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Management practices to minimize volatile and dislodgeable foliar residues of turfgrass pesticides.

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MANAGEMENT PRACTICES TO MINIMIZE VOLATILE AND DISLODGEABLE FOLIAR RESIDUES OF TURFGRASS PESTICIDES

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by

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ABSTRACT

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May 2002

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Pesticide applications to turfgrass are a common practice in the maintenance of lawns and golf courses across the U.S.A. As golf and related turfgrass uses become more urbanized, additional research and development of best management practices for the application of turfgrass pesticides will be necessary to reduce the potential for exposure to humans, wildlife and adjacent environments. Major routes of pesticide exposure for humans following application to turf are primarily through dermal and respiratory tract penetration.

Previous research on pesticide fate following applications to turfgrass determined that volatile and dislodgeable foliar residues were greatest immediately following application. Dissipation occurred in a diurnal pattern (greatest at mid-day) over a 14-day sampling period (1,2). Post-application irrigation (1.3-cm) greatly reduced the level of volatile and dislodgeable foliar residues and their consequent USEPA hazard quotient assessments. Hazard quotients (HQs) are calculated from the dose received from volatile or dislodgeable foliar pesticide residue concentrations divided by the pesticide reference dose (NOEL divided by uncertainty factors). A calculated HQ value greater than 1.0 indicates an exposure that cannot be deemed

completely safe. Although using 1.3-cm irrigation significantly decreased volatile and dislodgeable foliar residues, organophosphorous insecticides that have high vapor pressures and high inherent toxicity (low reference doses) were problematic as judged by the USEPA HQ criteria. Additionally there was an increase in the conversion of trichlorfon to DDVP, a more volatile and toxic insecticide.

Subsequent research determined Inhalation Hazard Quotients (IHQs) and Dermal Hazard Quotients (DHQs) following the application of 14 commonly used pesticides on turfgrass (3). Of the 13 pesticides, 3 resulted in IHQ values greater than 1.0: ethoprop, diazinon, and isazofos (all of which, are no longer used on golf courses). For DHQs, 7 of the compounds resulted in values greater than 1.0; ethoprop, diazinon, isazofos, isofenphos, trichlorfon, chlorpyrifos, and bendiocarb. The incorporation of spray-tank adjuvants (Aqua Gro-L® and Exalt 800®) and thatch management (dethatching and aeration) as a means to reduce the level of volatile and dislodgeable foliar residues was resulted in no significant reductions in the levels of volatile or dislodgeable foliar residues by either practice.

In the current study, volatile and dislodgeable foliar residues from pesticide-treated turfgrass (chlorpyrifos, isofenphos, trichlorfon, triadimefon and bendiocarb) were evaluated as mitigation practices that reduce the exposure risk potential. Daily volatile pesticide residues were collected by high-volume air sampling and dislodgeable foliar residues were collected by H_2O dampened cheesecloth wipes and used to assess potential exposure using USEPA HQ criteria.

The use of an extending-type adjuvant (Silwet L-77®) resulted in no significant reduction in the level of volatile or dislodgeable foliar residues of chlorpyrifos, isofenphos and bendiocarb or in their consequent HQ determinations (t-test, $P > 0.05$ and $P > 0.025$ for IHQ and DHQs, respectively). At no time during any of the experiments did IHQ values exceed 1.0. The highest was for isofenphos (IHQ of 0.2) and occurred in the presence of Silwet L-77 with 1.3-cm irrigation. Without Silwet L-77 in the presence of 1.3-cm post-application irrigation, all calculated DHQ values were below 1.0 by the end of Day 1. Chlorpyrifos and bendiocarb had DHQs less than 1.0 at the 15 min post-application irrigation sample interval and the DHQ value for isofenphos was less than 1.0 by the 2nd sampling at 2 hrs.

Increasing irrigation from 0.63- to 1.3-cm, lowered the ∑IHQ and ∑DHQ values by 1.7- and 1.9-fold, respectively. The 0.32-cm level was not an effective management practice and resulted in higher IHQ and DHQ values.

To simulate the application of pesticide to 1/2 or 1/4 of the golf course, application rates were reduced from full to 1/2 and 1/4 rates. This practice lowered the ∑IHQ values at both rates by ~3.0-fold and the ∑DHQ values by 4.0- and 4.6-fold, respectively, for both chlorpyrifos and isofenphos.

The potential for conversion to more toxic substances was examined by the hydrolysis of trichlorfon to DDVP and triadimefon to triadimenol in the presence of 0.63- and 0.32-cm post-application irrigation. No IHQ or DHQ values exceeded 1.0 for either DDVP or triadimenol following either irrigation level.

The exposure potential of golfers following application of turfgrass pesticides appears to be best managed by increased rates of post-application irrigation and applying pesticides to 1/2 of the course or less on a daily basis.

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INTRODUCTION AND LITERATURE REVIEW

1.1. Potential for Human Exposure to Turfgrass Pesticides from Volatile and Dislodgeable Foliar Residues.

Pesticide applications to turfgrass are a common practice in the maintenance of lawns and golf courses across the U.S.A. As golf and related turfgrass uses become more urbanized, additional research and development of best management practices for the application of turfgrass pesticides will be necessary to reduce the potential for exposure to humans, wildlife and adjacent environments. Major routes of pesticide exposure for humans following application to turf are primarily through dermal and respiratory tract penetrations.

1.2. Pesticide Volatility and Dislodgeable Foliar Residues.

Previous research established that pesticides volatilized throughout the first day following application to turf and then decrease diurnally over the next few days (Murphy et al., 1996ab). Volatile residues were highest immediately following application. The initial high concentration of volatile pesticides detected immediately following application rapidly dissipated to a lower level over a period of 2-3 hrs, usually increased by mid-day as solar radiation increased and then steadily declined throughout the evening. Subsequently on each additional day, volatile residues were highest at mid-day. This pattern of dissipation continued until the volatile residues reached their detection limits, usually 3 to 5 days following application and irrigation.

In the absence of post-application irrigation, dislodgeable foliar residues were highest immediately following pesticide application and then dissipated diurnally over time until non-detectable, usually 3-5 days post-application. Initial levels of dislodgeable foliar residues were greatly diminished by post-application irrigation and, depending on the water solubility of the pesticide, the occurrence of the highest level of residues was delayed to subsequent sampling intervals. Dislodgeable foliar residues then dissipated in a similar manner as for those applied without irrigation.

The above original research primarily examined volatile and dislodgeable foliar residues that occurred following application to turf of some commonly used pesticides (isazofos; MCPP; triadimefon; trichlorfon and DDVP, a degradative product of trichlorfon) to determine if exposure situations existed that could be hazardous for golfers, other recreational turf users and bystanders (Murphy et al., 1996ab). The extent of pesticide volatilization was examined by collecting volatile residues onto XAD-4 polymeric resin during high-volume air sampling (Kilgore et al., 1984). The extent of dermal exposure was assessed by collecting dislodgeable foliar residues onto H_20-dampened cheesecloth wipe samples (Thompson et al., 1984; Murphy et al., 1994).

The hazards associated with inhalation and dermal exposures was estimated using the United States Environmental Protection Agency (USEPA) Inhalation and Dermal Hazard Quotient (IHQ and DHQ, respectively) determinations. The highest calculated IHQ values were 0.002, 0.6, **5.0**, 0.2 and 0.001 and DHQ values were 0.1, 4.6, **14.3**, 0.8 and 0.2 for trichlorfon, DDVP, isazofos, MCPP and triadimefon, respectively (Murphy et al., 1996ab). Hazard quotients are calculated using the predicted inhalation or dermal exposure divided by a USEPA assigned reference dose (Rfd). These RfD values are the No Observable Effect Levels (mg/kg/day) divided by an uncertainty factor (10, 100, 1000), which is based on the amount of toxilogical data available for each pesticide. A calculated IHQ or DHQ value greater than 1.0, indicates, exposure to that pesticide cannot be deemed as completely safe.

Trichlorfon and isazofos applications were followed by 1.3-cm post-irrigation and MCPP and triadimefon were not irrigated (Murphy et al., 1996ab). The study concluded that exposure to certain pesticides (e.g. isazofos, DDVP) following applications to turfgrass cannot be deemed completely safe using the USEPA HQ criteria.

The problematic pesticides were isazofos and DDVP, both organophosphates with high volatility and inherent high toxicity. Additionally, post-application irrigation at 1.3-cm H_2O was found to increase the hydrolytic conversion of trichlorfon to DDVP, a more volatile and toxic metabolite. Thus, the level of post-application irrigation appeared to be an important consideration when making pesticide applications. Increasing irrigation may convert some pesticides to more toxic, environmentally mobile products, while reducing irrigation may increase the initial level of volatilization and dislodgeable foliar residues creating a greater potential for human exposure.

1.3. Mitigation Practices for Turfgrass Pesticides that have a Potential for Hazardous Human Exposure.

Subsequent research by Clark et al. (2000) examined 14 commonly used turfgrass pesticides, which elicited a wide range of volatility and toxicity, to estimate the potential hazard of each by determining volatile and dislodgeable foliar residues and calculating HQ values. The pesticides were grouped into three vapor pressure categories: high (vapor pressures > 1.3 mPa), intermediate (vapor pressures between 1.3 and 0.013 mPa) and low (vapor pressures < 0.013 mPa). Of the 14 pesticides examined, 11 never resulted in IHQ values greater than 1.0 (DDVP, chlorpyrifos, trichlorfon, bendiocarb, isofenphos, chlorothalonil, propiconizole, carbaryl, thiophanate-methyl, ipridione and cyfluthrin) and

5 pesticides never exceeded DHQ values of 1.0 (DDVP, propiconizole carbaryl, cyfluthrin, ipridione and thiophanate-methyl). Pesticides with high to intermediate vapor pressures and lower assigned reference doses (RfD, low RfD values = inherently high toxicity) had corresponding IHQs and DHQs values greater than 1.0 indicating a potential for hazardous exposure. These pesticides were all of the organophosphorous-type of insecticides (ethoprop, isazofos, diazinon, isofenphos, DDVP, trichlorfon and chlorpyrifos) with the exception of a carbamate (bendiocarb).

The use of spray tank adjuvants (Aqua Gro-L® and Exalt 800®) and incorporating thatch management protocols (aeration and dethatching) also were examined and preliminary results determined that neither practice had any significant effect on reducing volatile and dislodgeable foliar residues following applications and hence were not likely to attenuate exposure (Clark et al.; 2000).

1.4. Predicting Pesticide Volatility through Vapor Pressures and Weather Parameters.

A portion of most pesticides volatize when applied to turfgrass (Spencer et al, 1990). The levels of volatilization are dependent upon the pesticide's vapor pressure, ambient air temperature, soil moisture and surface type (Nash et al., 1990). The extent of volatilization and subsequent inhalation exposure will increase as the temperature of the air and wind speed is increased over the turfgrass surface. Thus, a model to predict the potential of human exposure to volatilized pesticides following application to turfgrass would be useful. Recently, the modeling of human exposure to volatile turfgrass pesticides using vapor pressure has been studied by Haith et al. (2000). Previously, no useful models had been reported that efficiently predict inhalation exposure hazards associated with pesticide applications to turf, primarily because of the difficulty in measuring numerous parameters involved in this process.

Volatilization of a pesticide is most directly affected by its vapor pressure (p_v, mPa) and its Henry constant (K_h or h, dimensionless). Vapor pressure is an indicator of the general tendency of a pesticide to volatilize from a solution. A Henry constant is the ratio of the vapor density or gas concentration (g, $\mu g\ m^{-3}$) to the solution density or dissolved concentration (d, $\mu g\ m^{-3}$) of pesticide at equilibrium ($h = g\ d^{-1}$). Vapor density is calculated from the p_v of a pesticide using the ideal gas law [Eq. 1]

[Eq. 1] $$g = (Mp_v) / (RT)$$

where M = molecular weight, R = gas constant (8300 mPa-m^3 / mol- °K) and T = temperature (°K). An increase in temperature increases the vapor pressure, solubility and Henry constant of a pesticide, h typically doubling with each 10 °C increase. A higher temperature increases the proportion of pesticide molecules that will have the kinetic energy necessary to escape as a vapor (Haith et al., 2000). Thus, the temperature of the turfgrass surface plays a crucial role in volatilization as evidenced by the diurnal variation in the volatilization rates of pesticides.

However, there are other factors that influence the pesticide loss from turfgrass, particularly, the absorption of pesticides occurring in thatch, leaf and water droplets (Haith et al., 2000). This relation is given by equation [Eq. 2], which estimates the total pesticide in the environment following application.

[Eq. 2] $$P = A + C + G$$

where A = the total pesticide absorbed in the thatch, and leaf, etc, C = the total pesticide dissolved in water in the environment and G = the total pesticide in gaseous form.

With this in mind, the volatility of pesticides following twenty weeks of applications and associated weather data for collections made over the summer months of 1996 and 1997 was used to construct a model (Haith et al., 2000). Initially the model used application rates of the total pesticide (P, g ha^{-1}), Henry constant (h, dimensionless), vapor pressure (p_v, mPa), and the organic carbon partition coefficient (K_{oc}, cm^3 g^{-1}), to estimate pesticide vapor concentration. These indices were further simplified to yield a final index that estimates total gaseous pesticide mass in turfed environments with the equation, $G / V \approx (h\ P)\ 10^6 / (k_{oc}, V)$, where G = the total gaseous pesticide mass, 10^6 is added as a scaling factor and both sides of the equation are divided by wind speed (V, m s^{-1}) because air movement would dilute the pesticide concentrations. This model was able to explain 70-90 % of the observed variation in gaseous concentrations for 8 of the 14 pesticides but predicting concentrations using regressions had significantly high errors. Haith et al., (2000) concluded that using models and regression extrapolation might not be as effective or as feasible as using volatilization measurements to determine ambient pesticide concentrations and calculating Hazard Quotients directly.

1.5. Potential for Reducing Inhalation and Dermal Exposures using the Adjuvant Silwet L-77®, Post-application Irrigation and Reduced Application Rates of Pesticides.

The objectives of this current thesis research were developed and based upon the findings of the previously mentioned turfgrass pesticide research (Murphy et al., 1996ab, Clark et al., 2000, Haith et al., 2000).

The effects of spray tank adjuvants and post-application irrigation were expanded upon during the growing seasons of 1998 and 1999. During the 1998 growing season, the organosilicone wetting-agent adjuvant, Silwet L-77®, was applied with the expectations of improving thatch penetration, suppressing volatilization and dislodgeable foliar residues and reducing inhalation and dermal exposures. Ranges of post-application irrigation levels from 0.32- to 1.3-cm H_2O were applied to plots immediately following pesticide application. In the 1999 growing season, the effect of post-application irrigation was examined further by reducing pesticide applications to 1/2 and 1/4 the maximum recommended label rates (1/2 and 1/4 full-rates).

All previous work by Murphy et al., (1996ab) and Clark et al., (2000) examined exposures at the maximum recommended label rates for pesticide applications to turfgrass. This worst-case scenario was used to simulate the greatest potential risk to golfers exposed for 4 hours on a golf course fairway that had been treated entirely at these maximum label rates. By reducing application rates, it should create an exposure scenario as if only 1/2 or 1/4 of the course had received treatment, respectively. Therefore, HQs can be estimated following exposure situations more likely to occur on actual golf courses and thus provide more realistic risk determinations.

1.6. Selection of Pesticides, Modes of Action and Exposure Routes.

1.6.1. Organophosphorous Insecticides.

In general, organophosphorous insecticides (OPs) do not persist in surface waters and very few incidences of high concentration of OPs have been found in ground water in the U.S.A. (Larsen et al., 1999). Nevertheless, all routes of exposure (dermal, oral and inhalation) are likely to occur during and shortly after these pesticides are applied. In fact, OPs ranked first as the pesticides most often implicated in symptomatic illnesses, according to the American Association of Poison Control Centers (Toxic Exposure

Surveillance System, 1996). Because OPs are widely used insecticides on golf courses and share a common mechanism of action as cholinesterase inhibitors, it becomes imperative to monitor the potential for multiple routes of exposure to avoid serious additive toxicity (EPA, 1999).

In normal functioning cholinergic neurons, an action potential depolarizes the presynaptic nerve terminal and a burst of neurotransmitter (acetylcholine) is released into the synaptic cleft (Baron et al., 1991). Released acetylcholine diffuses across the synaptic cleft and binds at a specific postsynaptic cholinergic receptor, which depolarizes the adjacent neurons and results in chemical transmission between neurons. To prevent over-stimulation of the postsynaptic receptor, acetylcholine is rapidly inactivated by the enzyme acetylcholinesterase, which hydrolyzes acetylcholine to choline and acetic acid. OPs such as chlorpyrifos, isofenphos, trichlorfon and DDVP, all act as irreversible cholinesterase inhibitors and cause an accumulation of acetylcholine in the nervous system (Gallo et al., 1991). Excess acetylcholine leads to mimicking of the muscarinic, nicotinic and central nervous system actions of acetylcholine. Primary symptoms of OP poisoning include tightness of chest, wheezing, increased salivation and lacrimation, nausea, vomiting, defecation, muscle weakness, elevation of blood pressure, tension, anxiety, restlessness, slurred speech, tremor and convulsions (Murphy et al., 1986).

Three OPs (chlorpyrifos, isofenphos and trichlorfon) were selected for this current study (Table 1).

Chlorpyrifos is one of the most commonly used insecticides in recent times and was selected because of the well-documented research on human exposure (Nolan et al., 1984, 1993; Shurdut et al., 2000; Racke et al., 1984; Vaccaro et al., 1987, 1993). It is used to control a variety of insects, including those on turfgrass, such as Chinch bugs, billbugs, cutworms and webworms. Chlorpyrifos has a high vapor pressure (2.4 mPa at 25 °C) and is readily absorbed through the skin, lungs and orally (Extoxnet, 1998). It has an oral LD_{50} value between 82 to 270 mg kg^{-1} for rats (USEPA Toxicity Category II, Extoxnet, 1998). The USEPA reference dose is 0.003 mg kg^{-1} day^{-1}. It has not been found to have any carcinogenic, mutagenic or teratogenic effects (Extoxnet, 1998). Research by Clark et al., (2000) determined that the highest IHQ value for full-rate chlorpyrifos application to turf never exceeded 0.15. However, DHQ values were 2.3 and 1.8 at 5 and 8 hrs, respectively, following 0.63-cm post-application irrigation on Day 1. Thus, it is very likely that the exposure potential of chlorpyrifos can be reduced by better management practices.

Isofenphos is used to control soil-dwelling insects on turf, vegetables and fruit crops. Isofenphos is readily absorbed through the skin, lungs and orally. It has an oral LD_{50} value between 28 to 38 mg kg^{-1} for rats (USEPA Toxicity Category I, Extoxnet, 1998). Although isofenphos is an intermediate vapor pressure compound (0.53 mPa at 25 °C), evidence suggests it has a very high inhalation toxicity (studies on hamsters determined an LC_{50} of 0.23 mg L^{-1} in a 4 hour inhalation period, Extoxnet, 1998). Its USEPA RfD is lower than chlorpyrifos' (0.0005 mg kg^{-1} day^{-1}; a lower value increases the calculated HQ) due to an incomplete human exposure data set (Extoxnet, 1998). There are no reported mutagenic, carcinogenic or teratogenic effects from long-term exposure to isofenphos (Extoxnet, 1998). During the study by Clark et al., (2000), isofenphos application never resulted in an IHQ value greater than 1.0 but had DHQ values of 5.7, 5.7, 1.1 and 1.1 at 5 hrs and 8 hrs on Day 1 and at mid-day on Days 2 and

3, respectively, following 0.63-cm post-application irrigation. Isofenphos was selected for use in this current study because of its potential to replace other similar but more toxic OPs, which are no longer used on turfgrass (e.g., ethoprop, isazofos and diazinon).

Trichlorfon is an all-purpose OP used on turfgrass, crops, ornamentals and agricultural premises and even for the control of fish parasites. It has an intermediate vapor pressure (0.50 mPa at 25 °C) and an USEPA assigned reference dose of 0.002 mg kg^{-1} day^{-1} (Extoxnet, 1998). Trichlorfon is readily absorbed through the skin, lungs and orally. For rats, its oral LD_{50} value is between 150 to 649 mg kg^{-1} and the LC_{50} value in air is 1300 mg m^{-3} (USEPA Toxicant Category II, Extoxnet, 1998). Trichlorfon has a high water solubility (120,000 mg L^{-1}) compared to other OPs such as chlorpyrifos (1.4 mg L^{-1}) and isofenphos (24 mg L^{-1}), is mobile in soils and has potential for ground water contamination (Extoxnet, 1998). Research on trichlorfon implies that it is teratogenic, mutagenic and carcinogenic in mammals (Extoxnet, 1998). Clark et al., (2000) found trichlorfon to have IHQ values well below 1.0, but its DHQ values were 1.1, 0.9 and 0.5 on Days 1,2 and 3, respectively. Murphy et al., (1996a) determined trichlorfon to have DHQ values of 27, 15, 13 and 9 without post-application irrigation, and 0.3, 0.2, 3.9 and 3.4 with 1.3-cm irrigation, at 3, 8, 27 and 51 hrs post-application, respectively

Trichlorfon rapidly hydrolyzes to dichlorvos (DDVP) following post-application irrigation at increased levels (1.3-cm) (Murphy et al., 1996a). Trichlorfon is not widely applied to turfgrass (more regularly used for spot treatments) due to its toxicity, which results from the conversion from trichlorfon to DDVP. DDVP has the highest vapor pressure (2133 mPa at 25 °C) of any insecticidal OP (Pesticide Manual, 1997). It has an oral LD_{50} value of 40-80 mg kg^{-1} and a dermal LD_{50} value of 75-100 mg kg^{-1} for rats, making it a relatively toxic insecticide (USEPA Toxicant Category I-II, Pesticide Manual, 1997). It has a USEPA RfD of 0.0005 mg kg^{-1} day^{-1}, the same value as isofenphos. DDVP is not as water soluble as its parent compound trichlorfon (120,000 mg L^{-1}) but it has the second highest water solubility (18000 mg L^{-1}) of the pesticides used in this study (Table 1). Murphy et al., (1996a) determined DDVP to have IHQ values below 1.0 with and without irrigation. However, conversion to DDVP was greatly increased in the presence of 1.3-cm irrigation resulting in significantly greater IHQ values (the highest IHQ value without irrigation was 0.2 on Day 3 but with 1.3-cm irrigation the IHQ was 0.6 occurred on Day 2). Clark et al., (2000) determined DDVP to have IHQ values well below 1.0 (the highest IHQ value was 0.06 on Day 1) for the entire sampling period in the presence of 0.63-cm post-application irrigation. Murphy et al., (1996a) determined DDVP to have DHQ values of 0.1, 0.0, 0.0 and 0.0 without irrigation and reported 0.3, 0.1, 4.5 and 2.7 values with 1.3-cm irrigation, both at 3, 8, 27 and 51 hrs post-application. Clark et al., (2000) determined DDVP in the presence of 0.63-cm post-application irrigation to yield the highest DHQ value of (0.3) on Day 1, however, it was not detected on Days 2 or 3. Clark et al., (2000) concluded that the judicial use of post-application irrigation in combination with managed spray volumes may be an effective means to attenuate the hazards associated with exposure to volatile and dislodgeable foliar residues following pesticide treatment to turfgrass.

1.6.2. Carbamate Insecticides.

Similar to the OPs, insecticidal carbamates, such as bendiocarb, aldicarb and carbaryl, act by inhibiting acetylcholinesterase (herbicidal carbamates do not), which allows acetylcholine to accumulate at cholinergic junctions (Baron et al., 1991).

Although both OPs and carbamates act as acetylcholinesterase inhibitors, the chemistry of the carbamates is substantially different from OPs. The carbonyl carbon of carbamates attacks the acetylcholinesterase as opposed to the phosphoxon group in OPs and allows the carbamate to be a reversible inhibitor due to its relationship to acetic acid formed during the enzymatic hydrolysis of acetylcholine by acetylcholinesterase.

Bendiocarb was selected for the present study because of its extensive use on turf, low to moderate toxicity (USEPA Toxicity Category II) and for having an intermediate vapor pressure (0.46 mPa at 25 °C) (Extoxnet, 1998). Bendiocarb is used to control a wide range of turfgrass pests, mostly soil dwelling insects (Extoxnet, 1998). It is readily absorbed through the skin, lungs and orally, with skin being the most likely route of exposure. Bendiocarb has an oral LD_{50} value between 35 to 156 mg kg^{-1} for rats (USEPA Toxicity Category I-II, Extoxnet, 1998). Exposure to bendiocarb during higher temperature and humidity poses a greater risk as it is more readily absorbed during these conditions. It does not accumulate in mammalian tissue due to detoxification through xenobiotic metabolism and is rapidly excreted in the urine (Extoxnet, 1998). In research by Clark et al., (2000), bendiocarb application did not elicit an IHQ value above 1.0, however, DHQ values of 0.7, 1.1 and 0.7, were reported at 5, 8 and 27 hrs post-application irrigation, respectively. It is a relatively water-soluble insecticide (260 mg L^{-1}) and was selected to examine its volatility and dislodgeable foliar residues when applied with adjuvants.

1.6.3. Sterol Biosynthesis Inhibiting Fungicides.

Triadimefon and triadimenol (toxic metabolite of triadimefon) are azoles belonging to the class of sterol biosynthesis inhibiting (SBI) fungicides, which have a wide spectrum of uses including fungicides, growth regulators and antidandruff shampoos, etc. (Kramer et al., 1986).

Triadimefon is commonly used on turfgrass and is included in the present study because of its moderate toxicity and an available turfgrass research database (Schumann et al., 2000; Murphy et al., 1996b). Triadimefon has an oral LD_{50} value of 1000 mg kg^{-1} in rats (USEPA Toxicity Category III, Pesticide Manual, 1997) and has a low vapor pressure (0.02 mPa at 25 °C) (Pesticide Manual, 1997). The water solubility of triadimefon is 64 mg L^{-1} making it slightly mobile in soil environments (Pesticide Manual, 1997). Murphy et al., (1996b) determined the greatest level of dislodgeable foliar residues of triadimefon to be 2,230 μg m^{-2} at 3 hrs post-application in the absence of irrigation. The highest calculated IHQ and DHQ values were 0.001 and 0.2, respectively. Using turfed soil cores, Schumann et al., (2000) determined triadimefon to be most associated with the thatch layer following post-application irrigation at 1.3-cm. The concentration in the leaf layer, the most likely source for dermal exposure was 71,890 μg m^{-2}. This amount is 32-fold greater than the amount of triadimefon estimated from dislodgeable foliar residues and indicates that much of triadimefon is taken up by the waxy layer of the turfgrass blades and is not as readily available via dislodgeable foliar residues as determined using H_2O-dampened cheesecloth.

Similar to trichlorfon, triadimefon undergoes a hydrolytic conversion to its breakdown product triadimenol. Triadimenol is a more toxic than triadimefon with an oral LD_{50} of 700 mg kg^{-1} in rats and a very low vapor pressure compared to triadimefon (0.0006 mPa at 25 °C) (Pesticide Manual, 1997). The fate of triadimenol has yet to be examined at different irrigation levels (1.3-cm post-application irrigation was used by

Murphy et al., 1996b and Schumann et al., 2000) to determine if conversion occurs at lower levels of post-application irrigation. Triadimenol has a similar water solubility (62 mg L^{-1} at 25 °C) as triadimefon, making it only slightly mobile in the turfgrass environment (Pesticide Manual, 1997). Research on pesticide runoff found triadimefon and triadimenol to be present in runoff water only after very high irrigation events (much higher rates of irrigation than used in turf management practices, Watschke et al., 2000). Murphy et al., (1996b) examined dislodgeable foliar triadimefon residues without post-application irrigation and found most of the residues to be available in the first 3 days (1, 0.6 and 0.6 % of total applied, respectively) and greatly reduced by Days 5, 7, 11 and 15 (0.04 %, on Day 5 and less than 0.01 % on Day 15). Schumann et al., (2000) examined triadimefon and triadimenol following application using turfed soil cores and determined that triadimefon was completely converted to triadimenol by Day 7. Because most (~80%) of the triadimenol in the thatch, soil, leaf and roots is still present at Day 28, it becomes appropriate to speculate on the fate of triadimenol residues. Do they accumulate with additional applications, and then become mobile during fall and spring recharge?

Because chlorpyrifos, isofenphos, trichlorfon and bendiocarb have DHQ values only slightly above or close to 1.0, it should be possible to attenuate their exposure and reduce their hazard quotients with the aid of management practices on turf including the use of adjuvants, post-application irrigation, and reduced rates of applied pesticides.

Trichlorfon and triadimefon were added to this study primarily to study the conversion in the environment to their more toxic and mobile metabolites, DDVP and triadimenol, respectively. Monitoring the toxic conversion of these two pesticides is necessary due to the proposed management practice of adjusting post-application irrigation.

1.7. Exposure Routes.

In order for toxicants to pass through the epidermis (dermal penetration), they must pass through many layers of dead, densely packed, keratinized cells before coming into contact with the highly vasculated dermis (Klaassen et al., 1986). Dermal penetration for many toxicants (in this case, pesticides) typically occurs by passive transport and depends on the partition coefficient (K_{ow}), with polar pesticides moving through the hydrated stratum corneum and non-polar pesticides using the lipid matrix of the membrane (Emmet et al., 1986). The larger the molecule, the slower and more difficult the passage is through the epidermis (Klaassen et al., 1986). Once in the dermis, the toxicant is passed into the systemic blood system and distributed to organs receiving high levels of blood flow (liver, kidneys, heart, nervous system and brain).

Fortunately, the skin is not usually a highly permeable barrier for many pesticides. For this study, a 10 % dermal penetration factor has been assigned when determining dose in the DHQ assessment. Where human subjects received a direct dermal exposure (0.5 or 5.0 mg kg^{-1}) of chlorpyrifos and urine was collected for 24 hrs following exposure, only 3 % of the total applied chlorpyrifos appeared in the urine as the principle urinary metabolite, 3,5,6-trichloro-2-pyridinol (3,5,6-TCP) (Nolan et al., 1983). Thus, penetration factors are dependent on the physical and chemical properties of each compound and the 10 % value is considered a worst-case scenario for the pesticides examined.

In this study, the pesticides applied have relatively higher vapor pressures (the exception is triadimefon), higher toxicities and intermediate partition coefficients compared to many other pesticides currently used on turfgrass. Therefore, the potential for toxicologically significant exposure via inhalation and dermal penetration is accentuated by the choice of the above test pesticides.

Pesticides that volatilize or form aerosols during application are likely to be taken into the lung due to their particle size (smaller than 1 μm) and penetrate the alveolar sacs. Absorbance is rapid because of the large surface area of the lung (50 to 100 m^2 compared to the skin 2 to 5 m^2) (Klaassen et al., 1986). The alveolar membrane also is very thin, which allows toxicants to pass more easily into the blood stream by passive transport than in the thicker, more keratinous layers of the epidermis. Inhalation of OPs and other volatile insecticides also is a direct penetration event into the pulmonary blood and systemic circulation system without passing through the liver. It is the combination of these factors (large surface area, thin cell layer and direct exposure to systemic circulation) that makes the lung a highly susceptible route of exposure to pesticides.

In order for significant dermal penetration to occur, pesticides must be nonpolar, nonionic and lipid soluble. Pesticides that have intermediate Partition Coefficients (PC) are termed amphipathic. Although the skin is mostly composed of epidermal cells, there are many sebaceous gland cells and hair follicles that provide multiple routes of penetration for these lipophilic and amphipathic pesticides.

The gastrointestinal or oral route is another possibility for pesticides to enter the body, however, it is the least likely route of exposure for golfers and will not be emphasized in this study.

With two probable exposure routes established for OPs and other pesticides, improvements in reducing the volatile and dislodgeable foliar residues of these compounds become imperative. The chemical structures of the pesticides used in this study are given in Figure 1 and physical properties of each in Table 1.

Table 1. Chemical and physical properties of selected pesticides used on turf.

Pesticide	Molecular Weight	Vapor Pressure (mPa, 25 °C)	Water Solubility (mg L^{-1}, 25 °C)	OPP RfD‡ (mg kg^{-1} day^{-1})
Chlorpyrifos	350.6	2.40	1.4	0.003
Trichlorfon	257.4	0.50	120000	0.002
DDVP	221.0	2133	18000	0.0005
Isofenphos	345.4	0.53†	24	0.0005
Bendiocarb	223.2	0.46	260	0.005
Triadimefon	293.8	0.02 †	64	3.0
Triadimenol	295.8	0.0006	62	1.25

† Vapor pressure at 20 °C.
‡ OPP RfD values were taken from the USEPA Office of Pesticide Programs Reference Dose Tracking Report, 4/14/95, and are determined by the no observable effect level (NOEL) values divided by the uncertainty factor.

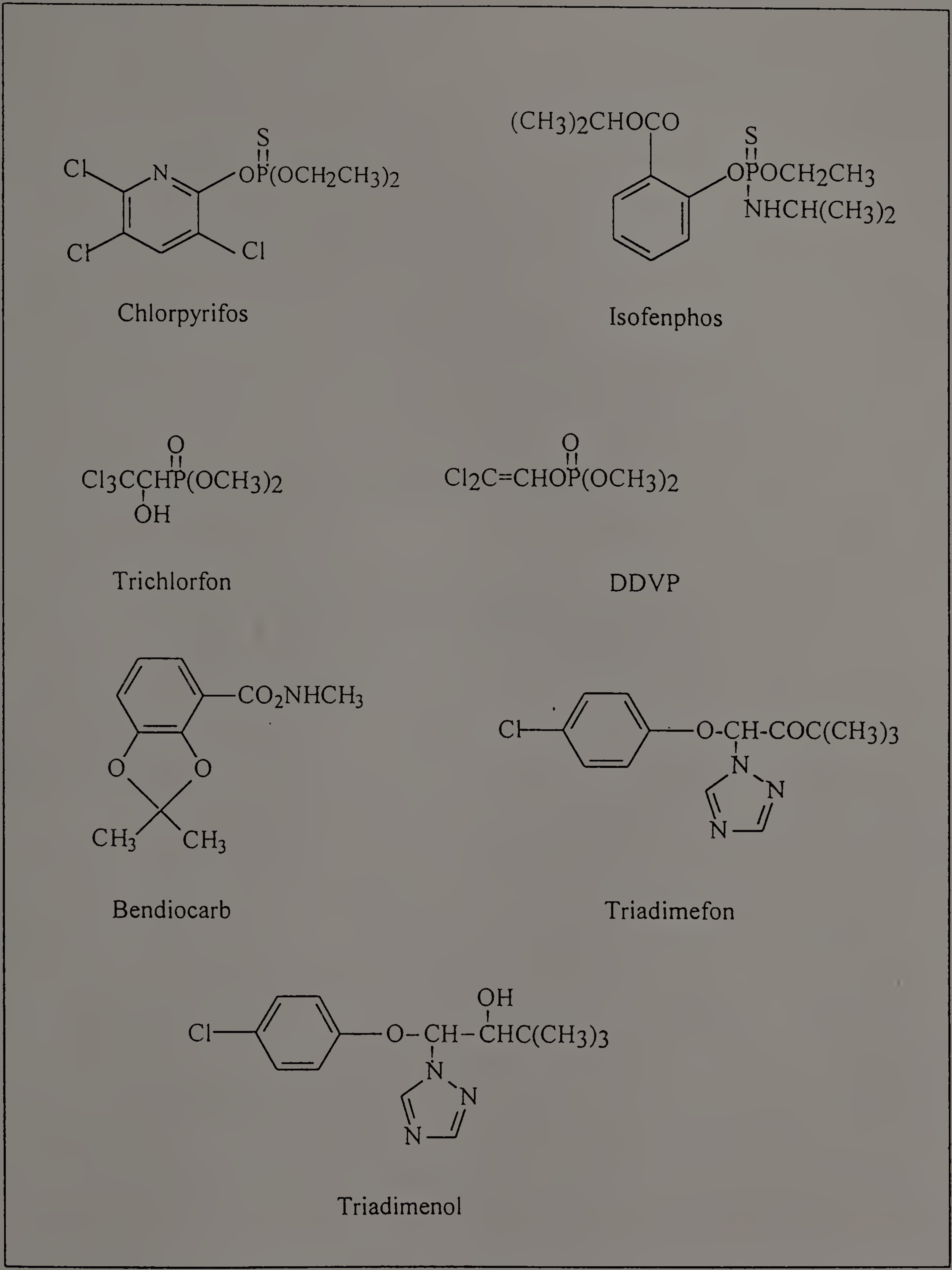


Fig. 1. Chemical structures of pesticides used in this study.

CHAPTER 2

METHODS AND MATERIALS

2.1. Experimental Site.

All pesticide applications made during the summers of 1998 and 1999 took place at the University of Massachusetts Turfgrass Research Center in Deerfield, MA. The 10-meter radius circular plots were seeded with 'Penncross' creeping bentgrass and maintained as golf course fairway, cut at 1.3-cm three times a week and irrigated as needed. The plots were located at least 100 meters apart and marked with turf paint every 50-cm around the circumference.

2.2. Pesticide Applications.

Applications were made to circular turfgrass plots in a manner and at a rate of application commonly used for the selected pesticides on golf courses and according to the manufacturer's instructions. Applications were made between the days when mowing occurred. Two individuals were involved in the application process. One walked with the sprayer made straight passes over the plot while the other monitored the pesticide tank level and aided with the hosing to maintain a constant rate of pesticide application. Pesticide was applied at approximately 4 gallons total water / formulated material per 1000 ft^2. A Rogers Sprayer (Innovative Equipment Inc.), equipped with a wind foil, skirt (Saskatoon, Saskatchewan Canada GF 1500) and six spray nozzles fitted with VisiFlo® Flat Spray Tips (TeeJet® Wheaton, Illinois), was used for all applications. The sprayer pressure was set at typically 35-40 psi. The addition of a skirt to the sprayer aided in reducing pesticide drift and increased the consistency of pesticide applications. A total of 8 applications were made during the summer months of 1998 and 1999.

Sampling occurred following each application for up to one week (see Tables 2 and 3 for sampling schedule for years 1 and 2, respectively). Applications were timed at least two weeks apart to reduce the possibility of residue carry-over and to reduce the possibility of turf damage (greater risk when using multiple pesticides in tank mixtures). Presamples were not included because five years of research data determined only non-detectable levels occurred at the site (Murphy et al., 1996ab and Clark et al., 2000).

2.3. Formulations and Spray-tank Adjuvants.

2.3.1. Year 1 (1998).

Formulated pesticides were applied in 13.5 gallons (51.1 L) of water to each plot. Tank mixtures consisted of 18.75 fl oz (555 mL) of Dursban Pro® (22.5 % active ingredient, chlorpyrifos, O, O-diethyl O-3, 5, 6-trichloro-2-pyridyl phosphorothioate), 11.25 fl oz (333 mL) of Oftanol ® 2 (22 % active ingredient, isofenphos, O-ethyl O-2 isopropoxycarbonylphenyl isopropylphosphoroamidathioate) and 0.470 lbs (213 g) of Turcam® (76 % active ingredient, bendiocarb, 2,3-isopropylidenedioxyphenyl methylcarbamate) per 15 gallons (57 L) of water. The adjuvant, Silwet L-77® (Witco), was added to one of the two tank mixtures for paired plot application at a rate of 0.1 % (v/v). There were a total of 8 applications (4 with and 4 without adjuvant), alternating between plots. Following pesticide application, either 0.63- (weeks 1 and 2) or 1.3-cm (weeks 3 and 4) post-application irrigation was applied to examine volatile and dislodgeable foliar loss. Each application was followed by one week of volatile and dislodgeable residue sample collection (Table 2). A total of 264 samples were collected from the 8 applications.

2.3.2. Year 2 (1999).

Formulations of chlorpyrifos, isofenphos, trichlorfon and triadimefon were applied in the same manner as for Year 1 applications except pesticides rates were reduced to 1/2 and 1/4 of the full label rates of the pesticides used in Year 1. Following pesticide application, 0.63- and 0.32-cm post-application irrigation was applied. Each tank mixture consisted of 1/2 or 1/4 full-rates of pesticides formulations as follows: 9.4 or 4.7 fl oz (278 or 138 mL) of Dursban Pro® (chlorpyrifos); 5.6 or 2.8 fl oz (166 or 82 mL) of Oftanol® 2 (isofenphos), 0.47 or 0.24 lbs (213 or 110 g) of Dylox® 80 (80 % active ingredient, trichlorfon, dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate) and 0.25 lbs / 0.13 lbs (113 or 59 g) of Bayleton® 25 (25 % active ingredient, triadimefon, 1-(4-chlorophenoxy)-3,3-dimethyl-1- (1H-1, 2, 4-triazol-1-yl) butan-2-one). respectively, per 15 gallons of water. A total of 180 samples were collected from the 8 applications (Table 3).

Table 2. A 24 hr sampling schedule for turfgrass pesticide applied from 7/98 - 9/98 (Year 1).

Day 1	Days 2 & 3	Days 5 & 7
Volatile Residues		
0700-0800 Application	0700-1100 # 5	1100-1500 # 8
0800-0900 #1 Air Sample	1100-1500 # 6	
0900-1100 #2	1500-1900 # 7	
1100-1500 #3		
1500-1900 #4		
Dislodgeable Foliar Residues		
0700-0800 Application	1200 #4 & #5	1200 #6 & #7
0815 # 1 Cheesecloth Wipe		
1000 # 2 (2 hrs. Post Application)		
1300 #3 (5 hrs. Post Application)		

Table 3. A 24 hr sampling schedule of pesticide applications from 7/99 - 9/99 (Year 2).

Day 1 (Presample)	Day 2	Day 3 & 4
Volatile Residues		
1100-1300 #1	0700-0800 Application	0700-1100 #6
	0800-0900 #2 Air Sample	1100-1500 #7
	0900-1100 #3	1500-1900 #8
	1100-1500 #4	
	1500-1900 #5	
Dislodgeable Foliar Residues		
1200 #1	0700-0800 Application	1200 # 5 & 6
	0815 #2 Cheesecloth Wipe	
	1000 #3 (2 hrs. Post Application)	
	1300 #4 (5 hrs. Post Application)	

2.4. Post-application Irrigation.

Post-application irrigation levels were applied by adjusting the time allowed for the water irrigation system to pass over the turf plots at a specific flow rate. An interval of 15 min delivered approximately 0.63-cm of water level using a Toro™ irrigation system. Irrigation was administered to the plots immediately following pesticide applications (approximately 2-3 min following application). Irrigation over 3 different time intervals, 7.5, 15, and 30 min, delivered 0.32, 0.63, and 1.3-cm, respectively. No additional irrigation was applied to the plots during the first day (Day 1) following the initial post-application irrigation event. In the following days, plots were irrigated as often as necessary to avoid drought stress.

2.5. Volatile Residues.

Pesticide volatility ($\mu g\ m^{-3}$) was measured with a single TF1A high-volume air sampler (Staplex Co., Brooklyn, NY) placed in the center of the circular plot using the methodology of Kilgore et al., (1984) as modified by Murphy et al., (1994). The air sampler cartridge was filled with approximately 150 mL of acetone / soxhlet-extracted (6-8 hrs) XAD-4 resin (Rohm and Haas). The Theoretical Profile Shape (TPS) method of Wilson et al., (1982) was used because of the simplicity of determining source flux from a relatively small area, which allows reproducibility and requires only a single wind speed measurement from the center of the plot. A more detailed examination of the validity for flux determination from turfgrass using this model has been reviewed previously (Jenkins et al., 1990, Murphy et al., 1993, and Clark et al., 2000).

A single air sampler was suspended at the center of a plot on a cross bar positioned at a ZINST (z-intercept) value of 70 cm above the soil surface using Wilson's equation (1982) for our plot conditions (10 m radius and having a roughness height of 0.2

cm). Ambient air was drawn through the air sampler at an average rate of 0.8 m^3 min^{-1}. The atmospheric wind speed was determined and used to estimate the horizontal source flux or trajectory. Horizontal source flux in this case is defined as the product of the atmospheric wind speed times the pesticide air concentration in air above the center of the designated plot. Although source flux was determined for modeling purposes (see Haith et al., 2000), results from the volatile samples (μg in the air for a 4 hr sampling period) were used to determine the pesticide concentration (μg m^{-3}) and to calculate IHQs. The maximum amount of pesticide residue per hr collected over the entire sampling period was used to determine the IHQ for that application.

Following volatile sample collection, the resin was removed from the packed cartridges and placed into a 500 mL Erlenmeyer flask. Approximately 150 mL of acetone was added to the flask, sealed with Teflon tape and shaken for 1 hr on a wrist-action shaker. The resin slurry was filtered through Whatman # 1 filter paper contained in a large glass funnel and rinsed with 3 x 50 mL portions of acetone into a 500 mL amber jar (Fisher Scientific). Extracts were pooled, placed in a refrigerator until the end of each day and transported to the MA Pesticide Analysis Laboratory (MPAL) where they were freezer stored at -15 °C until analysis.

Weather data were collected using a CR10 storage module data logger, equipped with wind speed, wind direction, temperature, solar radiation and rain fall sensors from Campbell Scientific Inc (Logan, UT). Data from the storage module were transferred to a spreadsheet program (Excel, Microsoft) for storage and analysis. Two weather stations were used, one on each plot. On plot I, wind speed, wind direction, solar radiation, rainfall and both surface and air temperature were measured. Because plot II was located close to trees and a road, a separate weather station was used to account for a possible difference in wind vectors. Only wind speed and surface temperature probes were measured at this site. Weather data were transferred from data modules to a computer at MPAL. Wind speed measurements were used in determining source flux of volatile compounds using the TPS model. Pesticide applications were scheduled when weather was predicted to be seasonal and steady for several days.

2.6. Dislodgeable Foliar Residues.

Dislodgeable foliar residues samples were collected by wiping dH_2O-dampened (distilled, de-ionized water, ddw) 9 x 23 cm pieces of cheesecloth (Fisher Scientific) onto randomly selected 30 x 30 cm sections of pesticide-treated turfgrass. Three replicates samples were collected from each plot for each collection day. The dampened cheesecloth was transferred to a 500 mL Erlenmeyer flask, sealed with Teflon tape, 150 mL of acetone was added, and the flask was shaken for 1 hr using a wrist-action shaker. The extract was filtered into a 500 mL amber jar via Whatman # 1 filter paper. The flask, filter paper and cheesecloth were sequentially rinsed three times with 30-40 mL portions of acetone, which were combined with the initial extract. Foliar residue extracts were freezer stored at -15 °C.

2.7. Residue Analysis.

Both volatile and dislodgeable foliar residues extracts were solvent-reduced before being analyzed. Each 500 mL amber jar, which contained 200-300 mL of acetone and pesticide residue, was brought to room temperature and solvent-reduced in a Turbo-Vap (Zymark©, Hopkinton, MA) to 1 mL. The reduced extracts were quantitatively transferred in acetone to a 10 mL centrifuge tube and brought to 50, 10 or 6 mL final volumes. The actual final volume was dependent on the time over which the sample was collected and whether it was a volatile or dislodgeable foliar sample.

2.7.1. Group 1 Analytes: Chlorpyrifos, Isofenphos, and Bendiocarb.

Group 1 pesticides were analyzed simultaneously using a Hewlett Packard 5890 Gas Chromatograph (GC) equipped with a Mass Selective Ion Detector (MSD). Initially, breakdown of bendiocarb occurred during the temperature program, making extrapolation more difficult. Introduction of a pressure-pulse program (see below) after each injection in the temperature program reduced this breakdown (see chromatograph in Appendix 1 to view eluted compounds.) Each extract was filtered through a 0.45 μm filter, GelmanSciences (Ann Arbor, MI) before being quantitatively transferred to an auto sampler vial for instrumental analysis. The GC temperature settings were as follows; inlet 200 °C, detector 280 °C, with an initial holding temperature of 100 °C for 1 min, increasing at 15°C min^{-1} up to 300 °C and held for a final 8.67 min interval. The pressure pulse program was as follows; initial pressure of 10.9 psi, ramped up to 40 psi at a rate of 90 psi min^{-1} for 30 sec, and back to the initial rate of 10.9 psi at the end of the run. Compounds were analyzed in the selective ion mode (SIM) using the mass ions: 126, 151 and 223 for bendiocarb; 197,199 and 314 for chlorpyrifos; and 121, 213 and 255 for isofenphos (see chromatographs, Appendix 1 and 2). The carrier gas (He) flow rate was 0.86 mL min^{-1}. The limit of detection (LOD) was set at 0.25 μg mL^{-1} for bendiocarb, isofenphos, and chlorpyrifos, and the limit of quantitation (LOQ) was 1.25 μg.

2.7.2. Group 2 Analytes: Trichlorfon and DDVP.

Trichlorfon was analyzed separately because it degraded to DDVP during standard Group 1 analysis conditions. Because we wished to monitor and determine trichlorfon and DDVP, a new method was developed. Both trichlorfon / DDVP residues were analyzed on a Hewlett Packard 5890 GC equipped with a flame photometric detector (FPD) and a short 5 m x 0.53 mm I.D. silicone test column, (2.65 µm film thickness, Hewlett Packard). The GC temperature settings were as follows; inlet 125 °C, detector 250 °C, with an initial holding temperature of 50 °C for 1 min, increasing at 10 °C min^{-1} to 125 °C and held for 1 min interval, then increasing at 30 °C min^{-1} to 220 °C and held for 1 min. An injection volume of 3 µL was used. Breakdown of the standards during initial trial runs indicated an unclean injection port that caused trichlorfon to be partially converted to DDVP. This unwanted feature was remedied by changing the septa, seal or sleeve. A cyclosplitter sleeve (Hewlett Packard) was more effective than other inlet sleeves in preventing trichlorfon breakdown. Sleeves were sonicated in acetone for up to 30 min, returned to the injection port and the injection port temperature was increased to 250 °C for 1 hr. The carrier gas (He) flow rate was 14.3 mL min^{-1} and the detector gases were H_2 and O_2 were 3 and 14 mL min^{-1}. The LOD was set at 0.5 µg mL^{-1} for trichlorfon, DDVP, chlorpyrifos and isofenphos and the LOQ was 2.5 µg. (see chromatograph, Appendix 3).

2.7.3. Group 3 Analytes: Triadimefon and Triadimenol.

Triadimefon and triadimenol were analyzed separately on a Hewlett Packard 6890 GC equipped with a nitrogen phosphorous detector (NPD) and a 30 m x 0.25 mm I.D. DB-200 column (0.25 µm film thickness, J&W Scientific Inc., Folsom, CA). The GC temperature settings were as follows; inlet 250 °C with 26.27 psi, detector at 250 °C, and the initial holding temperature of the column of 130 °C for 1 min, increasing at 8 °C min^{-1} up to 180 °C and held for a 1 min interval, then increased at 8 °C min^{-1} to 250 °C. The carrier gas (He) flow rate was 2.0 mL min^{-1}. The detector gases, H_2 and O_2 were 3.0 and 600 mL min^{-1}, respectively. The makeup gas (N_2) was 10 mL min^{-1}. (See chromatograph, Appendix 4). The injection volume was 1 μL using a 7673 Hewlett Packard series injector. The LOD was 0.1 μg mL^{-1} for triadimefon, triadimenol, chlorpyrifos and isofenphos (Year 2 analysis) and the LOQ was 0.5 μg.

2.7.4. Quantification.

All compounds were quantified using a 4-5 point standard curve (0.1, 0.5, 2.5, 5.0 and 10.0 μg mL^{-1}). The concentration of low standard for each pesticide was set at a five to one signal peak to baseline noise ratio and was dependent on the sensitivity of the instrument being used.

2.8. Volatile Residue Calculations and Source Flux.

2.8.1. High Volume Air Sampling and Volatile Residue Determination.

The flow rates from the high volume air samplers (ft^3 min^{-1}) were multiplied by the total minutes of air sampling and then by 0.0283 (a conversion factor) to give a total volume of air sampled as cubic meters (m^3) (Eq [2]). As mentioned previously, volatile residue sample extracts were reduced to either 10 or 6 mL to determine the final amount of the analyte (μg) collected from each sampling period. The amount of analyte was then divided by the result of the cubic meter calculation to yield a final pesticide concentration (C) in μg m^{-3} in the sample to be used in the Source Flux and IHQ determinations (Eq [3]).

[2] $31\ ft^3\ min^{-1}$ x $0.0283\ m^3\ ft^{-3}$ x 240 min = $210.550\ m^3$ of air per 4 hour sampling period.

[3] 22 μg / $210.55\ m^3$ = $0.105\ \mu g\ m^{-3}$ = final pesticide concentration (C) in the sample.

2.8.2. Source Flux using Theoretical Profile Shape (TPS) Method.

Using the TPS method from Wilson et al., (1982), a 10-meter radius plot with a roughness height (average difference in the height of turfgrass blades) of 0.2 cm and a ZINST height (air sampling height) of 70 cm has a calculated normal horizontal flux (NHF) value of 2.9 when determined under neutral or unstable atmospheric conditions. Neutral conditions are described as periods of daytime cloudiness in the early morning and late afternoon and on clear days when the wind speed is > 2.0 m s^{-1}. Unstable conditions are defined as sunny to partly cloudy with wind speeds < 2.0 m s^{-1}. A NHF value of 2.0 is used for stable atmospheric conditions. All experimental sampling periods in the current study were defined as unstable or neutral. Source flux [$F_z(0)_{field}$] is calculated by first multiplying wind speed (S) in m s^{-1} by the pesticide concentration (C) in ug m^{-3} then dividing by Wilson's NHF value of 2.9 (Eq. [4]). Results of source flux ($F_z(0)_{field}$) were given as μg $m^{-2}\ s^{-1}$ Eq. [5].

[4] $$F_z(0)_{field} = (SC / NHF)$$

[5] $$F_z(0)_{field} = \mu g\ m^{-2}\ s^{-1}$$

Source flux was finally converted to micrograms per square meter per hour by Eq [6] to compare air concentration in an hour of sampling (source flux, see below).

[6] $$\mu g\ m^{-2}\ s^{-1} \times 3600\ s\ h^{-1} = \mu g\ m^{-2}\ h^{-1}$$

2.8.3. Exposure and Hazard Quotient Determinations.

Determinations of volatile pesticide residue concentrations from the high volume air samples (Eq. [3]) were used to calculate the daily inhaled dose (D_i, ug kg^{-1}) of pesticide (Eqs. [7]).

[7] $$C \times R \times 4\ hr / 70\ kg = D_i$$

where C = measured pesticide concentration in air ($\mu g\ m^{-3}$) at 70 cm above the center of the circular plot, R = breathing rate for a human during moderate activity (2.5 $m^3\ h^{-1}$), (USEPA Exposure Factors Handbook, 1989), and the exposure time was set at 4 hrs for an average round of golf, divided by 70 kg (average adult weight). The calculated D_i is divided by the USEPA assigned chronic reference dose (RfD) for that specific pesticide (see explanation of NOELs and RfDs, section 2.8.2.) to yield the IHQ value (Eq. [8]) for estimating potential human risk.

[8] $$D_i / RfD = IHQ$$

2.9. Dislodgeable Foliar Residue and Dermal Hazard Quotient Determinations.

2.9.1. Dislodgeable Foliar Residues.

Dislodgeable foliar residue concentrations (F_r) are determined from extracted cheesecloth samples as previously described. Analytical results are given as $\mu g\ mL^{-1}$ and multiplied by the total volume (mL) to give a sample concentration of dislodgeable foliar residue as μg ft^{-2}. This value was divided by 0.0929 to convert μg ft^{-2} to μg m^{-2} (Eq. [9]). Typically, three dislodgeable foliar residue samples were collected from each plot in a sampling period. A total of six samples (combining replicates from other sampling week) were averaged before calculating DHQ values. The average of the dislodgeable foliar residue from (Eq. [9]) was used to calculate the daily dermal dose (D_d) using Eqs. [10] and [11], where S = the dislodgeable foliar residue concentration (F_r) multiplied by the dermal

[9] Dislodgeable Foliar Residue (F_r) = 39 μg ft^{-2} / 0.0929

$$F_r = 427\ \mu g\ m^{-2}$$

[10] $$S = (F_r = 427\ \mu g\ m^{-2}) \times (\text{Transfer Coefficient} = 0.5\ m^2\ h^{-1})$$

[11] $$S \times P \times 4\ h / 70\ kg \times 1000\ \mu g\ mg^{-1} = D_d$$

transfer coefficient of 0.5 m^2 h^{-1} (Zweig et al., 1985), multiplied by P = the dermal permeability of 0.1 (10% USEPA estimation, 1993), multiplied by 4 hours (time to complete a typical 18-hole round of golf) and divided by 70 kg and 1000 μg mg^{-1}. The dermal dose (D_d) (Eq. 11) is then divided by the Rfd resulting in the Dermal Hazard Quotient (DHQ) (Eq. [12]).

[12] $$D_d\ /\ Rfd = DHQ$$

2.9.2. NOELs and Chronic Reference Doses.

NOELs are the no observable effect levels based on available chronic toxicological data where an amount of pesticide per unit of weight (usually mg kg^{-1}) of the test subject's body weight has no observable adverse effect when a test subject is exposed to this amount on a daily basis over their lifetime. Chronic reference doses (RfDs) are estimated by the USEPA using existing NOEL values and are dependent on the amount and quality of available toxicity data. RfD values are determined by dividing NOELs by uncertainty factors. Uncertainty factors are assigned by the USEPA in multiples of 10 (10, 100, 1000, etc.) depending on the completeness of the human toxicity data set.

2.9.3. Data Analysis and Statistical Treatment.

Source flux and dislodgeable foliar residues concentrations of different treatments were compared between the same sampling intervals using an unpaired t-test ($P < 0.05$, for source flux and $P < 0.025$ for dislodgeable foliar residues, Excel, Microsoft). If all the sampling intervals were significantly different between treatments on Day 1, the treatments were considered determined as either significantly reduced or increased in the results section.

To make overall comparisons between treatments over the entire experimental intervals, the $\sum$ (sum) of IHQ and DHQ values ($\sum$ IHQ, $\sum$ DHQ) over the 7-day (Year 1) or 3-day (Year 2) sampling intervals as well as the percent loss of total applied pesticide were calculated. However, volatile residues were sampled continuously (0700-1900 hrs) and dislodgeable foliar residues were collected only at selected sampling intervals, typically the hottest times of the day (1200 hrs) and do not represent the average dislodgeable foliar residues over the entire day. Therefore, $\sum$ IHQ, $\sum$ DHQ and the percent loss of total applied cannot be compared between each sampling type (source flux versus dislodgeable foliar residues) but can only be used to gauge relative trends, increases or decreases, in volatile or dislodgeable foliar residues, respectively.

2.10. Chemicals Supplies.

2.10.1. Analytical Pesticide Standards.

Standards for the pesticides, chlorpyrifos, isofenphos. trichlorfon, dichlorvos (DDVP) and bendiocarb, were received from the USEPA (Beltsville, MD). Chlorpyrifos was 99 % pure. Isofenphos was 92 % pure liquid. Trichlorfon was 98 % pure. Bendiocarb was 99 % pure. Triadimefon was received from Mobay and was 98 % pure. Dichlorvos (2,2-dichlorovinyl dimethyl phosphate) was 99 % pure liquid form.

2.10.2. Solvents.

Pesticide-grade acetone was the solvent used for all extraction and chromatography purposes and was purchased from Fisher Scientific Company (Springfield, NJ).

2.10.3. Preparation of XAD-4 Resin.

Before use, XAD-4 resin was processed to remove the impurities, which can interfere with instrumental analysis. The resin is shipped in a sodium chloride and sodium bicarbonate salts buffer (pH 10.6), which retard microbial growth. The resin was cleaned by placing 700-1200 mL of resin into a 2.0 L Erlenmeyer flask and filling it with distilled water. The slurry was magnetically stirred and a 40 % HCl solution was added drop wise until the solution pH was approximately 5.6. The slurry was set aside until the water and resin separate, and the water was siphoned off. The resin was rinsed 2-3 times with distilled water to remove most of the storage salts and acidic water. The resin was filtered through Whatman # 1 filter paper, rinsed with 3 x 50 mL portions of acetone to remove any residual water and air dried over night. The acid-washed resin was soxhlet extracted with acetone for 6-8 hrs and fully air-dried before being used in the air sampler cartridges.

Pesticide breakthrough studies of XAD-4 resin were carried out to determine possible pesticide loss over a 4 hr sampling period. Two mL acetone aliquots containing 200, 50 and 10 μg of pesticides were applied to 120 mL portions of XAD-4 resin. The acetone was allowed to evaporate and the spiked resin portions were used to fill the cartridges. After attaching the cartridge to a high volume air sampler, the sampler was run for 3 hrs. Resin spiked samples were transferred to 500 mL Erlenmeyer flasks and extracted with acetone as previously described above.

CHAPTER 3

RESULTS

3.1. Method Validation.

Breakthrough studies of XAD-4 resin amended with a range of concentrations (50, 100, and 200 μg) of the test pesticides yielded the following average recoveries: 78.5 % for chlorpyrifos (n = 10) with a S.D. of ± 12.1 %; 83.4 % for isofenphos (n = 8) with a S.D. of + 12.8 %; 98 % for bendiocarb (n = 6) with a S.D. of ± 14.2 %; 88 % for trichlorfon (n = 8) with a S.D. of ± 10.5 %; 79.2 % for triadimefon (n = 5) with a S.D. of ± 4.0 %; 62.5 % for DDVP with a S.D. of ± 5.1 %; and 72% for triadimenol with a S.D. of ± 11.8 %. Pesticide-fortified cheesecloth samples (n = 3) yielded the following average recoveries: 104 % for chlorpyrifos (all pesticides with three triplicates) with a S.D. of ± 11.3 %; 91.7 % for isofenphos with a S.D. of ± 11.8 %; 99.0 % for bendiocarb with a S.D. of ± 15.2 %; 97.3 % for trichlorfon with a S.D. of ± 4.5%; 98 % for triadimefon with a S.D. of ± 8.6 %; 95.5 % for DDVP with a S.D. of ± 8.3 % and 100.3 % for triadimenol with a S.D. of ± 5.2 %.

Daily performance amendments were made to resin at 50, 100, and 200 μg (high for first day, lower for the consecutive days) and resulted in the following average recoveries: 91.2 % for chlorpyrifos with a S.D. of ± 19.5 %; 86.0 % for isofenphos with a S.D. of ± 9.5; 90.7 % for bendiocarb with a S.D. of ± 12.5 %; 93.4 % for trichlorfon with a S.D. of ± 4.5 %; 102.1 % for triadimefon with a S.D. of ± 12.3 %; 84.3 % for DDVP with a S.D. of ± 2.6 % and 86.6 % for triadimenol with a S.D. of ± 3.7 %. Daily performance amendments of pesticide to cheesecloth resulted in the following average recoveries: 86 % for chlorpyrifos with a S.D. of ± 12.0 %; 83.9 % for isofenphos with a

S.D. of $\pm$ 11.3 %; 100.4 % for bendiocarb with a S.D. of $\pm$ 16.2 %; 93.8 % for trichlorfon with a S.D. of $\pm$ 5.2 %; 93.0 % for triadimefon with a S.D. of $\pm$ 9.4.0 %; 91 % for DDVP with a S.D. of $\pm$ 6.4 %; and 98.4 % for triadimenol with a S.D. of $\pm$ 7.3 %.

Standard curves were constructed before and after each daily analysis using a set of pesticide standards (10, 5, 2.5, 0.5, 0.1 μg mL^{-1}). The calibration curve ($r^2 > 0.998$ being acceptable for quantitation) was used to estimate pesticide concentration of the collected field samples. The limit of detection (LOD) ranged from 0.1 to 0.2 μg mL^{-1} and depended on the signal to noise ratio (typically 5 to 1) for the detector. The limit of quantitation (LOQ) ranged from 0.5 to 0.8 μg mL^{-1}. Before instrumental analysis, samples were reduced to not less than 5 mL (on Days 5 and 7 in Year 1 and Day 3 in Year 2), which resulted in concentrations greater than the LOD for each instrument to avoid background interferences contained in the volatile and dislodgeable foliar residue samples.

3.2. Effect of Silwet L-77 and Post-application Irrigation on Inhalation and Dermal Hazard Quotients.

3.2.1. Volatile Residues.

3.2.1.1 Chlorpyrifos. Overall, the volatilization of chlorpyrifos as measured by source flux was most prevalent immediately following application and irrigation (Figs. 2A and 3A). Volatile chlorpyrifos residues decreased over time in a diurnal pattern on Days 1 through 3 and then became much less pronounced over the remainder of the 7-day experiment. At no time in any experiments did the IHQ values determined from volatile chlorpyrifos residues exceed 1.0 (Figs. 2B and 3B).

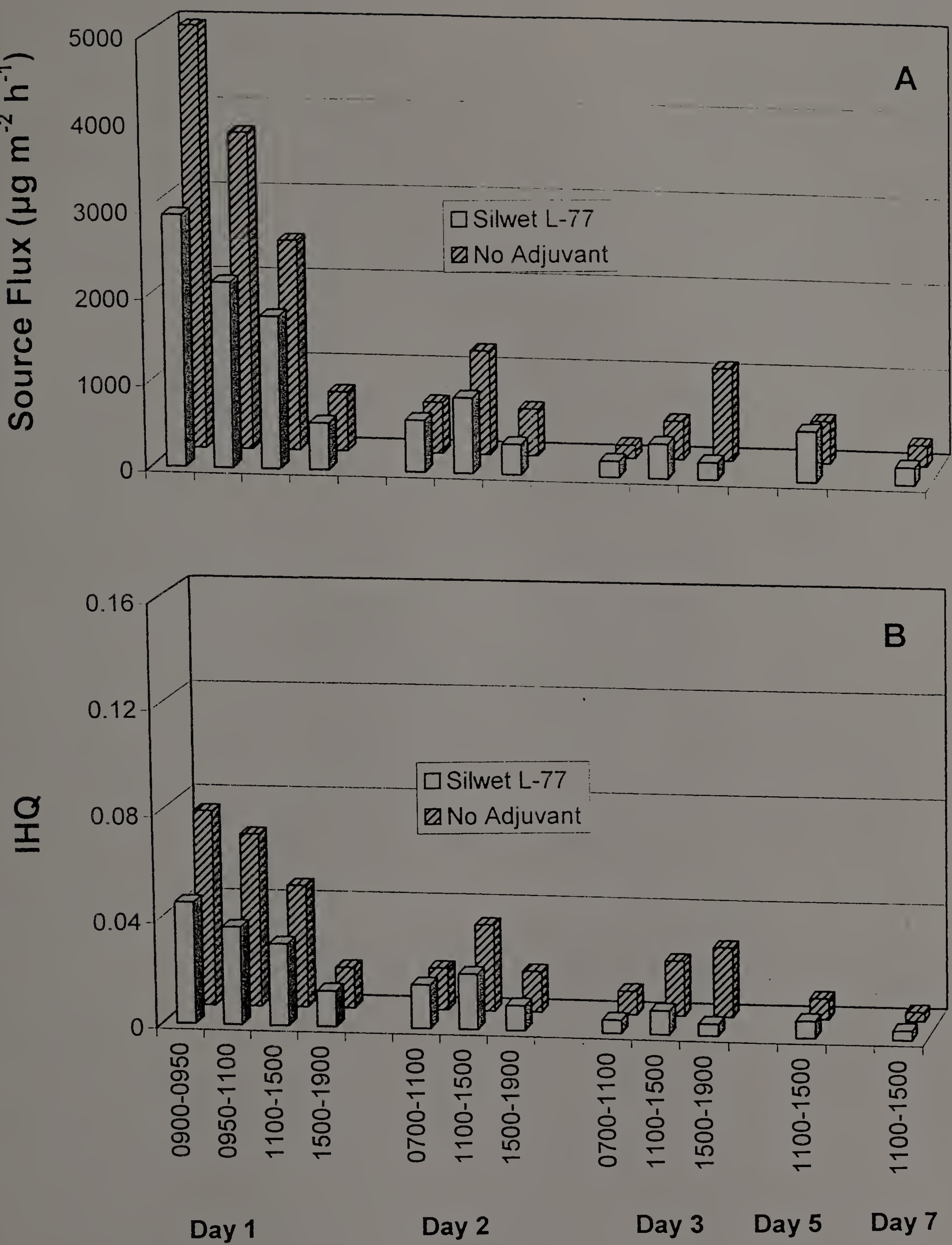


Figure 2. Source flux (panel A) and inhalation hazard quotient (IHQ, panel B) determinations over a 7-day period following application with full-rate chlorpyrifos, 0.63-cm post-application irrigation and with and without Silwet L-77. Values not significantly different at the 0.05 level.

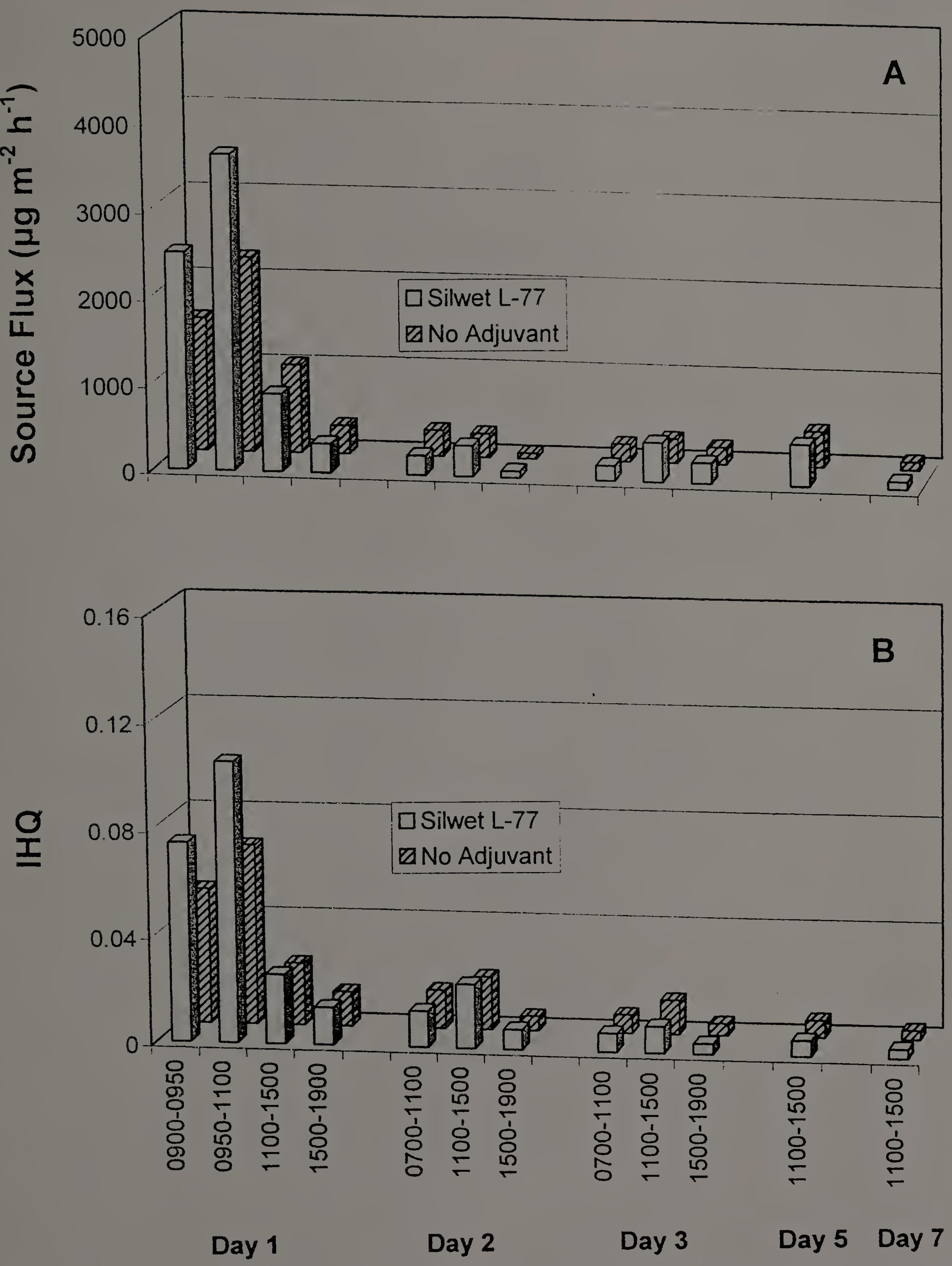


Figure 3. Source flux (panel A) and inhalation hazard quotients (IHQ, panel B) determinations over a 7-day period following application with full-rate chlorpyrifos, 1.3-cm post-application irrigation and with and without Silwet L-77. Values not significantly different at the 0.05 level.

There was no consistently significant reduction in the level of volatile residues following the application of full-rate chlorpyrifos in the presence of 0.1 % (v/v) Silwet L-77 compared to applications without adjuvant at either the 0.63- (Fig. 2A, t-test, $P > 0.05$) or 1.3-cm post-application irrigation treatment (Fig. 3A, t-test, $P > 0.05$). However, volatile residues generally were decreased following the higher rate (1.3-cm) of post-application irrigation, particularly in the absence of adjuvant. Overall, the percent loss of total applied chlorpyrifos as volatile residues in the presence of 1.3-cm post-application irrigation was reduced 2.4-fold compared to the loss following 0.63-cm irrigation (Table 4). In the presence of Silwet L-77, percent loss of total applied chlorpyrifos as volatile residues were increased some 1.2-fold following 1.3-cm post-application irrigation but decreased 1.4-fold following 0.63-cm post-application irrigation compared to the respective applications made without adjuvant (Table 4).

The highest level of volatile chlorpyrifos occurred without Silwet L-77 during the first hour following 0.63-cm post-application irrigation (0900-0950 hr, Fig. 2A). During this interval, the chlorpyrifos source flux was 5000 $\mu g\ m^{-2}\ h^{-1}$ (1.1 % of total applied) and resulted in an IHQ value of 0.08 (Fig. 2B). The loss of volatile chlorpyrifos residues on Day 1 at 1.3-cm irrigation was 3.0 and 2.5 % of the total applied, with and without adjuvant, respectively (Table 4). The highest level of volatile chlorpyrifos when applied with Silwet L-77 in the presence of 1.3-cm post-application irrigation occurred between 0950-1100 hrs and resulted in a source flux of 3600 $\mu g\ m^{-2}\ h^{-1}$ (Fig. 3A, 1.1 % of total applied) and an IHQ value of 0.1 (Fig. 3B).

Table 4. The summation of percent loss of total applied pesticide over the entire sampling period (7 days with or without Silwet L-77, and 3 days for 1/2 and 1/4 full-label rates of pesticide application).

Pesticide and residue type	Percent Loss of Total Applied Pesticides							
	1.3-cm[†]		0.63-cm		0.63-cm		0.32-cm	
	Full[‡]	Full	Full	Full	1/2	1/4	1/2	1/4
	+[§]	-	+	-	-	-	-	-
Chlorpyrifos								
Dislodgeable	0.36	0.39	0.57	0.36	0.38	0.38	0.49	0.59
Volatile	5.17	4.41	7.35	10.60	6.91	13.78	4.14	12.93
Isofenphos								
Dislodgeable	0.39	0.48	0.75	0.66	0.22	0.27	0.32	1.01
Volatile	1.75	0.63	0.78	1.21	0.70	1.24	0.65	0.90
Bendiocarb								
Dislodgeable	0.69	0.37	1.01	1.00	---	---	---	---
Volatile	1.63	1.73	1.75	2.53	---	---	---	---
Trichlorfon								
Dislodgeable	---	0.77	---	---	0.66	1.15	1.13	2.04
Volatile	---	4.81	---	---	1.08	2.33	1.11	3.15
DDVP								
Dislodgeable	---	0.18	---	---	0.00	0.00	0.00	0.00
Volatile	---	5.64	---	---	0.86	1.76	1.05	1.18
Triadimefon								
Dislodgeable	---	---	---	---	0.26	0.40	0.35	0.61
Volatile	---	---	---	---	1.00	3.06	0.98	3.55
Triadimenol								
Dislodgeable	---	---	---	---	0.17	0.30	0.11	0.35
Volatile	---	---	---	---	0.00	0.00	0.00	0.00

† Post-application irrigation rate (1.3-, 0.63- or 0.32-cm).
‡ Pesticide treatment rate at full-, 1/2 full-, or 1/4 full-label rates used on turfgrass (see section 2.3 for full-rate amounts used).
§ Silwet L-77 treatment (+). No treatment (-).

3.1.1.2. Isofenphos. Overall, the volatilization of isofenphos as measured by source flux was most prevalent immediately following application and irrigation. Volatile isofenphos residues decreased over time in a diurnal pattern on Days 1 through 3 and then became much less pronounced over the remainder of the 7-day experiment. At no time in any experiments did the IHQ values determined from volatile isofenphos residues exceed 1.0 (Figs. 4B and 5B).

There was no consistently significant reduction in the level of volatile residues following the application of full-rate isofenphos in the presence of 0.1% (v/v) Silwet L-77 compared to applications without adjuvant at either 0.63-cm (Fig. 4A, t-test, $P > 0.05$) or the 1.3-cm post-application irrigation treatment (Fig. 5A, t-test $P > 0.05$). However, volatile residues generally were decreased following the higher rate (1.3-cm) of post-application irrigation, particularly in the absence of Silwet L-77. Overall, the percent loss of total applied isofenphos as volatile residues was reduced 1.9-fold compared to the loss following 0.63-cm post-application irrigation. In the presence of Silwet L-77, percent loss of total applied isofenphos as volatile residues was increased some 2.8-fold following 1.3-cm post-application irrigation but decreased 1.6-fold following 0.63-cm post-application irrigation compared to the respective applications made without adjuvant (Table 4).

The highest level of volatile isofenphos occurred during the first hour following application without Silwet L-77 and with 0.63-cm post-application irrigation (0950-1100 hrs, Fig. 4A). During this interval, the isofenphos source flux was 922 $\mu g\ m^{-2}\ h^{-1}$ (0.5 % of total applied) and resulted in an IHQ value of 0.07 (Fig. 4B). The volatile loss of isofenphos residues on Day 1 at 1.3-cm irrigation was 0.9 and 1.2 % of the total

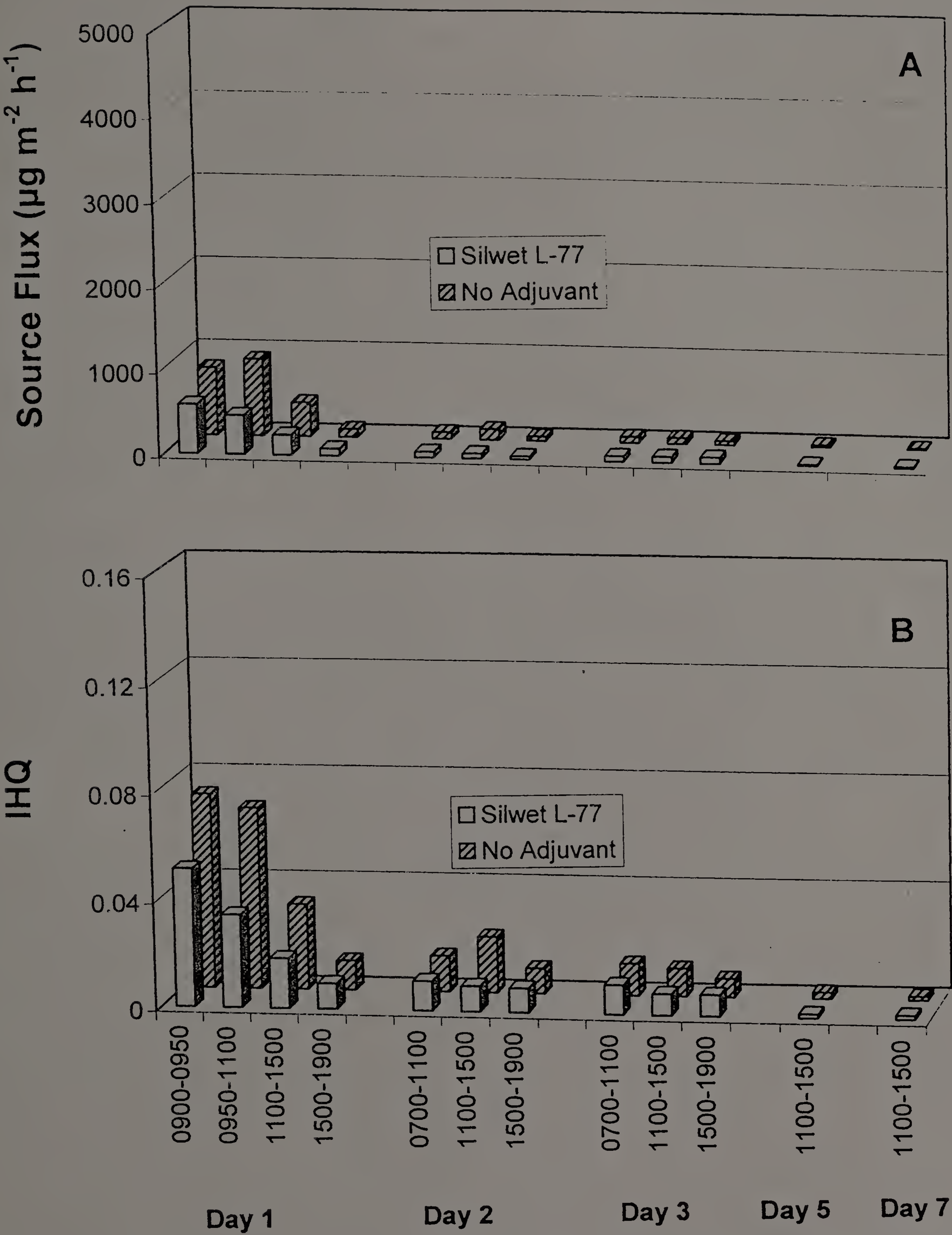


Figure 4. Source flux (panel A) and inhalation hazard quotients (IHQ, panel B) determinations over a 7-day period following application with full-rate isofenphos, 0.63-cm post-application irrigation and with and without Silwet L-77. Values not significantly different at the 0.05 level.

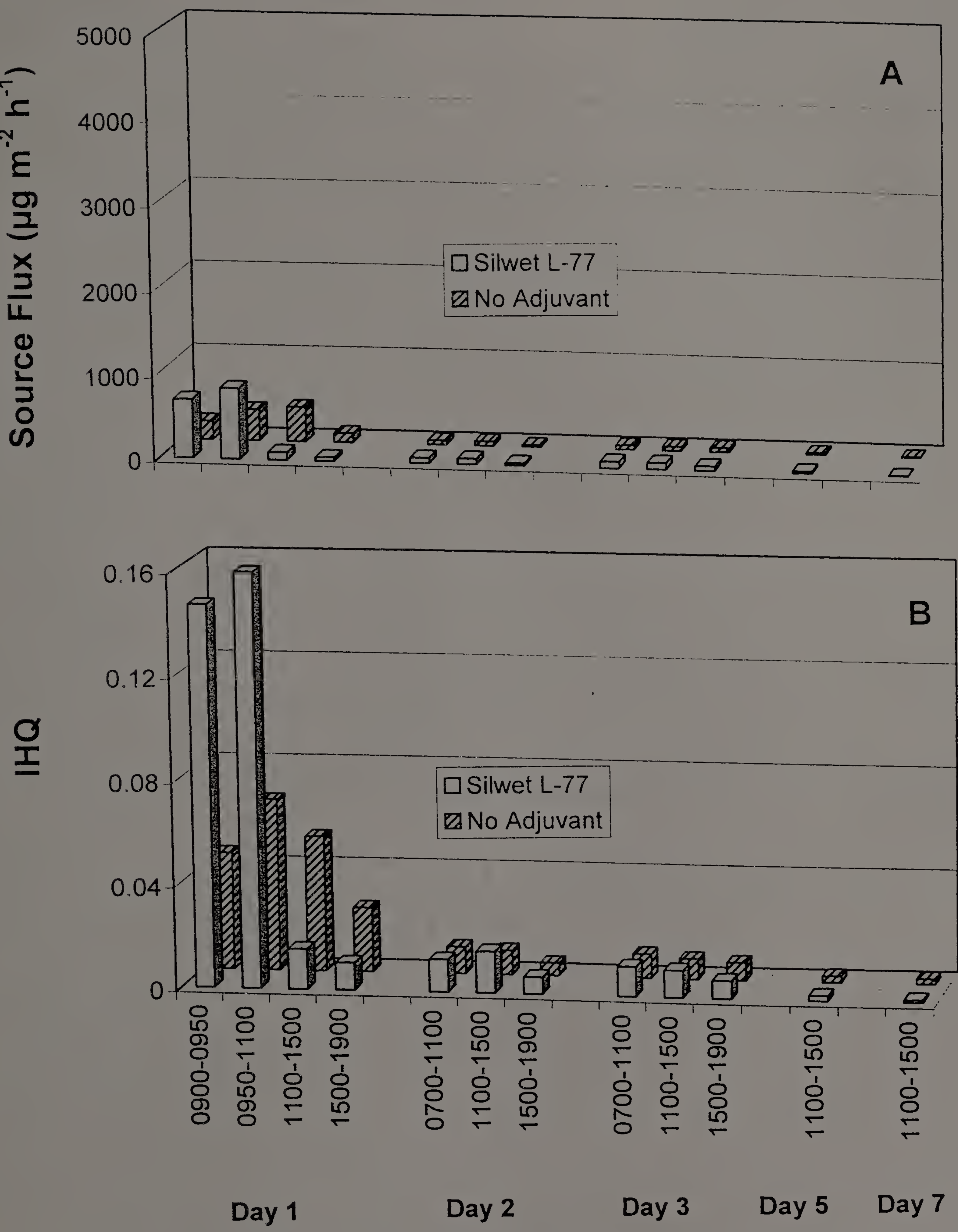


Figure 5. Source flux (panel A) and inhalation hazard quotients (IHQ, panel B) determinations over a 7-day period following application with full-rate isofenphos, 1.3-cm post-application irrigation and with and without Silwet L-77. Values not significantly different at the 0.05 level.

applied, with and without adjuvant, respectively. The highest level of volatile isofenphos occurred when applied with Silwet L-77 in the presence of 1.3-cm post-application irrigation occurred between 0950-1100 hrs and resulted in a source flux of 842 $\mu g\ m^{-2}\ h^{-1}$ (Fig. 5A, 0.74 % of applied), and an IHQ value of 0.16 (Fig. 5B).

3.2.1.3. Bendiocarb. Overall, the volatilization of bendiocarb as measured by source flux was most prevalent following application and irrigation (Figs. 6A and 7A). Volatile bendiocarb residues decreased over time (more gradually than chlorpyrifos and isofenphos) in a diurnal pattern on Days 1 through 5 and then became much less pronounced by Day 7 of the 7-day experiment. At no time in any experiments did the IHQ values determined from volatile bendiocarb residues exceed 1.0 (Figs. 6B and 7B).

There was no consistently significant reduction in the level of volatile residues following the application of full-rate bendiocarb in the presence of 0.1% (v/v) Silwet L-77 compared to applications without adjuvant at either 0.63- (Fig. 6A, t-test, $P > 0.05$) or 1.3-cm post-application irrigation treatment (Fig. 7A, t-test, $P > 0.05$). However, volatile residues generally were less following the higher rate (1.3-cm) of post-application irrigation, particularly in the absence of adjuvant. Overall, the percent loss of total applied bendiocarb as volatile residues in the presence of 1.3-cm post-application irrigation was reduced 1.5-fold compared to the loss following 0.63-cm post-application irrigation, both without adjuvant (Table 4). In the presence of Silwet L-77, the percent loss of total applied bendiocarb as volatile residues was increased 1.1-fold following 1.3-cm post-application irrigation and reduced 1.3-fold following 0.63-cm irrigation (Table 4).

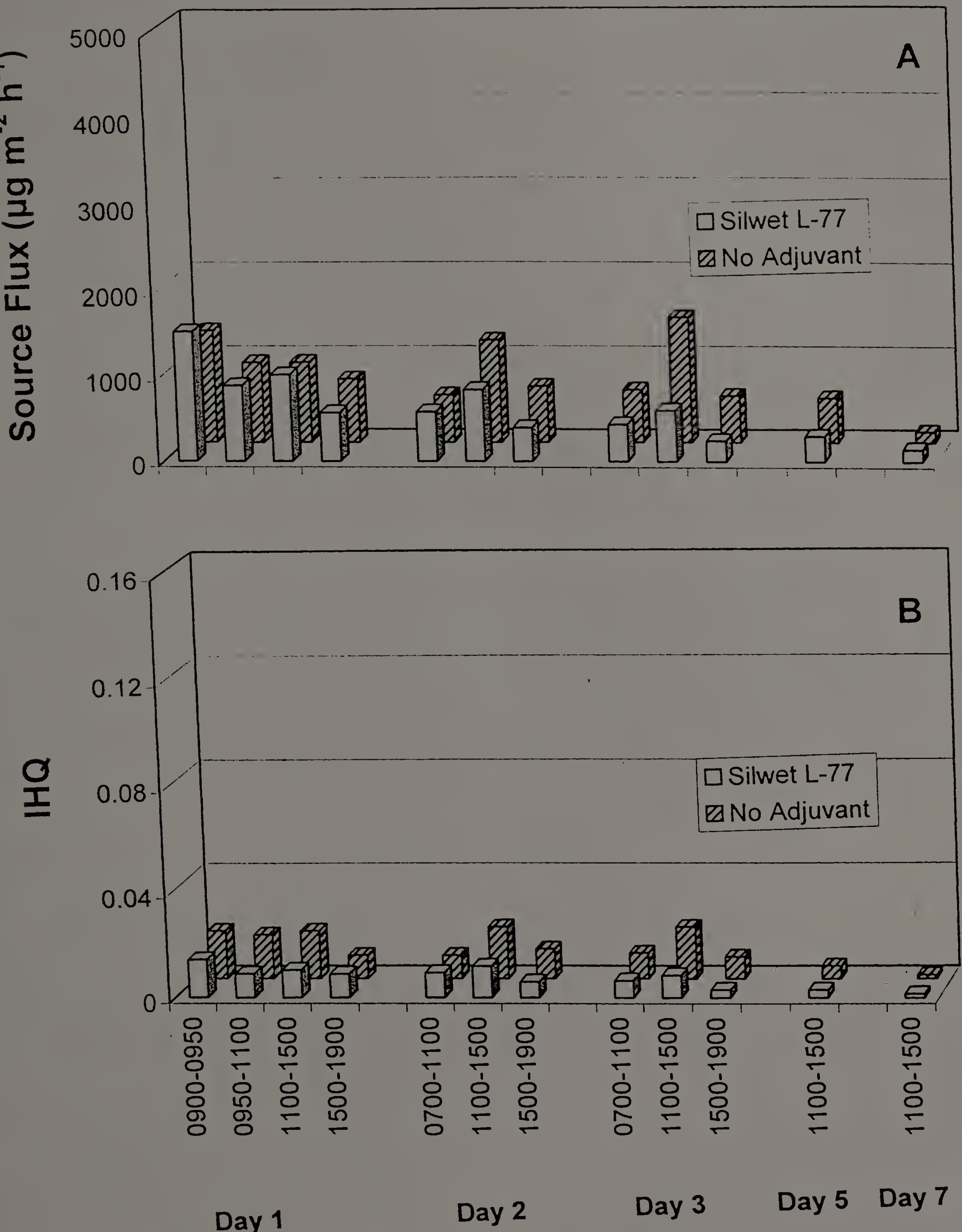


Figure 6. Source flux (panel A) and inhalation hazard quotients (IHQ, panel B) determinations over a 7-day period following application with full-rate bendiocarb, 0.63-cm post-application irrigation and with and without Silwet L-77. Values not significantly different at the 0.05 level.

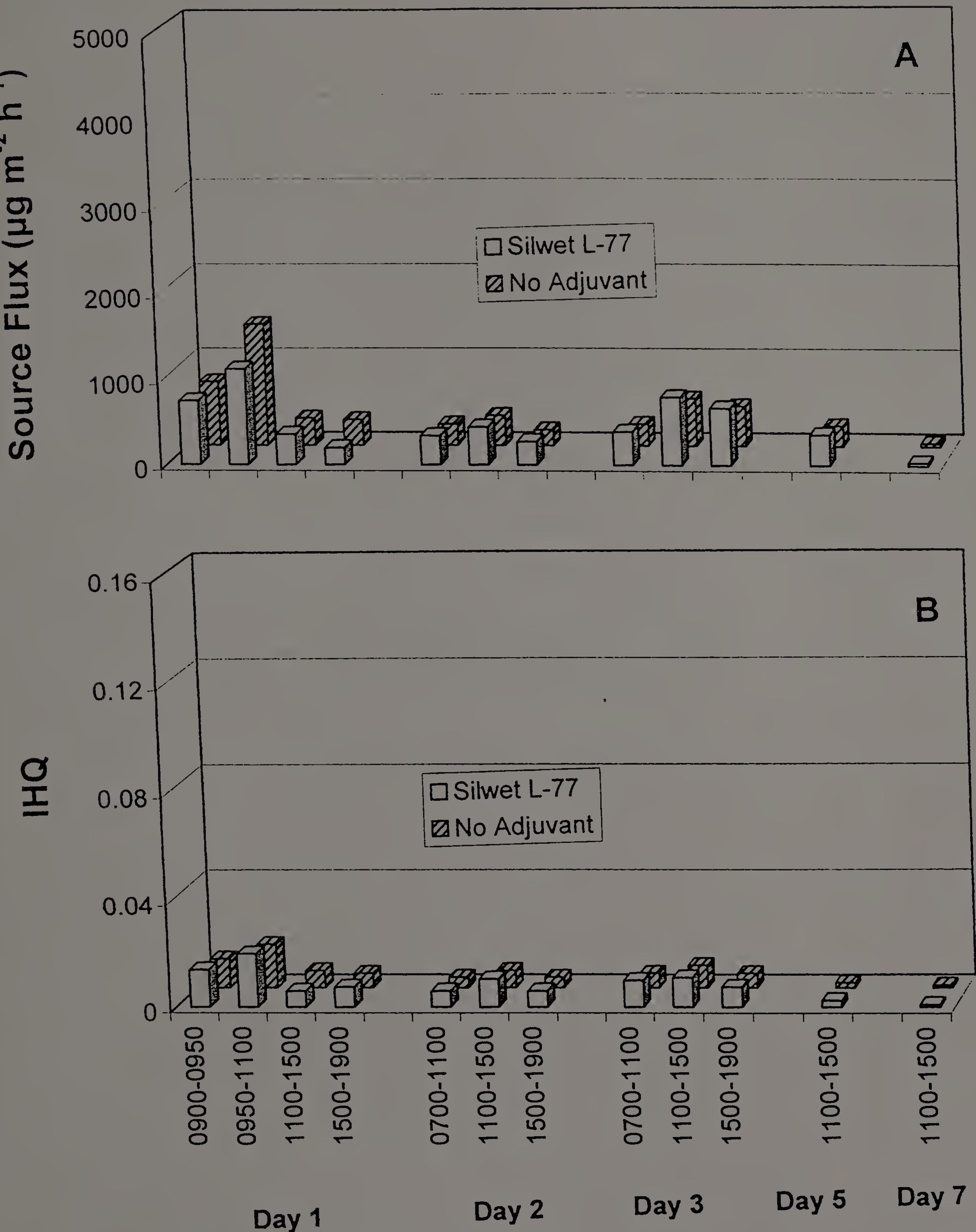


Figure 7. Source flux (panel A) and inhalation hazard quotients (IHQ, panel B) determinations over a 7-day period following application with full-rate bendiocarb, 1.3-cm post-application irrigation and with and without Silwet L-77. Values not significantly different at the 0.05 level.

The highest level of volatile bendiocarb occurred during the first hour with Silwet L-77 (0900-0950 hr, Fig. 6A) and on Day 3 (1100-1500 hr, Fig. 6A) in the absence of Silwet L-77 with 0.63-cm post-application irrigation. During these intervals, the bendiocarb source fluxes were both approximately 1500 $\mu g\ m^{-2}\ h^{-1}$ (Fig. 6A, 0.33 % of total applied). The volatile loss of bendiocarb residues on Day 1 at 0.63-cm irrigation was 1.9 and 2.0 % of the total applied, with and without adjuvant, respectively (Fig. 6A). The volatile loss of bendiocarb on Day 1 at 1.3-cm irrigation was 0.92 and 1.04 % of the total applied, with and without Silwet L-77, respectively (Fig. 7A).

3.2.2. Dislodgeable Foliar Residues.

3.2.2.1. Chlorpyrifos. Overall, dislodgeable foliar residues of chlorpyrifos were most available immediately following application and irrigation (15 min post-application irrigation, Figs. 8A and 9A). Dislodgeable foliar residues then decreased over time for the remainder of the 7-day experiment, regardless of irrigation level or presence of adjuvant.

In the absence of Silwet L-77, DHQ values never exceeded 1.0 at either the 0.63- (Fig 8B) or 1.3-cm (Fig. 9B) levels of post-application irrigation. Although dislodgeable foliar residues of chlorpyrifos were statistically reduced at 51 and 75 hrs (Days 3 and 5, respectively) in the presence of 0.1% (v/v) Silwet L-77 compared to its absence at both 0.63- and 1.3-cm post-application irrigation levels (Fig. 8A and 9A, t-test, $P \leq 0.025$), the presence of the adjuvant did not consistently reduce dislodgeable foliar chlorpyrifos residues.

The percent loss of total applied chlorpyrifos as dislodgeable foliar residues were 0.57 and 0.36 % at 0.63-cm post-application irrigation and 0.36 and 0.39 % at 1.3-cm irrigation, with and without Silwet L-77, respectively (Table 4). In the presence of

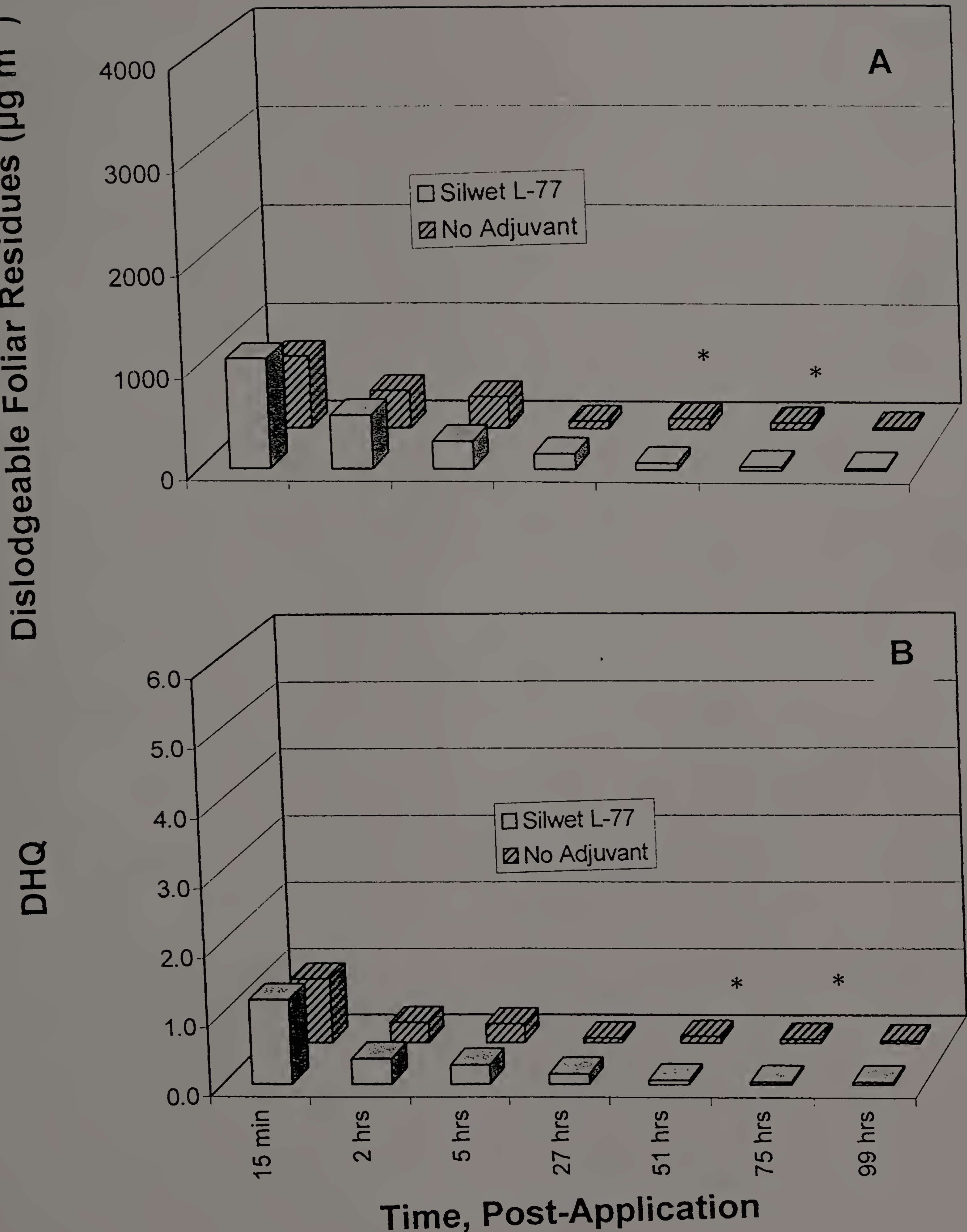


Figure 8. Dislodgeable foliar residues (µg m^{-2}, panel A) and dermal hazard quotient (DHQ) determinations (panel B) following applications of full-rate chlorpyrifos, 0.1% Silwet L-77 and 0.63-cm post application irrigation. * significant at the 0.025 level.

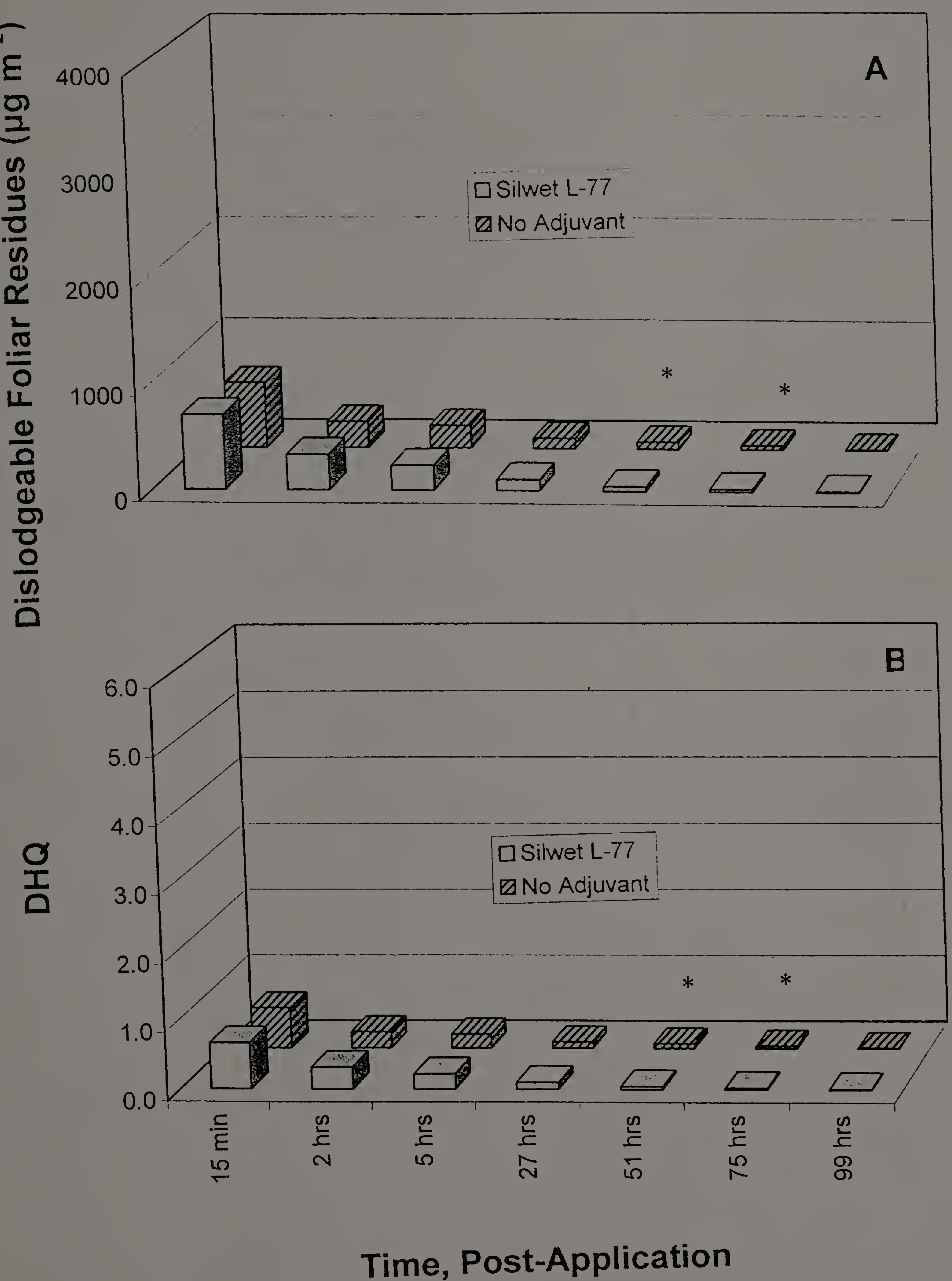


Figure 9. Dislodgeable foliar residues (µg m^{-2}, panel A) and dermal hazard quotient (DHQ) determinations (panel B) following applications of full-rate chlorpyrifos, 0.1% Silwet L-77 and 1.3-cm post application irrigation. * significant at the 0.025 level.

adjuvant and 1.3-cm post-application irrigation, dislodgeable foliar residues were decreased 1.6-fold compared to the 0.63-cm irrigation level (Figs. 8A and 9A). Without adjuvant and in the presence of 1.3-cm post-application irrigation, the level of dislodgeable foliar chlorpyrifos residues increased 1.1-fold compared to that obtained at 0.63-cm irrigation (Table 4).

The highest dislodgeable foliar residues occurred during the first sample collections in the presence of Silwet L-77 at both levels of post-application irrigation (15 min following post-application irrigation, Figs. 8A and 9A). At 0.63-cm irrigation, the highest chlorpyrifos dislodgeable foliar residue was 1090 $\mu g\ m^{-2}$ (0.28 % of total applied) with a DHQ value of 1.3 (the only DHQ value above 1.0 for chlorpyrifos) (Fig 8A and B). At 1.3-cm irrigation, the highest dislodgeable foliar residue was 720 $\mu g\ m^{-2}$ (0.19 % of total applied) with a DHQ value of 0.71 (Fig. 9A and B).

3.2.2.2. Isofenphos. Overall, dislodgeable foliar residues of isofenphos were most available immediately following application and irrigation (15 min post-application irrigation, Figs. 10A and 11A). Dislodgeable foliar residues then decreased over time for the remainder of the 7-day experiment, regardless of irrigation level or presence of adjuvant (Figs. 10A and 11A).

Of the three pesticides studied in Year 1, only isofenphos resulted in DHQ values substantially above 1.0 (Fig. 10B and 11B). All Day 1 samples had dislodgeable foliar isofenphos residues that were close to or above 1.0 regardless of irrigation level or presence of adjuvant. All DHQ values for full-rate isofenphos dropped below 1.0 by Day 2 (27 hrs) regardless of irrigation or adjuvant regime (Fig. 10B).

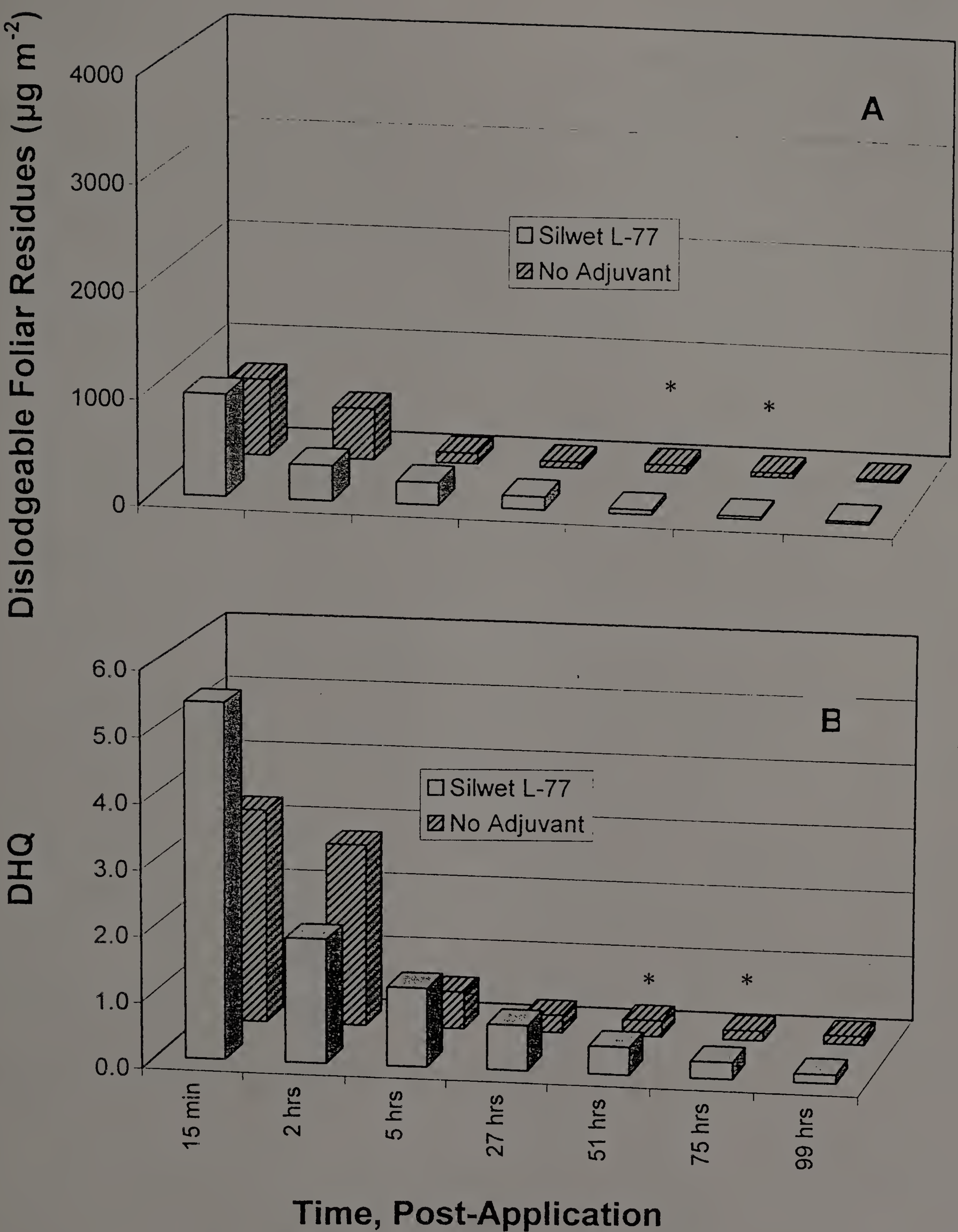


Figure 10. Dislodgeable foliar residues (µg m^{-2}, panel A) and dermal hazard quotient (DHQ) determinations (panel B) following applications of full-rate isofenphos, 0.1% Silwet L-77 and 0.63-cm post application irrigation. * significant at the 0.025 level.

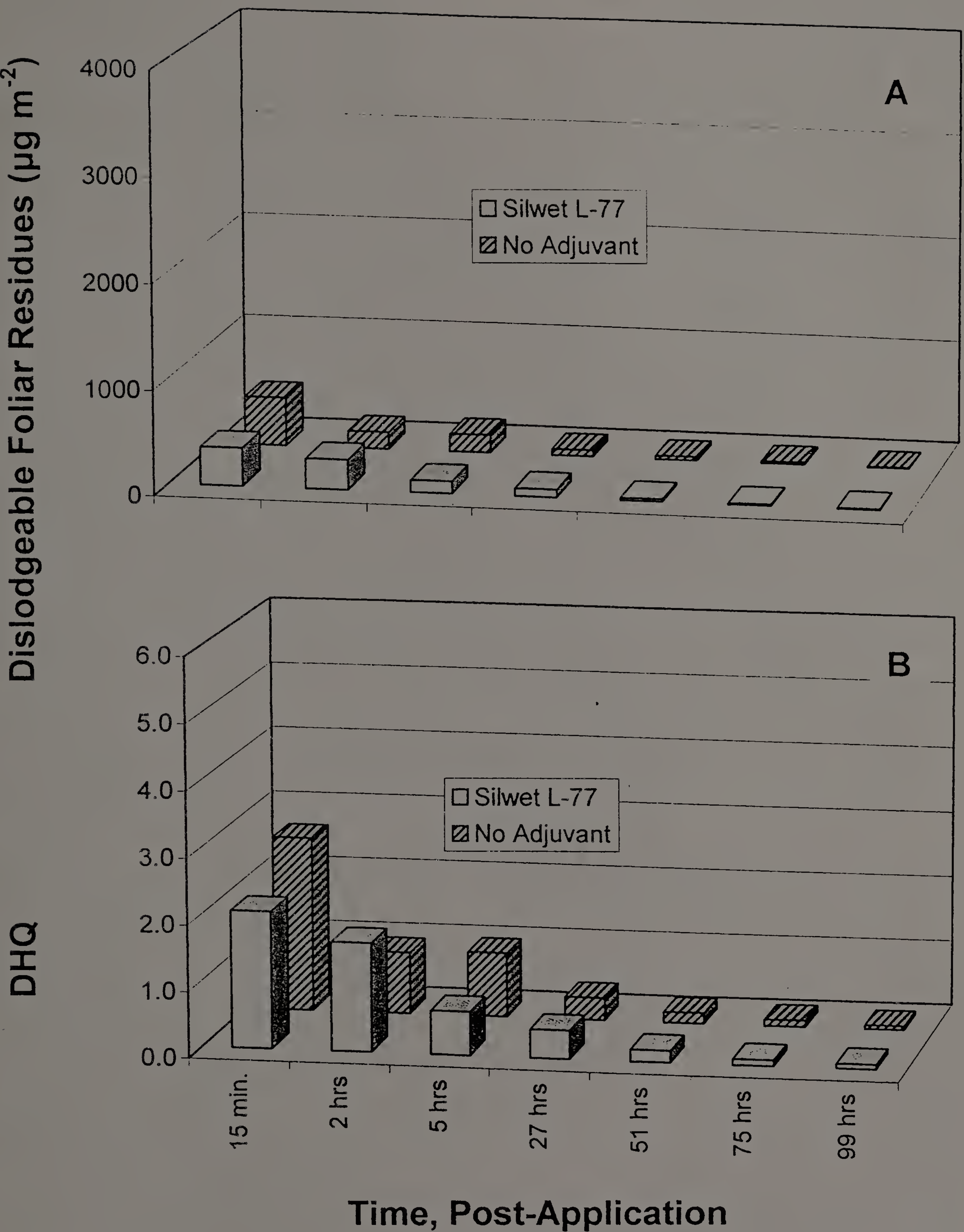


Figure 11. Dislodgeable foliar residues (µg m^{-2}, panel A) and dermal hazard quotient (DHQ) determinations (panel B) following applications of full-rate isofenphos, 0.1% Silwet L-77 and 1.3-cm post application irrigation. Values not significantly different at the 0.025 level.

The presence of 0.1 % (v/v) Silwet L-77 did not significantly reduce the level of dislodgeable foliar isofenphos residues at either the 0.63- (Fig. 10A, $P > 0.025$) or 1.3-cm (Fig. 11A, t-test, $P > 0.025$) post-application irrigation levels. However, increasing post-application irrigation from 0.63- to 1.3-cm generally decreased the availability of dislodgeable foliar isofenphos residues, regardless of the presence or absence of adjuvant (Fig 10A versus 11A).

The percent loss of total applied isofenphos as dislodgeable foliar residues was 0.57 and 0.36 % at 0.63-cm irrigation and 0.36 and 0.39 % at 1.3-cm irrigation with and without adjuvant, respectively (Figs. 10A and 11A). Without adjuvant in the presence of 1.3-cm post-application irrigation, the level of dislodgeable foliar isofenphos residues decreased some 1.4-fold compared to 0.63-cm irrigation (Table 4).

The highest DHQ values for isofenphos occurred at the 15 min sampling interval with 0.63-cm post-application irrigation; DHQ values were 5.4 (1000 $\mu g\ m^{-2}$, 0.44 % of total applied) and 3.1 (720 $\mu g\ m^{-2}$, 0.31 % of total applied) with and without Silwet L-77, respectively (Fig. 10B and 11B). At 1.3-cm post-application irrigation, DHQ values for isofenphos were below 1.0 by 27 hrs (Day 2) without adjuvant, but were below 1.0 by 5 hrs in the presence of Silwet L-77 (Fig. 11B). The highest DHQ values for isofenphos at 1.3-cm post-application irrigation were 2.7 (465 $\mu g\ m^{-2}$, 0.20 % of total applied) and 2.1 (363 $\mu g\ m^{-2}$, 0.16 % of total applied) with and without Silwet L-77, respectively (Fig. 11B).

3.2.2.3. Bendiocarb: Overall, dislodgeable foliar residues of bendiocarb were most prevalent immediately following application and irrigation (15 min post-application irrigation, Fig. 12A and 13A). Dislodgeable foliar residues continued to decrease over time for the remainder of the 7-day experiment (Fig. 12A and 13A).

Bendiocarb DHQ values never exceeded 1.0 at either the 0.63- (Fig. 12B) or 1.3-cm (Fig. 13B) levels of post-application irrigation. The presence of Silwet L-77 did not significantly reduce the level of dislodgeable foliar bendiocarb residues at either 0.63-cm or 1.3-cm post-application irrigation (Fig. 12A and 13A, t-test, $P > 0.025$). Likewise, irrigation alone (without the presence of Silwet L-77) had no significant reduction on DHQ values (Fig. 12B).

However, the percent loss of total applied bendiocarb as dislodgeable foliar residues was 0.82 and 0.81 % at 0.63-cm post-application irrigation and 0.52 and 0.27 % at 1.3-cm irrigation, with and without adjuvant, respectively (Table 4). Without adjuvant and in the presence of 1.3-cm post-application irrigation, the percent loss of total applied bendiocarb as dislodgeable foliar residues was reduced 2.7-fold compared to residue at 0.63-cm post-application irrigation (Table 4).

The highest bendiocarb dislodgeable foliar residues occurred at the15 min sampling interval in the presence of Silwet L-77 and 0.63-cm post-application irrigation and resulted in a DHQ of 0.95 (2400 μg m^{-2}, 0.51 % of applied, Fig. 12A and B).

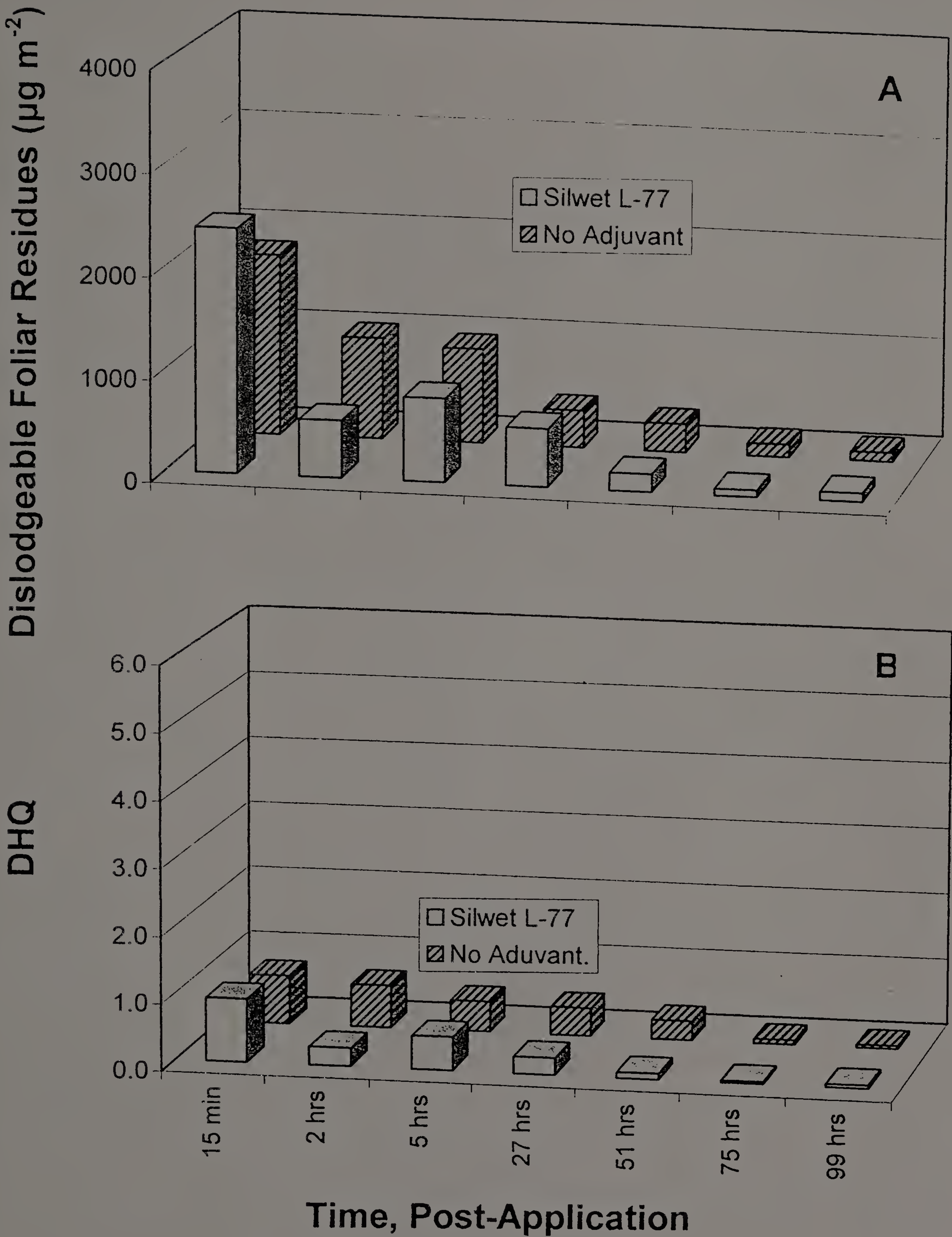


Figure 12. Dislodgeable foliar residues (μg m^{-2}, panel A) and dermal hazard quotient (DHQ) determinations (panel B) following applications of full-rate bendiocarb, 0.1% Silwet L-77 and 0.63-cm post application irrigation. Values not significantly different at the 0.025 level.

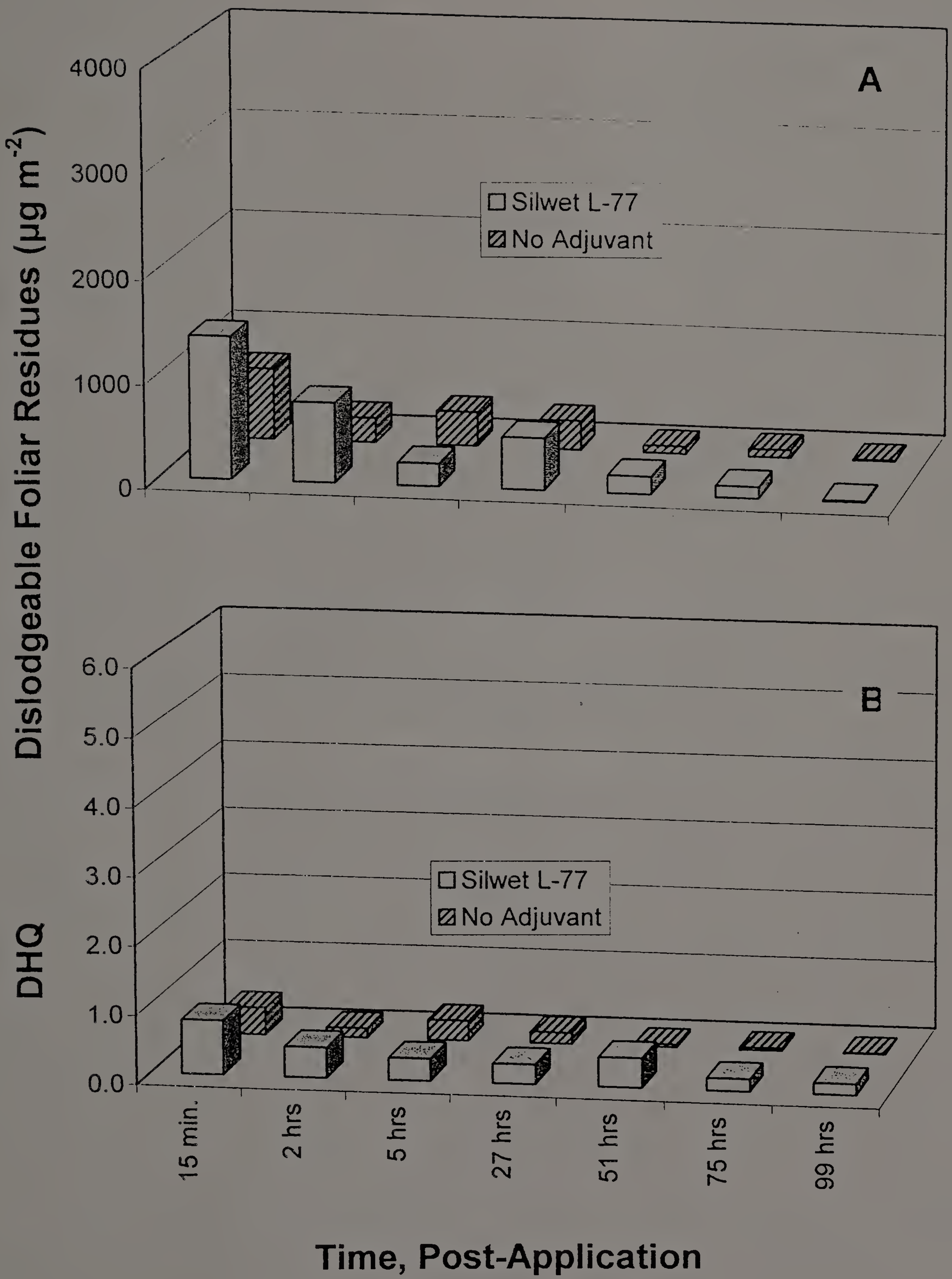


Figure 13. Dislodgeable foliar residues (µg m^{-2}, panel A) and dermal hazard quotient (DHQ) determinations (panel B) following applications of full-rate bendiocarb, 0.1% Silwet L-77 and 1.3-cm post-application irrigation. Values not significantly different at the 0.025 level.

3.3. Effect of Reducing Pesticide Application Rates on Exposure Potentials.

3.3.1. Volatile Residues and IHQ Values at 1/2 or 1/4 Full-rate Application in the Presence of 0.63- or 0.32-cm Post-application Irrigation.

3.3.1.1. Chlorpyrifos. Overall, the volatilization of 1/2 and 1/4 full-rate chlorpyrifos as measured by source flux was most evident immediately following application with post-application irrigation at either the 0.63- or 0.32-cm level (Figs. 14A and 15A). Volatile residues decreased over time in a diurnal pattern on Days 1 through 3 becoming much less pronounced by Day 3 of the 3-day experiment. Under these conditions, IHQ values never exceeded 0.08 (Figs. 14B and 15B).

Reducing applications from full to 1/2 full-rate at 0.63-cm post-application irrigation significantly reduced the level of volatile chlorpyrifos residues (Fig. 2A versus 14A, t-test, $P \leq 0.05$). The average source flux (n=2) in the first hour of sampling following application at 1/2 full-rate was decreased 2.5-fold compared to full rate chlorpyrifos (Fig. 2A and 14A, 0900-0950 hr). Over the entire 3-day collection, the source flux of 1/2 full-rate chlorpyrifos was 2.2-fold less than full-rate (Fig. 2A versus 14A).

Reducing applications from full to 1/2 full-rate at 0.32-cm post-application irrigation significantly reduced the level of volatile chlorpyrifos residues. The average source flux (n = 2) in the first hour of sampling following chlorpyrifos application at 1/2 full-rate was decreased 1.8-fold compared to full-rate (Fig. 2A versus 14A, t-test, $P \leq 0.05$). Over the entire 3-day collection, the source flux of 1/2 full-rate chlorpyrifos was 3.4-fold less than full-rate (Fig. 2A versus 14A).

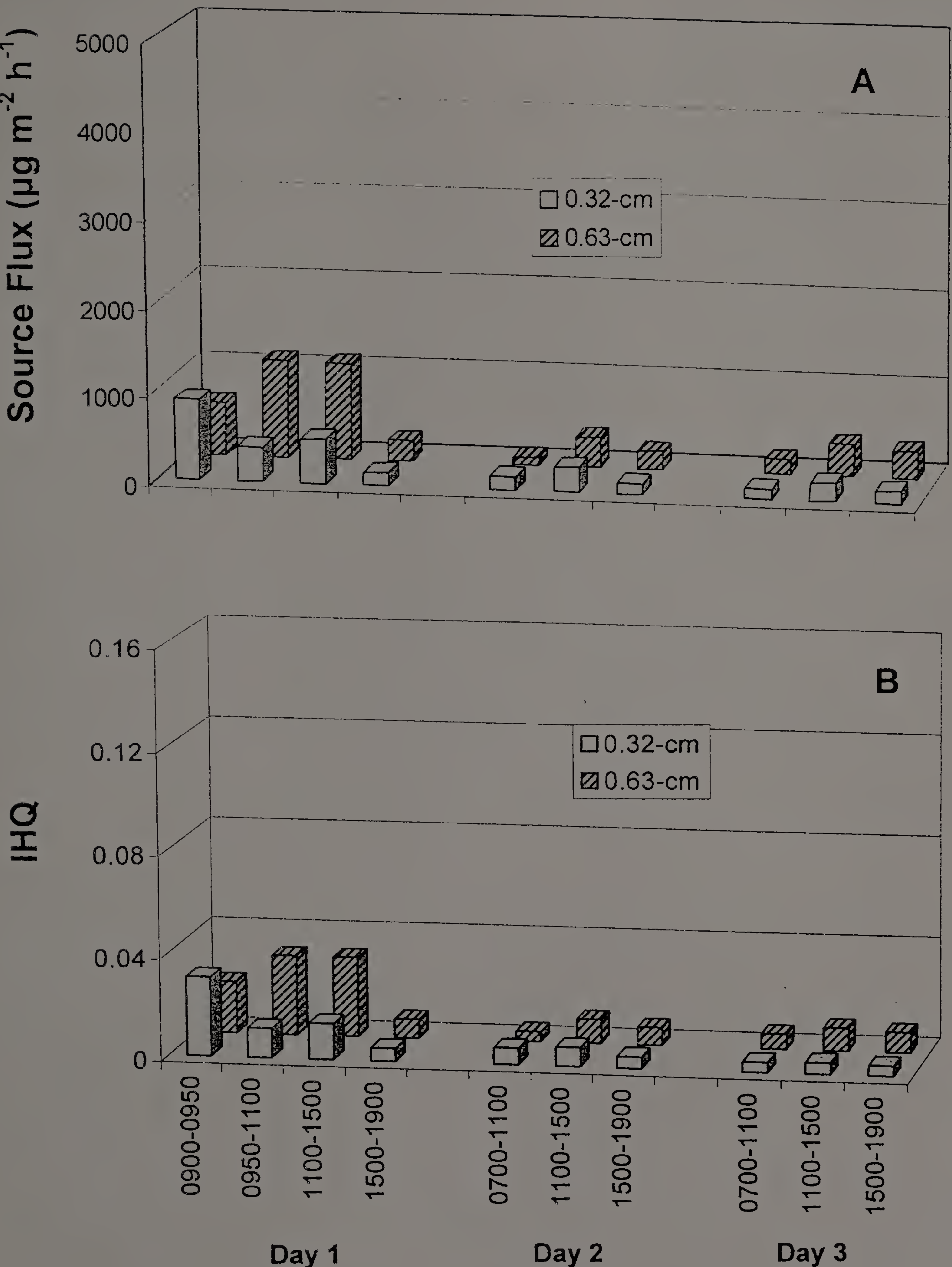


Figure 14. Source flux (panel A) and inhalation hazard quotient (IHQ, panel B) determinations over a 3-day sampling period following application with chlorpyrifos at 1/2 full-rate with either 0.32- or 0.63-cm post-application irrigation. Values not significantly different at the 0.05 level.

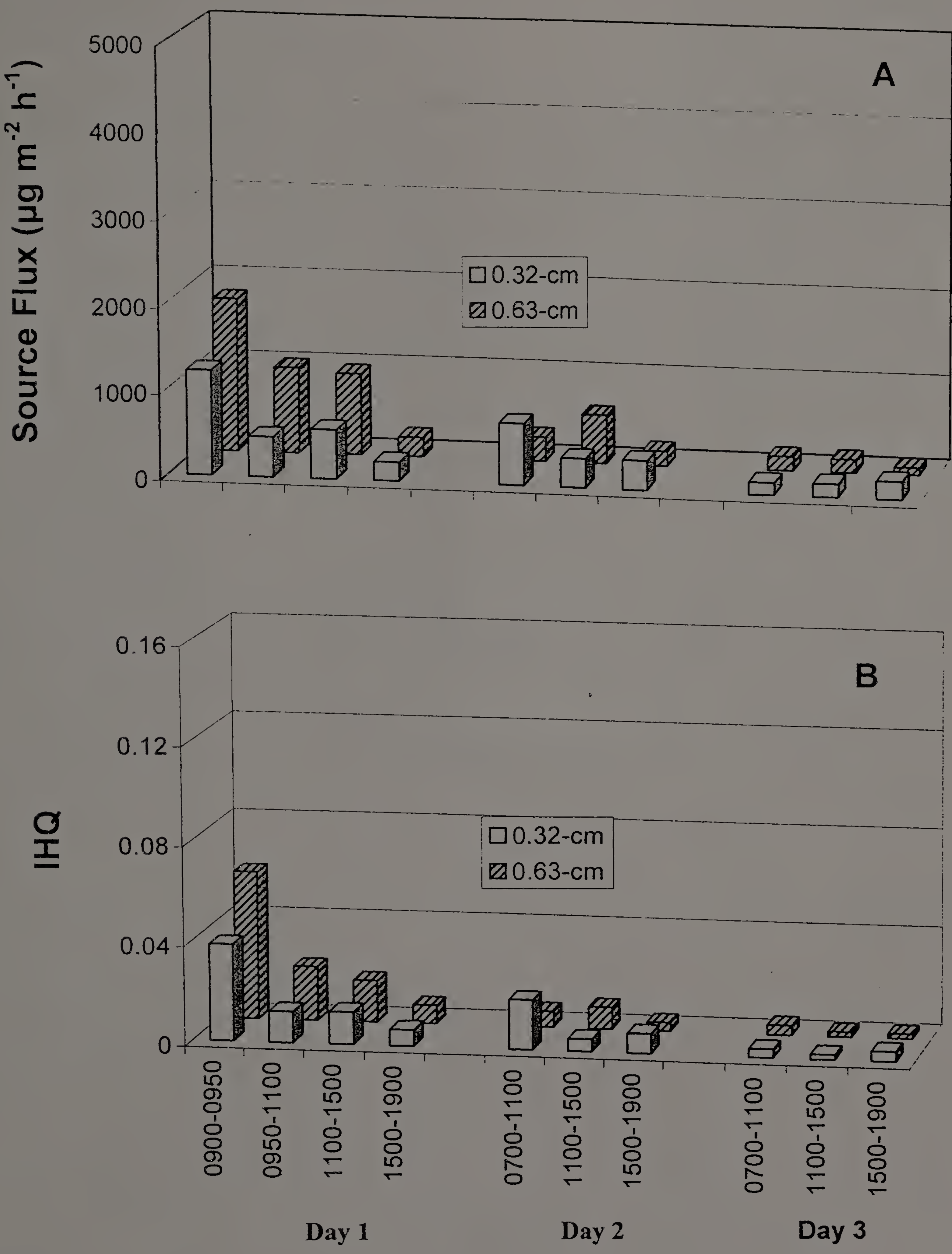


Figure 15. Source flux (panel A) and inhalation hazard quotient (IHQ, panel B) determinations over a 3-day sampling period following application with chlorpyrifos at 1/4 full-rate with either 0.32- or 0.63-cm post-application irrigation. Values not significantly different at the 0.05 level.

Reducing application from full to1/4 full-rate at 0.63-cm post-application irrigation significantly reduced the level of volatile chlorpyrifos residues during Day 1 (Fig. 2A and 15A, t-test, $P \leq 0.05$). The average source flux (n=2) in the first hour of sampling was decreased 2.8-fold when full-rate compared to 1/4 full-rate, following application with 0.63-cm irrigation (Fig. 2A versus 15A, 0900-0950 hr). Over the entire 3-day collection, the source flux at 1/4 full-rate chlorpyrifos was 1.9-fold less than at full-rate (Fig. 2A versus 15A).

Reducing application from full to 1/4 full-rate at 0.32-cm post-application irrigation significantly reduced the level of volatile chlorpyrifos residues (Figs. 2A and 15A, t-test, $P \leq 0.05$). The average source flux (n = 2) in the first hour of sampling following chlorpyrifos application at 1/4 full-rate was decreased 4.1-fold compared to full- rate (Fig. 2A versus 15A, 0900-0950 hr). Over the entire 3-day collection, the source flux at 1/4 full-rate chlorpyrifos was 2.3-fold less than at full-rate (Fig. 2A versus 15A, 0900-0950 hr).

Overall, reducing application from 1/2 to 1/4 full-rate followed by either 0.63- or 0.32-cm post-application irrigation did not significantly reduce the level of volatile chlorpyrifos residues over the 3-day collection (Fig. 14 versus 15, t-test, $P \geq 0.05$).

3.3.1.2. Isofenphos. Overall, the volatilization of 1/2 or 1/4 full-rate isofenphos as measured by source flux was most evident immediately following application at either the 0.63- or 0.32-cm irrigation levels (Figs. 16A and 17A). Volatile residues decreased over time in a diurnal pattern on Days 1 through 3 becoming much less pronounced by Day 3. Under these conditions, IHQ values never exceeded 0.03 (Fig. 16B and 17B).

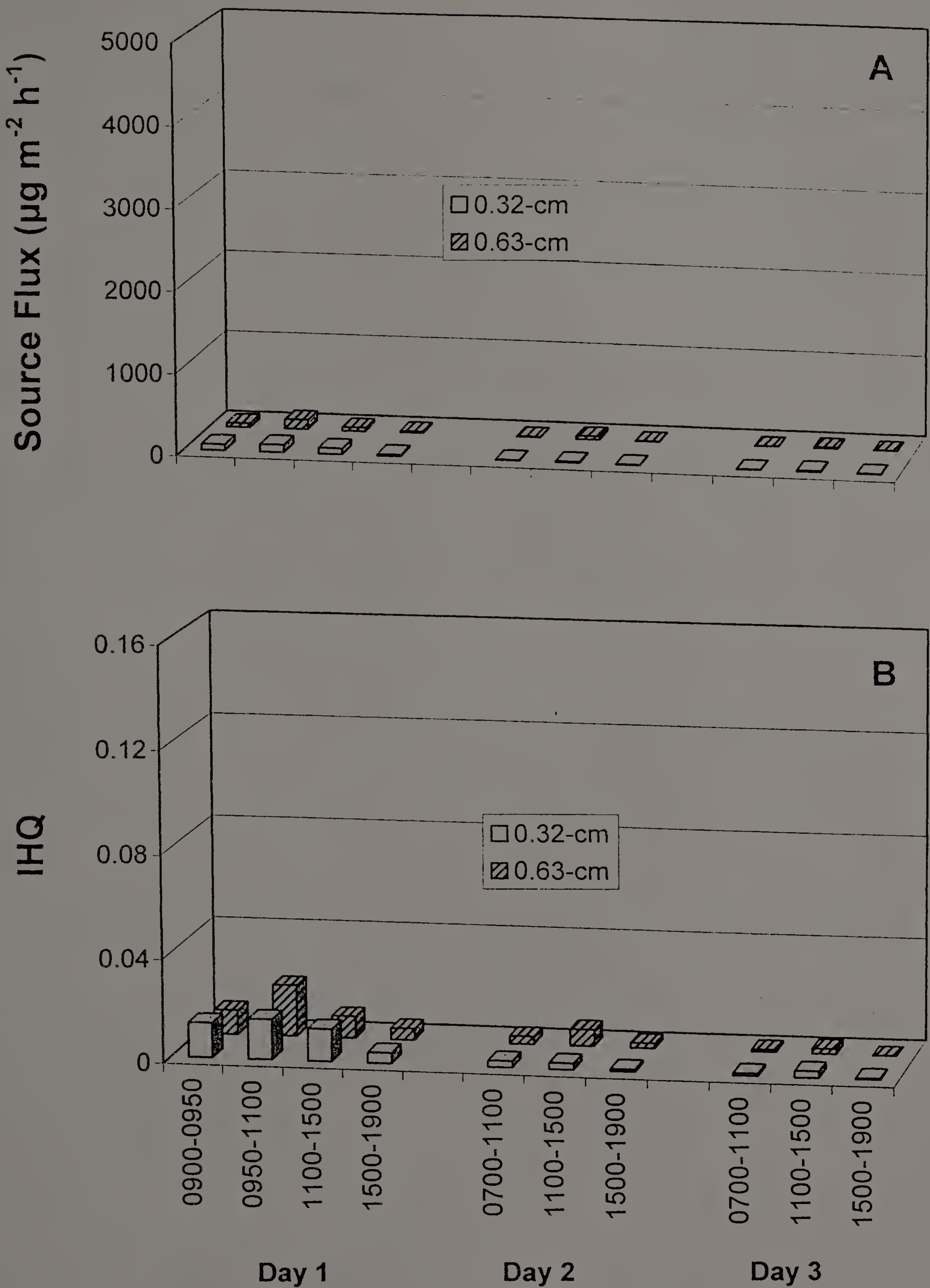


Figure 16. Source flux (panel A) and inhalation hazard quotient (IHQ, panel B) determinations over a 3-day sampling period following application with isofenphos at 1/2 full-rate with either 0.32- or 0.63-cm post-application irrigation. Values not significantly different at the 0.05 level.

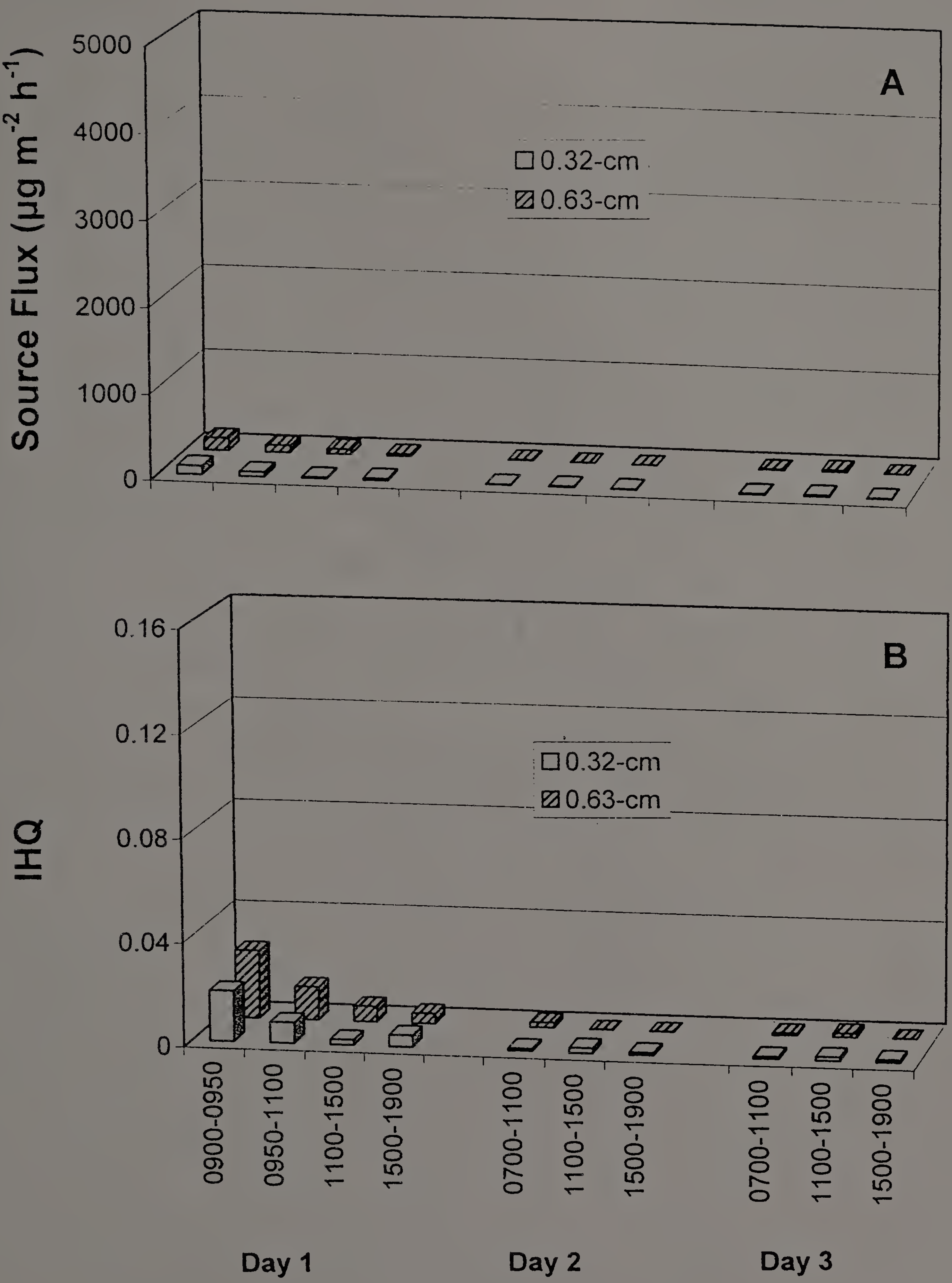


Figure 17. Source flux (panel A) and inhalation hazard quotient (IHQ, panel B) determinations over a 3-day sampling period following application with isofenphos at 1/4 full-rate with either 0.32- or 0.63-cm post-application irrigation. Values not significantly different at the 0.05 level.

Reducing applications from full to 1/2 full-rate at 0.63-cm post-application irrigation significantly reduced the level of volatile isofenphos residues (Fig. 4A versus 16A, t-test, $P \leq 0.05$). The average source flux in the first hour of sampling following isofenphos application at 1/2 full-rate was decreased 15.8-fold compared to full-rate (Fig. 4A and 16A, 0900-0950 hr). Over the entire 3-day collection, the source flux at 1/2 full-rate isofenphos was 8.3-fold less than full-rate (Fig. 4A versus 16A).

Reducing application from full to 1/2 full-rate at 0.32-cm post-application irrigation significantly reduced the level of volatile isofenphos residues. The average source flux (n = 2) in the first hour of sampling following isofenphos application at 1/2 full-rate was decreased 11.3-fold compared to full-rate (Fig. 4A and 16A). Over the entire 3-day collection, the source flux at 1/2 rate isofenphos was 8.8-fold less than at full-rate (Fig. 4A versus 16A).

Reducing application from full to1/4 full-rate at 0.63-cm post-application irrigation significantly reduced the level of volatile isofenphos residues (Fig. 4A versus 17A, t-test $P \leq 0.05$). The average source flux (n=2) in the first hour of sampling following isofenphos application at 1/4 full-rate was decreased 5.6-fold compared to full-rate (Fig. 4A and 17A, 0900-0950 hr). Over the entire 3-day collection, the source flux at 1/4 full-rate isofenphos was 7.7-fold less than at full-rate (Fig. 4A versus 17A).

Reducing application from full to 1/4 full-rate at 0.32-cm post-application irrigation significantly reduced the level of volatile isofenphos residues. The average source flux (n = 2) in the first hour of sampling following isofenphos application at 1/2 full-rate was decreased 8.1-fold compared to full-rate (Fig. 4A and 17A, t-test, $P \leq 0.05$). Over the entire 3-day collection, the source flux at 1/4 full-rate isofenphos was 11-fold less than at full-rate (Fig. 4A versus 17A).

Overall, reducing applications from 1/2 to 1/4 full-rate followed by either 0.63- or 0.32-cm post-application irrigation did not significantly reduce the level of volatile isofenphos residues over the 3-day collection (Figs. 16A versus 17A, t-test, P > 0.05).

3.3.1.3. Trichlorfon. Overall, the volatilization of 1/2 or 1/4 full-rate trichlorfon as measured by source flux was most evident immediately following application at either the 0.63- or 0.32-cm irrigation level (Figs. 18A and 19A). Volatile residues decreased over time in a diurnal pattern on Days 1 through 3 becoming much less pronounced by Day 3. Under these conditions, IHQ values never exceeded 0.04 (Figs. 18B and 19B).

Reducing applications from full to1/2 full-rate at either 0.63- or 0.32-cm post-application irrigation did not significantly reduce (n = 2) the level of volatile trichlorfon residues (Fig. 18A versus Clark et al., 2000, Table VI, table not shown, t-test, P > 0.05).

Reducing treatment from full to 1/4 full-rate at either 0.63- or 0.32-cm post-application irrigation did not significantly reduce (n = 2) the level of volatile trichlorfon residues (Fig. 19A, versus Clark et al., 2000, Table VI, table not shown, t-test, P > 0.05).

Reducing treatments from 1/2 to 1/4 full-rate followed by either 0.63- or 0.32-cm post-application irrigation did not significantly reduce (n = 2) the level of volatile trichlorfon residues over the 3-day collection (Figs. 18A versus 19A, t-test, P > 0.05).

3.3.1.4. Triadimefon. Overall, the volatilization of 1/2 or 1/4 full-rate triadimefon as measured by source flux was most evident immediately following application at either the 0.63- or 0.32-cm irrigation (Fig. 20 A and B). Volatile residues decreased over time in a diurnal pattern on Days 1 through 3 becoming much less pronounced by Day 3. Under these conditions, IHQ values never exceeded 0.00001 (Fig.

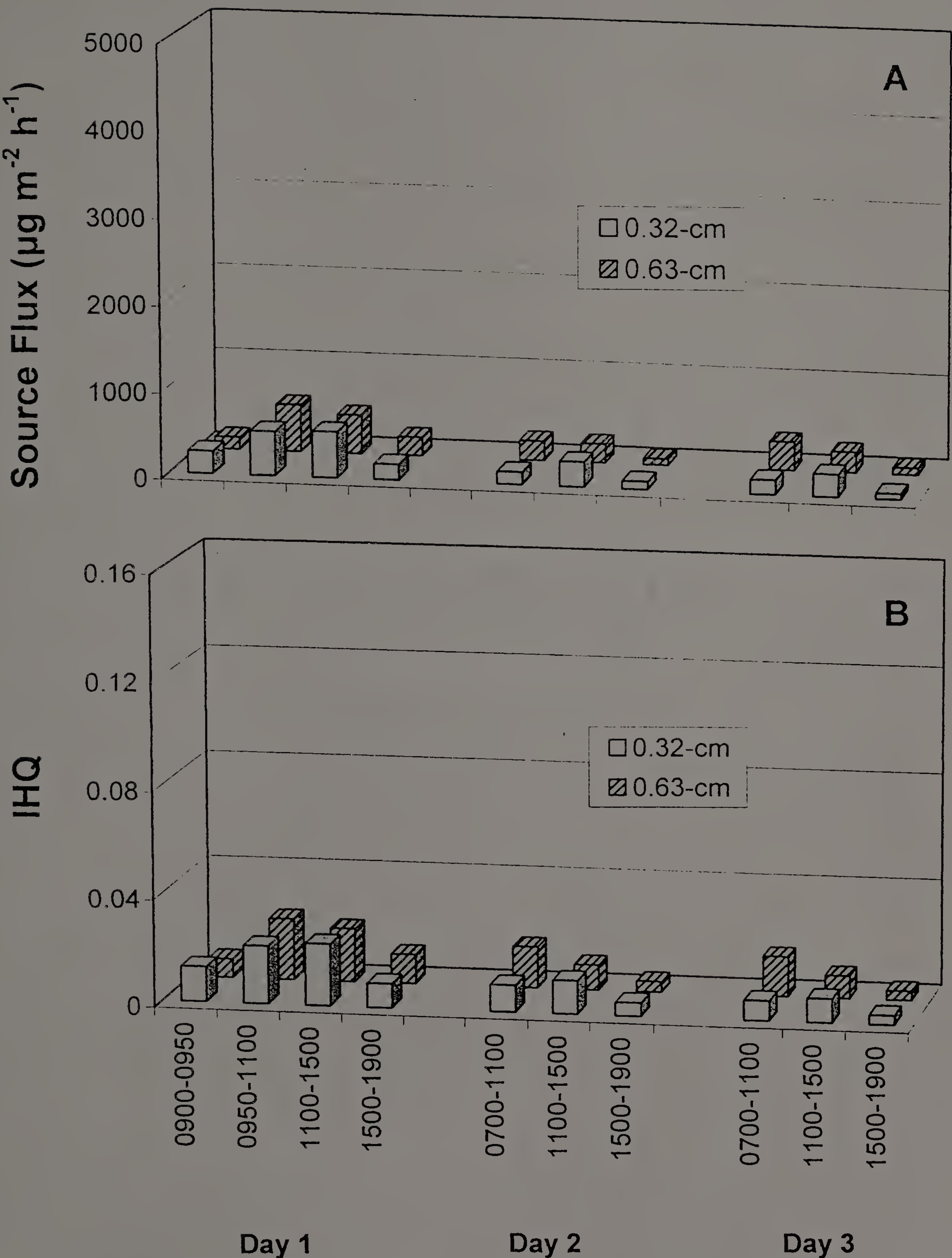


Figure 18. Source flux (panel A) and inhalation hazard quotient (IHQ, panel B) determinations over a 3-day sampling period following application with trichlorfon at 1/2 full-rate with either 0.32- or 0.63-cm post-application irrigation. Values not significantly different at the 0.05 level.

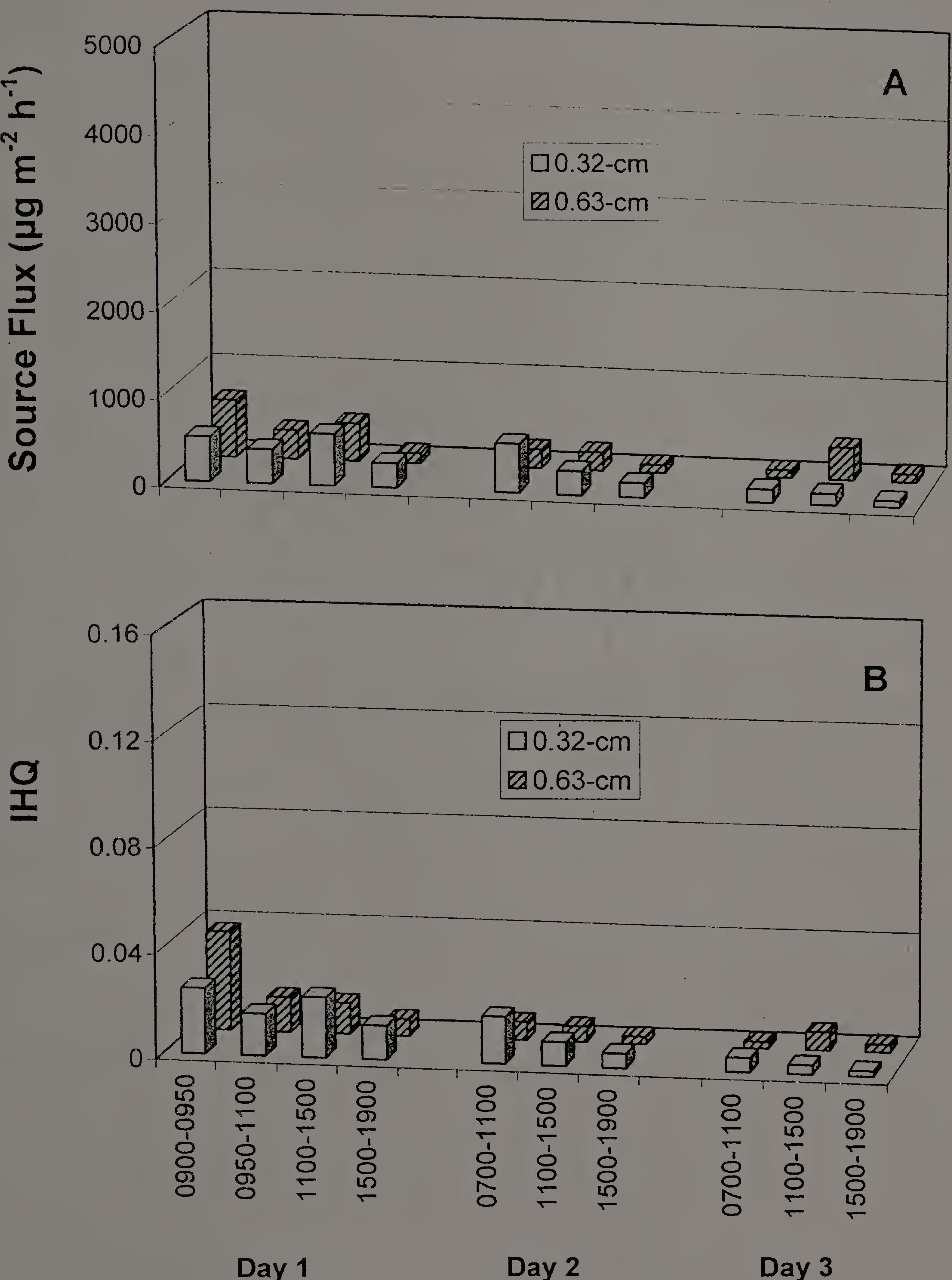


Figure 19. Source flux (panel A) and inhalation hazard quotient (IHQ, panel B)) determinations over a 3-day sampling period following application with trichlorfon at 1/4 full-rate with either 0.32- or 0.63-cm post-application irrigation. Values not significantly different at the 0.05 level.

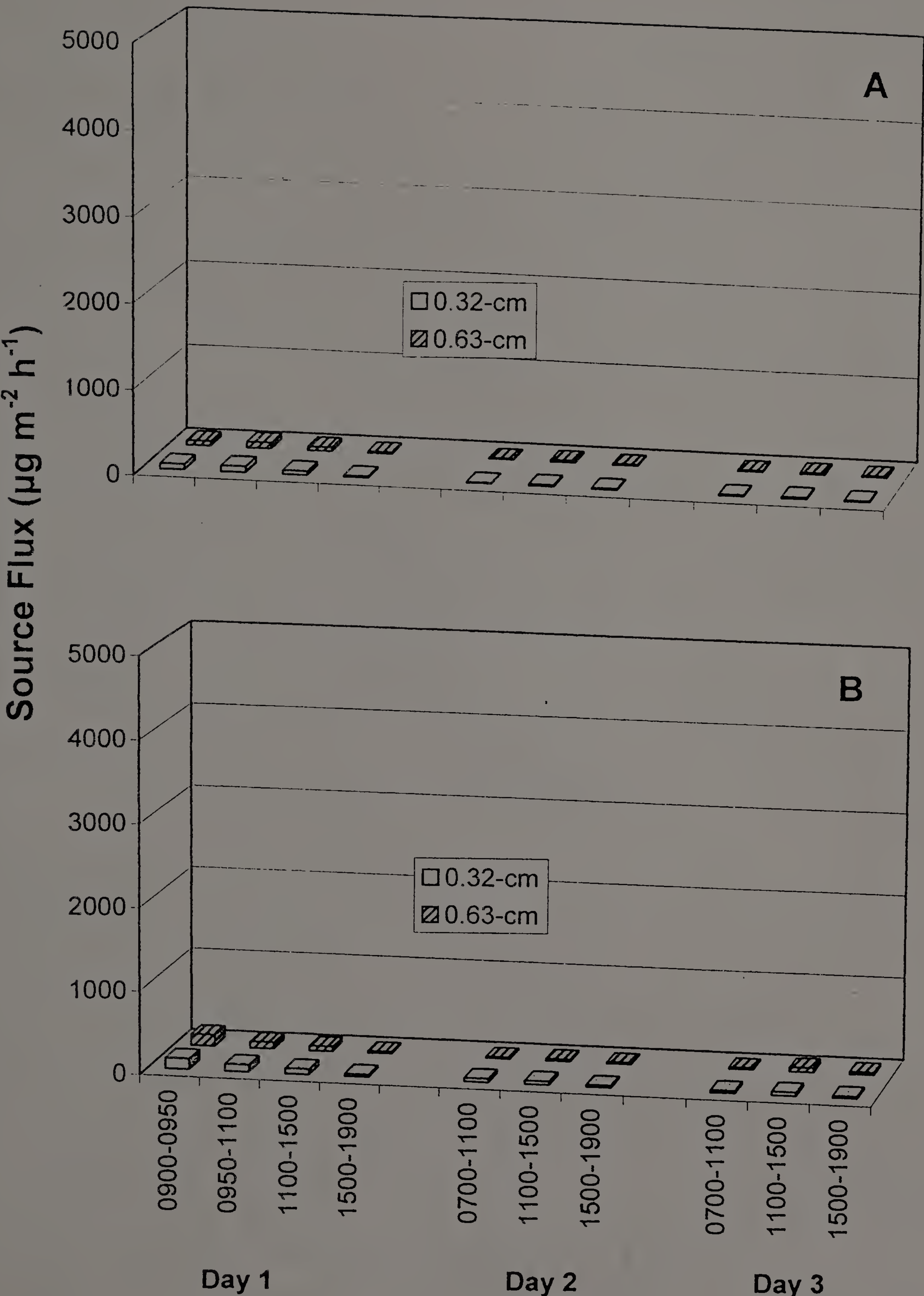


Figure 20. Source flux of triadimefon at 1/2 full-rate (panel A) and 1/4 full-rate (panel B) over a 3-day sampling period following either 0.32- or 0.63-cm post-application irrigation. Values not significantly different at the 0.05 level.

20A and B, IHQ values not shown).

Volatile triadimefon residues as determined by source flux were detectable but at very low levels (< 140 μg m^{-2} h^{-1}) immediately following application at 1/2 or 1/4 full-rates in the presence of either 0.63- or 0.32-cm post-application irrigation (Fig.20A and B). Previous examination of the environmental fate of full-rate triadimefon at 1.3-cm irrigation (Schumann et al., 2000) did not measure its volatility so direct comparison was not possible. However, comparisons can be made with the results of Murphy et al, (1996b), which examined volatility following application of full-rate triadimefon without post-application irrigation.

Reducing application from full to 1/2 full-rate at 0.63-cm post-application irrigation significantly reduced (n = 2) the level of volatile triadimefon residues compared to full-rate without post-application irrigation (Fig. 20A versus Murphy et al., 1996b, Fig. 1, t-test, $P \leq 0.05$). The average source flux (n=2) in the first hour of sampling following triadimefon application at 1/2 full-rate was decreased 10.5-fold compared to full-rate triadimefon without post-application irrigation (Fig. 20A versus Murphy et al., 1996b, Fig 1, 0900-0950 hr, t-test, $P \leq 0.05$). Over the entire 3-day collection, the source flux at 1/2 full-rate triadimefon was 9.7-fold less than at full-rate without post-application irrigation (Fig. 20A versus Murphy et al., 1996b, Fig. 1, t-test, $P \leq 0.05$).

Reducing application from full to 1/2 full-rate at 0.32-cm post-application irrigation significantly reduced the level of volatile triadimefon residues (Fig. 20B versus Murphy et al., 1996b, Fig. 1, t-test, $P \leq 0.05$). The average source flux (n = 2) in the first hour of sampling following triadimefon application at 1/2 full-rate was decreased 9.2-fold compared to full-rate without post-application irrigation (Fig. 20A versus Table 3, Murphy et al., 1996b). Over the entire 3-day collection, the source flux at 1/2 full-rate triadimefon was 9.7-fold less than at full-rate without post-application irrigation (Fig. 20A versus Murphy et al., 1996b, Fig. 1).

Reducing application from full to1/4 full-rate at 0.63-cm post-application irrigation significantly reduced the level of volatile triadimefon residues (Fig. 20B versus Murphy et al., 1996b, Fig. 1, t-test, $P \leq 0.05$). The average source flux (n=2) in the first hour of sampling following triadimefon application at 1/4 full-rate was decreased 4.2-fold compared to full-rate without post-application irrigation (Fig. 20B versus Murphy et al., 1996b, Fig. 1, t-test, $P \leq 0.05$). Over the entire 3-day collection, the source flux of 1/4 full-rate isofenphos was decreased 6.4-fold compared to full-rate without post-application irrigation (Fig. 20B versus Murphy et al., 1996b, Fig 1).

Reducing application from full to 1/4 full-rate at 0.32-cm post-application irrigation significantly reduced the level of volatile triadimefon residues. The average source flux (n = 2) in the first hour of sampling following trichlorfon application at 1/2 full-rate was decreased 4.6-fold compared to full-rate without post-application irrigation (Fig. 20B versus Table 3, Murphy et al., (1996b), t-test, $P \leq 0.05$). Over the entire 3-day collection, the source flux at 1/4 full-rate triadimefon was 5.5-fold less than at full-rate without post-application irrigation (Fig. 20B versus Murphy et al., 1996b, Fig. 1).

Overall, reducing applications from 1/2 to 1/4 full-rate followed by either 0.63- or 0.32-cm post-application irrigation did not significantly reduce the level of volatile triadimefon residues over the 3-day collection (Fig. 20A versus 20B, t-test, $P > 0.05$).

3.3.2. Dislodgeable Foliar Residues at 1/2 or 1/4 Full-rates in the Presence of 0.63- or 0.32-cm Post-application Irrigation.

3.3.2.1. Chlorpyrifos: Overall, dislodgeable foliar residues at 1/2 and 1/4 full-rate chlorpyrifos were most evident immediately following application and irrigation on Day 1 (15 min, Figs. 21A and 22A). Dislodgeable foliar residues continued to decrease over time for the remainder of the 3-day experiment. At no time in the 3-day experiment did DHQ values for chlorpyrifos exceed 1.0 (Figs. 21B and 22B).

Reducing application rates from full to 1/2 full-rate in the presence of 0.63-cm post application irrigation significantly reduced the level of dislodgeable foliar chlorpyrifos residues (Fig. 8A versus 21A, t-test, $P \leq 0.025$). Dislodgeable foliar residues of chlorpyrifos following application at 1/2 full-rate were decreased 1.7- and 5.8-fold over the first two sampling intervals compared to full-rate (15 min and 2 hrs post-application irrigation, respectively, Fig. 8A versus 21A). The highest DHQ value (0.4) was obtained in the first sampling interval (15 min post-application irrigation, Fig. 21B). Over the entire 3-day collection, the dislodgeable foliar residues at 1/2 full-rate chlorpyrifos were decreased 2.3-fold compared to full-rate (Fig. 8A versus 21A).

Reducing application rates from full to 1/2 full-rate with 0.32-cm post-application irrigation significantly reduced the level of dislodgeable foliar chlorpyrifos residues (Fig. 8A versus 21A, t-test, $P \leq 0.025$). Dislodgeable foliar residues of chlorpyrifos under these experimental parameters over the first day of sampling were reduced 2.0-fold compared to full-rate (Fig. 8A versus 21A). The highest DHQ value (0.5) was obtained in the first sampling interval (15 min post-application irrigation, Fig. 21B). Over the entire 3-day

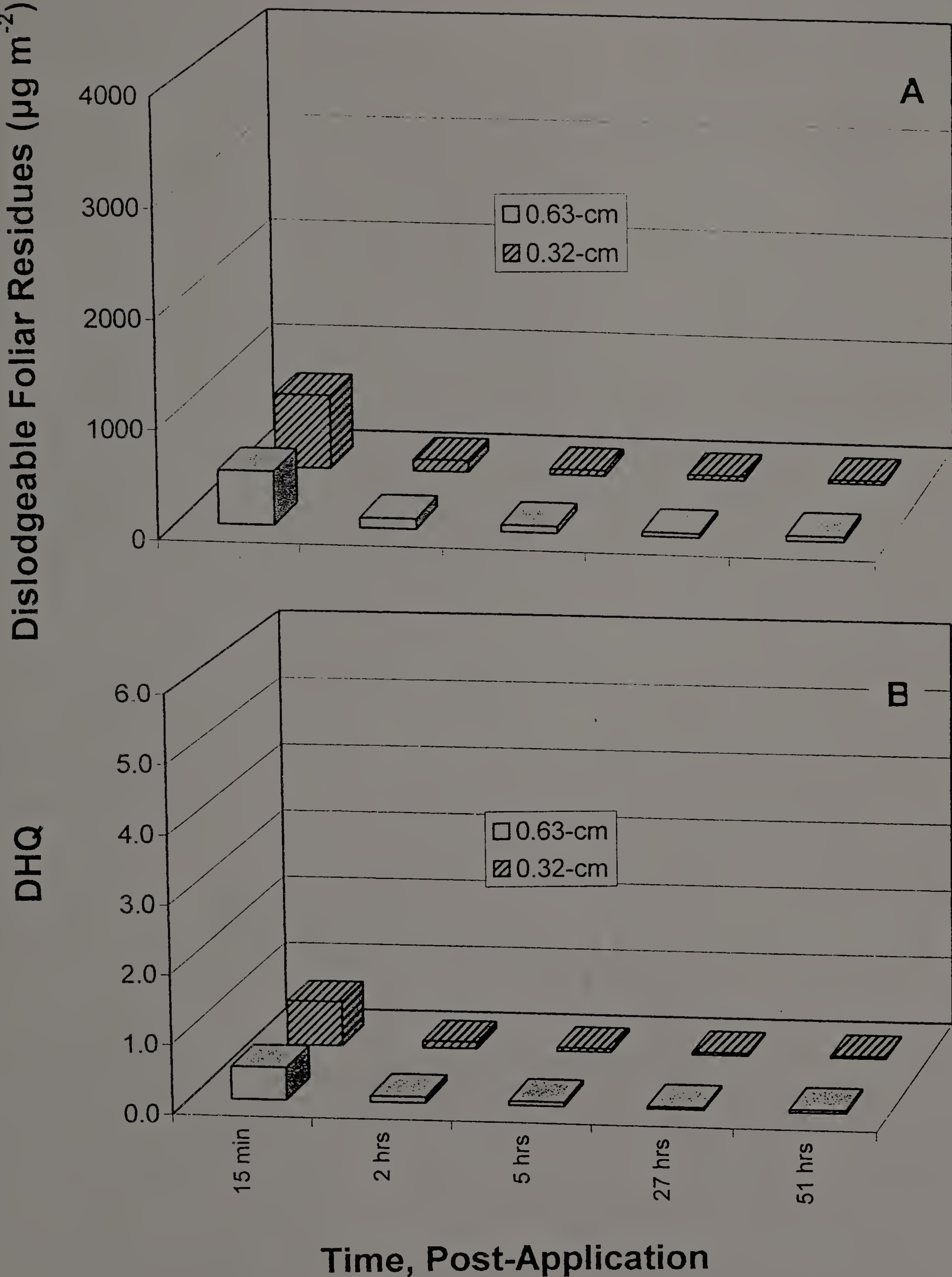


Figure 21. Dislodgeable foliar residues (µg m^{-2}, panel A) and dermal hazard quotient (DHQ) determinations (panel B) following applications of 1/2 full-rate chlorpyrifos at two levels of post-application irrigation (0.63- and 0.32-cm). Values not significantly different at the 0.025 level.

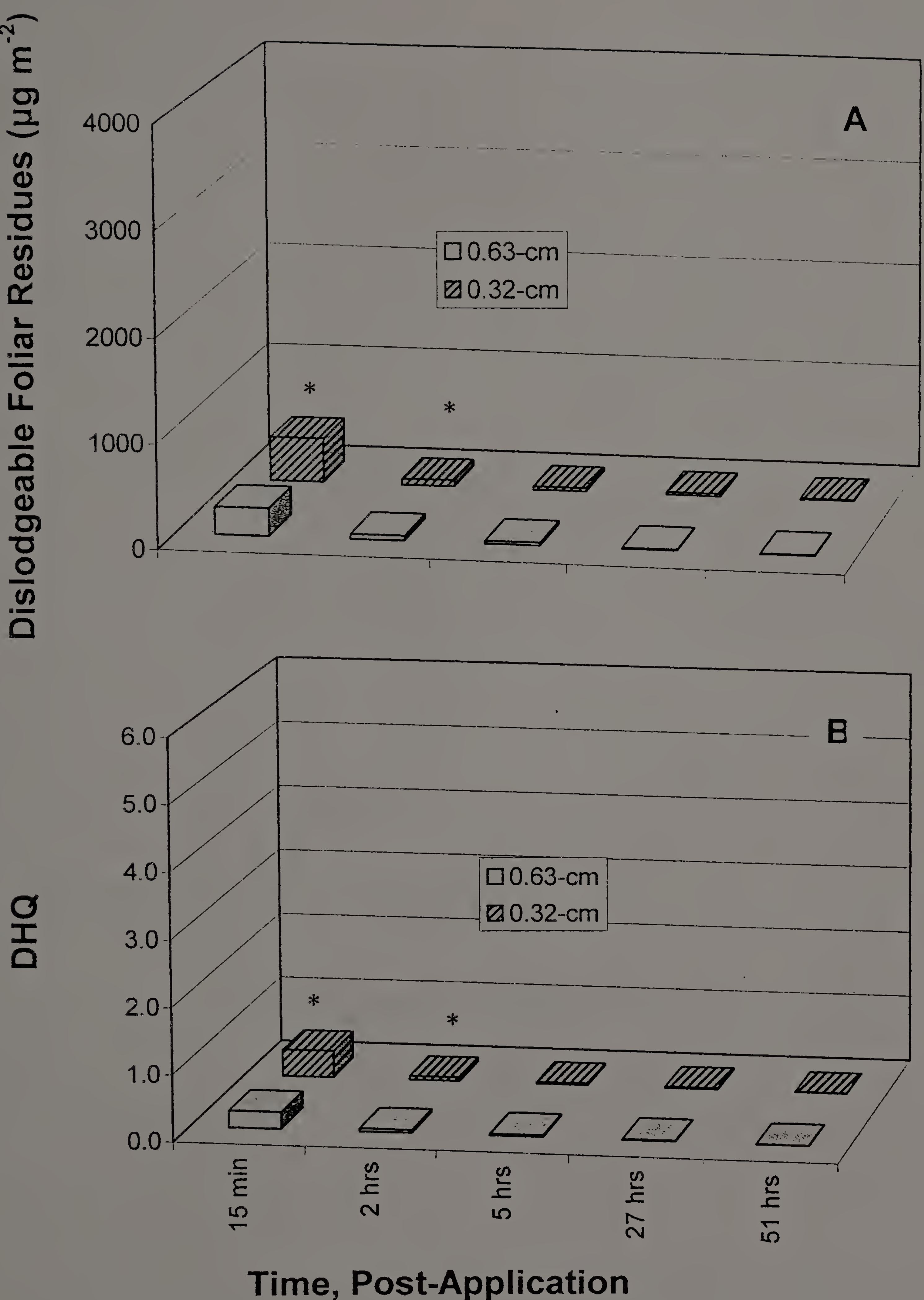


Figure 22. Dislodgeable foliar residues (µg m^{-2}, panel A) and dermal hazard quotient (DHQ) determinations (panel B) following applications at 1/4 full-rate chlorpyrifos at two levels of post-application irrigation (0.63- and 0.32-cm). *significant at the 0.025 level.

collection, the dislodgeable foliar residues at 1/2 full-rate chlorpyrifos were decreased 1.8-fold compared to full-rate (Fig. 8A versus 21A).

Reducing application rates from full to 1/4 full-rate in the presence of 0.63-cm post-application irrigation significantly reduced the level of dislodgeable foliar chlorpyrifos residues (Fig. 8A versus 22A, t-test, $P \leq 0.025$). Dislodgeable foliar residues of chlorpyrifos following application at 1/4 full-rate were decreased 2.6- and 7.5-fold in the first two sampling intervals compared to full-rate (15 min and 2 hrs post-application irrigation, respectively, Fig. 8A versus 22A). The highest DHQ value (0.25) was obtained in the first sampling interval (15 min, Fig. 22B). Over the entire 3-day collection, the dislodgeable foliar residues at 1/4 full-rate chlorpyrifos were decreased 4.7-fold compared to full-rate (Fig. 8A versus 22A).

Reducing application rates from full to 1/4 full-rate with 0.32-cm post-application irrigation significantly reduced the level of dislodgeable foliar chlorpyrifos residues (Fig. 8A and 22A, t-test, $P \leq 0.025$). Dislodgeable foliar residues of chlorpyrifos following application at 1/4 full-rate were decreased 1.8- and 5.0-fold in the first two sampling intervals compared to full-rate (15 min and 2 hrs post-application irrigation respectively, Fig. 8A and 22A). The highest DHQ value (0.4) was obtained in the first sampling interval (15 min post-application irrigation, Fig. 22B). Over the entire 3-day collection, the dislodgeable foliar residues of 1/4 full-rate chlorpyrifos were decreased 3.1-fold compared to full-rate (Fig. 8A versus 22A).

Reducing the application rate from 1/2 to 1/4 full-rate in the presence of 0.63-cm post application irrigation significantly reduced the level of dislodgeable foliar chlorpyrifos residues (excluding Day 3, Fig. 21A versus 22A). At 0.32-cm irrigation, significant reduction was seen at 2, 5 and 51 hrs post-application irrigation (Fig. 21A versus 22A).

3.3.2.2. Isofenphos. Overall, dislodgeable foliar residues of 1/2 and 1/4 full-rate isofenphos were most evident immediately following application and irrigation on Day 1 (15 min, Figs. 23A and 24A). Dislodgeable foliar residues continued to decrease over time for the remainder of the 3-day experiment. DHQ values only exceeded 1.0 on Day 1 during the 3-day experiment (Figs. 23B and 24B).

Reducing application rates from full to 1/2 full-rate in the presence of 0.63-cm post-application irrigation significantly reduced the level of dislodgeable foliar isofenphos residues (Fig. 10A and 23A, t-test, $P \leq 0.025$). Dislodgeable foliar residues of isofenphos following application at 1/2 full-rate were decreased 4.9- and 15.1-fold in the first two sampling intervals compared to full-rate (15 min and 2 hrs post-application irrigation, respectively, Fig. 10A versus 23A, t-test, $P \leq 0.025$). The highest DHQ value (0.9) was obtained in the first sampling interval in the presence of 0.63-cm post-application irrigation (15 min, Fig. 23B). Over the entire 3-day collection, the dislodgeable foliar residues of 1/2 full-rate isofenphos were decreased 6.1-fold compared to full-rate (Fig. 10A versus 23A).

Reducing application rates from full to 1/2 full-rate in the presence of 0.32-cm post-application irrigation resulted significantly reduced the level of dislodgeable foliar isofenphos residues (Fig. 10A and 23A, t-test, $P \leq 0.025$). Dislodgeable foliar residues of isofenphos following application at 1/2 full-rate were decreased 3- and 10-fold in the first two sampling intervals compared to full-rate (15 min and 2 hrs post-application irrigation, respectively, Fig. 10A versus 23A, t-test, $P \leq 0.025$). The highest DHQ value

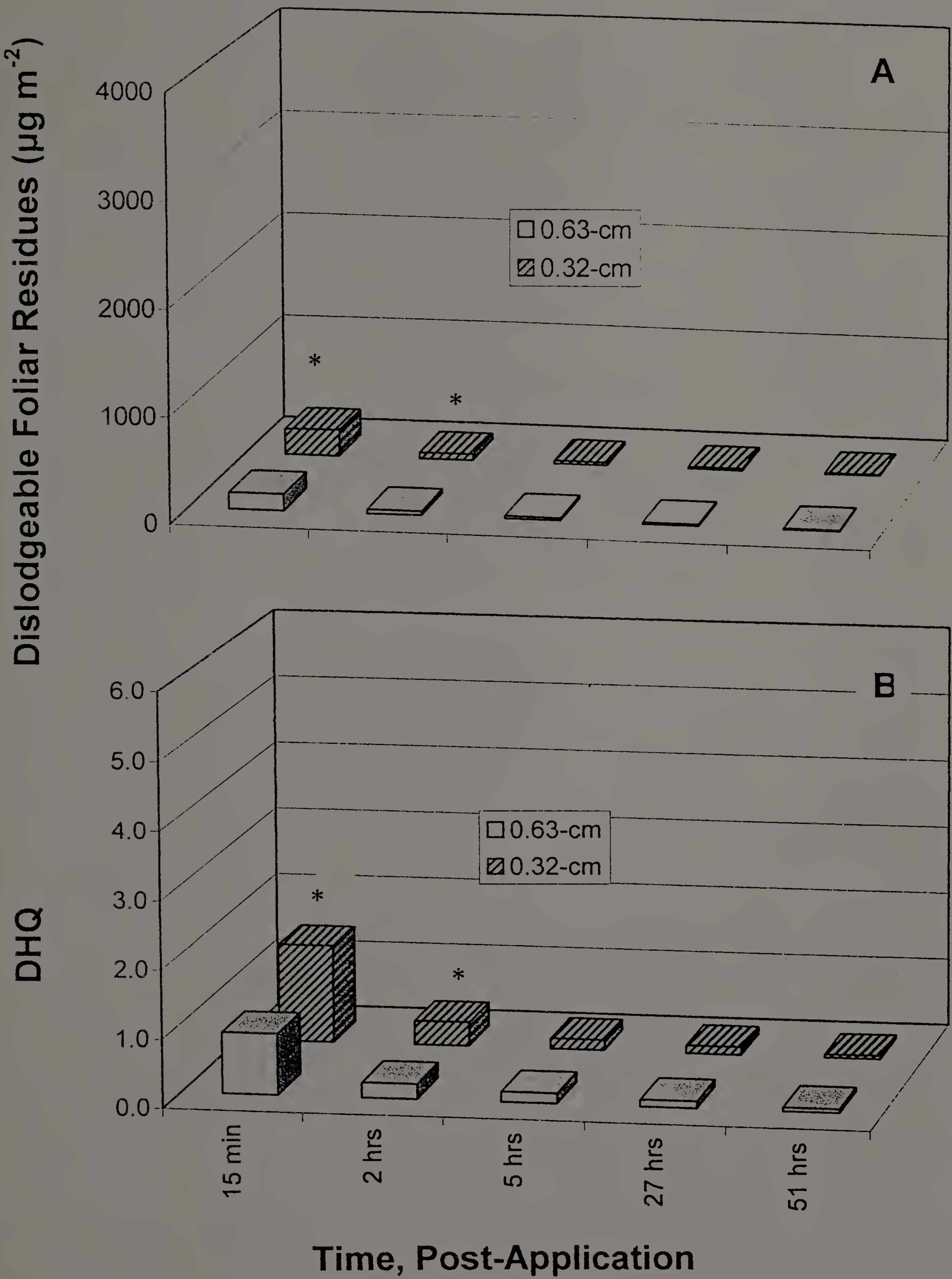


Figure 23. Dislodgeable foliar residues (µg m^{-2}, panel A) and dermal hazard quotient (DHQ) determinations (panel B) following applications of 1/2 full-rate isofenphos at two levels of post-application irrigation (0.63- and 0.32-cm). * significant at the 0.025 level.

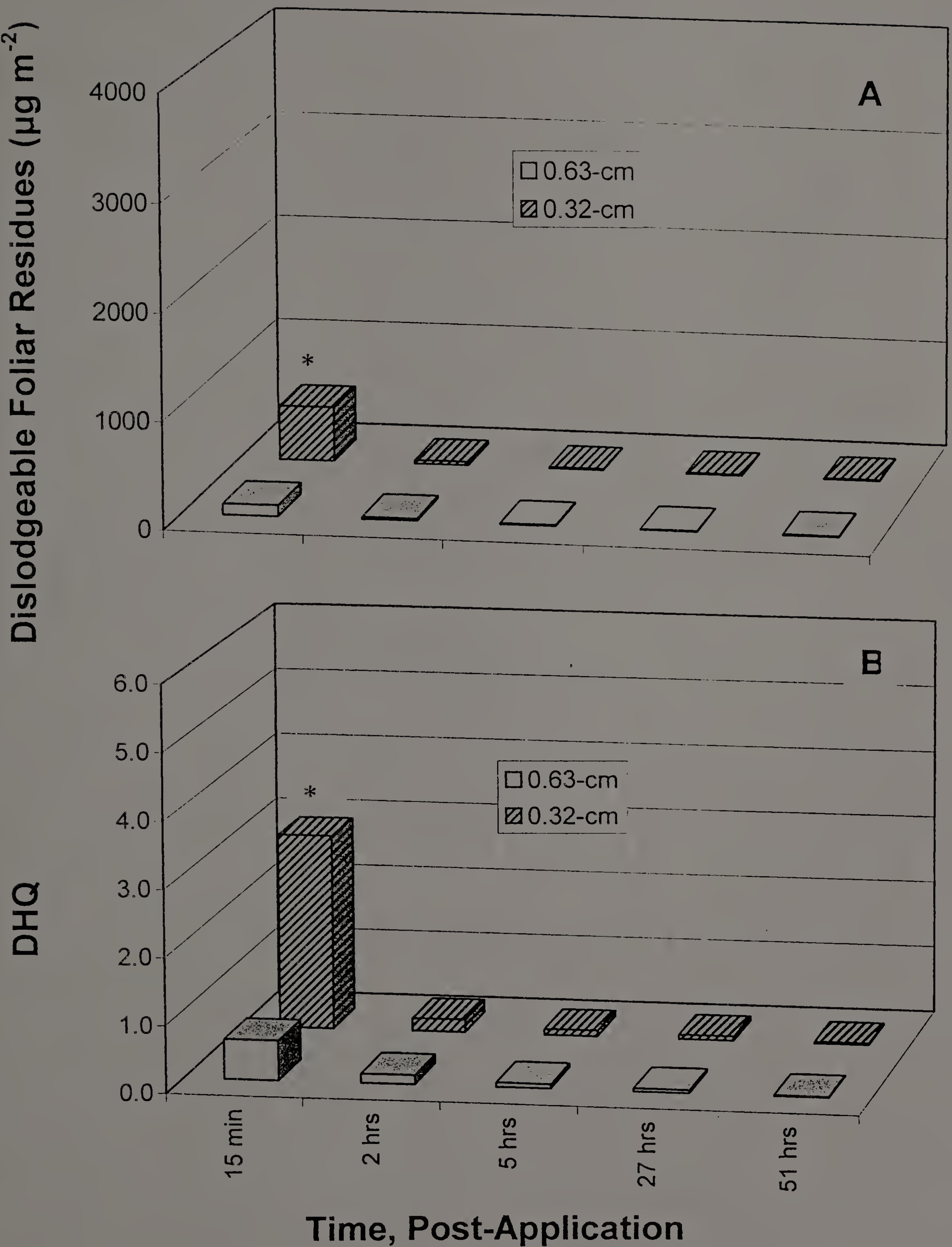


Figure 24. Dislodgeable foliar residues (µg m^{-2}, panel A) and dermal hazard quotient (DHQ) determinations (panel B) following applications of 1/4 full-rate isofenphos at two levels of post-application irrigation (0.63- and 0.32-cm). * significant at the 0.025 level.

(1.4) was obtained in the first sampling interval (15 min, at 0.32-cm irrigation, Fig. 23B). Over the entire 3-day collection, the dislodgeable foliar residues of 1/2 full-rate isofenphos were decreased 9.7-fold compared to full-rate (Fig. 10A versus 23A).

Reducing application rates from full to 1/4 full-rate in the presence of 0.63-cm post-application irrigation significantly reduced the level of dislodgeable foliar isofenphos residues (Fig. 10A versus 24A, t-test, $P < 0.025$). Dislodgeable foliar residues of isofenphos following application at 1/2 full-rate were significantly decreased 4.9- and 15.1-fold in the first two sampling intervals compared to full-rate (15 min and 2 hrs post-application irrigation, respectively, Fig. 10A and 24A, t-test, $P < 0.025$). The highest DHQ value (0.9) was obtained in the first sampling interval (15 min post-application irrigation, Fig. 24B at 0.63-cm irrigation). Over the entire 3-day collection, the dislodgeable foliar residues of 1/2 full-rate isofenphos were decreased 4.2-fold compared to full-rate (Figs. 10A versus 24A).

Reducing application rates from full to 1/4 full-rate in the presence of 0.32-cm post-application irrigation significantly reduced the level of dislodgeable foliar isofenphos residues (Figs. 10A and 24A, t-test, $P \leq 0.025$). Dislodgeable foliar residues of isofenphos following application at 1/2 full-rate were decreased 1.5- and 16.7-fold in the first two sampling intervals compared to full-rate (15 min and 2 hrs post-application irrigation, respectively, Figs. 10A and 24A, t-test, $P \leq 0.025$). The highest DHQ value (2.8) was obtained in the first sampling interval (15 min post-application irrigation, Fig. 24B at 0.32-cm irrigation). Over the entire 3-day collection, the dislodgeable foliar residues of 1/4 full-rate isofenphos were decreased 2.6-fold compared to full-rate (Figs. 10A versus 24A).

Reducing application rate from 1/2 to 1/4 full-rate in the presence of 0.63-cm post-application irrigation significantly reduced the level of dislodgeable foliar isofenphos residues at 15 min, 5, and 27 hrs post-application irrigation (Figs. 23A and 24A, t-test, $P \leq 0.025$).

Reducing application rate from 1/2 to 1/4 full-rate in the presence of 0.32-cm post-application irrigation did not significantly reduce the level of dislodgeable foliar isofenphos residues (except at 5 hrs post-application irrigation) (Figs. 23A and 24A, t-test, $P > 0.025$). At 15 min post-application, there were significantly higher residues at the 1/4 full-rate treatment.

3.3.2.3. Trichlorfon. Overall, dislodgeable foliar residues at 1/2 and full-rate trichlorfon were most prevalent immediately following application and irrigation on Day 1 (15 min, Figs. 25A and 27A). Dislodgeable foliar residues continued to decrease over time for the remainder of the 3-day experiment (Figs. 25A and 27A). At 1/2 full-rate, DHQ values only exceeded 1.0 on Day 1 during the 3-day experiment at 0.63-cm post-application irrigation. At 0.32-cm post-application irrigation however, they exceeded 1.0 on Day 2 (Fig. 25B).

In research by Clark et al., (2000), dislodgeable foliar residues and DHQ values for trichlorfon were not reported at sampling intervals less than the 5 hr sample interval. Therefore, only the 5, 27 and 51 hr (see below) post-application irrigation collections could be compared for trichlorfon in this research (Fig. 26A). Dislodgeable foliar residues of trichlorfon following application at full-rate were 510, 615, and 330 $\mu g\ m^{-2}$ at 5, 27, and 51 hrs post-application irrigation, respectively.

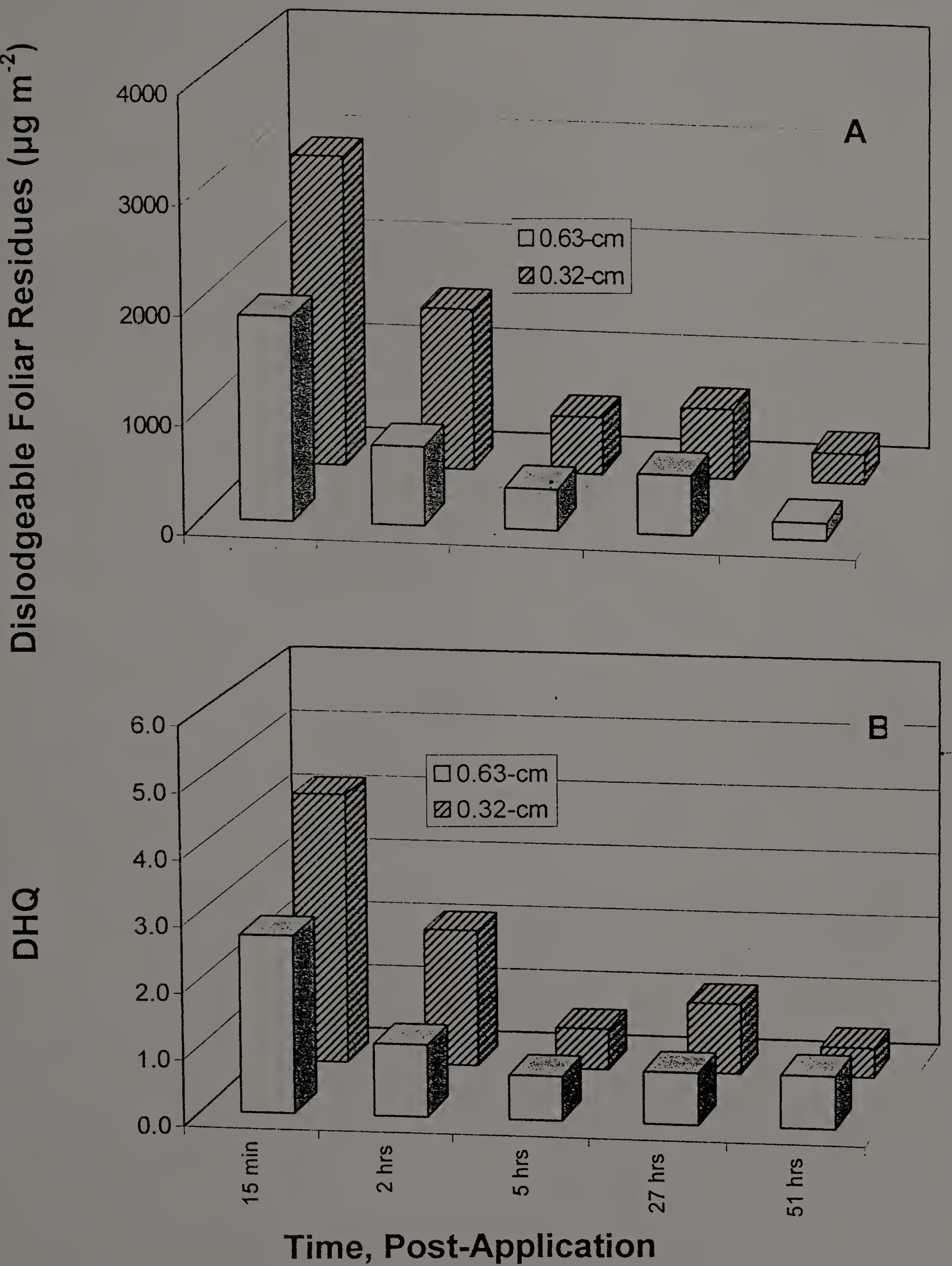


Figure 25. Dislodgeable foliar residues (µg m^{-2}, panel A) and dermal hazard quotient (DHQ) determinations (panel B) following applications of 1/2 full-rate trichlorfon and two levels of post-application irrigation (0.63- and 0.32-cm). Values not significantly different at the 0.025 level.

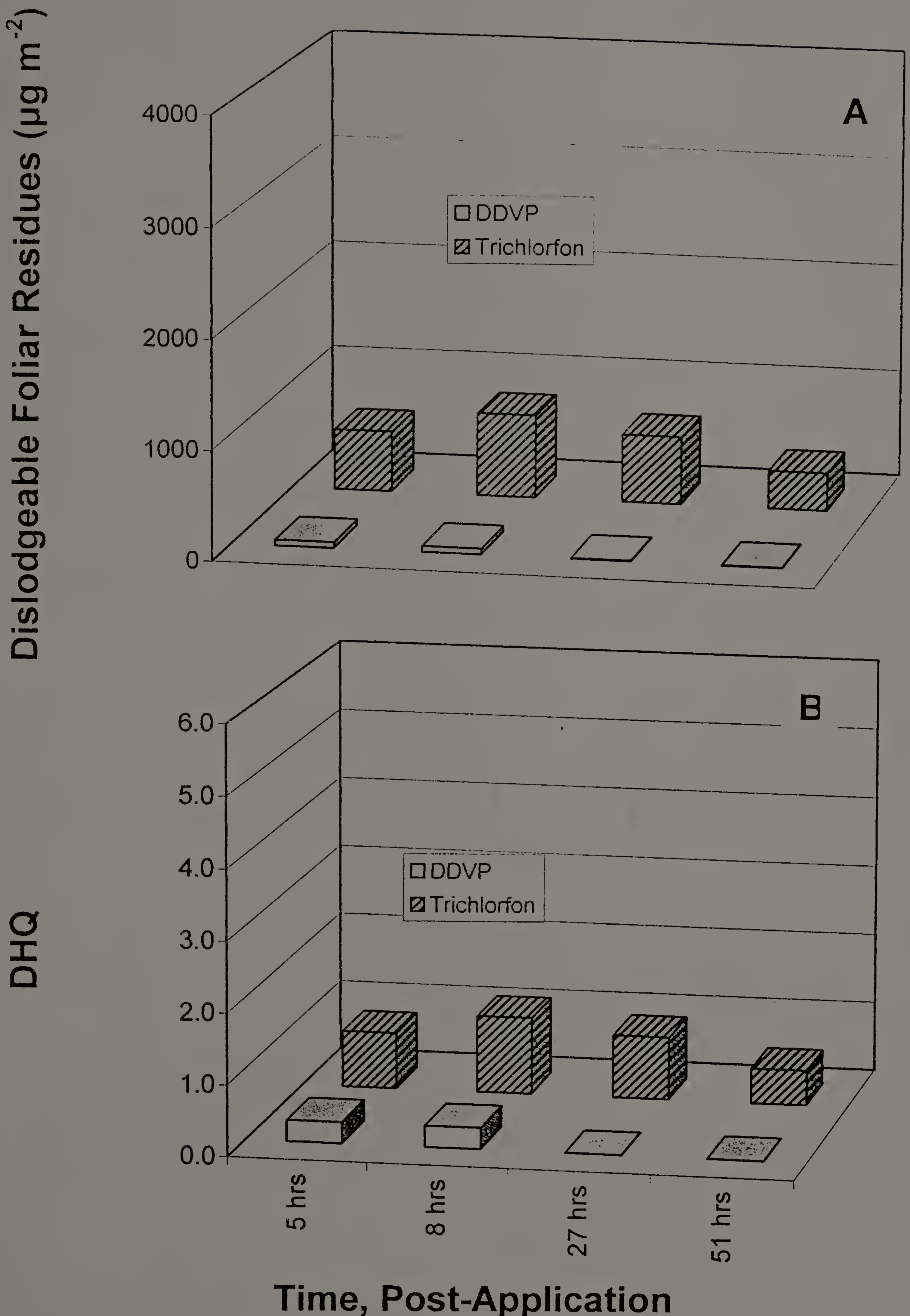


Figure 26. Dislodgeable foliar residues (µg m^{-2}, panel A) and dermal hazard quotient (DHQ) determinations (panel B) of DDVP and trichlorfon following application of full-rate trichlorfon with post-application irrigation at 0.63-cm (Clark et al., 2000).

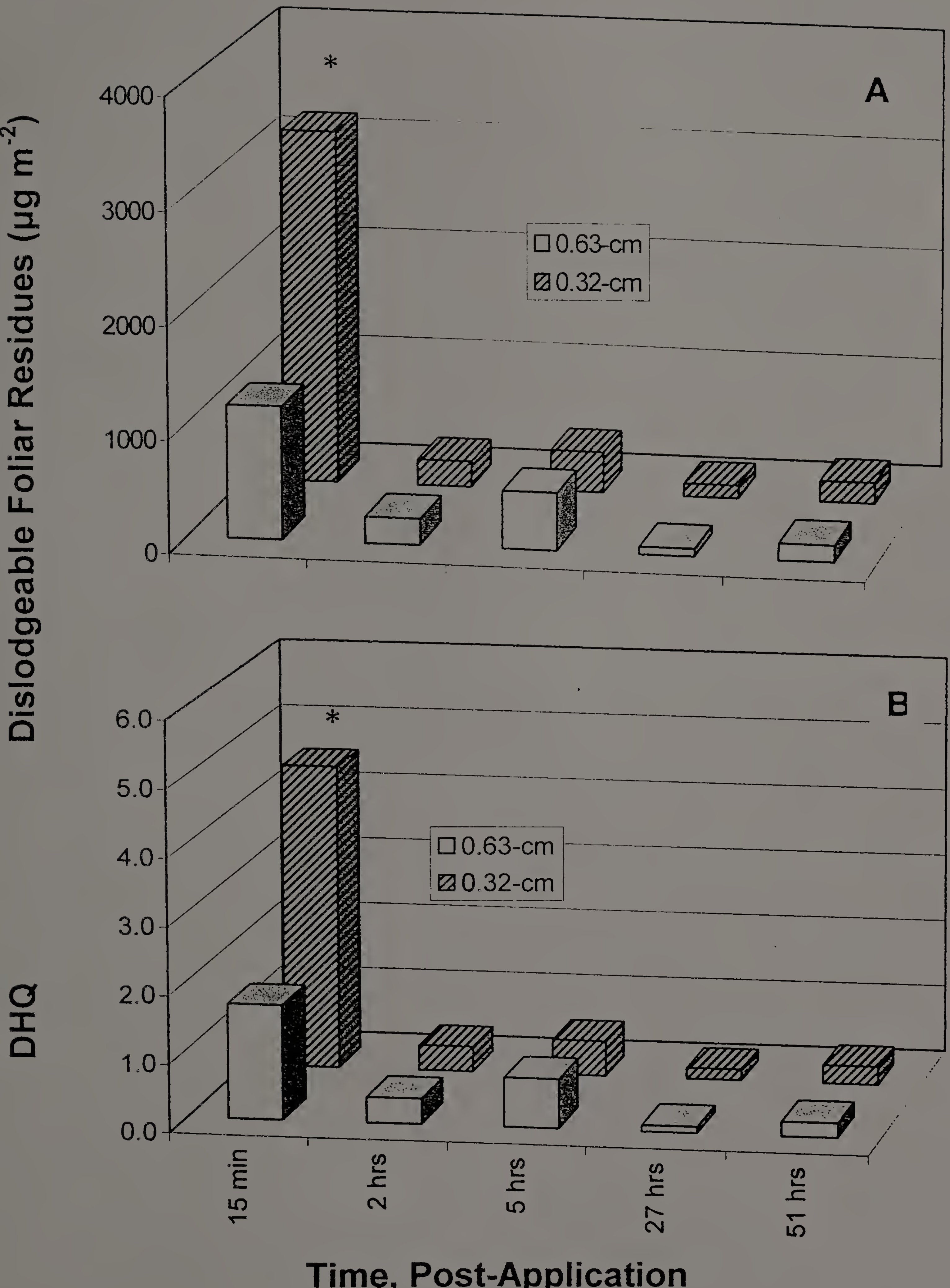


Figure 27. Dislodgeable foliar residues (µg m^{-2}, panel A) and dermal hazard quotient (DHQ) determinations (panel B) following applications of 1/4 full-rate trichlorfon and two levels of post-application irrigation (0.63- and 0.32-cm). * Significant at the 0.025 level.

Reducing application rates from full to 1/2 full-rate in the presence of 0.63-cm post-application irrigation did not significantly reduce the level of dislodgeable foliar trichlorfon residues (Fig. 26A versus 25A, t-test, $P > 0.025$). Dislodgeable foliar residues of trichlorfon following application at 1/2 full-rate were reduced 1.1-, increased 1.1- and reduced 2-fold, at 5, 27 and 51 hrs post-application irrigation, respectively (Fig. 26A versus 25A, t-test, $P > 0.025$). The highest DHQ value (2.7) was obtained in the first sampling interval (15 min post-application irrigation, Fig. 25B).

Reducing application rates from full to 1/2 full-rate in the presence of 0.32-cm post-application irrigation did not significantly reduce the level of dislodgeable foliar trichlorfon residues (Fig. 25A versus 26A, t-test, $P > 0.025$). Dislodgeable foliar residues of trichlorfon following application at 1/2 full-rate were 0-fold different, increased 1.4-fold, and were 0-fold different at 5, 27 and 51 hrs post-application irrigation, respectively (Fig. 26A versus 25A, t-test, $P > 0.025$). The highest DHQ value (4.1) was obtained in the first sampling interval (15 min post-application irrigation, Fig. 25B at 0.32-cm irrigation).

Reducing application rates from full to 1/4 full-rate in the presence of 0.63-cm post-application irrigation significantly reduced the level of dislodgeable foliar trichlorfon residues (Fig. 26A versus 27A, t-test $P \leq 0.025$). Dislodgeable foliar residues following application of 1/4 full-rate trichlorfon were decreased by 0-, 10.8-, 3.5-fold compared to full-rate at 5, 27 and 51 hrs post-application irrigation, respectively (Fig. 26A versus 27A, t-test, $P \leq 0.025$). The highest DHQ value (1.8) was obtained in the first sampling interval (15 min post-application irrigation, Fig. 27B).

Reducing application rates from full to 1/4 full-rate in the presence of 0.32-cm post-application irrigation significantly reduced the level of dislodgeable foliar trichlorfon residues (Fig. 26A versus 27A, t-test, $P \leq 0.025$). Dislodgeable foliar residues of trichlorfon following application at 1/4 full-rate were decreased by 1.3- 8.7- and 3.5-fold compared to full-rate 5, 27 and 51 hrs post-application irrigation, respectively (Fig. 26A versus 27A, t-test, $P \leq 0.025$). The highest DHQ value (4.5) was obtained in the first sampling interval (15 min post-application irrigation, Fig. 27B).

3.3.2.4. Triadimefon: Overall, dislodgeable foliar residues of triadimefon were most prevalent immediately following application and irrigation (15 min on Day 1). Dislodgeable foliar residues continued to decrease over time for the remainder of the 3-day experiment (Figs. 28A and B).

There was no available research data of dislodgeable foliar triadimefon residues following application at full-rate in the presence of 0.63-cm post-application irrigation. However, research of triadimefon at full-rate was examined by Murphy et al., (1993b) without irrigation and Schumann et al., (2000) in the presence of 1.3-cm irrigation. In this research, examination of 1/2 and 1/4 full-rate triadimefon in the presence of either 0.63- or 0.32-cm irrigation was used to monitor conversion of triadimefon to triadimenol and to compare the results in the presence of higher level of irrigation (1.3-cm) or without irrigation. Dislodgeable foliar residues of triadimefon following application were nearly nondetectable at both irrigation levels (0.63- and 0.32-cm) and there was no DHQ value above 0.001 (Figs. 28A and B, DHQ values not shown).

Application rates at 1/2 full-rate in the presence of 0.63- or 0.32-cm post-application irrigation, however, resulted in significant reduction on the level of

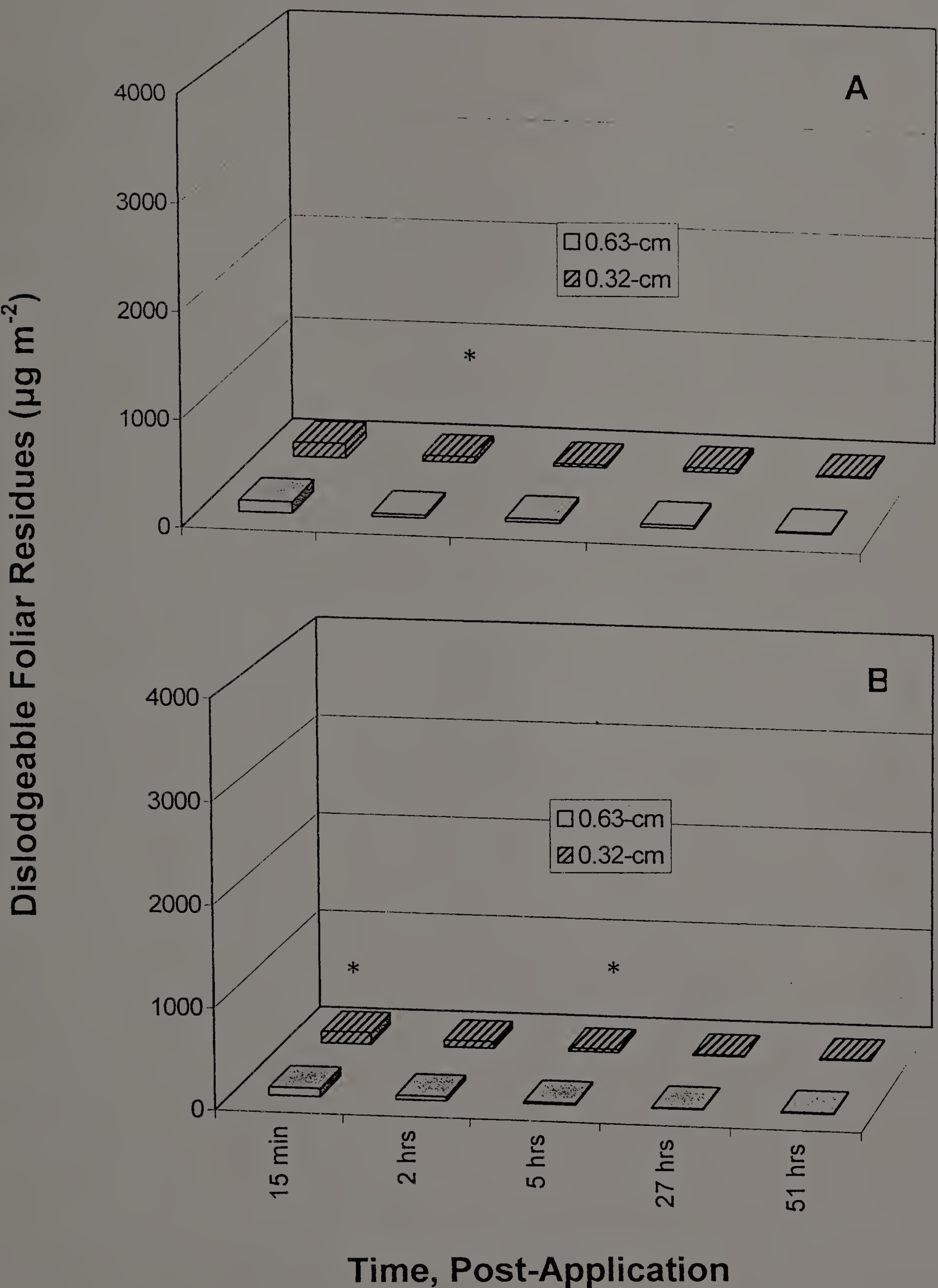


Figure 28. Dislodgeable foliar residues (µg m^{-2}) following application to turfgrass with triadimefon at 1/2 full-rate (panel A) and 1/4 full-rate (panel B) with post-application irrigation at either 0.63- or 0.32-cm. * significant at the 0.025 level.

dislodgeable foliar triadimefon residues compared to full-rate without irrigation (Fig. 28A versus Fig. 1., Murphy et al., 1996b, t-test, $P \leq 0.025$). Over the entire 3-day collection in the presence of 0.63- and 0.32-cm post-application irrigation, the dislodgeable foliar residues of 1/2 full-rate triadimefon were decreased 55- and 41-fold compared to full-rate without irrigation, respectively (Fig. 27A versus Fig. 1., Murphy et al., 1996b, t-test, $P \leq 0.025$).

Reducing application rates from full to 1/4 full-rate in the presence of 0.63- and 0.32-cm post-application irrigation resulted in a significant reduction in the level of dislodgeable foliar triadimefon residues compared to full-rate without irrigation (Fig. 27B versus Murphy et al., 1996b, Fig. 1, t-test, $P \leq 0.025$). Over the entire 3-day collection, the dislodgeable foliar residues of 1/4 full-rate triadimefon in the presence of 0.63- and 0.32-cm post-application irrigation were decreased 55- and 45-fold compared to full-rate without irrigation (Fig. 27B versus Murphy et al., 1996b, Fig. 1, t-test, $P \leq 0.025$).

3.4. Effect of Post-application Irrigation on Conversion of Trichlorfon and Triadimefon.

3.4.1. Conversion of Trichlorfon to DDVP.

3.4.1.1. Volatile Residues. Overall, the volatilization of DDVP following application of 1/2 and 1/4 full-rate trichlorfon as measured by source flux was most evident immediately following application at both the 0.63- or 0.32-cm levels of post-application irrigation (Figs. 29A and 30A). Volatile residues decreased over time in a diurnal pattern on Days 1 through 3 becoming much less pronounced by Day 3. Under these conditions, IHQ values never exceeded 0.11 (Figs. 29B and 30B).

Examination of previous research by Murphy et al., (1996a) of volatile trichlorfon residues at full-rate in the presence of 1.3-cm irrigation as determined by source flux

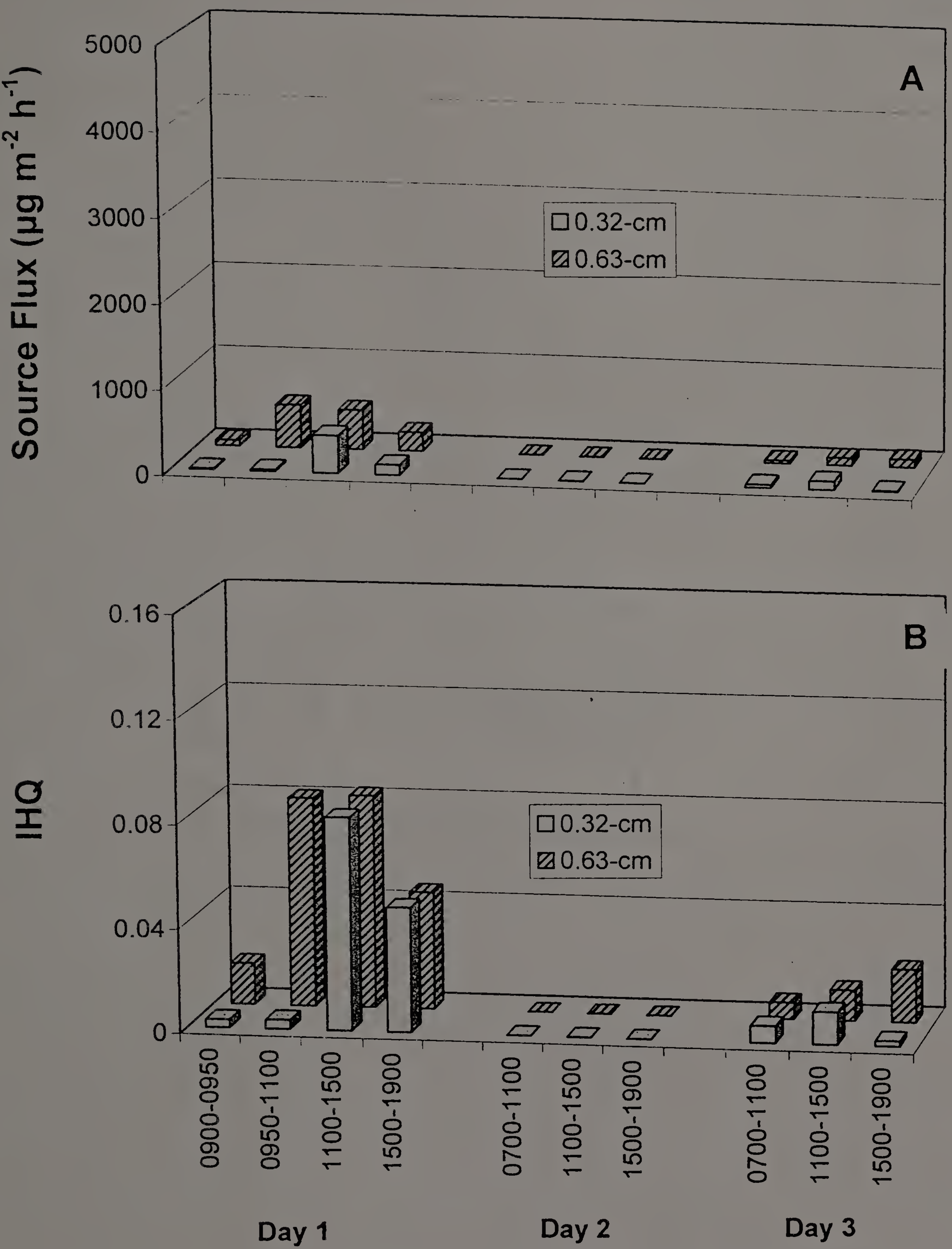


Figure 29. Source flux (panel A) and inhalation hazard quotient determinations (IHQ, panel B) of **DDVP** over a 3-day sampling period following application of trichlorfon at 1/2 full-rate with either 0.63- or 0.32-cm post-application irrigation. Values not significantly different at the 0.05 level.

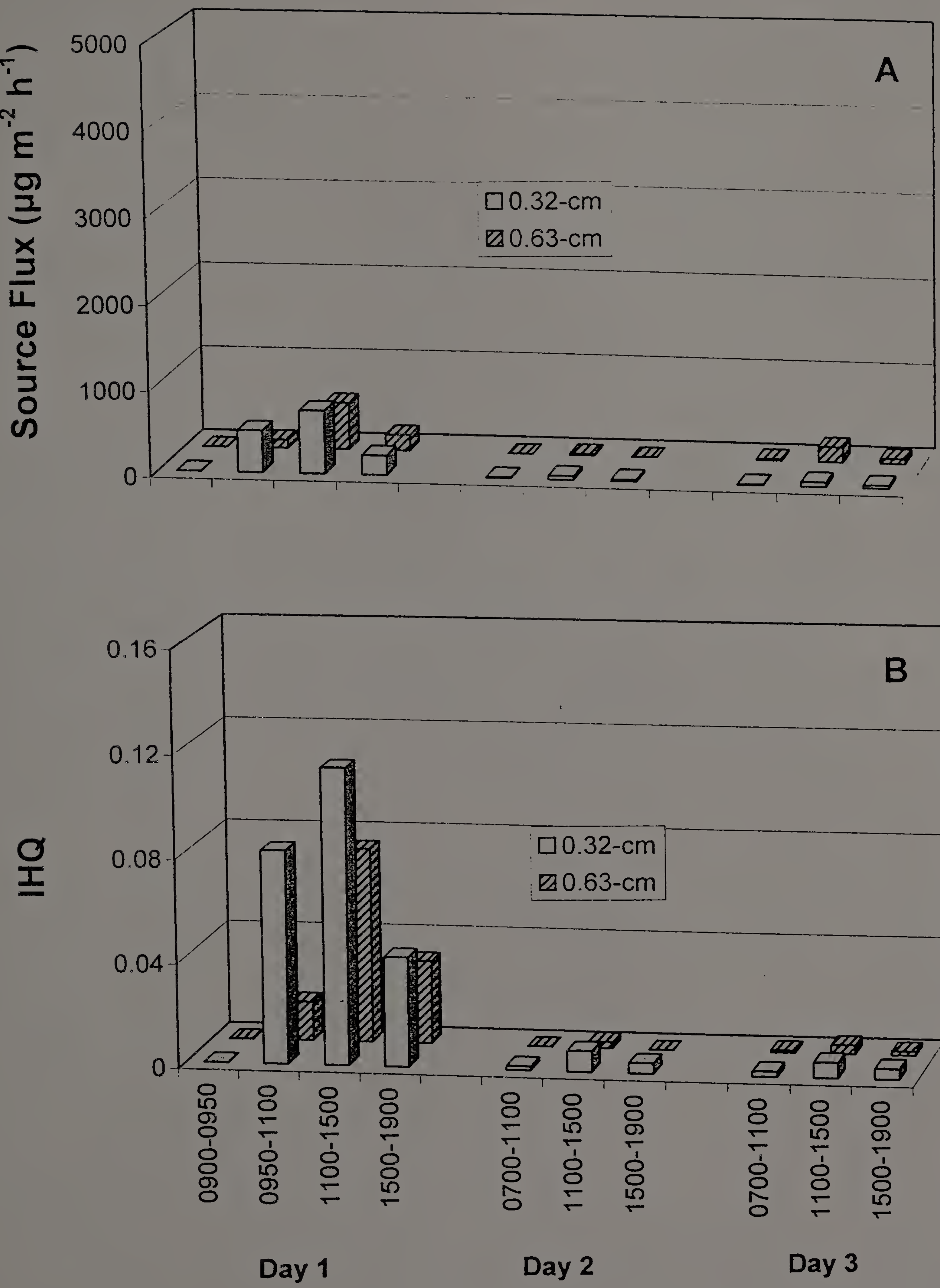


Figure 30. Source flux (panel A) and inhalation hazard quotient (IHQ, panel B) determinations of **DDVP** over a 3-day sampling period following application of trichlorfon at 1/4 full-rate with either 0.32- or 0.63-cm post-application irrigation. Values not significantly different at the 0.05 level.

resulted in a 2.5-fold increase in the conversion of trichlorfon to DDVP compared to full-rate application in the presence of 0.63-cm irrigation (Clark et al., 2000). Overall, the percent loss of total applied trichlorfon as volatile DDVP residues was 5.6 and 2.2 % at 1.3- and 0.63-cm irrigation, respectively (Table 4).

Reducing application rates from full to 1/2 full-rate in the presence of 0.63-cm post-application irrigation did not significantly reduce the level of volatile DDVP residues (Fig. 29A, versus Table VI, Clark et al., 2000, t-test, $P > 0.025$). The highest IHQ value (0.08) was obtained in the second and third sampling interval on Day 1 (0950-1500 hrs, Fig. 29B at 0.63-cm irrigation). Over the entire 3-day collection however, the source flux of volatile DDVP residues following 1/2 full-rate with 0.63-cm post-application irrigation was significantly decreased by 6.3- and 7.1-fold compared to full-rate trichlorfon without irrigation and 1.3-cm post-application irrigation, respectively (Fig 29A versus Figs. 1 and 2, Murphy et al., 1996a, t-test, $P < 0.05$).

Reducing application rates from full to 1/2 full-rate in the presence of 0.32-cm post-application irrigation did not significantly reduce the level of volatile DDVP residues (Fig. 29A versus Table VI, Clark et al., 2000, t-test, $P \leq 0.025$). The highest IHQ value (0.08) was obtained in the third sampling interval on Day 1 (1100-1500 hrs, Fig. 29B, 0.32-cm irrigation). Over the entire 3-day collection, however, the source flux of volatile DDVP residues following 1/2 full-rate with 0.32-cm post-application irrigation was significantly decreased 3.6- and 12.5-fold compared to full-rate trichlorfon without irrigation and with 1.3-cm post-application irrigation, respectively (Fig. 29A versus Figs. 1 and 2, Murphy et al., 1996a, t-test, $P < 0.05$).

Reducing application rates from full to 1/4 full-rate in the presence of 0.63-cm post-application irrigation did not significant reduce the level of DDVP volatile residues (Fig. 30A versus Table VI, Clark et al., 2000, t-test, $P > 0.025$). The highest IHQ value (0.08) was obtained in the third sampling interval on Day 1 (1100-1500 hrs Fig. 30B, at 0.63-cm irrigation). Over the entire 3-day collection, however, the source flux of volatile DDVP residues following 1/4 full-rate and 0.63-cm post-application irrigation was significantly decreased 4.8- and 8.4- fold compared to full-rate trichlorfon without irrigation and 1.3-cm post-application irrigation, respectively (Fig. 30A versus Figs. 1 and 2, Murphy et al., 1996a, t-test, $P < 0.05$).

Reducing application rates from full to 1/4 full-rate in the presence of 0.32-cm post-application irrigation resulted in no significant reduction on the level of DDVP volatile residues (Fig. 30A versus Table VI, Clark et al., 2000, t-test, $P > 0.025$). The highest IHQ value (0.11) was obtained in the third sampling interval on Day 1 (1100-1500 hrs, Fig. 29B, at 0.63-cm irrigation). Over the entire 3-day collection, however, the source flux of volatile DDVP residues following 1/4 full-rate and 0.32-cm post-application irrigation was significantly decreased 3.3- and 5.7-fold compared to full-rate trichlorfon without irrigation and 1.3-cm post-application irrigation, respectively (Fig. 30A versus Figs. 1 and 2, Murphy et al., 1996a, t-test, $P< 0.05$).

3.4.1.2. Dislodgeable Foliar Residues. Previous examination of dislodgeable foliar trichlorfon residues at full-rate in the presence of 1.3-cm irrigation (Fig. 31, Murphy et al., 1996a) compared to full-rate and 0.63-cm irrigation (Clark et al., 2000) resulted in a 2.5-fold increase in the conversion of trichlorfon to DDVP. The highest

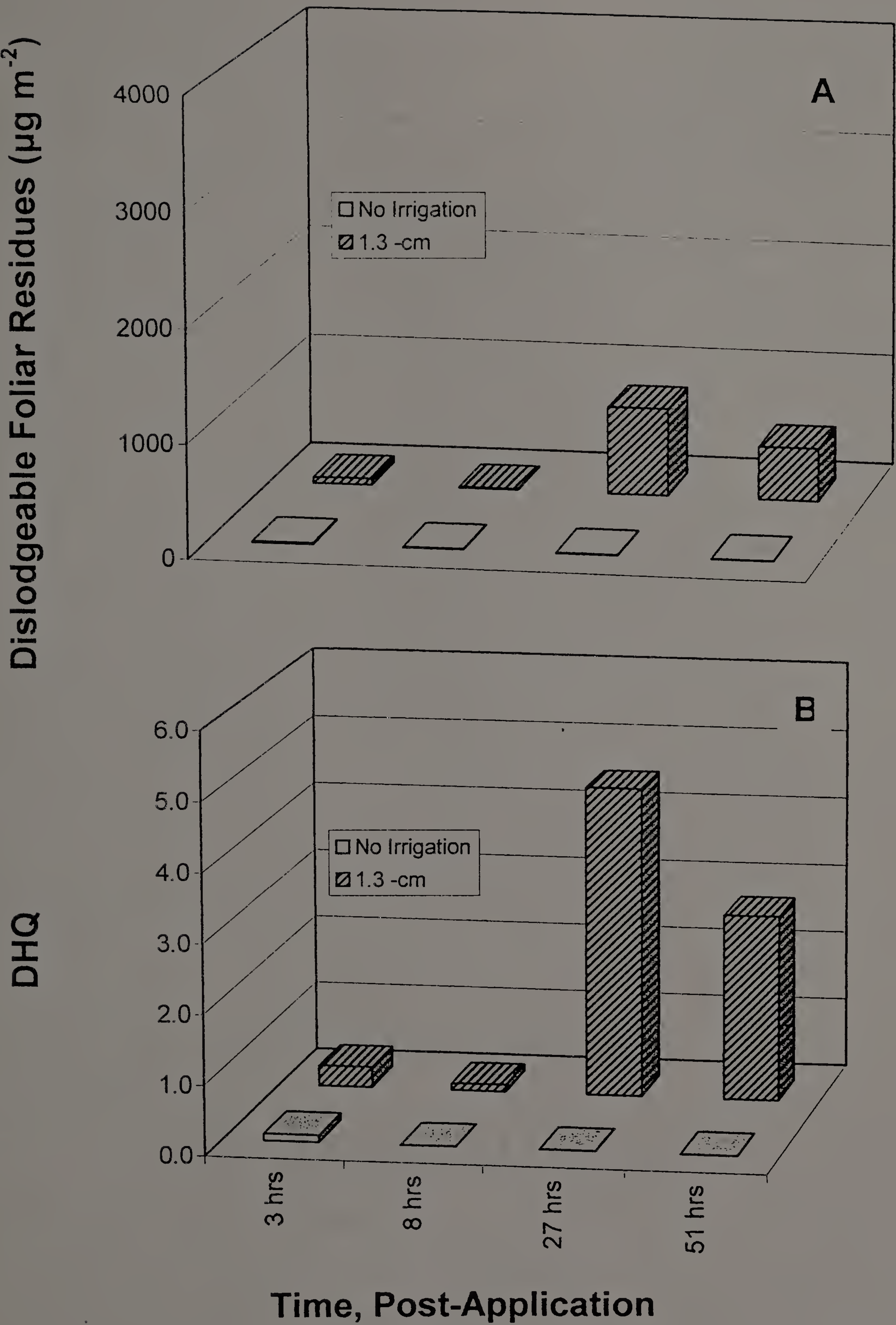


Figure 31. Dislodgeable foliar residues (µg m^{-2}, panel A) and dermal hazard quotient (DHQ) determinations (panel B) of **DDVP** following application of full-rate trichlorfon with 1.3-cm post-application irrigation or no irrigation (Murphy et al., 1996a).

determined DHQ values for DDVP were 4.6 and 0.3 at 1.3- and 0.63-cm post-application irrigation, respectively.

Under the current experimental protocols, there were no detectable dislodgeable foliar DDVP residues following treatment at 1/2 or 1/4 full-rate in the presence of either 0.63- or 0.32-cm post-application irrigation (data not shown). Therefore, DHQ values were not calculated.

3.4.2. Conversion of Triadimefon to Triadimenol.

Previous examination by Murphy et al., (1996b, Fig. 1, figure not shown) determined the source flux of full-rate triadimefon without irrigation to be present in the range of 4000 to 1000 μg m^{-2} (3 hrs and 51 hrs post-application, respectively) over the first 3 days of sampling and then continued to decline over days 5, 7, 11 and 15. The fate of triadimefon was examined at 1.3-cm post-application irrigation by Schumann et al., (2000) and was determined to be rapidly converted to triadimenol in all four turf matrices (leaf, thatch, soil and roots) and was not detectable at the end of the experiment (28 days). Triadimenol was never detected below the top 5.1-cm of the soil profile during the entire 28-day experiment.

The percent of total applied triadimefon in leaf was determined to be 20, 5 and 2 % on Days 1,2 and 3, following application, respectively. The leaf layer is considered to be the matrices where dislodgeable foliar residues are most available for dermal exposure, making it useful for this study. The percent of total applied of triadimenol in the leaf layer was determined to be 5 % by the end of Day 1 and maintained at this level over the remaining 28 days of sampling.

3.4.2.1. Volatile residues. Following application of 1/2 and 1/4 full-rate triadimefon in the presence of 0.63- or 0.32-cm post-application irrigation resulted in volatile residues of both triadimefon and triadimenol at only slightly greater than the detection limit and were not tabulated here (data not shown). Calculated IHQ values for triadimenol never exceeded 0.00001 under any experimental conditions examined.

3.4.2.2. Dislodgeable Foliar Residues. Generally, there were no detectable residues of triadimenol following application of 1/2 and 1/4 full-rate triadimefon in the presence of either 0.63- or 0.32-cm post-application irrigation (Fig. 32). The greatest level of dislodgeable foliar triadimenol residues occurred on Day 1 at 1/2 full-rate in the presence of 0.63-cm post-application irrigation and resulted in dislodgeable foliar residues of 46 and 51 $\mu g\ m^{-2}$ (both 0.001 % of applied) and DHQ values below 0.0001 (data not shown).

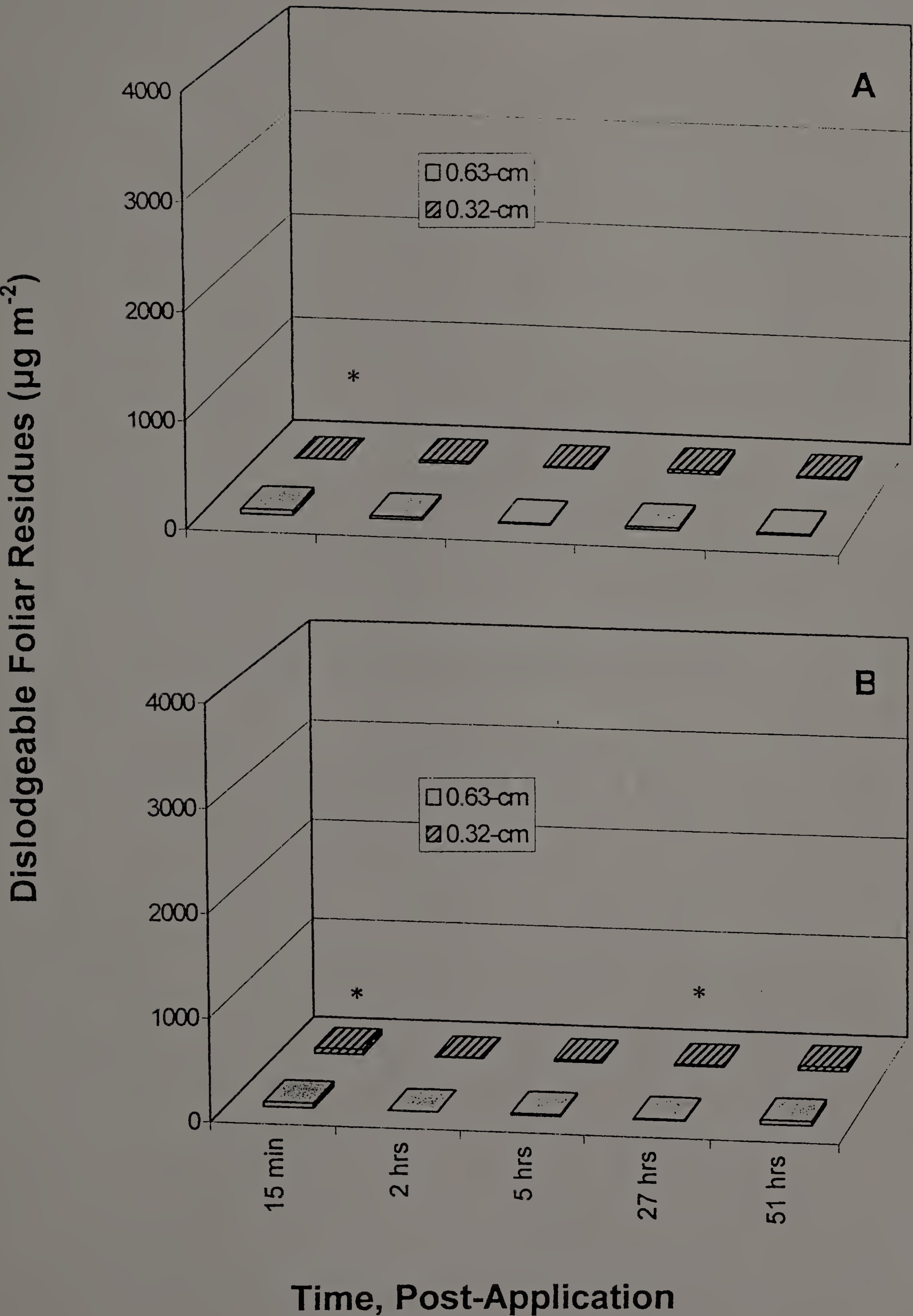


Figure 32. Dislodgeable foliar residues (µg m^{-2}) of **triadimenol** following application of triadimefon at 1/2 full-rate (panel A) and 1/4 full-rate (panel B) with post-application irrigation at either 0.63- or 0.32-cm. * significant at the 0.025 level.

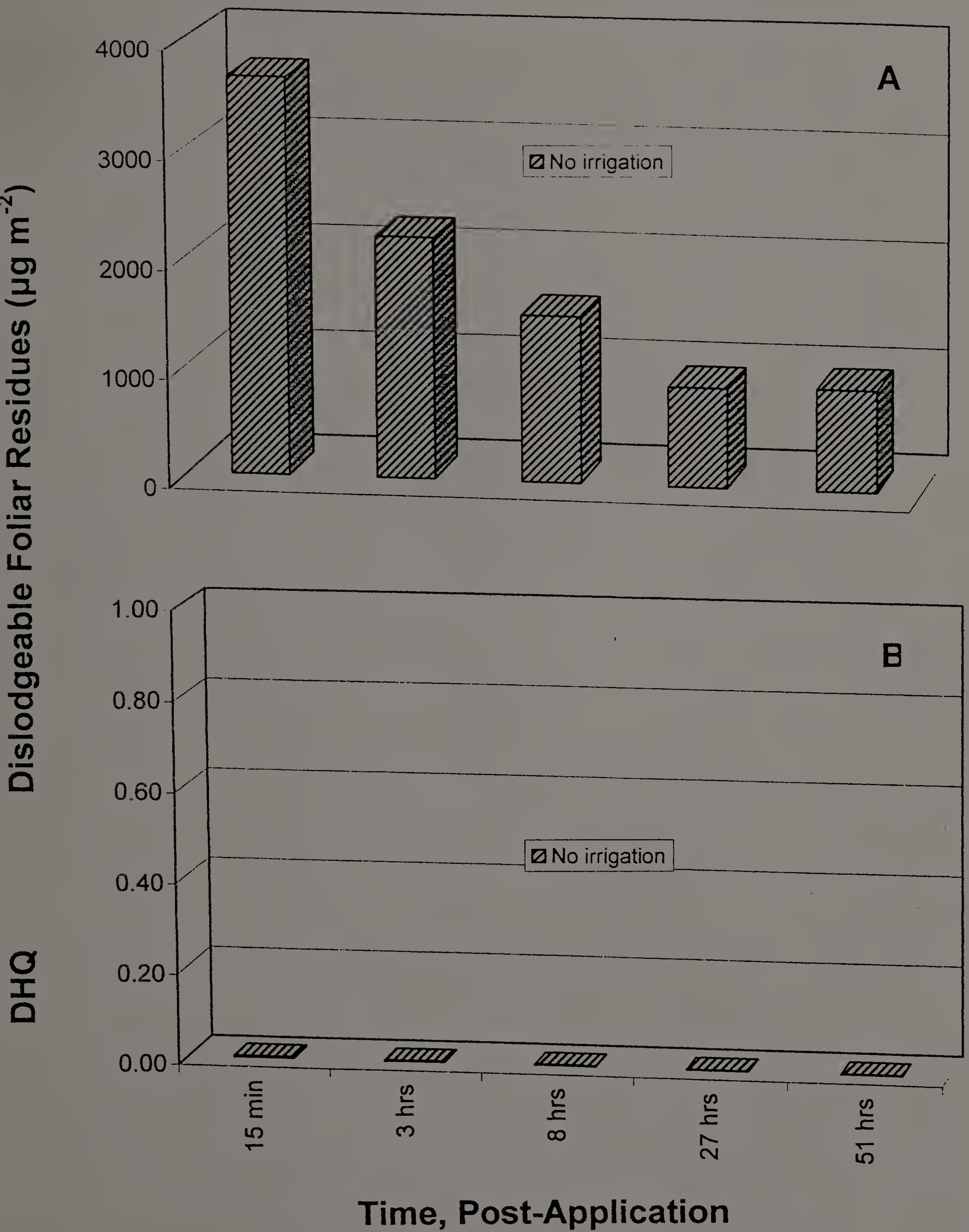


Figure 33. Dislodgeable foliar residues (µg m^{-2}, panel A) and DHQ determinations (panel B) following application to turfgrass with full-rate triadimefon with no post-application irrigation. (Murphy et al., 1996b).

Table 5. Inhalation hazard quotients (IHQs) during with or without adjuvant (Silwet L-77), at two post-application irrigation levels of 1.3-cm and 0.63-cm.

Treatments		Inhalation Hazard Quotients†					
Pesticide, Irrigation Level§	Adj‡.	Day 1	Day 2	Day 3	Day 5	Day 7	Σ IHQ
Isofenphos, 1.3-cm	+	**0.17**	**0.02**	**0.01**	**0.00**	**0.00**	**0.20**
	-	0.07	0.01	0.01	0.00	0.00	0.09
Isofenphos, 0.63-cm	+	**0.05**	**0.01**	**0.01**	**0.00**	**0.00**	**0.07**
	-	0.08	0.02	0.01	0.00	0.00	0.11
Chlorpyrifos, 1.3-cm	+	**0.11**	**0.02**	**0.01**	**0.01**	**0.00**	**0.15**
	-	0.07	0.02	0.01	0.01	0.00	0.11
Chlorpyrifos, 0.63-cm	+	**0.05**	**0.02**	**0.01**	**0.01**	**0.00**	**0.09**
	-	0.08	0.03	0.03	0.01	0.00	0.15
Bendiocarb, 1.3-cm	+	**0.02**	**0.01**	**0.01**	**0.00**	**0.00**	**0.04**
	-	0.02	0.01	0.01	0.00	0.00	0.04
Bendiocarb, 0.63-cm	+	**0.02**	**0.01**	**0.01**	**0.00**	**0.00**	**0.04**
	-	0.02	0.02	0.02	0.01	0.00	0.07

† The IHQ values reported in Table 5 are the maximum daily IHQs measured on that sampling day, and are the average of two experiments (n = 2).
‡ With (+) or without (-) Silwet L-77.
§ The pesticides in the presence of adjuvant / no adjuvant were applied during year 1.

Table 6. Dermal hazard quotients (DHQ values) over time following pesticide application at full pesticide label rates with or without adjuvant at two post-application irrigation levels (1.3- and 0.63-cm).

Treatment		Dermal Hazard Quotients.[†] (Time, Post-Application)							
Pesticide, Irrigation Level	Adj.‡	15 min.	2 hrs	5 hrs	27 hrs	51 hrs	75 hrs	99 hrs	Σ DHQ
Isofenphos, 1.3-cm	+	**2.07**	**1.64**	**0.66**	**0.43**	**0.18**	**0.09**	**0.07**	**5.14**
	-	2.66	0.94	0.98	0.35	0.17	0.10	0.06	5.26
Isofenphos, 0.63-cm	+	**5.42**	**2.39**	**1.65**	**0.69**	**0.25**	**0.15**	**0.13**	**10.68**
	-	3.29	1.71	1.37	0.27	0.20	0.25	0.13	7.22
Chlorpyrifos, 1.3-cm	+	**0.69**	**0.32**	**0.22**	**0.10**	**0.04**	**0.02**	**0.03**	**1.42**
	-	0.61	0.25	0.21	0.10	0.05	0.03	0.03	1.28
Chlorpyrifos, 0.63-cm	+	**1.23**	**0.37**	**0.28**	**0.15**	**0.06**	**0.04**	**0.04**	**2.17**
	-	0.95	0.30	0.28	0.07	0.10	0.06	0.04	1.80
Bendiocarb, 1.3-cm	+	**0.79**	**0.44**	**0.32**	**0.29**	**0.43**	**0.18**	**0.16**	**2.61**
	-	0.40	0.14	0.30	0.16	0.05	0.03	0.02	1.10
Bendiocarb, 0.63-cm	+	0.95	0.27	0.50	0.25	0.09	0.04	0.05	2.15
	-.	0.73	0.64	0.46	0.42	0.29	0.07	0.05	2.66

† Dermal Hazard Quotients are the average of two different sampling days (three triplicates from each plot, n = 6).
‡ With (+) or without (-) adjuvant (Silwet L-77).
§ The pesticides in the presence of adjuvant / no adjuvant were applied during year 1.

Table 7. Inhalation hazard quotients (IHQs) over time following application at 1/4 or 1/2 pesticide full-label rates in the presence of two post-application irrigation levels (0.63-cm and 0.32-cm).

Treatments		Inhalation Hazard Quotients. †			
Pesticide, Irrigation Level	**Rate**	**Day 1**	**Day 2**	**Day 3**	**Σ IHQ**
Isofenphos, 0.63-cm	**1/4**	**0.03**	**0.00**	**0.00**	**0.03**
	1/2	0.02	0.01	0.00	0.03
Isofenphos, 0.32-cm	**1/4**	**0.02**	**0.00**	**0.00**	**0.02**
	1/2	0.02	0.00	0.00	0.02
Chlorpyrifos, 0.63-cm	**1/4**	**0.06**	**0.01**	**0.00**	**0.07**
	1/2	0.03	0.01	0.00	0.04
Chlorpyrifos, 0.32-cm	**1/4**	**0.04**	**0.02**	**0.00**	**0.06**
	1/2	0.03	0.01	0.00	0.04
Trichlorfon, 0.63-cm	**1/4**	**0.04**	**0.00**	**0.00**	**0.04**
	1/2	0.02	0.00	0.00	0.02
Trichlorfon, 0.32-cm	**1/4**	**0.03**	**0.01**	**0.00**	**0.04**
	1/2	0.02	0.00	0.00	0.02
DDVP, 0.63-cm	**1/4**	**0.08**	**0.00**	**0.00**	0.08
	1/2	0.08	0.00	0.02	0.08
DDVP, 0.32-cm	**1/4**	**0.11**	**0.01**	**0.00**	0.11
	1/2	0.08	0.00	0.01	0.08

† The IHQ values reported in Table 7 are the maximum daily IHQs measured on that sampling day, and are the average of two experiments (n = 2).

Table 8. Dermal hazard quotients (DHQs) over time following application at 1/4 and 1/2 pesticide full-label rates in the presence of two post-application irrigation levels (0.63- and 0.32-cm).

Treatments		Dermal Hazard Quotients. †					
Pesticide, Irrigation Level	Rate	15 min. ‡	2 hrs	5 hrs	27 hrs	50 hrs	Σ DHQ
Isofenphos, 0.63-cm	**1/4**	**0.54**	**0.20**	**0.07**	**0.05**	**0.01**	**0.87**
	1/2	1.00	0.22	0.15	0.10	0.05	1.52
Isofenphos, 0.32-cm	**1/4**	**0.95**	**0.19**	**0.09**	**0.07**	**0.03**	**1.33**
	1/2	1.44	0.36	0.16	0.12	0.06	2.14
Chlorpyrifos, 0.63-cm	**1/4**	**0.25**	**0.05**	**0.03**	**0.01**	**0.00**	**0.34**
	1/2	0.47	0.06	0.06	0.04	0.04	0.61
Chlorpyrifos, 0.32-cm	**1/4**	**0.41**	**0.06**	**0.03**	**0.03**	**0.01**	**0.54**
	1/2	0.54	0.10	0.05	0.04	0.03	0.76
Trichlorfon, 0.63-cm	**1/4**	**1.70**	**0.38**	**0.73**	**0.10**	**0.21**	**3.12**
	1/2	3.64	1.10	0.67	0.79	0.80	7.00
Trichlorfon, 0.32-cm	**1/4**	**4.54**	**0.38**	**0.53**	**0.17**	**0.27**	**5.89**
	1/2	3.21	2.10	0.63	1.08	0.45	7.47
Triadimefon, 0.63-cm	**1/4**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
	1/2	0.00	0.00	0.00	0.00	0.00	0.00
Triadimefon, 0.32-cm	**1/4**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
	1/2	0.00	0.00	0.00	0.00	0.00	0.00

† Dermal Hazard Quotients are the average of two different sampling days (three triplicates from each plot, n = 6).
‡ Time, post-application.

Table 9. Total ∑IHQ and ∑DHQ values of pesticides over the entire sampling period (7days with or without Silwet L-77 adjuvant and 3 days for 1/2 and 1/4 rates of application).

Pesticide and residue type	Summation of IHQ and DHQ values							
	1.3-cm		0.63-cm		0.63-cm		0.32-cm	
	Full‡	Full	Full	Full	1/2	1/4	1/2	1/4
	+§	-	+	-	-	-	-	-
Chlorpyrifos								
IHQ	0.3	0.2	0.2	0.3	0.1	0.1	0.1	0.1
DHQ	1.4	1.3	2.2	1.8	0.7	0.3	0.9	0.5
Isofenphos								
IHQ	0.4	0.2	0.2	0.3	0.1	0.1	0.1	0.1
DHQ	5.1	5.2	10.0	7.4	1.4	0.9	2.1	3.3
Bendiocarb								
IHQ	0.1	0.1	0.1	0.2	---	---	---	---
DHQ	2.6	1.1	4.3	5.3	---	---	---	---
Trichlorfon								
IHQ	---	0.4†	---	---	0.1	0.1	0.1	0.1
DHQ	---	7.8†	---	---	7.1	3.1	7.5	5.9
DDVP								
IHQ	---	1.5†	---	---	0.3	0.1	0.2	0.3
DHQ	---	7.6†	---	---	0.0	0.0	0.0	0.0

† Sum of HQ values over three days.
‡ Pesticide treatment rate (full-, 1/2 - 1/4 rate).
§ Silwet L-77 treatment (+). No treatment (-).

Table 10. Weather data for Year 1 Week 1 (chlorpyrifos, isofenphos and bendiocarb applications).

Day and sampling period	Minutes air sampled	Surface temperature, Plot 1	Surface temperature, Plot 2	Wind Speed, Plot 1	Wind Speed, Plot 2
	min	°C	°C	ms^{-1}	ms^{-1}
Day 1					
9:00-9:50	50	26.8	29.2	2.4	2.8
9:50-11:10	70	27.1	37.0	3.1	3.2
11:10-3:05	235	32.1	36.7	2.9	3.0
3:05-7:00	235	32.2	27.9	2.1	2.1
Day 2					
7:00-11:00	240	22.6	†	1.5	†
11:00-3:00	240	31.8	†	2.2	†
3:00-7:00	240	28.3	†	2.4	†
Day 3					
7:00-11:00	240	27.2	†	1.6	†
11:00-3:00	240	31.8	†	1.7	†
3:00-7:00	90	33.2	†	1.6	†
Day 5					
11:00-3:00	240	34.8	†	1.7	†
Day 7					
11:00-3:00	240	32.3	†	3.0	†

† Weather data on Plot 2 was not collected; therefore weather parameters from Plot 1 were used for both.

Table 11. Weather data for Year 1 Week 2 (chlorpyrifos, isofenphos and bendiocarb applications).

Day and sampling period	Minutes air sampled	Surface temperature, Plot 1	Surface temperature, Plot 2	Wind Speed, Plot 1	Wind Speed, Plot 2
	min	°C	°C	ms^{-1}	ms^{-1}
Day 1					
9:00-9:45	45	24.2	†	2.4	2.8
9:45-11:15	70	26.9	†	1.4	3.2
11:15-3:10	235	33.3	†	1.4	3.0
3:10-7:00	230	33.5	†	1.2	2.1
Day 2					
7:00-11:00	240	22.6	†	1.3	1.3
11:00-3:00	240	31.8	†	1.1	1.1
3:00-7:00	240	28.32	†	1.0	1.0
Day 3					
7:00-11:00	240	27.2	†	1.3	1.3
11:00-3:00	240	30.8	†	1.8	1.8
3:00-7:00	240	30.0	†	1.8	1.8
Day 5					
11:00-3:00	240	33.8	†	1.7	1.7
Day 7					
11:00-3:00	240	32.3	†	3.0	3.0

† Weather station on Plot 2 was not collected; therefore weather parameters from Plot 1 were used for both.

Table 12. Weather data for Year 1 Week 3 (chlorpyrifos, isofenphos and bendiocarb applications).

Day and sampling period	Minutes air sampled	Surface temperature, Plot 1	Surface temperature, Plot 2	Wind Speed, Plot 1	Wind Speed, Plot 2
	min	°C	°C	ms^{-1}	ms^{-1}
Day 1					
9:00-9:50	50	19.4	†	1.5	†
9:50-11:10	70	22.0	†	1.5	†
11:10-3:10	240	26.1	†	1.5	†
3:10-7:00	230	27.0	†	1.0	†
Day 2					
7:00-11:00	240	28.3	19.0	1.4	1.9
11:00-3:00	240	21.7	28.0	1.0	1.2
3:00-7:00	240	21.7	24.1	0.7	0.9
Day 3					
7:00-11:00	240	24.9	24.3	0.5	1.0
11:00-3:00	240	33.6	32.4	1.7	1.7
3:00-7:00	240	33.1	28.2	2.4	1.8
Day 5					
11:00-3:00	240	18.7	24.1	1.7	1.3
Day 7					
11:00-3:00	240	33.6	†	1.7	†

† Weather station on Plot 2 was not collected; therefore, weather parameters from Plot 1 were used for both source flux determinations at both Plot 1 and 2.

Table 13. Weather data for Year 1 Week 4 (chlorpyrifos, isofenphos and bendiocarb applications).

Day and sampling period	Minutes air sampled	Surface temperature, Plot 1	Surface temperature, Plot 2	Wind Speed, Plot 1	Wind Speed, Plot 2
	min	°C	°C	ms^{-1}	ms^{-1}
Day 1					
9:00-10:00	60	15.4	14.3	0.8	1.0
10:00-11:20	80	26.9	21.4	1.0	0.9
11:20-3:10	230	25.0	24.0	1.9	1.3
3:10-7:00	230	20.9	19.2	1.0	0.9
Day 2					
7:00-11:00	240	16.7	18.7	0.9	1.0
11:00-3:00	240	25.5	28.0	1.3	0.9
3:00-7:00	240	25.5	24.1	1.2	1.3
Day 3					
7:00-11:00	240	19.0	19.0	1.2	1.5
11:00-3:00	240	27.9	29.2	1.5	1.7
3:00-7:00	240	27.8	26.0	1.9	1.9
Day 5					
11:00-3:00	240	25.2	†	3.9	†
Day 7					
11:00-3:00	240	24.4	†	1.0	0.9

† Weather station on Plot 2 was inoperable; therefore, weather data collected from Plot 1 was used for source flux determinations at both Plot 1 and 2.

Table 14. Weather data for Year 2 Week 5 (chlorpyrifos, isofenphos, trichlorfon, DDVP, triadimefon and triadimenol applications).

Day and sampling period	Minutes air sampled	Surface air temperature†	Wind Speed †
	min	°C	ms^{-1}
Day 1			
9:00-10:00	60	28.7	1.4
10:00-11:20	120	35.6	1.4
11:20-3:10	180	45.0	1.4
3:10-7:00	240	40.9	1.2
Day 2			
7:00-11:00	240	39.7	0.8
11:00-3:00	240	46.9	1.6
3:00-7:00	240	41.8	1.3
Day 3			
7:00-11:00	240	40.0	1.2
11:00-3:00	240	46.0	2.0
3:00-7:00	240	40.9	2.0

† Weather station on Plot 2 was inoperable; therefore, weather data collected from Plot 1 was used for source flux determinations at both Plot 1 and 2.

Table 15. Weather data for Year 2 Week 6 (chlorpyrifos, isofenphos, trichlorfon, DDVP, triadimefon and triadimenol applications).

Day and sampling period	Minutes air sampled	Surface air temperature†	Wind Speed†
	min	°C	ms^{-1}
Day 1			
9:00-10:00	60	29.4	1.0
10:00-12:00	120	35.2	1.5
12:00-3:00	180	35.1	2.1
3:00-7:00	240	29.8	1.6
Day 2			
7:00-11:00	240	23.3	2.0
11:00-3:00	240	29.8	3.0
3:00-7:00	240	26.5	1.9
Day 3			
7:00-11:00	240	23.3	2.0
11:00-3:00	240	29.8	3.0
3:00-7:00	240	26.5	1.9

† Weather station on Plot 2 was inoperable; therefore, weather data collected from Plot 1 was used for source flux determinations from both Plot 1 and 2.

Table 16. Weather data for Year 2 Week 7 (chlorpyrifos, isofenphos, trichlorfon, DDVP, triadimefon and triadimenol applications).

Day and sampling period	Minutes air sampled	Surface air temperature†	Wind Speed †
	min	°C	ms^{-1}
Day 1			
9:00-10:00	60	29.4	1.0
10:00-11:30	90	35.2	1.5
11:30-3:00	210	35.1	2.1
3:00-7:00	240	29.8	1.6
Day 2			
7:00-11:00	240	23.3	2.0
11:00-3:00	240	29.8	3.0
3:00-7:00	240	26.5	1.9
Day 3			
7:00-11:00	240	23.3	2.0
11:00-3:00	240	29.8	3.0
3:00-7:00	240	26.5	1.9

† Weather station on Plot 2 was inoperable; therefore, weather data collected from Plot 1 was used for source flux determinations from both Plot 1 and 2.

Table 17. Weather data for Year 2 Week 8 (chlorpyrifos, isofenphos, trichlorfon, DDVP, triadimefon and triadimenol applications).

Day and sampling period	Minutes air sampled	Surface air temperature†	Wind Speed †
	min	°C	ms^{-1}
Day 1			
9:00-10:20	80	21.5	1.0
10:20-11:50	90	27.4	1.5
11:50-3:20	210	29.9	1.5
3:20-6:50	210	21.2	1.2
Day 2			
7:00-11:00	240	18.9	0.9
11:00-3:00	240	24.5	1.3
3:00-7:00	240	21.9	1.0
Day 3			
7:00-11:00	240	20.0	1.1
11:00-3:00	240	24.0	1.6
3:00-7:00	240	20.5	1.5

† Weather station on Plot 2 was inoperable; therefore, weather data collected from Plot 1 was used for source flux determinations from both Plot 1 and 2.

CHAPTER 4

DISCUSSION

4.1. Volatile Residues / IHQs.

Similar to other research on pesticide dissipation, most pesticide loss following application to turf occurred in the first two days following application and the use of post-application irrigation significantly reduced the total level of pesticide residues compared to no irrigation (Hurto et al., 1993). Volatile chlorpyrifos, isofenphos, bendiocarb, trichlorfon, DDVP and triadimefon residues decreased over time in a diurnal pattern over the 3 and 7 day sampling intervals. IHQ values determined for chlorpyrifos, isofenphos, bendiocarb, trichlorfon, DDVP and triadimefon (not shown) never exceeded 1.0 under any experimental conditions (the IHQ for isofenphos was the highest at 0.2) (Tables 5 and 7).

4.1.1. Use of Spray-tank Adjuvant, Silwet L-77.

In the presence of 0.1% Silwet L-77 at either 0.63- or 1.3-cm post-application irrigation level, there was no significant reduction in volatile chlorpyrifos, isofenphos and bendiocarb residues or their respective calculated IHQ values (t-test, $P \leq 0.05$). The application of chlorpyrifos, isofenphos and bendiocarb with or without Silwet L-77 never resulted in IHQ values that exceeded 0.17, 0.11 or 0.02 over the entire sampling interval, respectively (Table 5).

The percent loss of total applied pesticides as volatile chlorpyrifos, isofenphos, and bendiocarb residues in the presence of Silwet L-77 and 0.63-cm irrigation were reduced 1.4-, 1.6- and 1.4- fold compared to no adjuvant, respectively (Table 4). This reduction did not occur in the presence of adjuvant at the 1.3-cm post-application irrigation level and, in fact, volatile chlorpyrifos and isofenphos residues actually increased under these conditions (Table 4).

The $\sum$ IHQ values for chlorpyrifos, isofenphos and bendiocarb over the entire seven-day experimental interval in the presence of 1.3-cm irrigation post-application irrigation were increased 1.5-, 2.0- and 0-fold in the presence of Silwet L-77 verses without adjuvant, respectively (Table 9). At 0.63-cm post-application irrigation, the $\sum$ IHQ values for chlorpyrifos, isofenphos and bendiocarb were reduced 1.5-, 1.5- and 2.0-fold in the presence of Silwet L-77 (Table 9).

4.1.2. Effects of Post-application Irrigation.

There was no significant reduction in the level of volatile chlorpyrifos, isofenphos, and bendiocarb residues by increasing post-application irrigation from 0.63- to 1.3-cm (t-test, $P > 0.05$) at full-rate applications. However, the percent loss of total applied pesticides as volatile chlorpyrifos, isofenphos and bendiocarb residues in the presence of 1.3-cm post-application irrigation were reduced 2.1-, 1.9- and 1.5- fold compared to 0.63-cm post-application irrigation, respectively (Table 4).

Reducing post-application irrigation from 0.63- to 0.32-cm at 1/2 full-rates decreased the percent loss of total applied pesticides for volatile chlorpyrifos and isofenphos residues by 1.7- and 1.1-fold, respectively (Table 4). The percent loss of total applied pesticides for volatile trichlorfon and triadimefon residues at 1/2 full-rate were not effected by reducing post-application irrigation from 0.63- to 0.32-cm. Volatile DDVP residues were increased by 1.2-fold when reducing post-application irrigation from 0.63- to 0.32-cm (Table 4).

Reducing post-application irrigation from 0.63- to 0.32-cm at 1/4 full-rates decreased the percent loss of total applied pesticides for volatile chlorpyrifos, isofenphos and DDVP residues by 1.4-, 1.4- and 1.5-fold, respectively (Table 4). The percent loss of total applied pesticides for volatile trichlorfon and triadimefon residues at 1/4 full-rate and 0.32-cm post-application irrigation were increased 1.4- and 1.2-fold compared to 0.63-cm. (Table 4).

The $\sum$ IHQ values for chlorpyrifos, isofenphos and bendiocarb over the entire 7-day experimental interval in the presence of 1.3-cm post-application irrigation were reduced 1.5-, 1.5- and 2.0-fold compared to 0.63-cm post-application irrigation, respectively (Table 9). Reducing post-application irrigation from 0.63- to 0.32-cm at 1/2 and 1/4 full-rates did not significantly increase the $\sum$ IHQ values for chlorpyrifos, isofenphos, trichlorfon, and triadimefon residues (Table 9). The $\sum$ IHQ values for DDVP were decreased 1.5-fold for 1/2 full-rate and increased 3.0-fold for 1/4 full-rate when post-application irrigation was decreased from 0.63- to 0.32-cm (Table 9).

4.1.3. Reduced Rates of Applied Pesticides.

Reducing the pesticide label rates from full to 1/2 full-rate in the presence of 0.63-cm post-application irrigation significantly reduced the level of volatile chlorpyrifos, isofenphos and triadimefon residues. Over the entire 3-day collection, volatile chlorpyrifos, isofenphos and triadimefon residues were decreased 2.2-, 8.3- and 9.7-fold compared to full-rate, respectively (Figs. 14A, 16A and 20A versus Figs. 2A, 4A and Table 3, Murphy et al., 1996b). Reducing the pesticide label rates from full to 1/2 full-rate in the presence of 0.63-cm post-application irrigation significantly reduced the $\sum$IHQ values for both chlorpyrifos and isofenphos by 3.0-fold (Table 9). The $\sum$IHQ values for triadimefon at 1/2 full-rate were not compared because there were no IHQ values above 0.00001 under any experimental conditions examined.

Reducing the pesticide label rates from full to 1/4 full-rate in the presence of 0.63-cm post-application irrigation significantly reduced the level of volatile chlorpyrifos and isofenphos residues. Over the entire 3-day collection, volatile chlorpyrifos and isofenphos residues were decreased 4.7- and 4.2-fold compared to full-rate, respectively (Figs. 15A and 17A versus Figs. 2A, 4A and Table 3, Murphy et al., 1996b, respectively). Reducing the pesticide label rates from full to 1/4 full-rate in the presence of 0.63-cm post-application irrigation significantly reduced the ∑IHQ values for both chlorpyrifos and isofenphos by 3.0-fold (Table 9). The ∑IHQ values for triadimefon at 1/4 full-rate were not compared because there were no IHQ values above 0.00001 under any experimental conditions examined.

Bendiocarb was not examined at reduced rates because full-rates at 0.63-cm post-application irrigation did not result in IHQ and DHQ values above 1.0. Likewise, reduced rates of trichlorfon and DDVP in the presence of 0.63-cm post-application irrigation could not be compared to full-rates due to the lack of comparable data (Clark et al., 2000).

4.1.4. Conversion of Trichlorfon to DDVP and Triadimefon to Triadimenol.

IHQ values for volatile DDVP residues were never greater than 0.11 under any experimental conditions examined. Reducing post-application irrigation from 1.3- to 0.63-cm decreased the level of volatile DDVP residues by 2.5-fold (Murphy et al., 1996a versus Clark et al., 2000). In the present study reducing post-application irrigation from 0.63- to 0.32-cm (at 1/2 and 1/4 full-rates) did not significantly reduce the level of volatile DDVP residues. However, reducing pesticide label rates from full-rate in the presence of 1.3-cm post-application irrigation to 1/2 and 1/4 full-rates in the presence of 0.63-cm reduced the overall (for 3-days) volatile DDVP residues by 7.1- and 8.4-fold (Figs. 29A and 30A versus Murphy et al., 1996a, Fig. 2). Under the same conditions, reducing post-application irrigation to 0.32-cm reduced the overall volatile DDVP residues by 12.5- and 5.7-fold (Figs. 29A and 30A versus Murphy et al., 1996a, Fig. 2).

Expectedly, there were no detectable levels of volatile triadimenol under any of the experimental conditions examined or IHQ values above 0.00001.

4.2. Dislodgeable Foliar Residues / DHQs.

Dislodgeable foliar chlorpyrifos, isofenphos, bendiocarb, trichlorfon and triadimefon residues were greatest immediately following post-application irrigation and decreased over time during the 7 and 3 day sampling intervals (Tables 6 and 8). Dislodgeable foliar residues resulted in DHQ values above 1.0, particularly for isofenphos and trichlorfon applied at full-rates, 1/2 and 1/4 (only trichlorfon) full-rates with or without Silwet L-77 and in the presence of 1.3-, 0.63-, or 0.32-cm post-application irrigation (Tables 6 and 8). Nevertheless, all the pesticides examined (chlorpyrifos, isofenphos, bendiocarb, trichlorfon, DDVP, triadimefon and triadimenol) had DHQ values below 1.0 by the end of Day 1 (Tables 6 and 8).

4.2.1. Use of Spray-tank Adjuvant, Silwet L-77.

In the presence of 0.1% Silwet L-77 at either 0.63- or 1.3-cm post-application irrigation level, there was no significant reduction on the level of dislodgeable foliar chlorpyrifos, isofenphos and bendiocarb residues or their calculated DHQ values. The highest calculated DHQ of any pesticide examined was full-rate isofenphos (DHQ of 5.4), which occurred in the presence of Silwet L-77 and 0.63-cm post-application irrigation. The only time chlorpyrifos and bendiocarb exceeded DHQ values 1.0 (1.2 and 1.0, respectively) occurred in the presence of Silwet L-77 and 0.63-cm post-application irrigation. Without Silwet L-77 and in the presence of 1.3-cm post-application irrigation, all calculated DHQ values were below 1.0 by Day 1.

The percent loss of total applied pesticides as dislodgeable foliar chlorpyrifos, isofenphos and bendiocarb residues in the presence of Silwet L-77 and 0.63-cm irrigation increased 1.6-, 1.1- and 0-fold compared to no adjuvant treatments respectively, (Table 4).

In the presence of adjuvant and 1.3-cm post-application irrigation, the percent loss of total applied chlorpyrifos and isofenphos were reduced 1.1- and 1.2-fold when compared to no adjuvant treatments, respectively (Table 4). The percent loss of total applied bendiocarb was increased 1.9-fold when compared to no adjuvant treatment (Table 4).

The $\sum$ DHQ values for chlorpyrifos, isofenphos and bendiocarb over the entire 7-day experimental sampling interval in the presence of 1.3-cm irrigation post-application irrigation resulted in 1.1-, 0- and 2.4-fold increases in the presence of Silwet L-77 verses no adjuvant treatments, respectively (Table 9). At 0.63-cm post-application irrigation, the $\sum$ DHQ values for chlorpyrifos and isofenphos were increased 1.2- and 1.4-fold in the presence of Silwet L-77 when compared to no adjuvants treatments, respectively (Table 9). For bendiocarb, the $\sum$ DHQ values were reduced 1.2-fold in the presence of Silwet L-77 when compared to no adjuvant treatments (Table 9).

4.2.2. Effects of Post-application Irrigation.

There was no significant reduction in the level of dislodgeable foliar chlorpyrifos, isofenphos and bendiocarb residues when increasing post-application irrigation from 0.63- to 1.3-cm. Using 1.3-cm post-application irrigation, however, reduced the percent loss of total applied isofenphos and bendiocarb residues by 1.4- and 2.7-fold compared to 0.63-cm irrigation, respectively (Table 4). The percent loss of total applied chlorpyrifos in the presence of 1.3-cm post-application irrigation was increased 1.1-fold compared to the 0.63-cm level.

Reducing post-application irrigation from 0.63- to 0.32-cm at 1/2 full-rates increased the percent loss of total applied pesticides as dislodgeable foliar chlorpyrifos, isofenphos, trichlorfon and triadimefon residues by 1.3-, 1.5-, 1.7- and 1.3-fold, respectively (Table 4).

Reducing post-application irrigation from 0.63- to 0.32-cm at 1/4 full-rates increased the percent loss of total applied pesticides as dislodgeable foliar chlorpyrifos, isofenphos, trichlorfon and triadimefon residues by 1.6-, 3.7-, 1.8- and 1.6-fold, respectively (Table 4).

Increasing post-application irrigation from 0.63- to 1.3-cm, although not statistically significant, reduced the $\sum$DHQ for chlorpyrifos, isofenphos and bendiocarb by 1.4-, 1.4- and 4.8-fold, respectively. Reducing post-application irrigation from 0.63- to 0.32-cm at 1/2 and 1/4 full-rates did not significantly increase the $\sum$DHQ values for chlorpyrifos, isofenphos, trichlorfon, and triadimefon residues (Table 9). However, the $\sum$DHQ values for chlorpyrifos, isofenphos and trichlorfon residues were increased 1.3-, 1.5- and 1.1-fold for 1/2 full-rate and 1.7-, 3.7- and 1.9-fold for 1/4 full-rate in the presence of 0.32-cm post-application irrigation, respectively (Table 9).

4.2.3. Reduced Rates of Applied Pesticides.

Reducing the pesticide label rates from full to 1/2 full-rate in the presence of 0.63-cm post-application irrigation significantly reduced the level of dislodgeable foliar chlorpyrifos and isofenphos residues. Over the entire 3-day collection, dislodgeable foliar residues chlorpyrifos and isofenphos residues were decreased 2.3- and 6.1-fold compared to full-rate, respectively (Figs. 21A and 23A, versus Figs. 8A and 10A). Reducing the pesticide label rates from full to 1/2 full-rate in the presence of 0.63-cm post-application irrigation significantly reduced the $\sum$DHQ values for chlorpyrifos and isofenphos by 2.3- and 5-fold, respectively (Figs. 21A and 23A versus Figs. 8A and 10A).

Reducing the pesticide label rates from full to 1/4 full-rate in the presence of 0.63-cm post-application irrigation significantly reduced the level of volatile chlorpyrifos and isofenphos residues. Over the entire 3-day collection, volatile chlorpyrifos and isofenphos residues were decreased 4.7- and 4.2-fold compared to full rate, respectively (Figs. 22A and 24A versus Figs. 8A and 10A). Reducing the pesticide label rates from full to 1/4 full-rate in the presence of 0.63-cm post-application irrigation significantly reduced the $\sum$DHQ values for chlorpyrifos and isofenphos by 5.3- and 7.8-fold, respectively (Figs. 22A and 24A versus Figs. 8A and 10A).

Reducing pesticide application rates from 1/2 to 1/4 full-rates did not result in significantly reduced levels of dislodgeable foliar residues (Tables 4 and 9). This apparent lack of reduction probably occurred due to smaller actual differences between 1/2 versus 1/4 full-rate compared to full versus 1/2 or 1/4 full-rates.

Bendiocarb was not examined at reduced rates because full-rates at 0.63-cm post-application irrigation did not result in DHQ values above 1.0. Reduced rates of trichlorfon, DDVP and triadimefon in the presence of 0.63-cm post-application irrigation could not be compared to full-rates by the percent loss of total applied or the $\sum$ DHQ values due to an incomplete data set from previous research (Clark et al., 2000).

4.2.4. Conversion of Trichlorfon to DDVP and Triadimefon to Triadimenol.

The use of 1.3-cm post-application irrigation increased the level of dislodgeable foliar DDVP residues following application of trichlorfon by 2.5-fold compared to no irrigation (Murphy et al., 1996a) and triadimenol was present in the leaf and thatch layer as early as Day 1. At 1/2 and 1/4 rates full-rate application, however, there were no detectable levels of dislodgeable foliar DDVP residues (figure not shown) and triadimenol residues levels were near the LOD (Fig. 32).

4.3. Additional Factors Influencing Dissipation.

4.3.1. Pesticide Chemistry Effects.

Henry's constant (K_H) is defined as the ratio of vapor phase to solution concentration of a pesticide and is different for each pesticide, which influences the rate of volatilization. A higher K_H value decreases the time for a pesticide to move from solution to the vapor phase and increased volatilization. Water solubility is a crucial factor in influencing the K_H of a pesticide and determines its pattern of volatile and dislodgeable foliar residues loss (Spencer et al., 1990).

Keeping vapor pressure and water solubility in mind, the decreasing order in the reduction of DHQ values for the pesticides tested is worth examining. The order of vapor pressures of the pesticides used in this study during year 1 examination from highest to lowest is; chlorpyrifos, isofenphos and bendiocarb. For water solubility, the order is; bendiocarb, isofenphos and chlorpyrifos. Isofenphos, which has both an intermediate vapor pressures and water solubility, resulted in the greatest overall reduction of DHQ values over its period in the presence of either levels of irrigation (Table 5). Chlorpyrifos resulted in the second greatest reduction of DHQ values, likely due to its relatively high vapor pressure that increases volatilization and its low water solubility that may hold the pesticide on the turfgrass blade or in the thatch. Bendiocarb had the least amount of reduction at either irrigation level and this reduction is likely due to its greater water solubility making it more prone to dislodgement by the H_2O-dampened cheesecloth wipe.

4.3.2. Weather Data.

Although pesticide applications days are selected on the days where the highest temperatures will be reached at mid-day, weather is always unpredictable and may make the volatilization and dislodgeable foliar residue data difficult to interpret. During the summers of 1998 and 1999, applications began in July and ended in September. In 1998, the average surface temperatures of the plots for a week of sampling following the 4 applications were 30.0, 29.6, 25.8 and 23.4 ° C, respectively (Appendix, Tables 10,11,12 and 13). In 1999, the average surface temperatures of the plots for a week of sampling following the 4 applications were 40.6, 28.9, 26.3, and 22.9 ° C, respectively (Appendixes, Tables 14,15,16 and 17).

At 1/4 full-rate application, the levels of volatile and dislodgeable foliar pesticide residues are similar to those obtained following 1/2 full-rate applications at the early sampling periods (greatest potential for exposure). An explanation for this finding could be the scheduling of the pesticide applications. Applications at 1/4 full-rate occurred in the hotter times (July) during the summer while applications at 1/2 full-rate were made in later in the summer or early in the fall (August and September). Another possible explanation is that the actual differences in the amount actually applied at 1/2 and 1/4 full-rate is not substantially large and the sampling errors were larger than the actual difference. More than likely, an experiment comparing 1/2 to 1/8 full-rates would find a more significant reduction in the level of volatile and dislodgeable foliar residues.

CHAPTER 5

CONCLUSION

At no time in any of the experiments did IHQ values exceed 1.0. The highest IHQ value was determined for isofenphos (0.2) and occurred in the presence of Silwet L-77 with 1.3-cm post-application irrigation. Dermal exposures appear to be of greater concern as determined by DHQ values, particularly those associated with full-rate chlorpyrifos (0.63-cm, DHQ 0.95), full-rate isofenphos (1.3-cm, DHQ 2.7; 0.63-cm, DHQ 3.3), 1/2 full-rate isofenphos (0.32-cm, DHQ 1.4) and 1/2 and 1/4 full-rate trichlorfon (0.63-cm, DHQs of 3.6 and 1.4, respectively; and 0.32-cm, DHQs of 3.2 and 4.5, respectively). With 1.3-cm post-application irrigation, however, all DHQ values were below 1.0 by the 2 hr sampling period for all pesticides examined.

Similar to the research by Clark et al., (2000) that examined Aqua Gro-L, a penetrant, and Exalt 800, a spreader-sticker, the extending-type adjuvant, Silwet L-77, likewise was not effective in reducing the level of volatile or dislodgeable foliar residues when incorporated into spray tank mixtures at 0.1%. Although Silwet L-77, Aqua Gro-L and Exalt 800 did not significantly reduce the level volatile and dislodgeable foliar pesticide residues, research examining the efficacy of these adjuvants at reduced pesticide application rates (1/2 or 1/4) would be useful. Ideally, applications could be made at 1/2 or 1/4 full-rate with Silwet L-77 and insect damage and overall turfgrass quality assessed.

Increasing post-application irrigation from 0.63- to 1.3-cm, although not significant ($P > 0.025$, $n = 6$), consistently reduced DHQ values of the year 1 pesticides examined (chlorpyrifos, isofenphos and bendiocarb) by 1.7- 1.9- and 2.7-fold, respectively, whereas the 0.32-cm level was not an effective management practice.

Although there was no significant reduction on volatile residues when comparing individual sampling periods, increasing post-application irrigation from 0.63- to 1.3-cm also clearly reduced the percent loss of total applied pesticides as volatile residues by 2.4-, 1.9- and 1.5-fold for full-rate chlorpyrifos, isofenphos and bendiocarb, respectively.

The potential for conversion to more toxic products also was examined in the presence of 0.63- and 0.32-cm irrigation with the degradation of trichlorfon to DDVP and triadimefon to triadimenol. As previously determined Murphy et al., (1996b) and Schumann et al., (2000), 1.3-cm post-application irrigation was found to increase the conversion of trichlorfon to DDVP and triadimefon to triadimenol, respectively. Nevertheless, there was no significant difference in the amount of conversion found at either the 0.63- or 0.32-cm irrigation level. Furthermore, no IHQ or DHQ values exceeded 1.0 for either DDVP or triadimenol in any experiment. The conversion of trichlorfon to DDVP at 1/2 rate in the presence of 0.63-cm post-application irrigation resulted in the highest IHQ value (0.11). The conversion of triadimefon to triadimenol appears to be not toxologically relevant in that the greatest IHQ and DHQ values were < 0.0001 and < 0.001, respectively.

Reducing pesticide application rates from full to 1/2 or 1/4 full-rates significantly lowered the level of volatile and dislodgeable foliar residues and their calculate IHQ and DHQ values at both the 0.63- or 0.32-cm post-application irrigation levels (t-test, $P < 0.05$ and $P < 0.025$ for IHQ and DHQs, respectively). This practice lowered the $\sum$IHQ values at both reduced rates by 3.0-fold for both chlorpyrifos and isofenphos and the $\sum$DHQ values for both chlorpyrifos and isofenphos by 4.0- and 4.6-fold, respectively.

Overall, reducing pesticide application rates was the most effective strategy in reducing potential exposure. Obviously applying pesticides to only 1/2 the golf course or less in any single day could result in greatly attenuated exposures. Post-application irrigation should be maintained at 1.3-cm and reduced below 0.63-cm only with caution. The use of spray-tank adjuvants are by themselves not effective means to reduce exposure but may be useful when used as extending agents when reduced rates of pesticides are used.

Recommendations to reduce golfer exposure should include at least 0.63-cm post-application irrigation (preferably 1.3-cm, except trichlorfon), reentry periods of at least two hours and pesticide application to 9 or less holes per 24 hr interval.

Lastly, the USEPA hazard quotient (HQ) determinations are theoretically worst-case scenarios of pesticide exposure and cannot replace the usefulness of actual dosimeters and biological monitoring of golfers following pesticide applications to turfgrass. DHQ values in the present study are determined from Zwieg's transfer coefficient, which estimates exposure to strawberry pickers over a four-hour interval and is currently the best available dermal exposure estimate to golfers (Zweig et al., 1985). Most likely, a golfer is not handling turfgrass comparable to a strawberry picker over a 4 hr interval. A study involving whole body dosimetry (cotton pants, hand washes and personal air samplers) and biological monitoring (urinary metabolites, blood acetylcholinesterase levels, etc.) and a concurrent USEPA IHQ and DHQ assessment study would allow for more realistic determination of transfer coefficient and golfer exposure. These results would allow the reexamination of past research using the USEPA IHQ and DHQ assessments by employing more realistic transfer factors.

APPENDIX: Chromatographs from each Detector

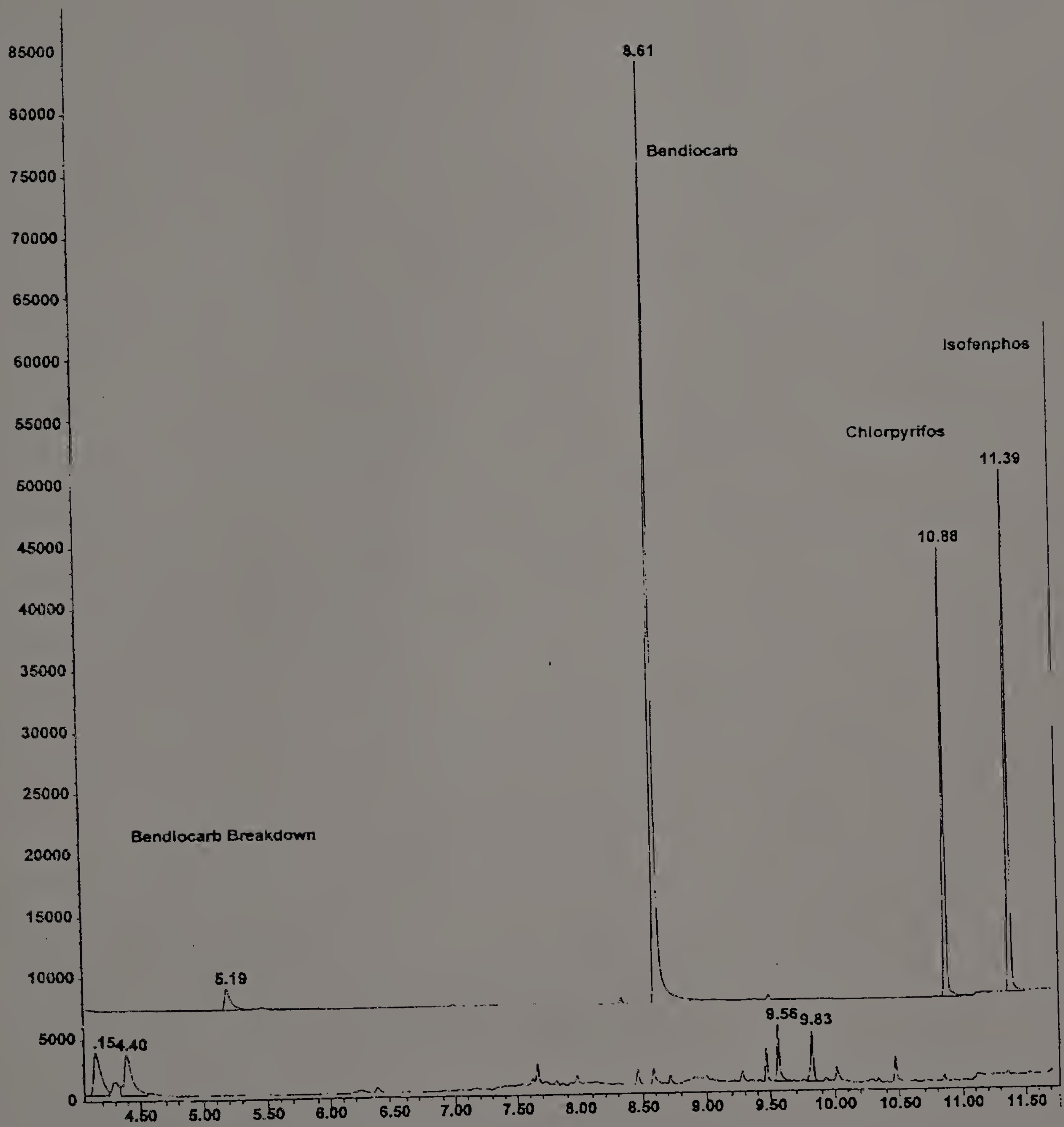
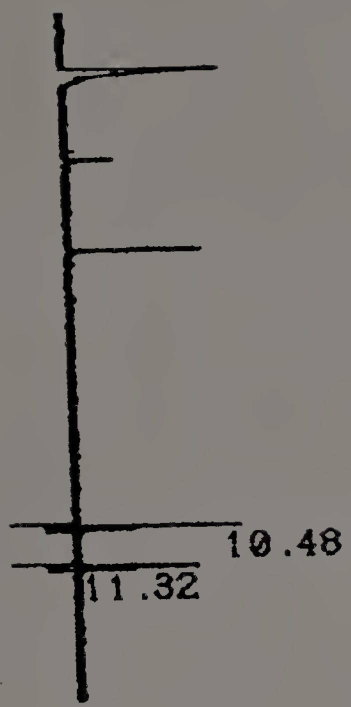
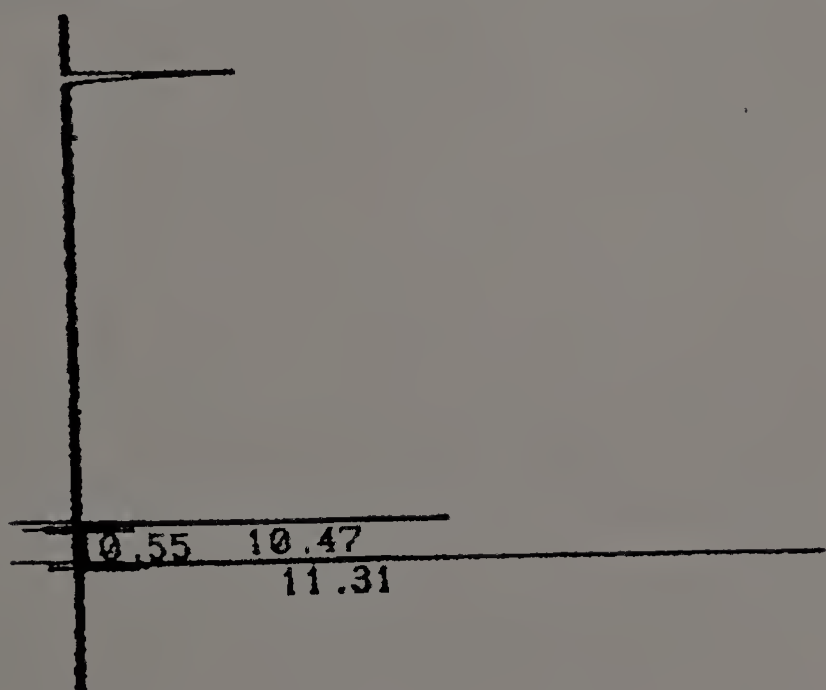


Figure 34. Chromatograph of year 1 analysis of bendiocarb, chlorpyrifos and isofenphos on a GC equipped with a mass selective ion detector (MSD).

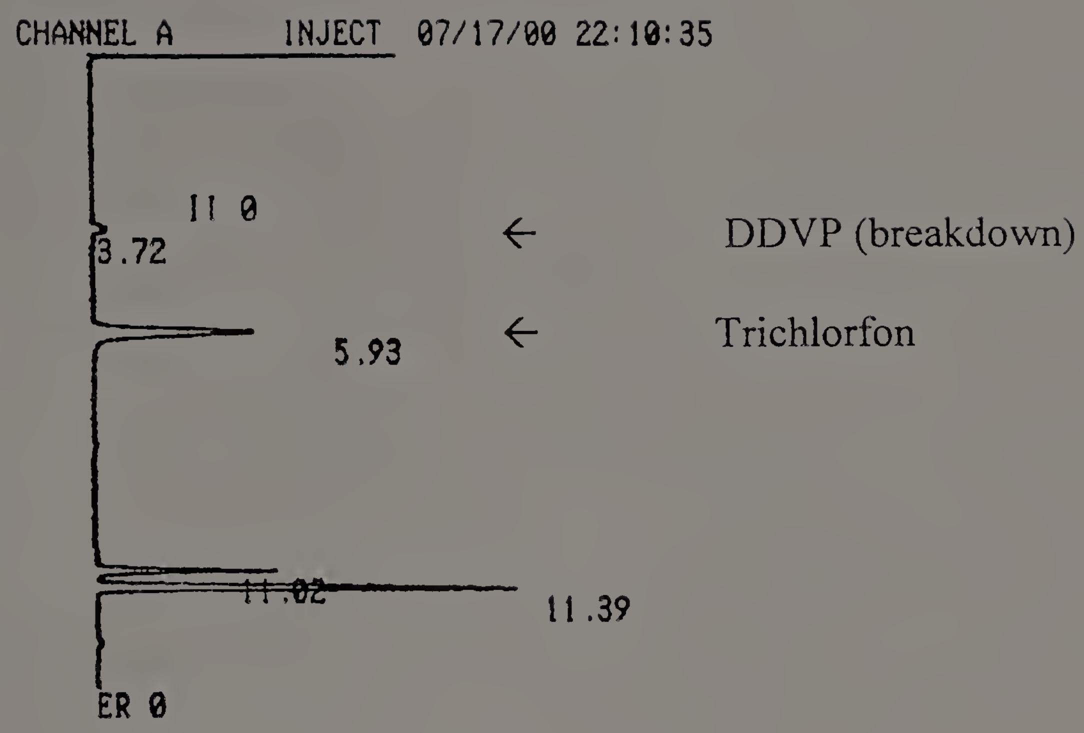


NAME	ug/ml	RT	AREA	BC
Chlorpyrif	0.	10.48	19059	01
ISOFENPHOS	0.	11.32	14182	01



NAME	ug/ml	RT	AREA	BC
Chlorpyrif	0.	10.47	45297	03
ISOFENPHOS	0.	11.31	90906	01

Figure 35. Chromatograph of year 2 analyses of chlorpyrifos and isofenphos on a GC equipped with a flame photometric detector (FPD).



trichlorfon, DDVP 07/17/00 22:10:35 CH= "A" PS= 1.

FILE 1. METHOD 5. RUN 265 INDEX 1

VIAL 00

SAMPLE 1

NAME	CONC	RT	AREA BC	RF
DDVP	0.	3.72	9616 01	
Trichlorfo	0.	5.93	152990 01	
Isofenphos	0.	11.02	103887 01	
4	0.	11.39	244983 01	
TOTALS	0.		511476	

Figure 36. Chromatograph of year 2 analyses of trichlorfon, DDVP, isofenphos, and chlorpyrifos (peak 4) on GC equipped with a flame photometric detector (FPD).

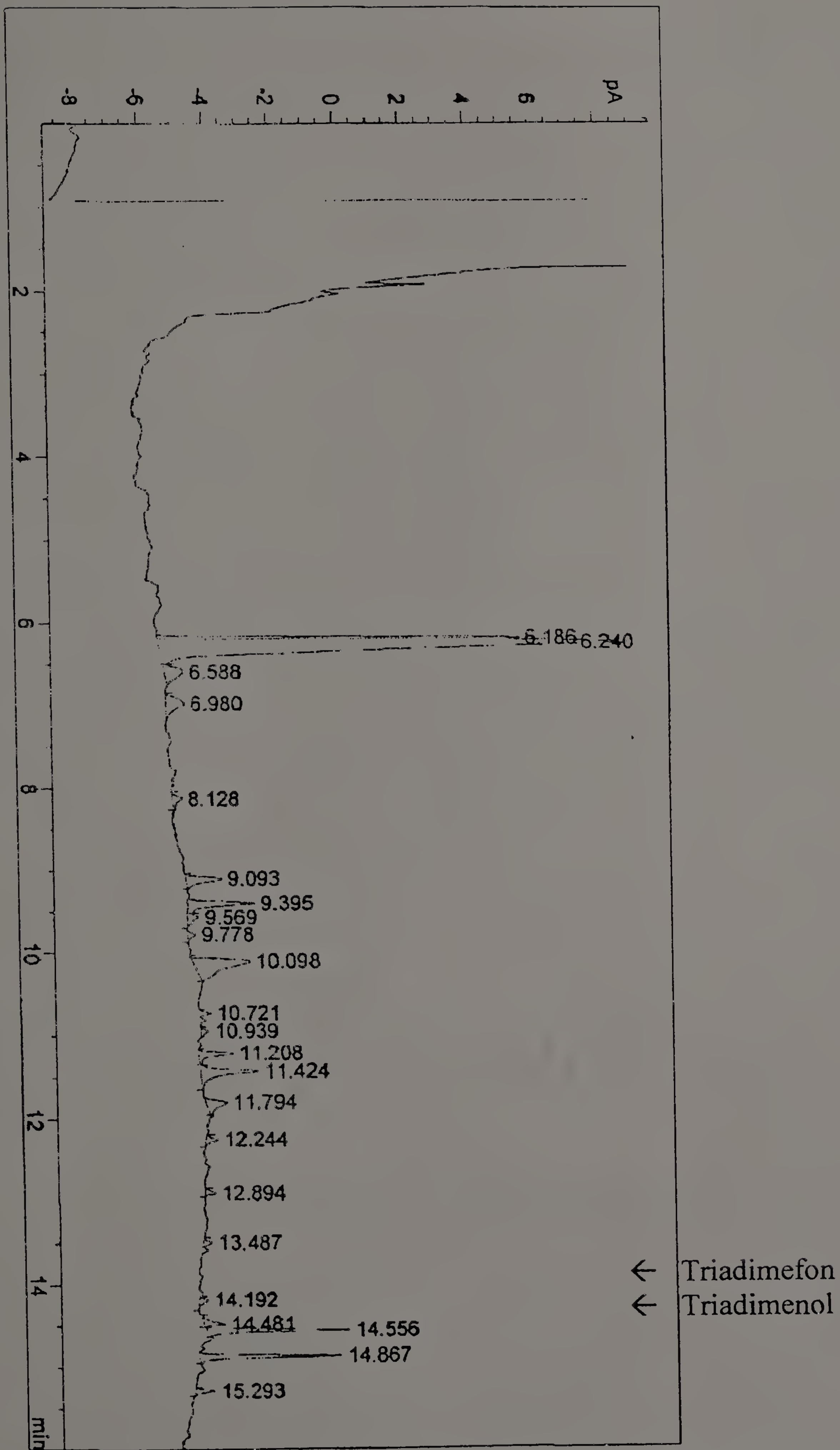


Figure 37. Chromatograph of year 2 analyses of triadimefon and triadimenol on GC equipped with a nitrogen phosphorous detector (NPD).

BIBLIOGRAPHY

Arya, S.P. Introduction to Micrometeorology. Academic Press. San Diego, CA., **1988,** Chapter 10, pp. 148-154

Baird, J.H.; Basta, N.T.; Huhnke, R.L.; Johnson, G.V.; Payton, M.E.: Storm, D.E.; Wilson, C.A.; Smolen, M.D.; Martin, D.L. and Cole, J.T. Best management practices to reduce pesticide and nutrient runoff from turf. In *Fate of Turfgrass Chemicals and Pest Management Approaches.* Eds. J.M Clark, M.P. Kenna, ACS Symposium Series 743, ACS Books, Washington, D.C. **2000**, pp. 268-293.

Baker, E.A.; Hayes, A.L.; Butler, R.C. Physicochemical properties of agrochemicals: Their effects on foliar penetration. *Pest. Sci.* **1992,** 34, 167-182.

Baron R.C. Carbamate insecticides. In *Handbook of pesticide toxicology.* Eds. Hayes W.J., Laws, E.R. Eds; Academic Press: New York. **1991,** Vol 3 pp. 1125-1189.

Bhowmik, P.C.; Wayne Bingham. Preemergence activity of dinitroaniline herbicides used for weed control in cool-season turfgrasses. *Weed Technology.* **1990** . Vol. 4:387-393.

Borgert, C.J.; Roberts, S.M.; Harbison, R.D.; Cisar, J.L.; Snyder, G.H. Assessing Chemical Hazards on Golf Courses..USGA Green Section Record. University of Florida. Ft. Lauderdale Research Center. **1994**, pp 11-14.

Brewer, L.W.; Hummell, R.A.; Kendall, R.J. Avian response to organophosphorous pesticides applied to turf. In *Pesticides in Urban Environments* ACS. Ed Ed., Racke, K. D.; Leslie, A.R.; ACS Symposium Series 522. **1993,** pp 320-330.

Bukovac, M.J.; Petracek, P.D. Characterizing pesticide and surfactant penetration with isolated plant cuticles. *Pest. Sci.*, **1993,** Vol 37, pp.179-194.

Casarett and Doull's toxicology: the basic science of poisons; Doull, J; Klaassen, C.; Amdur,M., Eds.; Macmillan: New York, **1980**; pp 26, 65, 413-15, 527-39.

Cisar, J.L.; Snyder, G.H. Mobility and persistence of pesticides applied to a USGA green.VI. Pesticides in percolate, thatch, soil and clippings and approaches to reduce fenamiphos and fenamiphos metabolite leaching. Environmental Horticulture Department, U. of Florida. Chapter 22.

Clark, J.M., G. Roy, J.J. Doherty and R.J Cooper. 1999. Hazard Evaluation and Management of Volatile and Dislodgeable Foliar Residues following Application to Turfgrass. In *Fate of Turfgrass Chemicals and Pest Management Approaches.* Eds. J.M Clark, M.P. Kenna. ACS Symposium Series 743, ACS Books, Washington, D.C. **2000**, pp.294-313.

Clark, J.M. Development and evaluation of best management systems for screening turfgrass pesticides for potential volatility and dislodgeable residues. *Turfgrass Field Book.* CFNR, UMASS-Amherst. **1997**, pp. 45-51.

Clark, J.M. Evaluation of management factors affecting volatile and dislodgeable foliar residues. *USGA 1996 Turfgrass and Environmental Research Summary.* USGA, Far Hills, NJ. **1996**, pp. 60-63.

Clark, J.M. Development and evaluation of best management systems for screening turfgrass pesticides for potential volatility and dislodgeable residues. *Turfgrass Field Book.* CFNR, UMASS-Amherst. **1997**, pp. 45-51.

Clendening, L.D.; Jury, W.A.; Ernst, F.F. A field mass balance study of pesticide volatilization, leaching, and persistence. In *Long Range Transport of Pesticides.* Ed. D.A. Kurtz. Lewis Publishers, Chelsea, Michigan. **1990**, pp. 47-60.

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

Cooper, R.J. Volatilization as an avenue for pesticide dissipation. International Turfgrass Society Research Journal 7. Eds. Carrow, R.N.; Christians, N.E. Overland Park, Kansas. **1993**, pp.116-126.

Cowell, J.E.; Adams, S.A.; Kunstman, J.C., Mueth, M.G. Comparison of foliar dissipation and turf dislodgeable residue sampling techniques. 19 In *Pesticides in Urban Environments: Fate and significance.* Ed., Racke, K. D.; Leslie, A.R.; ACS Symposium Series 522. **1993,** pp 100-112.

Exposure factors handbook. U.S. Environmental Protection Agency. Exposure Assessment Group, Office of Health and Environmental Assessment: Washington, D.C. USEPA, EPA-600/8-89-043, **1989.**

Extoxnet. Extension toxicology network. Eds Seyler, L.A.; Allan, J.W.; Rutz, D.A.; Kamrin, M.A. **1996-1999.**

Fenske, R. Nonuniform dermal deposition patterns during occupational exposure to pesticides. *Arch. Environ. Contam. Toxicol.* **1990.**

Fenske, R.; Elkner, K. Multiroute exposure assessment and biological monitoring of urban pesticide applicators during structural control treatments with chlorpyrifos. *Toxicol. Industrial Health,* **1990**, 6(3/4), pp 349-371.

Gallo, M.; Lawryk, N. Organic phosphorous pesticides. *Handbook of pesticide toxicology*; Hayes, W.; Laws, E, Jr., Eds; Academic Press: New York, **1991**: Volume 2, Chapter 16.

Glotfelty, D.; Taylor, A.; Turner, B.; Zoller, W. Volatilization of surface applied pesticides from fallow soil. *J. Agric. Food Chem.* **1984**, 32. 638-643.

Goh, K.; Edmiston, S; Maddy, K.; Margetich, S. Dissipation of dislodgeable foliar residues of chlorpyrifos and dichlorvos treated lawn: implication for safe reentry. *Bull. Environ. Contam. Toxicol.* **1986**, pp 37, 33-40.

Haith, D.A.; Disante, C.J.; Roy, G.R.; Clark J.M. Modeling approaches for assessment of Exposure from volatilized pesticides applied to turf. In *Fate and management of turfgrass chemicals*. ACS Symposium 743. Clark, J.M.; Kenna, M.P. Eds. **2000** pp. 255-267.

Harris, D.C. Quantitative chemical analysis: 4th edition. W.H. Freeman and Company, NewYork. **1996**. Chapter 4 and 22.

Hayes, W.J. Pesticide studied in man. Williams and Baltimore, London. **1982**, pp 284, 343, 351-356, 397-398.

Jenkins, J.; Cooper, R.; Curtis, A. Comparison of pendimethalin airborne and dislodgeable residues following application to turfgrass. In *Long range transport of pesticides*; Kurtz, D., Ed.; Lewis Publishers: MI, **1990**, Chapter 3.

Jenkins, J.; Curtis, A.; Cooper, R. Two-small plot techniques for measuring airborne and dislodgeable residues of pendimenthalin following application to turfgrass. In *Pesticides in Urban Environments*. Eds. Racke, K., Leslie A., ACS Symposium Series 522: American Chemical Society:Washington, **1993.**

Kenna, M.P, and Snow, J.T. The U.S. golf association turfgrass and environmental research program overview. In *Fate of Turfgrass Chemicals and Pest Management Approaches*. Eds. J.M Clark, M.P. Kenna. ACS Symposium Series 743, ACS Books, Washington, D.C. **2000** pp.2-35.

Kilgore, W.; et al. Human exposure to DEF/merphos. Residues Rev. 1984, 91, 71-77. Eds. Larsen, S.J.; Capel P.D.; *Pesticides in surface waters: distribution, trends, and governing factores*. Volume III. Pesticides in the Hydrologic System. **1999**, pp 190-194.

Kross, B.C.; Burmeister, L.F.; Ogilvie, L.K.; Fuortes, L.J. Proportionate mortality study of golf course superintendents. *Am J Ind Med.* **1996**, May; 29 (5): 501-506.

Larsen, S.J.; Capel P.D.; Majewski M. S. Pesticides in the Hydrologic System: Vol III Pesticides in Surface Waters, Distribution, Trends, and Governing Factors. Ann Arbor Press, Inc. Chelsea, Michigan, **1991**, pp 190-194.

Lee, Y.D.; Kim, H.J.; Chung J.B.; Jeong B.R. Loss of pendimethalin in runoff and leaching from turfgrass land under simulated rainfall. *J. Agric. Food Chem.* **2000**, Nov; 48 (11) 5376-82.

Majewski, M.; Glotfelty, D; Seiber, J. A comparison of the aerodynamic and the theoretical-profile-shape methods for measuring pesticide evaporation from soil. *Atmos. Environ.* **1989**, pp 23, 929-938.

Matsumura, F. *Toxicology of insecticides.* 2nd ed.; Plenum: New York, **1985**.

McChesney, M.M.; Seiber, J.N.; Modeling the volatilization of pesticides and their distribution in the atmosphere. In *Long range transport of pesticides*. Ed. Kurtz D.A. Lewis Publishers, Chelsea, Michigan 1990 pp. 61-81.

McGaughey, J.F. and Gangual, S.K. Comparison of three commercially available gass chromatographic flame photometric detectors in the sulfur mode. **1980**. *Anal. Chem.* 52:13 pp 2079-2083.

Mitra, S.; Bhowmik, P.C. and Xing, B. Synergistic effects of an oil and surfactant in influencing the activity of rimsulfuron in weed control. *Fifth International Symposium on Adjuvants for Agrochemicals*. Ed; McMullan, **1998** pp. 298-304.

Murphy, K.C.; Cooper, R.J.; Clark J.M. Volatile and dislodgeable foliar residues following trichlorfon and isazofos application to turfgrass and implication for human exposure. *Crop Sci.*, **1996**, *36*:1446-1454.

Murphy, K.C.; Cooper, R.J.; Clark J.M. Volatile and dislodgeable residues following Triadimefon and MCPP application and implication for human exposure. *Crop Sci.*, **1996**, *36*:1455-1461.

Murphy, K.C. The determination of volatile and dislodgeable residues from pesticide-treated turfgrass and an assessment of human exposure. Ph.D. dissertation, Dept. of Chemistry, Univ. of Massachusetts, Amherst.**1994**, pp. 1-135.

Nash, R.G.; Hill, B.D. Modeling Pesticide Volatilization and Soil Decline Under Controlled Conditions. In *Long range transport of pesticides*. Ed. Kurtz, D.A.; Lewis Publishers, **1990**, pp 17-28.

Nolan, R.J.;Rick, D.L.; Freshour, N.L.; Saunders, J.H. Chlorpyrifos: Pharmacokinetics in human volunteers. *Toxicol. App. Pharmacol.* **1984** 73: 8-15.

The Pesticide Manual: 11th Edition. CDS Tomlin. The British Crop Protection Council, Farnham, Surrey, United Kingdom, 1997.

Petrovic, A.M.; Young, R.G; Ebel, J.G. Jr.; Lisk. D.J. Conversion of triadimefon fungicide to triadimenol during leaching through turfgrass soils. *Chemosphere*, **1993**b, 26(8), 159-1557.

Policello, G.A., et al., The influence of pH on the performance of organosilicone surfactants. *Pesticide Formulations and Application Systems*: 14th Volume, ASTM STP 1234 Franklin R. Hall, Paul D. Berger, and Herbert M. Collins, Eds., American Society for Testing and Materials, Philadelphia, **1995**.

Racke, K.D. Environmental fate of chlorpyrifos. *Rev. Environ. Contam. Toxicol.* **1993**, Vol. 131: pp 1-154.

Racke, K.D. Fontaine, D.D., Lubinski, R.N., Miller J.R. Chlorpyrifos degradation in soil at termiticidal application rate. *Pestic. Sci.* **1994**, Vol 42: pp 43-51.

Racke, K.D.; Lubinski, R.N.; Fontaine, D.D.; Miller, J.R., McCall, Oliver, G.R.; Comparative fate of chlorpyrifos insecticide in urban and agricultural environments. In *Pesticides in urban environments: Fate and significance*. Ed., Racke, K. D.; Leslie, A.R.; ACS Symposium Series 522. **1993**, pp 70-85.

Reigart, J.R.; Roberts, J.R. Recognition and management of pesticide poisonings: 5th edition. Office of Pesticides. U.S.E.P.A. Washington D.C. **1999.**

Rosenthal, W.D. and Hipp, B.W. Field and Model estimates of pesticide runoff from turfgrass. Fate and significance. Ed., Racke, K. D.; Leslie, A.R.; ACS Symposium Series 522. **1993**, pp 209-213.

Runes, H.B., Jenkins J.J., Field, J.A. Method for the analysis of triadimefon and ethofumesate from dislodgeable foliar residues on turfgrass by solid-phase extraction and in vial elution. *J. Agric. Food Chem.* **1999** Aug; 47(8):3252-6.

Sánchez-Camazano, M.; Arienzo, M.; Sánchez-Martín, M.J.; Crisanto, T. Effect of different surfactants on the mobility of selected non-ionic pesticides in soil. *Chemosphere*. **1995**, Vol 31, No. 8, pp 3793-3801.

Schumann, G.L.; Clark, J.M.; Doherty, J.J.; Clarke, B.B. Application of DMI fungicides to turfgrass with three delivery systems. In *Fate and Management of Turfgrass Chemicals*. ACS Symposium 743. Eds. Clark, J.M.; Kenna, M.P. **2000** pp. 150-163.

Shurdut, B.A.; Vaccaro, J.R. Nolan R.J. Potential chlorpyrifos exposure to residents following turf treatment with a granular pesticide. Arch. *Env. Contam. Toxicol.* **1999.**

Shurdut, B.A.; Barraj L., Francis, M. Aggregate exposure under the food and quality protection act: An approach using chlorpyrifos. *Regul. Toxicol. Pharmacol.* **1998**. 28: 164-177.

Spencer, W.F.; Cliath, M.M. The solid-air interface: transfer of organic pollutants between the solid-air interface. In *Fate of pollutants in air and water environments*. Suffet, I., Ed; John Wiley and Sons: New York, **1977**, Part I; pp107-126.

Spencer, W.F.; Cliath, M.M. Movement of pesticides from soil to the atmosphere. In *Long range transport of pesticides*. Ed. Kurtz, D.A.; Lewis Publishers, **1990**, pp 1-16.

Taylor, A.; Spencer, W. Volatilization and vapor transport processes. In pesticides in the soil environments: Processes, impacts, and modeling; Cheng, H, Ed.; Soil Science Society of America: Wisconsin, **1990**; 213-265.

Thompson, D.G.; Stephenson, G.R.; Sears, M.K.; Persistence, distribution and dislodgeable residues of 2,4,-D following its application to turfgrass. *Pest. Sci.* **1984**, Vol 15, pp 353-360.

U.S Environmental Protection Agency. *Dermal exposure assessment: principles and applications*. Interem Report. EPA/600/8-91/011B. **1992.**

U.S Environmental Protection Agency. Exposure factors Handbook. Office of Pesticide Programs. Washingtion, D.C. **1989.**

U.S. Environmental Protection Agency. Office of Pesticide Programs Reference Dose Tracking Report. Washingtion, D.C. **1995.**

Vaccaro, J.R.; Nolan, R.J., Murphy, P.G., Berbich, D.B. The use of a unique study design to estimate exposure to adults and children to surface and airborne chemicals. American Society of Testing Materials, ASTM STP. **1993**, 1287: 166-183.

Vaccaro J.R. Risks with exposure to chlorpyrifos formulation components. In, Pesticides in Urban Environments: Fate and Significance. Ed., Racke, K. D.; Leslie, A.R.; ACS Symposium Series 522. **1993,** pp 297-306.

Watschke, T.L.; Mumma, R.O.; Linde, D.T.; Borger, J.A. and Harrison, S.A. Surface runoff of selected pesticides applied to turfgrasses. In *Fate of Turfgrass Chemicals and*

Pest Management Approaches. Eds. J.M Clark, M.P. Kenna. ACS Symposium Series 743, ACS Books, Washington, D.C. **2000**, pp. 94-105.

Wilson, J.D. et al., Verification of a simple micrometeorological method for estimating the rate of gaseous transfer from the ground to the atmosphere. *Agric. Meterology* **1983**, 29, pp 183-189.

Wilson, J.D. et al. Estimation of the rate of gaseous mass transfer from a surface plot to the atmosphere. *Atmosph. Environ.* **1982**, 16:1861-1867.

Xing, B. and Jin, Z. Sorption of organic chemicals by microfilters. *Journ. Env. Qual.* **1999**, Vol. 28 pp350-353.

Yeary, R.A.; Leonard, J.A. Measurement of pesticides in air during application to lawns, trees and shrubs in urban environments. In *Pesticides in urban environments: Fate and significance*. Eds., Racke, K. D.; Leslie, A.R.; ACS Symposium Series 522. **1993**, Chapter 23 pp. 275-281.

Zweig, G.: Gao, R.;Witt, J.; Popendorf, W.; Bogen, K. Dermal exposure to carbaryl by strawberry harvesters. *J. Agric. Food Chem.* **1984**, 32, 1232-1236.

Zweig, G.; Leffingwell, J.T.; Popendorf W. The relationship between dermal pesticide exposure by fruit harvesters and dislodgeable foliar residues. *Environ. Health*, **1985** B20(1):27-59