flow rates for the column, split vent, and septum purge vent were 2, 20, and 2.9 mL/min, respectively. Column hydrogen linear velocity was 55 cm/s. Detector makeup flow was 52 mL/min $ArCH_4$ (95:5 v/v). The retention time of chlorpyrifos under these conditions was 29.63 min. Quantitation was done using peak area compiled on a Hewlett-Packard 1000 E series computer equipped with Hewlett-Packard 3357 laboratory automation system software. Duplicate, blank, and fortified water and sediment were analyzed throughout the study to assess the method precision and accuracy and to determine detection and quantitation limits of chlorpyrifos.

Sediment moisture analysis was done by transferring approximately 1 g of drained sediment to a tared weighing pan. The sample and pan were dried in an oven at 105 °C overnight, cooled in a desiccator, and reweighed. Any loss in mass was attributed to moisture in the sample.

To obtain total volatile solids, dried sediment was ignited in a muffle furnace at 550 ± 50 °C for 1 h. The loss in weight represents the amount of volatile matter in the sample.

Sediment grain size was analyzed by homogenizing and washing samples through a set of preweighed standard sieves (wet sieving) size 10, 20, 30, 60, 120, and 230. The percent by weight retained on each sieve was recorded. Total residue, total volatile solids, and grain size analyses were performed in accordance with standard methods (U.S. Environmental Protection Agency, 1979).

Chlorpyrifos Adsorption onto Enclosure Barrier. Laboratory experiments were conducted to evaluate the effects of the plastic barrier material (Scrimweve) on chlorpyrifos distribution and mass balance. The experimental procedures followed those of Sharom and Solomon (1981) with the following modifications. A saturated solution of chlorpyrifos was prepared by adding an excess of solid chlorpyrifos to 1 L of deionized distilled water and stirring for approximately 4 h. A dilute solution was prepared from the saturated solution and quantitated by GLC prior to the experiment.

Scrimweve was cut into 1.62 cm diameter circles to fit into the caps of 20-mL scintillation vials. Vials were rinsed with acetone and hexane and autoclaved for 20 min. Scintillation vials (18) were each filled with 20 mL of the dilute aqueous chlorpyrifos solution, capped, inverted, and stored at 20 °C. Vials without lined caps served as controls and were not inverted. All vials were wrapped with black plastic to prevent photodegradation of chlorpyrifos. A set of three vials each from the lined and control sets were sampled at 6, 24, 48, 72, 96, 144, and 216 h. The water was extracted with isooctane and analyzed to determine time to adsorptive equilibrium.

Further experiments were conducted to determine the amount of chlorpyrifos sorbed as a function of initial concentration. Chlorpyrifos solutions were prepared from a saturated solution to achieve nominal concentrations of 0.2, 1.0, 2.0, 10, and 20 μg/L. Actual test solution concentrations were measured prior to the start of the experiment. Three vials from each concentration level and control were analyzed after equilibrium was achieved (as determined from the first experiment).

Table II. Mean Water Quality Data of Littoral Enclosures

parameter	units	mean	min	max	n
conductivity	μS/cm	283	177	662	96
pH		8.20	7.76	9.08	154
alkalinity	mg/L $CaCO_3$	140	76.1	300	154
color	PCU	51.5	15.0	200	154
turbidity	NTU	1.28	0.30	4.90	154
DOC	mg/L C	17.6	0.20	323	154
temp	°C	20.6	15.6	26.7	127

The data from these laboratory experiments were used to estimate the sorptive contribution of Scrimweve in the high-treatment enclosure. First, the amount of chlorpyrifos sorbed to the Scrimweve barrier (ng/cm²) was calculated using the laboratory-derived equilibrium relationship $Y = 7.463X + 0.315$ ($r^2 = 0.99$), where Y is the amount sorbed (ng/cm²) and X is the measured field concentration (ng/mL), at each sampling time (t). These results were then corrected for the nonequilibrium condition that initially exists, using the laboratory-derived relationship $Y = 0.497X + 8.88$ ($r^2 = 0.93$), where Y is the percent sorbed and X is the time (h). This estimate was converted to mass sorbed at time (t) using the Scrimweve surface area per enclosure. The mass sorbed was then plotted against time and the area under the curve integrated to obtain an estimate of the total mass sorbed over the entire study period (1 h–64 days).

RESULTS AND DISCUSSION

Quality Assurance. The recovery efficiency of chlorpyrifos from field fortified water samples was 78.3 ± 10.5% (mean ± SD, n = 13). The analysis precision measured by taking the mean relative percent differences for laboratory and field duplicate samples were 5.2 ± 5.9% (n = 5) and 12.3 ± 10.0% (n = 10), respectively. The minimum detectable quantity of chlorpyrifos in the water samples was estimated to be 0.01 μg/L (lowest standard/sample concentration factor). The minimum detectable quantity (Peters et al., 1974) of chlorpyrifos in sediment was 0.090 ng/g. The minimum detectable amount on a mass per enclosure (encl) basis was 0.020 mg/encl. Recovery efficiencies for laboratory and field fortified sediment samples were 97.4 ± 20.5% (n = 23) and 78.6 ± 13.1% (n = 5), respectively. Laboratory precision was 0.54 ± 0.47 ng/g (n = 4). The sediment data were adjusted for background and analyte recovery, based on the analysis of uncontaminated sediment and laboratory fortified samples.

Physical and Chemical Measurements. Analyses of the physical and chemical parameters for all enclosures in blocks 1 and 2 and the open pond were performed weekly to characterize the site water and to observe changes attributable to the application of chlorpyrifos (Table II). There were no changes observed in water chemistry of the littoral enclosures that could be directly attributed to the application of chlorpyrifos. An analysis of variance using a split plot design was used to analyze the weekly water chemistry data (Steel and Torrie, 1960). The data were tested for significant variance components due to block, treatment level, enclosure within block and treatment, day, block by day interaction, and treatment by day interaction. There was a significant ($p \leq 0.05$) variance in turbidity with treatment level which appears to have been caused by elevated turbidity in the control enclosures with respect to other treatment levels. There was also significant ($p \leq 0.05$) variance in DOC with treatment level and with block, which appears to be caused by elevated DOC in the 20.0 μg/L treatment level enclosures in block 2 as compared to those in block 1. Elevated conductivity and color were also observed in these enclosures. These changes could have been induced by the application of chlorpyrifos since increases were noted on treatment day. However, the 20.0 μg/L treatment level enclosures in block 1 showed no similar increases. Water temperatures in the littoral enclosures ranged from 15.6 to 26.7 °C with a mean daily temperature of 21.0 °C for the 68-day period starting June 12 and ending August 18, 1986.

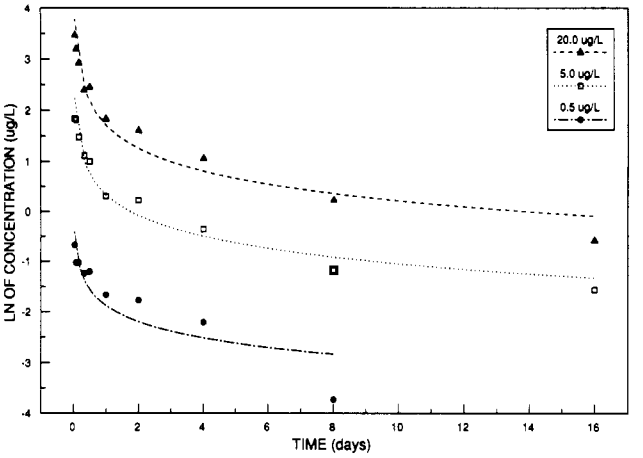

Figure 1. Dissipation of chlorpyrifos from littoral enclosure water at the three treatment concentrations. Each point represents the mean of all replicate enclosure concentrations at each treatment level (0.5 μg/L, n = 2; 5.0 and 20.0 μg/L, n = 4).

Residues within the Water Column. The maximum chlorpyrifos concentration in the water was measured 1 h after application at all treatment levels (Figure 1). The mean 1-h concentrations for the 0.5, 5.0, and 20.0 μg/L treatment enclosures were 0.51 ± 0.20 (n = 2), 6.29 ± 1.05 (n = 4), and 32.0 ± 5.3 (n = 4) μg/L, respectively. The mean coefficients of variation of replicate enclosures within a treatment level with respect to time for the 0.5, 5.0, and 20.0 μg/L treatments were 16.9%, 16.3%, and 20.6%, respectively. Measured chlorpyrifos concentrations at 1 h posttreatment were 0.37 and 0.65 μg/L in the two 0.5 μg/L treatments and ranged from 5.26 to 7.75 μg/L in the 5.0 μg/L treatment and from 24.1 to 35.7 μg/L in the 20.0 μg/L treatment enclosures. The 95% confidence intervals about the mean for each treatment level did not overlap throughout the study.

The measured concentrations were slightly to markedly higher than the estimated environmental concentrations (EEC) of 0.5, 5.0, and 20.0 μg/L. These differences could be influenced by the time after treatment, the accuracy of the mean depth and surface area measurements used in the EEC calculation, the efficiency of the application method, the pesticide formulation, and sampling biases such as depth discrimination. The 1 h posttreatment values exceeded the EEC by 2%, 20%, and 38% in the 0.5, 5.0, and 20.0 μg/L treatment levels, respectively. By 24 h after treatment, corresponding values declined to 62%, 73%, and 69% of the EEC. The similarity of the values from the 24-h data, when mixing is more complete, indicates that the top water stratum was oversampled during the 1-h sampling..

The loss rate and persistence of chlorpyrifos in the treated enclosure water was determined by calculating the half-life (DT_{50}) and time to 95% loss (DT_{95}). Initial concentrations were based on the 1-h measured values. The loss of chlorpyrifos at all treatment levels was described by linear regression analysis of ln concentration vs ln time (Table III). The linear regression for the 0.5 μg/L treatment had the lowest regression correlation (r^2 = 0.79) and failed to accurately predict the long-term loss time. Measured values indicated that the DT_{95} was achieved in about 8 days vs the calculated value of 49 days. Calculated loss times in the 20.0 and 5.0 μg/L enclosures agreed well with measured concentrations.

Table III. Estimated DT_{50} and DT_{95}[a] Values for Chlorpyrifos in the Water of Littoral Enclosures

nominal treatment level, μg/L	equation[b]	r^2	DT_{50}, days	DT_{95}, days
0.5	$\ln c = -1.875 - 0.462 (\ln t)$	0.79	0.33	49
5.0	$\ln c = 0.332 - 0.598 (\ln t)$	0.96	0.26	12
20.0	$\ln c = 1.708 - 0.650 (\ln t)$	0.96	0.20	7

[a] Time (days) for 50% and 95% dissipation, respectively. [b] From linear regression of ln concentration (μg/L) vs ln time (days).

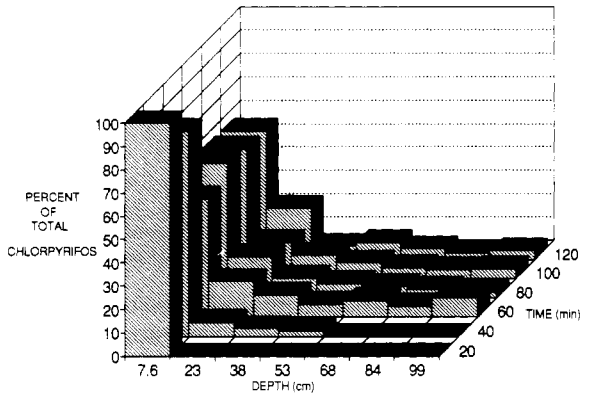

Figure 2. Vertical distribution of chlorpyrifos in a 20.0 μg/L treatment enclosure water column for the first 2 h following application (presented as the percent of total chlorpyrifos measured at each depth over time).

Studies included in a review by Marshall and Roberts (1978) reported a similar loss of chlorpyrifos in various test systems. Aqueous chlorpyrifos residues in general exhibit a rapid initial loss phase probably associated with degradation within the water column and volatilization processes occurring at the air–water interface. This initial loss phase is followed by a slower phase when partitioning into various sorptive pools competes with the degradation and volatilization processes. Half-lives reported in the review ranged from 0.5 to 4 days. Most studies do not include pesticide losses during the first 24 h, which results in a longer observed half-life. Ludwig et al. (1968) studied the loss of chlorpyrifos following aerial application to a salt marsh and reported a half-life of less than 4 h using water concentrations measured at 1 h posttreatment. Reimer and Webster (1980) applied chlorpyrifos to 0.1-m^3 artificial pools and found a half-life of 5 ± 3 h. These values agree closely with the 4.7–8-h half-life observed during this study.

The vertical mixing rate of chlorpyrifos was investigated in one of the 20.0 μg/L treatment enclosures. All of the chlorpyrifos was found in the top 7.6 cm of the water column 20 min after application, and none was detected near the bottom of the water column (1 m) until 1 h after application (Figure 2). By 2 h, 55% of the chlorpyrifos remained in the top 7.6 cm of water, while 3.6% had reached the bottom. Samples were not taken after 2 h posttreatment; however, it is expected that the enclosures would require 24 h or less to thoroughly mix after a surface application (Macek et al., 1972; Solomon et al., 1986).

With surface application, the mixing rate of chlorpyrifos in the enclosures could have significant effect on the outcome and interpretation of the chemical and concurrent biological studies. The sampling method utilized during this study did not allow the water data to be corrected for nonhomogeneity. Enclosure water samples collected for pesticide analysis may be biased by the sampling method, the location, and the distribution pattern of the pesticide. A composite sample of enclosure water for pesticide analysis should be integrated over the entire water column and at numerous locations within the enclosures to best represent the average water concentration. Otherwise, sample concentrations should be reported at preselected depth intervals until complete mixing has occurred. Sampling only surface water will yield artificially high concentrations if the values are extrapolated to represent concentrations at all depths. Comparisons of field data to the calculated EEC values must specify the sampling technique and time to allow for valid interpretations.

The vertical concentration gradient in the enclosures may also have significant biological implications. Organisms dwelling in the top 10 cm of water may be exposed to higher concentrations for shorter periods of time than deeper dwelling organisms. Organisms incapable of migrating may be impacted more than those which are more mobile. Caged fish and invertebrate bioassays are generally performed in the top 25 cm of water, which may result in higher pesticide exposure during bioassays than would be expected for free-ranging biota.

Adsorption onto the enclosure wall material (Scrimweve) is another source for toxicant uptake in addition to sediment and biota. The adsorption of chlorpyrifos to the Scrimweve was not measured in situ but was estimated from laboratory experiments. The total mass adsorbed throughout the study period (1 h–64 days) was estimated to be 3.8% of the initial mass measured at 1 h. This value has been adjusted for a nonequilibrium condition which exists for up to 200 h after treatment and assumes a static system. The water in the littoral enclosures is generally calm, and vertical movement due to wind is diminished by the enclosure barrier; therefore, it is reasonable to assume that adsorption determined without agitation in the laboratory is a good representation of field conditions. Sharom and Solomon (1981) provide evidence that adsorption of permethrin onto a polymer from a finite reservoir may be limited by diffusion processes. They studied experimental laboratory systems containing an aqueous solution of the pesticide in contact with polyethylene and poly(vinyl chloride) that was allowed to equilibrate both with and without physical agitation. Systems that were agitated attained equilibrium in less than 24 h, whereas the same system without agitation did not reach equilibrium in 120 h. The kinetic energy imparted by agitation may have accelerated adsorption by causing more frequent solute polymer collisions. If this is true, adsorption to the barrier in an enclosed aquatic system is a slow process unless the system is sufficiently agitated by natural processes or the system has a small volume-to-barrier surface area ratio.

The volume-to-surface area ratio of our laboratory system was 0.0097 L/cm^2, compared to a ratio of 0.18 L/cm^2 for the littoral enclosures. If adsorption is diffusion limited, it would be slower in littoral enclosures than laboratory results would predict. Sharom and Solomon (1981) found that increasing the volume-to-surface area ratio resulted in a decrease in the adsorption of permethrin to glass. It is reasonable to assume that adsorption to plastic would act comparably.

Residues within the Sediment. The sediment results presented are from 16 in-situ sediment vessels collected over 420 days after chlorpyrifos application from one enclosure at each treatment level. The sediment was predominantly fine grained, consisting of 37% silt and clay (<63 μm) and 63% sand (63–600 μm) with an organic carbon content of 11.6 ± 2.22% (mean ± SD, n = 43).

Chlorpyrifos in sediment reached maximum concentration 1 day after application at the 20 μg/L treatment level, decreased to 50% of the maximum by 16 days, and was still 14% of the maximum after 420 days (Figure 3). Chlorpyrifos in sediment at the 5.0 μg/L treatment level reached maximum concentration 2 days after application,

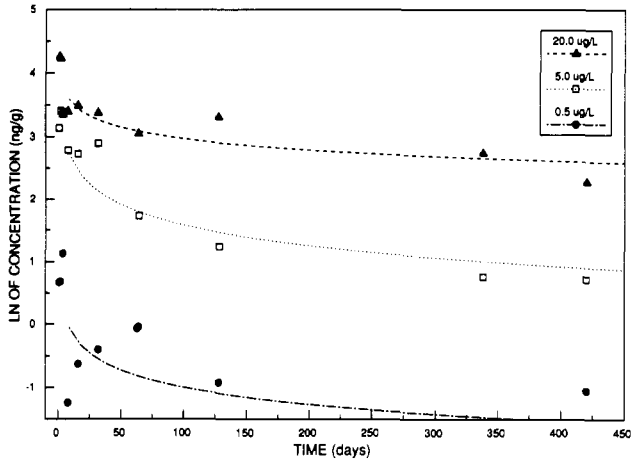

Figure 3. Sediment concentration vs time plots for three littoral enclosures.

Table IV. Estimated DT_{50} and DT_{95}[a] Values for Chlorpyrifos in the Sediment of Littoral Enclosures

nominal treatment level, μg/L	equation[b]	r^2	DT_{50}, days	DT_{95}, days
0.5	$\ln c = 0.796 - 0.389 (\ln t)$	0.59	0.83	7.6
5.0	$\ln c = 3.760 - 0.473 (\ln t)$	0.87	16.3	249
20.0	$\ln c = 4.150 - 0.256 (\ln t)$	0.81	9.6	≫420

[a] Time (days) for 50% and 95% dissipation, respectively. [b] From linear regression of ln concentration (ng/g) vs ln time (days).

decreased to 50% of the maximum by 16 days, and was 6.8% of the maximum after 420 days. Whereas the chlorpyrifos in sediment in the 20.0 and 5.0 μg/L enclosures reached a maximum and then decreased smoothly with time, chlorpyrifos in the sediment at the 0.5 μg/L treatment level reached a maximum at 4 days, decreased to 9% of the maximum at 8 days, and fluctuated between 3% and 32% of the maximum through 420 days after application. Sediment from a control enclosure contained no measurable chlorpyrifos. The relative amount of chlorpyrifos observed in the sediment is similar to the data in the literature for small ponds and enclosures (Hurlbert et al., 1970; Mulla et al., 1973; Hughes et al., 1980). In all cases, however, our values were slightly lower and the maximum concentration was observed more rapidly.

Persistence in the Sediment. The time to 50% and 95% degradation of chlorpyrifos in sediment (DT_{50} and DT_{95}, respectively) was derived using the linear regression of ln chlorpyrifos concentration in the sediment (ng/g) vs ln time (days) (Table IV). The DT_{50} values for the 20.0 and 5.0 μg/L enclosures followed the expected pattern of greater DT_{50} values with decreasing concentration and were similar to half-life values found in other field sediment samples in the literature (Schimmel et al., 1983). The DT_{95} in the 20.0 μg/L enclosure was ≫420 days, which indicated persistence of trace quantities of chlorpyrifos in the sediment of littoral enclosures. In the 20.0 μg/L treatment enclosure, the maximum concentration of chlorpyrifos was observed in the initial sample, collected at 24 h, which may lead to a slight overestimation of the long-term persistence of chlorpyrifos in the sediment as measured by DT_{95}. The DT_{95} value for the 5.0 μg/L enclosure was 249 days, which indicated a fairly long persistence of trace quantities of chlorpyrifos at this treatment level as well. The DT_{50} and DT_{95} values for the 0.5 μg/L enclosure are included in Table IV, but the low correlation coefficient of 0.59 reflects the erratic nature of the data at this treatment level.

The persistence of chlorpyrifos in the sediment of littoral enclosures could be influenced by the sampling technique, the polypropylene barrier, or the nature of the pond and the climatic conditions during the study period. The sampling technique used in this study does not disturb the sample surface during collection and storage, which should result in a minimum of chlorpyrifos loss. The in-situ sediment vessels were placed into each enclosure 14 days before pesticide application. During this time the sediment changed from black to a light brown matching the color of the surrounding sediment, indicating some degree of similarity between the two sediment types. The sediment was quite uniform in size and texture after a coarse sieving and had a substantial organic carbon content of 11.6%. The mean water temperatures, derived from hourly data collected on 3-day periods from −1 day through 64 days, were 19.7, 21.1, and 20.7 °C for the 20.0, 5.0, and 0.5 μg/L treatment enclosures, respectively. The above factors and conditions would tend to favor the sorption of chlorpyrifos onto the sediment and its persistence there (Hughes et al., 1980).

Table V. Percent of Measured Chlorpyrifos in Sediment by Depth

time, days	20.0 μg/L		5.0 μg/L		0.5 μg/L	
	1 cm	2 cm	1 cm	2 cm	1 cm	2 cm
1	95.5	4.18	92.1	7.91	94.6	5.36
2	96.1	2.56	91.2	8.80	89.0	11.0
4	95.7	4.25	91.2	8.85	89.3	10.7
8	97.8	2.23	94.5	5.55	100	ND[a]
16	88.3	11.7	90.6	9.41	100	ND
32	93.2	6.82	96.7	3.14	82.9	17.2
64	89.4	10.6	86.5	13.5	38.0	62.0
128	77.9	22.1	72.8	27.2	38.2	61.8
338	77.5	22.5	66.3	33.7	8.95	91.1
420	74.8	25.3	91.4	8.65	100	ND

[a] ND, below the analytical detection limit of 0.090 ng/g.

Partitioning within the Sediment. The in-situ sediment samples were fractionated into 1-cm layers in the laboratory. The major proportion of chlorpyrifos measured in the sediment was in the top 1-cm layer at all treatment levels. The amount and proportion decreased with time with an increase in the proportion measured in the second 1-cm layer. The top 1-cm layer contained mean values of 88%, 87%, and 74% of measured chlorpyrifos in the 20.0, 5.0, and 0.5 μg/L treatment enclosures, respectively (Table V). The second centimeter layer contained the remainder of chlopyrifos. The third centimeter contained only trace amounts (0.18–0.80 ng/g) on days 1 and 2 in sediment from the 20.0 μg/L enclosure.

The occurrence of chlorpyrifos in the second centimeter layer of sediment indicates a certain amount of bioturbation within the in-situ sediment vessels. During the analysis many oligochaetes were seen in the frozen sediment samples. No attempt was made to quantify or estimate the actual biomass of these biota, but their presence in the samples could account for the transport of chlorpyrifos into the second centimeter layer of sediment. Diffusion as a transfer mechanism within the sediment would be minimal on the basis of the log k_{oc} of 3.06 for chlorpyrifos in the littoral enclosure sediment.

Chlorpyrifos Distribution. To determine the distribution of chlorpyrifos within littoral enclosures, the amount of chlorpyrifos in each compartment, water, and sediment was calculated on a mass per enclosure basis. In this manner the data were normalized with respect to the size of each compartment of interest within each enclosure.

The distribution of chlorpyrifos between the water and sediment of littoral enclosures was similar at each treatment level. Initially, the majority of the chlorpyrifos at each treatment level was measured in the aqueous phase (Figure 4). By 16–32 days the amount in the sediment

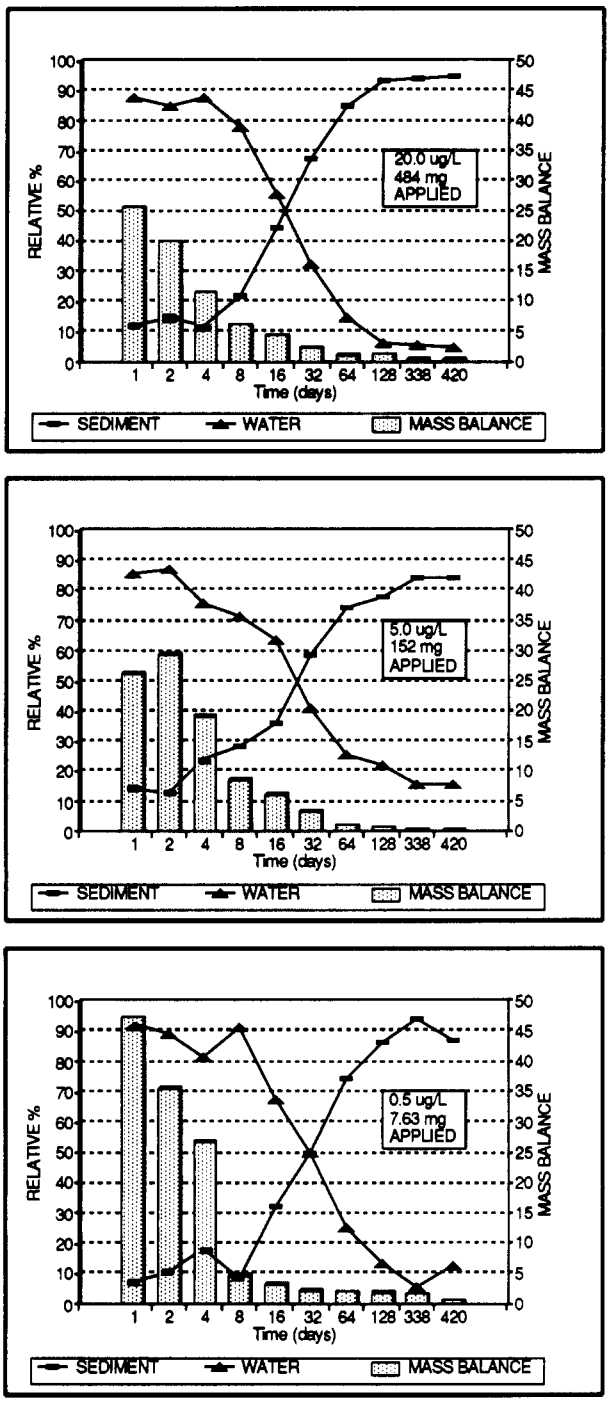

Figure 4. Percent of chlorpyrifos in the water and sediment relative to the amount measured (left axis) and the mass balance of chlorpyrifos relative to the amount applied (right axis, bar graph) to the three littoral enclosures. All data are on a milligram per enclosure basis.

was equal to that in the water with the majority of the measured chlorpyrifos residing in the sediment after that time.

Analysis of system compartments other than water and sediment was beyond the scope of this investigation; however, dissipation pathways can be proposed on the basis of available literature. Marshall and Roberts (1978) identified degradation, sorption and desorption, volatilization, and system mixing as key processes. In a pond study, Hurlbert et al. (1970) found that sorption to suspended solids accounted for half of the water column chlorpyrifos residue and found trace amounts in the sediments and greater residue amounts associated with the aquatic vegetation. The microbial degradation of chlorpyrifos in the enclosures is likely to be small. Walker et al. (1988) found the degradation of chlorpyrifos in estuarine water and sediment in the laboratory primarily due to abiotic factors. Schimmel et al. (1983) did find evidence of microbial degradation and reported the half-lives in nonsterile and sterile estuarine sediment as 24 and >28 days, respectively; however, there was an insufficient number of samples for statistical validation.

Past studies (Macek et al., 1972) have also allowed researchers to predict the distribution of chlorpyrifos in natural waters. Neely and Blau (1977) predicted by computer simulation that after 25 days, hydrolysis, volatilization, metabolism, soil and plants, and water accounted for 76%, 11.4%, 11%, 0.5%, and 0.8% of the total chlorpyrifos applied, respectively. Although this prediction shows the major dissipation compartments, the relative magnitude of each will differ depending on test system characteristics.

The importance of volatilization as a dissipation pathway is difficult to assess. Chlorpyrifos does have a moderate potential for volatility based on its physical properties (Neely and Blau, 1977); however, the application method, environmental conditions, and test system characteristics have considerable impact. In this study, the chlorpyrifos was applied to the surface as a dilute aqueous solution (2.5–200 000-fold dilution of the original formulation), which should result in faster mixing with the subsurface water, causing the volatilization process to become diffusion limited (MacKay and Wolkoff, 1973). It is feasible that a portion of the 16–34% of the applied chlorpyrifos unaccounted for on day 0 was lost due to volatilization.

These studies indicate that hydrolysis, volatilization, sorption to aquatic vegetation, and, to a lesser extent, sorption to sediment could be important chlorpyrifos dissipation pathways in the littoral enclosures. Although only trace amounts of chlorpyrifos were detected in the sediments of this and other studies (Hurlbert et al., 1970), the high toxicity and moderate persistence (Marshall and Roberts, 1978; Hughes et al., 1980; Schimmel et al., 1983; U.S. Environmental Protection Agency, 1986) of chlorpyrifos could still result in a toxicological risk to the biota present.

Chlorpyrifos Mass Balance. The mass balance of chlorpyrifos is discussed in terms of the total amount of chlorpyrifos measured in the water and sediment compartments (milligrams) as a percentage of the total amount applied at each treatment level.

For purposes of the mass balance, the aqueous chlorpyrifos concentration from 128–420 days posttreatment was estimated in the 20.0 and 5.0 μg/L enclosures using data from days 1–64 and the following regression equations, respectively: $Y = 3.42 - 1.15X$, $r^2 = 0.93$, $n = 7$, and $Y = 2.87 - 1.04X$, $r^2 = 0.89$, $n = 7$, where $Y = \log_{10}$ aqueous amount (μg/L) and $X = \log_{10}$ time (days). For the 0.5 μg/L enclosure data from days 1–8 were used to estimate aqueous amounts for days 32–420 using the linear regression $Y = 1.69 - 1.05X$, $r^2 = 0.77$, $n = 4$.

The water was the only compartment sampled during the first 12 h after chlorpyrifos application and contained mean values of 68%, 84%, and 66% of the applied pesticide in the 20.0, 5.0, and 0.5 μg/L treatment enclosures, respectively. The dissipation pattern after that time was similar at each treatment level with the total amount of chlorpyrifos accounted for (sum of water and sediment compartments) ranging from 47% at 1 day to 0.3% at 420 days (Figure 4).

Conclusions. The majority of the chlorpyrifos applied as an emulsifiable concentrate to littoral enclosures was initially in the aqueous phase but, after quickly dissipating from the water, trace amounts remaining where primarily associated with the sediment phase. Water column half-

lives ranged from 4.7 to 8 h, and it took 7–12 days for 95% of the chlorpyrifos residues to dissipate. The percent of the total chlorpyrifos residue found in the sediment averaged 1.6% in the 20.0 μg/L treatment enclosure and 2% in the 5.0 and 0.5 μg/L treatment enclosures.

The dissipation and persistence of chlorpyrifos measured in the littoral enclosures agreed well with literature data from other natural systems (Ludwig et al., 1968; Reimer and Webster, 1980; Schimmel et al., 1983). The enclosures have a volume-to-barrier surface area ratio large enough to diminish the impact of the polymer barrier on the persistence of chlorpyrifos. The test system design proved to be a feasible method for studying environmental chemistry. The method incorporates replication and allows containment and control of the toxicant; therefore, studies can be performed without impacting a large natural aquatic system.

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