Partitioning and Persistence of Trichlorfon and Chlorpyrifos in a Creeping Bentgrass Putting Green

L. Wu,* R. L. Green, G. Liu, M. V. Yates, P. Pacheco, J. Gan, and S. R. Yates

ABSTRACT

Golf course putting greens typically receive high pesticide applications to meet high quality demands. Research on pesticide fate in turf ecosystems is important to better understand the potential impact of pesticide use on the environment and human health. This research was conducted to evaluate the environmental fate of two commonly used insecticides—trichlorfon (dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate) and chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridylphosphorothioate)—in a creeping bentgrass (*Agrostis palustris* Huds.) putting green under customary field management practices at the University of California-Riverside Turf Research Facility during 1996 and 1997. The two insecticides were chosen because of their difference in water solubility, persistence, adsorption, and vapor pressure. Volatilization, clipping removal, and soil residues of the insecticides were quantified and leaching was monitored using lysimeters installed in putting green plots. Results showed trichlorfon volatilization, clipping removal, and leaching loss was insignificant (in the range of 0.0001–0.06% of applied mass) both in 1996 and 1997. No significant difference in clipping removal of trichlorfon and chlorpyrifos was observed in both years (0.06 and 0.05% of applied mass for trichlorfon and 0.15 and 0.19% of applied mass for chlorpyrifos, respectively, in 1996 and 1997), but significantly lower cumulative leaching and lower soil concentration was observed in 1997 than in 1996. Volatilization loss of chlorpyrifos was not significantly different between 1996 (2.05%) and 1997 (2.71%). Volatilization loss of trichlorfon in 1996 (0.01%) was significantly higher than in 1997 (0.008%). This study demonstrated the fraction of applied insecticides leaving the turf putting greens was minimal.

TURFGRASS provides a low-cost recreational and aesthetic surface (Beard and Green, 1994). Due to the high quality demands of recreational and aesthetic use, turfgrass is one of the most intensively managed biotic systems. In particular, golf courses usually receive more pesticides than turfgrass used for most other purposes (Kriner, 1985). Research on partitioning and persistence of pesticides in turfgrass is important for a better understanding of the potential impact of pesticide use on the environment and human health.

Sears and Chapman (1978) conducted research to determine the persistence and movement of four insecticides {chlordane (1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene), diazinon [O,O-diethyl 0-2-isopropyl-6-methyl (pyrimidine-4-yl)], chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridylphosphorothioate), and CGA 12223 [O,O-diethyl O-(1-isopropyl-5-chloro-1,2,4-triazolyl)]} in the grass–thatch layer, root zone, and underlying soil. They found that approximately 60% of the chlordane remained 56 d after application; but only 9% of chlorpyrifos still remained at the same time in the grass thatch layer. In contrast diazinon and CGA 12223 disappeared within 14 d after application. Niemczyk and Krueger (1987) found that 96 to 99% of the insecticide isazofos (O-5-chloro-1-isopropyl-1H-1,2,4-triazol-3yl O,O-diethyl phosphorothioate) remained in the thatch over an 8-wk experiment. Their study showed that irrigation immediately after treatment did not increase the residue level in the thatch during the first two weeks after treatment.

Most studies have focused on cool-season grasses grown on native soils. Relatively little is known about pesticide partitioning, including all avenues of pesticide persistence and loss, in putting greens with a modified sand root-zone. Snyder and Cisar (1993, 1995) and Cisar and Snyder (1997) observed considerable leaching of fenamiphos (ethyl 4-methylthio-m-tolyl isopropylphosphoramidate) metabolites (>10% of the applied mass) following its application to a green constructed to U.S. Golf Association (USGA) specifications. Cisar and Snyder (1996) measured dissipation of four organophosphate (OP) pesticides in clippings, thatch, soil, and percolate, and found that most of the applied OP pesticides was retained in the thatch layer, where they degraded over time. Less than 1% of the applied OP pesticides was found in clippings, but nearly 8% of chlorpyrifos and 1.2% of fonofos [O-ethyl S-phenyl (RS)-ethylphosphorodithioate] was removed in clippings when a granular formulation was used. Less than 0.1% of the OP pesticides was detected in the leachate.

Volatilization and mowing removal are associated with human exposure via inhalation and dermal contact. Murphy et al. (1996a) pointed out that volatilization was one of the major avenues of pesticide loss from treated areas. They found approximately 12% of the applied pesticides volatilized. Cooper et al. (1990) found that the volatile loss of pendimethalin [N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine] during the first 48 h following application totaled 6.1%, with an estimated loss of about 13% during the 5-d period. Murphy et al. (1996a,b) observed that about 8% of the applied triadimefon [1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl) butanone], and 12% of the applied trichlorfon (dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate) and isazofos was lost to volatilization within the first week after application.

It was reported that trichlorfon has a half-life between

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Abbreviations: OP, organophosphate; OC, organic carbon; GC, gas chromatograph; ECD, electron capture detector; PUF, polyurethane foam plugs.

3 and 27 d in aerobic soils, with an average of 10 d (Wauchope et al., 1992). Chlorpyrifos, on the other hand, is more persistent in soils. The half-life of chlorpyrifos in soil is usually between 60 and 120 d, but can range from 2 wk to >1 yr, depending on the soil type, climate, and other conditions (Wauchope et al., 1992; Howard, 1991). These observations reflect that partitioning and persistence of insecticides depend on their chemistry, the environmental settings, and management practices. Hence, site- and pesticide-specific assessment will be critical for best management practices (Perris, 1996). The concurrent distribution of trichlorfon and chlorpyrifos in air, grass, and water and dissipation in soil have not been well studied, although both insecticides are commonly used in the turf industry. Trichlorfon has a high water solubility, weak adsorption, low vapor pressure, and short persistence, while chlorpyrifos has a low water solubility, strong adsorption, high vapor pressure, and long persistence. The objective of this study was to characterize partitioning, persistence, and loss of trichlorfon and chlorpyrifos on a simulated golf putting green in southern California.

MATERIALS AND METHODS

Field Plots, Soil, and Chemicals

The site used for the field-plot study was located at the Turfgrass Research Facility of University of California in Riverside. A detailed description of the field site and plots is given elsewhere (Wu et al., 2002). In brief, the test site was constructed in 1992 and replanted with washed sod of creeping Bentgrass (*Agrostis palustris* Huds.) in 1995. It consisted of 12 plots of 3.7 by 3.7 m, and each plot contained a five-lysimeter assembly near the center of the plot. The lysimeter assembly (~1.22 m² surface area) had a metal drainpipe at the bottom, which extended to the edge of the field to allow easy collection of leachate. The constructed putting green soil consisted of three layers: a 7-cm layer of gravel (about 10 mm in diam.), a 43-cm layer of pea gravel (about 5 mm in diam.) in the middle, and a 45-cm top layer of soil, which was a Caltega IV green sand containing 10% (m³ m⁻³) sphagnum peat. The materials were manually packed into the lysimeters to ensure uniformity. The remainder of the plot was mechanically filled with the same gravel and soil mix.

Before the field experiment, soil cores were randomly removed from the field plots to determine soil properties and site-specific insecticide degradation rate constants. These cores were divided into the thatch (0–2 cm), mat (2–5 cm), and soil (below 5 cm) layers, and then finely chopped (thatch) or passed through a 2-mm sieve (mat and soil) before use. The organic carbon content (OC) was determined to be 6.6% for the thatch, 3.4% for the mat, and 0.3% for the soil layer. The same materials also were used in the following incubation experiment for obtaining degradation rate constants of trichlorfon and chlorpyrifos.

Standards of trichlorfon (98%) and chlorpyrifos (99.2%) were purchased from Chem Service (West Chester, PA). Solvents used for residue extraction and analysis were all analytical grade.

Laboratory Incubation Experiment

A laboratory incubation experiment was conducted to determine degradation rate of trichlorfon and chlorpyrifos in the thatch, mat, and soil medium. Briefly, 30 g of a medium (dry wt.) in a beaker was spiked with 3 mL of acetone solution containing 1 mg mL⁻¹ of trichlorfon or chlorpyrifos, and the treated medium was thoroughly mixed and then placed in a fume hood overnight to evaporate the solvent. The treated medium was then mixed with 270 g of untreated soil in a 500-mL Erlenmeyer flask and the water content was adjusted to 12% (w/w). The initial pesticide concentration in the substrate was 10 mg kg⁻¹ for each pesticide. The sample flasks were loosely covered with aluminum foil and incubated at 20°C. Two 10-g aliquots were removed from each flask and analyzed for insecticide concentration following solvent extraction on 0, 3, 7, 14, and 28 d after treatment for chlorpyrifos, and 0, 0.4, 1, 3, and 7 d after treatment for trichlorfon. The more frequent sampling for trichlorfon was because of its faster degradation than chlorpyrifos. Sample extraction was carried out on a Dionex ASE-200 accelerated solvent extractor (Dionex, Sunnyvale, CA) using a method similar to Gan et al. (1999). A mixture of acetone and dichloromethane (2:1, v/v) (acidified with 2% phosphoric acid) was used for the extraction. The extraction temperature, pressure, and duration were 13.8 MPa, 100°C, and 10 min, respectively. Extract from each sample was purged with N gas and collected in glass vials. The extract was concentrated in a rotary evaporator and reconstituted in 5 mL hexane. Two μL of the final extract was injected into an HP-5890 gas chromatograph (GC) using an auto-injector. Trichlorfon was analyzed with an electron capture detector (ECD) using a DB-608 column (30 m by 0.25 mm by 0.25 μm) at a flow rate of 1.3 mL min⁻¹ (He). The initial oven temperature was 50°C and then increased to 220°C at 30°C min⁻¹. The inlet and detector temperatures were 250 and 280°C, respectively. Chlorpyrifos was analyzed on the same system under similar conditions, except that the oven temperature was initially 100°C, and then ramped at 70°C min⁻¹ to 200°C. The detection limit for trichlorfon was about 0.01 g kg⁻¹ in soil, and that for chlorpyrifos was 0.002 g kg⁻¹.

The mean and standard deviation ($n = 3$) of the recovery rates for trichlorfon were 96.1 and 10.9% in the thatch, 58.4 and 4.1% in the mat, and 72.2 and 3.5% in the soil, respectively. The respective values ($n = 3$) for chlorpyrifos were 94.5 and 2.6% in the thatch, 88.5 and 1.1% in the mat, and 89.3 and 3.2% in the soil.

Field Experiments

The same treatment was repeated in 1996 and 1997 on different replicate plots at the field site. Trichlorfon was sprayed uniformly onto the grass canopy of each plot at 765 mg m⁻² (a.i.) and chlorpyrifos at 153 mg m⁻² (a.i.) using a backpack sprayer on 4 June 1996 and on 9 July 1997. Air, clipping, soil, and leachate samples were collected from four replicate plots in 1996 and three replicate plots in 1997. Other application conditions were as suggested by the formulation labels. In both years the insecticides were sprayed in the early morning with minimal wind. It should be noted that both insecticides were applied on the same replicate plots within each year. During the study, the plots were mowed four times per week at a 5-mm cutting height. Irrigation was applied to prevent visual drought symptoms. The total amount of irrigation water during the experimental period in 1996 was 56 cm and in 1997 was 57 cm, which was approximately 1.5 times of the potential evapotranspiration rate at the site for the period. The plots were fertilized at an annual N rate of 244 kg ha⁻¹ using 15.0–2.2–6.6 (N–P–K) and 6.0–0.9–0 (N–P–K) fertilizers.

Volatilization Measurement. Immediately following insecticide application, a flux chamber was placed on each of the treated plots to collect insecticide vapor in the atmosphere. The chambers were developed according to Gao et al. (1997), and had a base of 40 by 40 cm with an internal volume of 12.8 L. They found that the sampling efficiency of the chambers

was comparable to other volatilization measurement devices. The chamber body was made of sheet metal, and the outside was painted white to reflect heat. The chambers (one at each plot) were connected via a manifold to a vacuum source, which provided a constant airflow of 20 L min^{-1} for each chamber. Polyurethane foam plugs (PUF) were placed in the inlet and outlet of each chamber. The PUF plug in the inlet was used to filter any insecticide vapor in the inlet air, while the PUF in the outlet was used to trap insecticide vapor emitting from the measured area. The PUF samples were collected and replaced with unused plugs every 1 h on the first day, and every 6 to 8 h thereafter. The PUF samples in the outlet were stored in glass jars and kept in a freezer until analysis. Sampling for fluxes continued until 8 d after treatment, when the atmospheric concentration of insecticides became nondetectable using the sampling method. A Soxhlet device was used to extract the PUF samples, and the extraction duration was 8 h. The extracting solvent was a mixture of hexane and acetone (1:1, v/v), and the refluxing temperature was 60°C. Extracts were collected and concentrated to near dryness in a rotary evaporator before reconstituted in 5.0 mL hexane. An aliquot of the final extract was then transferred to a gas chromatography (GC) vial and quantified using the GC methods given in the laboratory experiment.

Analysis of Residues on Grass. Residues and persistence of insecticides on turfgrass were determined by analyzing insecticide concentrations in grass clippings. Clippings were collected from each of the entire treated plots when the plots were mowed as regular putting green maintenance. An aliquot of clippings from each plot was taken for determining the water content. A subsample of 20 g (fresh wt.) was transferred into a blender jar and 150 mL of a 35% water–acetone mixture was added. The sample was blended for 2 min at high speed. The mixture was filtered through a Buchner funnel into a 500-mL suction flask, and the filtrate was transferred to a separatory funnel containing 50 mL methylene chloride. Fifty milliliters of petroleum ether was added to the separatory funnel, which was then vigorously shaken for 1 min. The aqueous layer was transferred to a second separatory funnel, while organic extract was transferred to a 300-mL, flat-bottomed flask. Four grams of sodium chloride was added to the aqueous phase in second separator, which was shaken vigorously until the NaCl was dissolved. The methylene chloride extraction procedure was repeated two more times. The organic extract was combined and dried by passing through a layer of anhydrous sodium sulfate, and was further concentrated and prepared in 5.0 mL hexane for analysis by GC. The same GC conditions as given above were used for trichlorfon and chlorpyrifos quantification.

Monitoring of Residues in Leachate. Leaching of insecticides over time was determined by analyzing residues in the lysimeter drainage water. Drainage water samples were continuously collected for 72 d in 1996, and for 80 d in 1997. The volume of leachate was measured and recorded daily. If the daily leaching volume from a plot was <500 mL, the leachate samples from the following consecutive days were combined until the volume reached at least 500 mL. A 500-mL water sample was poured into a 1-L separatory funnel, and was mixed vigorously with 200 mL methylene chloride. After the organic and water phases were separated completely, the organic phase was collected in a 300-mL flat-bottom flask. The same extraction process was repeated for two more times, and the combined solvent extract was passed through a layer of anhydrous sodium sulfate to remove any residual water. The dried extract was further concentrated in a rotary evaporator and dissolved in 5.0 mL hexane for analysis by GC.

Analysis of Insecticide Distribution in Soil. To determine insecticide distribution and persistence in soil, soil core samples (5.4 cm i.d.) were taken immediately before and 0, 2, 7,

15, 29, 59, and 91 d after treatment in 1996; and 0, 2, 7, and 15 d after treatment in 1997. Four cores were randomly taken from each plot, in areas outside of the lysimeter assembly to avoid any disturbance inside the lysimeters. Soil cores were divided into sections of 0 to 2, 2 to 10, 10 to 20, 20 to 32, and 32 to 47 cm deep, and samples from the same plot and depth were pooled and mixed. Samples were stored in glass jars at 4°C until analysis. An aliquot of soil was removed for determining water content, and a subsample of 30 g (oven-dry wt.) was extracted using a Soxhlet extraction device. The extraction conditions were similar to those used for the PUF samples, except that the extraction time was 8 h.

RESULTS AND DISCUSSION

Loss of trichlorfon and chlorpyrifos due to volatilization, clipping removal, leaching loss, and residues in thatch, mat, and soil were monitored in 1996 and were repeated in 1997. The pattern of dissipation of the two insecticides was similar in 1996 and 1997, so only data for 1996 are shown while cumulative losses are presented for both years.

Laboratory Incubation

Degradation of trichlorfon and chlorpyrifos in the incubated samples was fitted to the first-order decay model. The fit was better for trichlorfon ($r^2 = 0.74$–0.94) than for chlorpyrifos ($r^2 = 0.65$–0.89). The first-order degradation half-lives of trichlorfon and chlorpyrifos in the thatch, mat, and soil layers are given in Table 1.

Table 1. Measured cumulative loss (in % of applied mass) of trichlorfon and chlorpyrifos in air, clipping removal, leachate, and soil dissipation half-life in 1996 and 1997; and estimated adsorption coefficients of the two insecticides in thatch, mat, and soil.

Pesticide	1996	1997
Trichlorfon		
Volatilization, applied %†	0.01 (0.001)	0.008 (0.001)
Clipping removal, applied %	0.06 (0.014)	0.05 (0.003)
Leaching, applied %	0.05 (0.01)	0.0001 (0.0002)
Soil dissipation half-life, d‡	1.07	6.00
Degradation half-life, d		
Thatch		1.0
Mat		7.7
Soil		0.5
Adsorption coefficient, L kg^{-1}§		
Thatch	0.66	
Mat	0.34	
Soil	0.28	
Chlorpyrifos		
Volatilization, applied %	2.05 (0.9)	2.71 (0.80)
Clipping removal, applied %	0.27 (0.12)	0.19 (0.04)
Leaching, applied %	0.006 (0.001)	0.0006 (0.0001)
Soil dissipation half-life, d	8.60	6.40
Degradation half-life, d		
Thatch		247.6
Mat		266.6
Soil		119.5
Adsorption coefficient, L kg^{-1}		
Thatch	399.7	
Mat	208.4	
Soil	17.6	

† Numbers are the means of four replications (treated plots). Numbers inside the parentheses are standard deviations.
‡ Soil dissipation half-life was estimated from measured pesticide concentration of soil samples taken from the experiment plots; degradation half-life was calculated from laboratory incubation experiments.
§ Adsorption coefficient was estimated from the K_{oc} of trichlorfon (10 L kg^{-1}) and chlorpyrifos (6070 L kg^{-1}) (Wauchope et al., 1992), and the organic C content of each layer.

Degradation of trichlorfon in materials from all depths was very fast, with half-lives of only <8 d. In comparison, chlorpyrifos was much more persistent in the three layers, with half-lives of 119.5, 247.6, and 266.6 d, respectively, for the soil, thatch, and mat layers.

Site-specific adsorption coefficients were estimated for trichlorfon and chlorpyrifos in different layers using the measured organic carbon content and the K_{oc} values given in a pesticide properties database (Wauchope et al., 1992). From the estimated K_d values (Table 1), trichlorfon would be weakly adsorbed in the thatch, mat, and soil layer. On the other hand, chlorpyrifos would be strongly adsorbed, especially in the thatch and mat layers.

Volatilization

Figure 1 shows volatilization fluxes ($\mu g \ m^{-2} \ d^{-1}$) of trichlorfon and chlorpyrifos for the 1996 study. Volatilization occurred mainly during the first 3 d. The two insecticides, however, showed substantial differences in volatilization fluxes. The highest volatilization flux for trichlorfon was 7 $\mu g \ m^{-2} \ d^{-1}$, compared with 427 $\mu g \ m^{-2} \ d^{-1}$ for chlorpyrifos. In 1997, the highest volatilization flux for trichlorfon was 1 $\mu g \ m^{-2} \ d^{-1}$, while for chlorpyrifos it was 134 $\mu g \ m^{-2} \ d^{-1}$. These results are consistent with the difference in Henry's constant for trichlorfon (1.50×10^{-9}) and chlorpyrifos (3.65×10^{-4}). Watanabe (1993) indicated that pesticide volatilization from soil surface was positively correlated to the vapor pressure and Henry's law constant, and inversely correlated to water solubility and soil adsorption constant. When a pesticide is adsorbed, it will be less available for volatilization. Although trichlorfon has a smaller adsorption coefficient (0.28–0.66 $m^3 \ Mg^{-1}$) than chlorpyrifos (17.6–399.7 $m^3 \ Mg^{-1}$), the reduction in vapor pressure due to higher adsorption of chlorpyrifos, however, was not able to account for the difference in vapor pressure of the two compounds. The net result is that chlorpyrifos has a higher volatilization loss.

Volatilization loss of trichlorfon in 1996 (0.01%) was slightly higher ($P < 0.05$) than in 1997 (0.008%), while volatilization loss of chlorpyrifos was not significantly different in the two years. The similar volatilization loss of the two insecticides in the 2 yr was attributed to the similar irrigation input and similar average air temperature during the sampling periods in 1996 (31°C) and in 1997 (32°C). Cumulatively, loss of insecticides from volatilization was very small. The cumulative loss of trichlorfon was 0.01 and 0.008% of applied mass in 1996 and 1997, respectively, whereas the total loss of chlorpyrifos was 2.05 and 2.71% of applied mass for the same years. These values are smaller than those reported by Murphy et al. (1996b) for triadimefon (~8%), but are comparable to MCPP [2-(4-chloro-2-methyl phenoxy) propionic acid] (~1%).

Insecticides in Clippings

Insecticide residues on grass were monitored for 45 d in 1996 and 16 d in 1997. The amount of insecticides found in grass clippings was the greatest on the first day after application, at about 400 and 300 $\mu g \ m^{-2} \ d^{-1}$, respectively, for trichlorfon and chlorpyrifos in 1996 (Fig. 2). The trichlorfon residue in grass clippings became nondetectable in about 3 d after its application, while chlorpyrifos became nondetectable in 5 d (Fig. 2). In 1997, the chlorpyrifos dissipation rate (both in terms of the magnitude and persistence) in clippings was very similar to that of 1996. The dissipation rate of trichlorfon, on the other hand, was slightly different from that of 1996: the first day clipping removal was not as high as in 1996, but it was more persistent than in 1996.
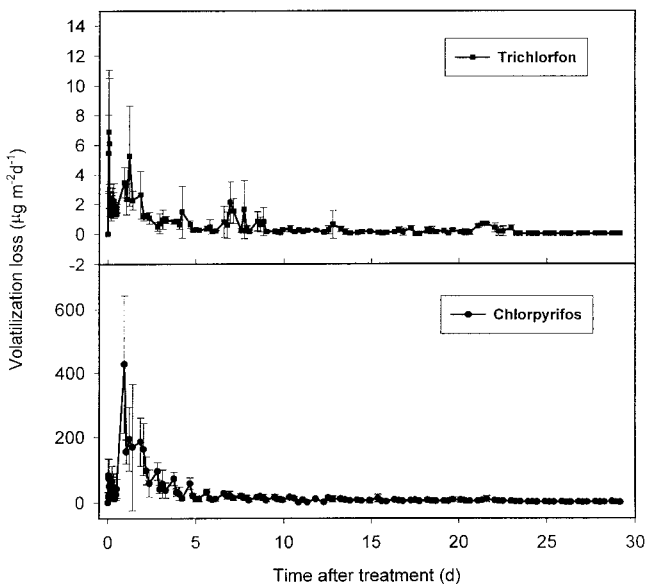

Fig. 1. Volatilization fluxes of trichlorfon and chlorpyrifos after application to a bentgrass putting green under southern California conditions. The data points (symbols) are the means of the four treated plots (replications) in 1996 and three plots in 1997, and the error bar represents 1 SD.
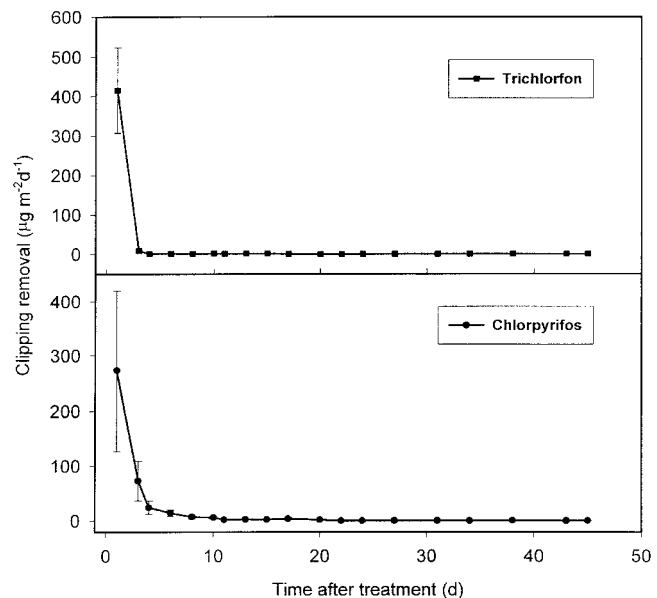

Fig. 2. Amount of trichlorfon and chlorpyrifos removed in turfgrass clippings after treatment ($\mu g \ m^{-2} \ d^{-1}$). The data points (symbols) are the means of four treated plots (replications) in 1996 and three plots in 1997, and the error bar represents 1 SD.

Both insecticides showed slightly more persistence in clippings in 1997 than in 1996, but the amount of cumulative clipping removal was very similar in both years. For trichlorfon, the clipping removal was 0.06% of the applied mass in 1996, compared with 0.05% in 1997. Cumulative clipping removal of chlorpyrifos was 0.27% in 1996, compared with 0.19% in 1997. There was no similar research to compare for the total amount of clipping loss for the two insecticides in the literature. However, the trend of the dissipation was similar to those observed by Cisar and Snyder (1996).

Distribution, Movement, and Dissipation in the Profile

Downward movement of trichlorfon was faster than chlorpyrifos, because the former has weaker adsorption to the soil than the later. Since the retardation factor increases linearly with adsorption coefficient, a insecticide with strong adsorption will move downward slowly. Nevertheless, both applied insecticides resided mainly in the top layers (0–2 cm thatch layer and 2–10 cm mat layer) during the measurement period, as shown in Fig. 3a and 3b. This implies that the two insecticides were retained in the thatch and mat layers because these layers had much higher organic matter contents and consequently higher potential for adsorption. Adsorption by the organic thatch layer was considered as the main reason in preventing downward movement of insecticides into underlying soil (Niemczyck et al., 1977). In a microecosystem experiment, Branham and Wehner (1985) found that 96% of the applied diazinon resided in the top 10 mm of the turf profile regardless of whether it was thatch or soil. Horst et al. (1996) also found that little chlorpyrifos moved through the thatch layer to the underlying soil during a 113-d experiment.

Insecticide degradation in soil profile is one of the major loss avenues. For an insecticide like chlorpyrifos with low mobility, dissipation occurred mainly in the thatch–mat layer (Fig. 3b). It was noticed that there was a big difference between field-measured dissipation half-life and the laboratory-measured degradation half-life for chlorpyrifos (Table 1). One of the main reasons can be attributed to the temperature difference between the field (approximately 37°C) and laboratory (approximately 20°C) conditions. Getzin (1981) found that chlorpyrifos degraded four times faster at 35°C than at 15°C. The shorter half-life in the field than in the laboratory can also be caused by other dissipation mechanisms such as metabolism by the plant, volatilization, and photo-decomposition under field conditions. Results from our experiment (Table 1) showed the consensus feature that the insecticides rapidly dissipated in the soil profile. Regression analysis indicated that the first-order dissipation (including degradation, volatilization, leaching, plant metabolism, and photo-decomposition) model could fit the data well ($R^2 > 0.95$ in all cases). The dissipation half-life for trichlorfon was 1.1 d in 1996 and 6.0 d in 1997. For chlorpyrifos, the dissipation half-life was 8.7 d in 1996 and 6.4 d in 1997, which are much shorter than approximately 1 to 2 mo, as reported by

Caux et al. (1996) in potato (*Solanum tuberosum* L.) culture. This suggests that pesticide dissipation rate varies considerably with its environmental conditions such as crop, soil moisture, and soil temperature.

Insecticides in Leachate

The volume and concentration of leachate was monitored for 72 d in 1996 and 80 d in 1997 after insecticide application. Unlike the clipping and volatilization that showed immediate insecticide detection on the first day, insecticides did not appear in the leachate until 20 d after treatment for trichlorfon and 30 d after treatment for chlorpyrifos (Fig. 4). The slower breakthrough of chlorpyrifos may be attributed to its stronger adsorption in soil. The highest amount of daily leaching of trichlorfon (71.3 μg m^{-2}) was much greater than chlorpyrifos (1.9 μg m^{-2}), which may be a result of their different water solubility and degradation rates (Table 1).

Irrigation management can also affect pesticide leaching. For a pesticide with a short half-life, the short-term leaching reduction might be significant since most of the applied pesticide will be degraded during the first few days. Using two different water application rates (heavy and light) but the same amount of water, Starrett et al. (1996) found that leaching was significantly reduced under light irrigation. Soil water regime can also affect pesticide degradation rate. Awasthi and Prakash (1997) found that chlorpyrifos was degraded rapidly in air-dried soils and slower in soils at field capacity and/or under submerged conditions. Our experiments, however, showed that irrigation management was fairly consistent in both years. The average cumulative volume of leachate for the first 72 d was 329 L and 350 L per lysimeter assembly, in 1996 and 1997, respectively. The concentrations of the insecticides, on the other hand, were considerably lower in 1997 than in 1996, which is consistent with the lower soil concentrations in 1997.

The cumulative residue in leachate only accounted for 0.05 and 0.01% of applied mass for trichlorfon and chlorpyrifos, respectively, in 1996, and 0.0001 and 0.0006% of applied mass, respectively, in 1997. Considering that the potential evapotranspiration rate at the experiment site was approximately 46 cm during the 72-d experimental period, the leachate collected was equivalent to approximately 50% of irrigation. This suggests there was excessive water applied to the green, which can happen in the golf industry. However, even under such heavy irrigation, the experimental data showed that the applied insecticides in the putting green had negligible potential for contaminating ground water.

SUMMARY

Runoff from the irrigated turf greens is usually a minor cause for pesticide loss, thus this research focused on volatilization and partitioning into grass, soil, and leachate. The same treatment was repeated in 1996 and 1997 to determine the partitioning, persistence, and loss of two insecticides—trichlorfon and chlorpyrifos—in a bentgrass putting green in southern California under customary field management practices. Insecticide loss
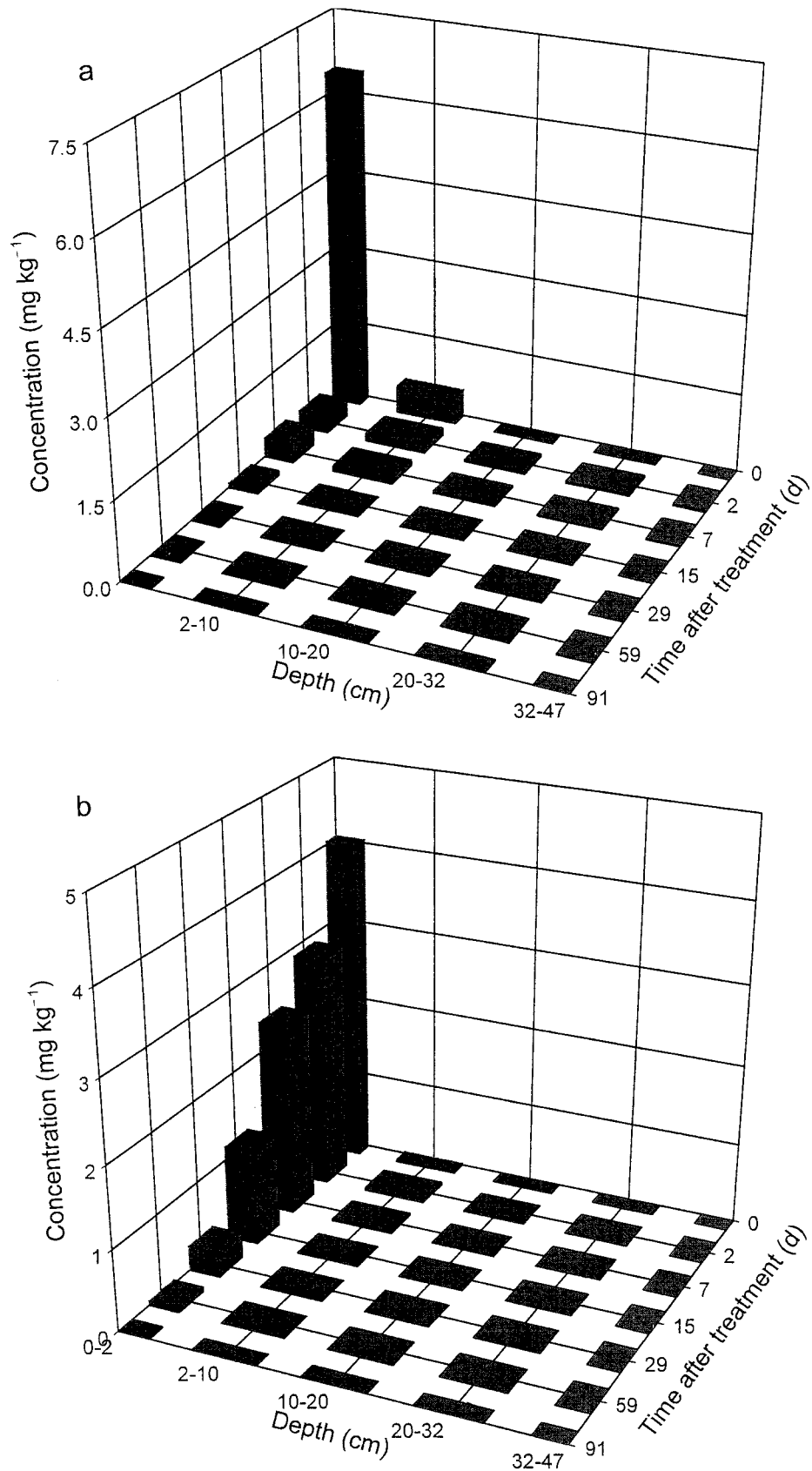
Fig. 3. (*a*) Distribution of trichlorfon at different depths in turf plots after application. (*b*) Distribution of chlorpyrifos at different depths in
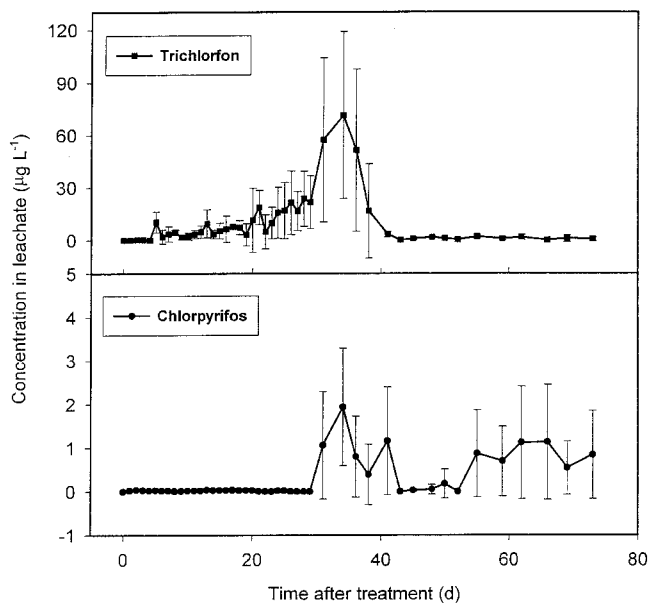   turf plots after application.

Fig. 4. Leaching rate (μg m^{-2} d^{-1}) of trichlorfon and chlorpyrifos in 1996. The data points (symbols) are the means of four treated plots (replications) in 1996 and three plots in 1997, and the error bar represents 1 SD.

via clipping removal and volatilization was found to be minor. Clipping removal and volatilization occurred mostly during the first 5 d after insecticide application. The insecticide (chlorpyrifos) with a higher Henry's law constant and a lower adsorption coefficient had a higher potential for volatilization. Total clipping removal loss was <0.5% of the applied mass. Leaching loss of the two insecticides was also minor. But it was clear that more mass leached out of root zone for an insecticide (trichlorfon) with higher solubility, longer half-life, and low adsorption rate. Thus, whenever it is possible, those with lower solubility, shorter half-life time, and stronger adsorption should replace such insecticides. Due to the high organic material content and low mobility, most of the insecticides' dissipation occurred at the thatch–mat layer. Therefore, although the putting greens normally receive high inputs of trichlorfon and chlorpyrifos, the fraction of applied insecticides leaving the greens were minimal.

REFERENCES

Awasthi, M.D., and N.B. Prakash. 1997. Persistence of chlorpyrifos in soils under different moisture regimes. Pestic Sci. 50:1–4.

Beard, J.B., and R.L. Green. 1994. The role of turfgrasses in environmental protection and their benefits to humans. J Environ Qual. 23:452–460.

Branham, B.E., and D.J. Wehner. 1985. The fate of diazinon applied to thatched turf. Agron. J. 77:101–104.

Caux, P.Y., C. Bastien, and A. Crowe. 1996. Fate and impact of pesticides applied to potato cultures: The Nicolet River basin. Ecotoxicol. Environ. Saf. 33:175–185.

Cisar, J.L., and G.H. Snyder. 1996. Mobility and persistence of pesticides applied to USGA green: III. Organophosphate recovery in clippings, thatch, soil, and percolate. Crop Sci. 36:1433–1438.

Cisar, J.L., and G.H. Snyder. 1997. Mobility and persistence of pesticides applied to USGA-type green: V. Irrigation management and fenamiphos leaching. Int. Turfgrass Soc. Res. J. 8:167–173.

Cooper, R.J., J.J. Jenkins, and A.S. Curtis. 1990. Pendimethalin volatility following application to turfgrass. J. Environ. Qual. 19:508–513.

Gan, J., S.K. Papiernik, W.C. Koskinen, and S.R. Yates. 1999. Evaluation of accelerated solvent extraction (ASE) for analysis of pesticide residues in soil. Environ. Sci. Technol. 33:3249–3253.

Gao, F., S.R. Yates, M.V. Yates, J. Gan, and F.F. Ernst. 1997. Design, fabrication, and application of a dynamic chamber for measuring gas emissions from soil. Environ. Sci. Technol. 31:148–153.

Getzin, L.W. 1981. Degradation of chlorpyrifos in soil: Influence of autoclaving, soil moisture, and temperature. J. Econ. Entomol. 74:158–162.

Horst, G.L. P.J. Shea, N.E. Christians, D.R. Miller, C. Stuefer-Powell, and S.K. Starrett. 1996. Pesticide dissipation under golf course fairway conditions. Crop Sci. 36:362–370.

Howard, P.H. 1991. Handbook of environmental fate and exposure data for organic chemicals. p. 5–13. *In* Vol. 3. Pesticides. Lewis Publ., Chelsea, MI.

Kriner, R.E. 1985. Final report on the results of a national survey of pesticide usage on golf courses in the U.S., conducted in July–September 1982. America Association of Retired Persons under a cooperative agreement with the Environmental Protection Agency. USEPA, Washington, DC.

Murphy, K.C., R.J. Cooper, and J.M. Clark. 1996a. Volatile and dislodgeable residues following trichlorfon and isazofos application to turfgrass and implications for human exposure. Crop Sci. 36:1446–1454.

Murphy, K.C., R.J. Cooper, and J.M. Clark. 1996b. Volatile and dislodgeable residues following triadimefon and MCPP application to turfgrass and implications for human exposure. Crop Sci. 36:1455–1461.

Niemczyk, H.D., and H.R. Krueger. 1987. Persistence and mobility of isazofos in turfgrass thatch and soil. J. Econ. Entomol. 80:950–952.

Niemczyk, H.D., H.R. Krueger, and K.O. Lawrence. 1977. Thatch influences movement of soil insecticides. Ohio Rep. 62:26–28.

Perris, J. 1996. The UK turfgrass market: An overview of customer needs and market opportunities: An agronomist's perception. Pestic. Sci. 47:379–383.

Sears, M.K., and R.A. Chapman. 1979. Persistence and movement of four insecticides applied to turfgrass. J. Econ. Entomol. 72:272–274.

Snyder, G.H., and J.L. Cisar. 1993. Mobility and persistence of pesticides in a USGA-type green: II. Fenamiphos and Fonofos. Int. Turfgrass Soc. Res. J. 7:987–983.

Snyder, G.H., and J.L. Cisar. 1995. Pesticide mobility and persistence in a high-sand-content green. USGA Green Section Rec. 33:15–18.

Starrett, S.K., N.E. Christians, and T. Al Austin. 1996. Movement of pesticides under two irrigation regimes applied to turfgrass. J. Environ. Qual. 25:566–571.

Watanabe, T. 1993. Relationship between volatilization rates and physicochemical properties of some pesticides. J. Pestic. Sci. 18:201–209.

Wauchope, R.D., T.M. Buttler, A.G. Hornsby, P.W.M. Augustijn-Beckers, and J.P. Burt. 1992. SCS/ARS/CES Pesticide properties database for environmental decisionmaking. Rev. Environ. Contam. Toxicol. 123:1–157.

Wu, L., G. Liu, M.V. Yates, R. Green, P. Pacheco, J. Gan, and S.R. Yates. 2002. Environmental fate of metalaxyl and chlorothalonil applied on a bentgrass putting green under southern California climate. Pest Manage. Sci. 58:(in press).