Organophosphorous pesticides in stormwater runoff from southern California

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ABSTRACT - Large quantities of the organophosphorous (OP) pesticides diazinon and chlorpyrifos are applied to agricultural and urban watersheds in California every year. Although water quality managers recognize the need to reduce OP pesticide inputs from stormwater runoff, little data are available on the sources of OP pesticides in urban watersheds. The goal of this study was to characterize diazinon and chlorpyrifos concentrations from different land uses indicative of source categories in urban southern California watersheds. This characterization included analysis of 128 runoff samples from eight different land uses over five storm events. In addition, 41 samples were collected from two sites located at the mouth of large, mixed land use watersheds during three different storm events.

Diazinon was consistently detected (93% of samples) during this study, whereas chlorpyrifos was not (12% of samples). Mixed agricultural land use had the highest flow weighted mean (FWM) concentration of diazinon (4,076 ng/L), which exceeded the next-highest land use categories (commercial, residential) by a factor of 10 to 100 (324 to 99 ng/L, respectively). Open space had the lowest concentration of diazinon (< 20 ng/L). Concentrations of diazinon at replicate land use sites and during replicate storm events at the same site were highly variable. The difference in diazinon FWM concentrations among replicate sites ranged from 1.5-fold to 45-fold. The difference in diazinon FWM concentrations among storms at the same site ranged from 1.25-fold to 30-fold. Part of this variability is a response to the temporal patterns observed within a storm event. The majority of land use site-events had peak concentrations prior to peak flow indicating a “first-flush” effect, but this was not always a predictable temporal trend. The first-flush effect was rarely evident in terms of mass loadings, which was mostly a reflection of flows in urban environments. Flow can range orders of magnitude during a single event in highly impervious urban watersheds, and this variability overwhelms the variability in diazinon concentrations attributable to first-flush effect.

INTRODUCTION

Large quantities of the organophosphorous (OP) pesticides diazinon (*O,O*-diethyl-*O*-[2-isopropyl-6-methyl-4-pyrimidinyl] phosphorothioate) and chlorpyrifos (*O,O*-diethyl-*O*-[3,5,6-trichloro-2-pyridyl] phosphorothioate) are applied to agricultural and urbanized watersheds in California every year. An estimated 387 metric tons (mt) of diazinon and another 927 mt of chlorpyrifos were applied in 1999 based upon records kept by agricultural applicators and by commercial pest control operators (Department of Pesticide Regulation 2000). Additional significant users of OP pesticides, particularly diazinon, are residential homeowners for exterior pest control. Unfortunately, there are no estimates of diazinon or chlorpyrifos use during home applications, although these pesticides can be purchased over-the-counter at most home improvement stores. In southern California, where more than 17 million people reside, residential use of OP pesticides has the potential to be enormous.

The OP pesticides are toxic to a wide variety of non-target aquatic organisms including fish and invertebrates (Menconi and Cox 1994a, 1994b). OP pesticide used in agricultural watersheds of California has entered ambient surface waters and resulted in toxicity to the cladoceran *Ceriodaphnia dubia* (DeVlaming *et al.* 2000). However, OP pesticide usage is not restricted to agricultural watersheds. Diazinon and chlorpyrifos have both been found in wet-weather runoff from urban watersheds and resulted in discharge and ambient water column toxicity (Bailey *et al.* 2000, Denton 2001). Diazinon and, to a lesser extent, chlorpyrifos have been identified as likely toxicants in stormwater discharges from a southern California watershed using *C. dubia* (Schiff *et al.* 2002). The consistent toxicity and concentrations of OP pesticides measured in urban wet-weather discharges have led State regulators to add at least 32 California streams to their list of impaired waterbodies (e.g., §303d list) for OP pesticides.

Despite the demonstrated toxicity of diazinon and chlorpyrifos to aquatic organisms, there is a lack of understanding of the major sources of these pesticides in an urbanized watershed. Source contributions are exacerbated in southern California's arid environment where streams are routinely dry unless it is raining, thus enabling longer time periods for OP pesticides to build up within urban watersheds. Moreover, when rain does occur, flow may change from < 0.03 cubic meters per second (cms) to > 283.2 cms in a matter of minutes to hours, enhancing pesticide transport to receiving waters (Tiefenthaler *et al.* 2001a). This fundamental lack of data regarding source contributions of OP pesticides in stormwater runoff is a serious impediment to water quality managers attempting to control the discharge of these compounds to receiving water bodies.

The objective of this study was to measure concentrations of OP pesticides in stormwater discharges from different land uses in order to characterize categorical sources during storm events. However, flow and water quality can be highly variable within storms in southern California; understanding these dynamic relationships in flow and concentration may help water quality mangers to determine the most effective actions for controlling OP pesticide in urban stormwater runoff. Therefore, a secondary goal of this study was to generate a time-concentration series of OP pesticides during storm events to facilitate the evaluation of flow and concentration dynamics.

METHODS

Sample Design

Southern California is a semi-arid environment that typically receives 12 to 14 storm events annually, averaging 28 cm of cumulative precipitation. The wet season extends from October to April, but most of the precipitation occurs from January to March (between 12 and 8 cm per month). Our sampling occurred between January and April, 2001.

Six different homogeneous land-use catchments, ranging in size from 0.5 to 2.6 km^2, were sampled throughout the Los Angeles region (Figure 1). These land uses included residential, commercial (COM), industrial (IND), recreational (REC), agricultural, and open (OPEN). Since residential and agricultural land uses were anticipated to be major sources of OP pesticides, replicate land use sites were examined to assess the variability within these land use categories. These replicates included high-density (HDR) and low-density (LDR) residential land use sites as well as row crop (AG-MIX) and commercial nursery (AG-NUR) agricultural sites. Variability in runoff characteristics may arise from changes at the same land use among different storm events. Therefore, each site was sampled for at least one storm event, and HDR, LDR, COM, IND, and AG-MIX were sampled for two storm events

In order to relate loading from land use categories to final concentration in receiving waters, flow and concentration were measured during replicate storm events in two major creeks draining the Santa Monica Bay watershed. These two creeks, Ballona Creek (ME-BAL) and Santa Monica Canyon (ME-SM), are separate drainage basins comprised of multiple land uses in varying proportions (Table 1). The sampling

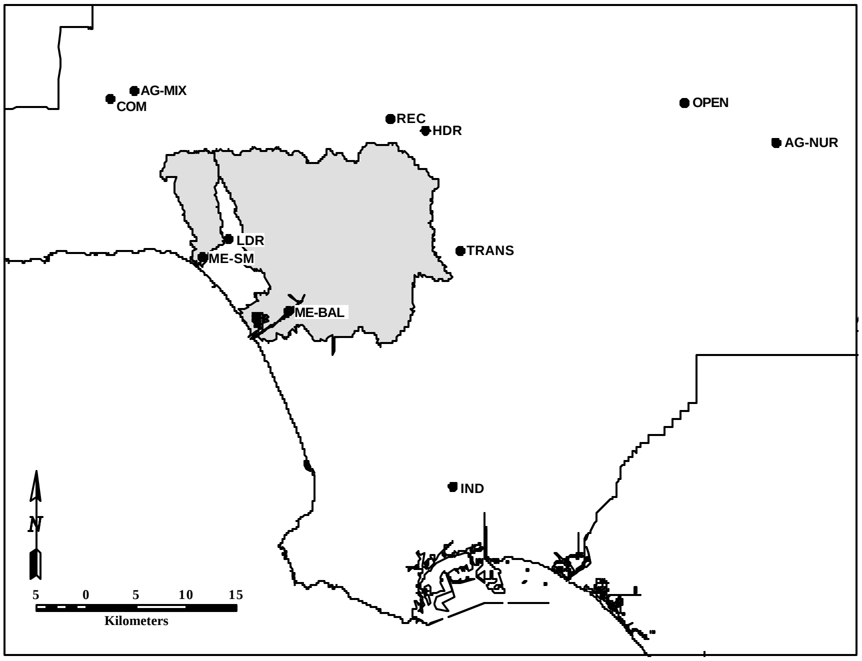

Figure 1. Map of land use and mass emission sites throughout the Los Angeles region (see text for abbreviations). Mass emission watersheds are highlighted.

Table 1. Land use characteristics of the mass emission watersheds.

	Percent of Land Use	
Land Use	Ballona Creek ($338\ km^2$)	Santa Monica Canyon ($41\ km^2$)
Agriculture	<0.1	-
Industrial	7.3	0.0
Commercial	15.5	0.7
High-Density Residential	50.3	11.6
Low-Density Residential	3.4	8.5
Mixed Urban	4.9	-
Recreation	1.3	1.6
Open	16.4	77.6
Water	0.9	<0.1
Total	100.0	100.0

sites, referred to mass emission (ME) sites, are located just upstream of where the creeks discharge to Santa Monica Bay. The specific land use sites sampled as part of this study were not necessarily located within ME-SM or ME-BAL. The land use sites were selected to be representative of this generic land use type regionally. Similarly, not all ME sites were sampled regionally, and ME-SM and ME-BAL were selected to be representative of a largely undeveloped and developed watershed, respectively.

Flow at the land use sites was measured at 15-minute intervals during most events, but extended to as much as 30 minutes during prolonged events, using either area-velocity meters in conjunction with stage measuring sensors or by estimating stage-discharge relationships using standard hydrologic equations. Flow at ME sites was estimated at 15-minute intervals using historically derived and calibrated stage-discharge relationships.

The goal of water quality sampling was to collect samples that were representative of the entire hydrograph including rising, peak, and tailing flows. Ten to 12 water quality samples were targeted for each site-event. This sample size was statistically determined to be optimal for southern California watersheds based on Leecaster *et al.* (2001). All samples were collected with one of three methods: (1) peristaltic pumps with Teflon® tubing and stainless steel intakes that were fixed at the bottom of the channel or pipe pointed in the upstream direction in an area of undisturbed flow; (2) direct filling of the sample bottle either by hand or using a pole; or (3) indirect filling using an intermediate bottle for securing large volumes. Samples were collected in pre-cleaned amber glass bottles and stored immediately at 4^{O}C until they were shipped to the laboratory for analysis.

Chemical Analysis

Water samples were extracted by passing 1L of sample through a preconditioned (ethyl acetate followed by methanol) 90 mm 3M C18 solid phase extraction (SPE) disk. Analytes were eluted from the SPE disk using ethyl acetate. The eluate was dried over sodium sulfate and rotoevaporated at 35°C to 1 mL with solvent exchange to hexane. The hexane extract was then concentrated under nitrogen to 0.5 mL for analysis.

Gas chromatographic (GC) analyses were performed using a Varian 3800 GC equipped with DB-XLB capillary column (60 m x 0.32 mm x 025 µm.) and a Varian Saturn 2000 Ion Trap. Helium was used as a carrier gas at constant flow of 1.2 mL/min. Samples were fortified with 1-Bromo-2-nitrobenzene as an internal standard and injected in splitless mode in an injector at 250°C. The oven temperature profile was: 50°C for 1 minute; 50-100°C at 25°C/minute; 100-310°C at 10°C/minute for 7 minutes.

Field and laboratory blanks, laboratory duplicates, and matrix spike samples were prepared and analyzed at a frequency of ≥ 5%. No blank samples contained target compounds at levels that exceeded the detection limit. Laboratory duplicates were all ≤ 20% reproducible percent different among paired samples. Matrix spiked samples were all ≤ 30% reproducible percent different from their nominal value.

Data Analysis

There were four steps for assessing wet-weather runoff concentrations of OP pesticides from urban areas. First, the flow-weighted mean (FWM) concentrations among the various land uses were compared to determine which land use had the greatest wet-weather concentration. The FWM was calculated according to Equation 1:

$$FWM = \frac{\sum_{i=1}^{n} C_i * F_i}{\sum_{i=1}^{n} F_i} \qquad \textbf{Equation 1}$$

where: *FWM* = Flow-weighted mean

C_i = Concentration of ith sample
F_i = Instantaneous flow at the time of ith sample
n = Number of samples per event

Event FWMs were calculated in a similar method to the annual FWM, except that only those samples for a single storm were used in the calculation. Samples below the detection limit in all instances were coded as the detection limit (20 ng/L for both diazinon and chlorpyrifos) for the purpose of estimating FWM concentrations. The FWM concentrations were used to compare among land use categories and within replicate land use categories, while event FWMs were used to compare concentrations between replicate storm events at the same land use site. Second, FWM concentrations were compared among ME sites to assess differences in concentrations among the two sub-basins. Third, time-concentration series from individual storm events were examined to determine the presence of runoff characteristics such as first flush or tail flush. Time-concentration series were plotted by graphing changes in concentration and flow over time. A storm event was included in the analysis if the sampling adequately covered the event. The criteria for adequate sampling coverage used for this study was initiation of sampling when flows were $\leq$ 20% of peak flows and continuous sampling through peak flows until flows subsided to $\leq$ 20% of peak flow. Since watersheds in southern California have highly variable flows that may increase orders of magnitude during storm events, these criteria are considered relatively conservative. Fourth, first-flush evaluations were also compared using estimates of cumulative emissions relative to cumulative volume discharged during the storm event similar to Bertrand-Jakowski (1998). When these curves are close to unity, then mass discharge is a function of flow. When these curves deviate from unity, there is an indication that some within-storm variance in mass discharge is occurring.

RESULTS

Five of seven possible rain events, ranging in size from 0.41 to 2.67 cm, were sampled throughout the study period of January 11–April 15, 2001 (Table 2). One to two storm events were sampled at each of the land use and mass emission sites during this period with storm flows lasting from 4 to 23 h. Mean flow ranged from 0.003 to 1.72 cms in the land use sites, and peak flows ranged from 0.008 to 3.8 cms. While both flow and pesticide concentrations were sampled at the open space site during the February 10, 2001, storm event, surface runoff flow infiltrated into the ground, so little change in flow was measured. At the two ME sites, average flows ranged from 0.088 to 38.1 cms, with peak flows of 107 cms recorded in Ballona Creek.

Comparison Among Land Use Types

The detection of diazinon and chlorpyrifos in runoff samples differed drastically. Diazinon was detected in 93% of all samples including 12 of 13 site-events at land use sites. Only the open land use site had diazinon concentrations below the detection limit. In contrast, only 12% of the samples had detectable chlorpyrifos concentrations encompassing 2 of 13 site-events. Only the mixed agriculture land use had FWM concentrations of chlorpyrifos above the detection limit. These event FWM concentrations were 49.3 ± 2.1 and 22.9 ± 1.8 ng/L for the February 19 and March 14, 2001, storm events, respectively, with a site FWM of 36.7 ± 1.4 ng/L. As a result of the low frequency of detection for chlorpyrifos, the remainder of this section will focus on diazinon.

The mixed agricultural land use site had the highest diazinon concentration, with a FWM concentration (4,076 ng/L) that was 10 to 100 times higher than that of any other land use type (Table 3). Commercial land use had the second highest concentration of diazinon (324 ng/L). The FWM from this site was three times that of the high-density residential land use (99 ng/L). The open space site had the lowest concentration of diazinon ($\leq$ 20 ng/L).

Inter-storm variability in diazinon concentration was high, as shown by the difference in event FWM concentrations at sites in which two storms were sampled. The mixed agriculture site showed the highest inter-storm variability, with a factor of 30 difference between storm events (Table 3). The variability between replicate storms was far less, but still substantial for the residential, commercial, and industrial land use types. The FWM concentrations among storm events ranged from a factor of 1.25 to 7 difference at these sites.

Comparisons within land use types, such as agricultural and residential, showed large variability in diazinon FWM concentrations. Runoff from the mixed agriculture site had site FWM concentration approximately 45 times higher than the other agricultural use measured (nursery areas; Table 3). The

Table 2. Land use and mass emission site sampling dates, rainfall quantity, duration of sampling, and mean and peak flow measured (cubic meters per second, cms).

	Date of Storm Event	Rainfall (cm)	Sampling Duration (hrs)	Mean Flow (cms)	Peak Flow (cms)
LAND USE SITES					
High-Density	2/10/2001	0.004	11	0.082	0.563
Residential	2/19/2001	0.004	10	0.061	0.233
Low-Density	2/19/2001	0.011	4	0.068	0.097
Residential	3/04/2001	0.027	8	0.019	0.071
Commercial	2/19/2001	0.011	4	0.004	0.008
	4/07/2001	0.019	6	0.008	0.018
Industrial	2/10/2001	0.008	23	0.253	1.801
	2/19/2001	0.004	11	0.205	0.774
Agriculture (Mixed)	2/19/2001	0.005	5	0.026	0.042
	3/04/2001	0.015	8	0.022	0.053
Agriculture (Nursery)	4/07/2001	0.021	7	1.723	3.801
Recreational	2/19/2001	0.004	5	0.017	0.044
Open Space	2/10/2001	0.004	6	<0.001[a]	<0.001
MASS EMISSION SITES					
Ballona Creek	2/19/2001	0.010	9	38.105	107.041
	4/07/2001	0.014	20	32.604	100.853
Santa Monica Canyon	2/19/2001	0.011	9	0.088	1.133
	4/07/2001	0.019	8	0.648	3.021

[a] Change in flow not detected at this site.

Table 3. Event flow-weighted mean (FWM) and site FWM concentration of diazinon by land use type.

Land Use Site	Sampling Dates	Sample Size	Event Flow-Weighted Mean Conc.±95%CI (ng/L)	Site Flow-Weighted Mean Conc.±95% CI (ng/L)
High-Density	2/10/2001	10	125.3 ± 6.1	99.2 ± 12.6
Residential	2/19/2001	10	90.1 ± 6.9	
Low-Density	2/19/2001	10	55.9 ± 5.9	67.6 ± 4.4
Residential	3/04/2001	11	94.6 ± 5.5	
Commercial	2/19/2001	10	66.2 ± 8.9	324.0 ± 57.0
	4/07/2001	10	440.9 ± 79.1	
Industrial	2/10/2001	10	106.5 ± 11.0	89.6 ± 8.7
	2/19/2001	7	53.6 ± 15.0	
Agriculture (Mixed)	2/19/2001	10	6999.8 ± 309. 8	4076.0 ± 178.3
	3/04/2001	10	219.6 ± 49.5	
Agriculture (Nursery)	4/07/2001	10	148.0 ± 11.5	148.0 ± 11.5
Recreational	2/19/2001	10	63.2 ± 11.8	63.2 ± 11.8
Open Space	2/10/2001	10	≤ 20 ± 0	≤ 20 ± 0

variability within land use was considerably less within residential land uses, where the FWM diazinon concentration at the high-density residential site was a factor of 1.5 higher than at the low-density residential site.

Comparison Among Mass Emission Sites

Diazinon was detected in 100% of the samples at both ME sites during the study. In contrast, chlorpyrifos was detected in only 3 of 41 samples taken at the ME sites (7%). All three of the samples were collected during the February 10, 2001, event at Santa Monica Canyon, yielding an event FWM concentration near the detection limit (20.5 ± 0.9 ng/L).

Santa Monica Canyon had a site FWM diazinon concentration that was 87% higher than that of Ballona Creek, but because of the high inter-storm variability in Santa Monica Canyon, these concentrations were not significantly different (Table 4). Event FWM concentrations during the February 19, 2001, storm were roughly equivalent between the two ME sites, while the April 7, 2001, event sampled in Santa Monica Canyon had a two-fold greater concentration than the same event in Ballona Creek. This contradicts some of the land use data since Santa Monica Canyon has more open land use while Ballona Creek is more developed and is comprised of predominantly urban land uses. Part of this intersite variability may have been due to localized differences in rainfall and flow. Unlike the February 19th event, where rainfall quantities were similar, Santa Monica Canyon received 25% more rainfall than Ballona Creek on April 7 (Table 2).

Temporal Variability Within Storm Events

There was no clear and consistent pattern of within-storm variability at each of the land use sites (Figure 2). The majority of land site-events showed evidence of a first flush of diazinon. Seven of the 13 total land use site-events had the maximum diazinon concentration prior to peak flow. These concentration maxima were 1.4-fold to 5.5-fold higher than concentration minima later in the storm event, depending upon the land use. Concentration maxima were also observed during peak and tailing flows at one site-event each, respectively. The remaining four land use site-events had no discernable pattern of changes in diazinon concentration within the storm event.

The first-flush relationship observed in diazinon concentrations from time-concentration series was not necessarily evident from estimates of loading (Figure 3). For example, the one-to-one relationship for cumulative mass versus cumulative volume for the commercial and industrial land use sites indicated emissions covaried with flow. In both of these instances, flow ranged over two orders of magnitude while concentrations of diazinon only ranged by a factor of 2 to 4 within a single storm event. A small first-flush effect was evident from the agricultural site where 30% of the cumulative mass was discharged within the first 15% of volume discharged. In this case, diazinon concentrations ranged four-fold while flow ranged by only a factor of two. Finally, a tail flush effect was evident at the high-density residential site. In this case, 40% of the diazinon mass was discharged during the last 20% of the storm volume.

DISCUSSION

Of all the sources evaluated, the agricultural land use generated the greatest concentrations of diazinon in stormwater runoff. Our measurements of diazinon from agricultural runoff is consistent with deVlaming *et al.* (2000), who measured significantly increased

Table 4. Event flow-weighted mean (FWM) and site FWM concentration of diazinon by mass emission site.

Mass Emission Site	Sampling Dates	Sample Size	Event Flow-Weighted Mean Conc.±95%CI (ng/L)	Site Flow-Weighted Mean Conc.±95% CI (ng/L)
Ballona Creek	2/19/2001	10	227.1 ± 37.4	242.9 ± 39.0
	4/07/2001	10	252.3 ± 57.9	
Santa Monica Canyon	2/19/2001	10	239.1 ± 49.3	452.3 ± 205.3
	4/07/2001	10	505.3 ± 255.9	

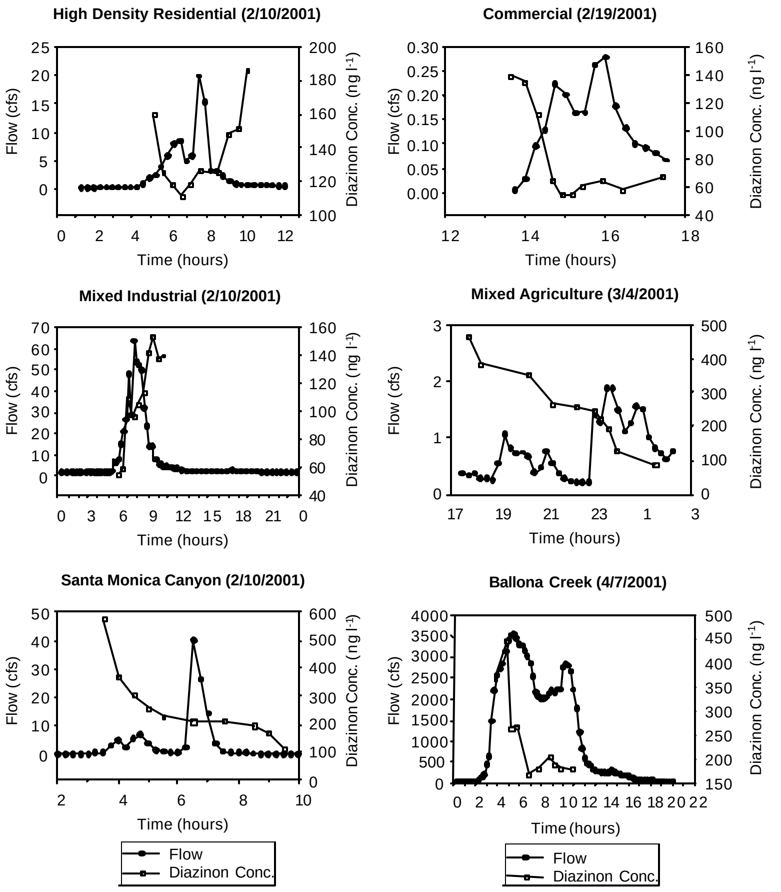

Figure 2. Time-concentration series for diazinon during storm events for various land use and mass emission sites in southern California.

concentrations of diazinon in ambient surface waters that received agricultural runoff, particularly those fields and orchards that recently received OP pesticide applications. Therefore, agricultural practices are often the major target considered when looking for the most effective and direct management actions. In urban watersheds, however, agriculture can be an insignificantly small proportion of the watershed. In our targeted mass emission watersheds, for example, agriculture comprised less than 0.1% of the total land use. Therefore, agricultural controls in an urban watershed will produce negligible effects on runoff water quality.

From an urban perspective, commercial and residential land uses had the greatest concentrations of diazinon. Although little work examining sources has been published, Bailey *et al.* (2000) showed that predominantly residential subwatersheds generated higher runoff concentrations of diazinon than predominantly industrial subwatersheds. This makes intuitive sense, since most urban applications of diazinon are either conducted by commercial pest control operators or by homeowners themselves. Unfortunately, the present study was not designed to assess the relative contribution among homeowners and commercial pest control operator applications in residential land use runoff. However, a total maximum daily load (TMDL) for diazinon in San Diego, California, estimated that commercial pest control operator applications represented less than 40% of the total diazinon use in that urban watershed (SDRWQCB 2000).

The variability of diazinon concentrations within land use replicates, or among different storms at the same land use, are likely a function of rainfall and OP pesticides use within the subwatershed. Variations in rainfall can alter the build-up and wash-off of pollutants within watersheds. For example, variations in antecedent rainfall and precipitation, as well as intensity and duration, are factors that can influence event mean concentrations for other constituents (Sansalone and Buchberger 1997, Bertrand-Krajewski *et al.* 1998). Recent studies in the Los Angeles Region have led to similar conclusions (Tiefenthaler *et al.* 2001b). However, pesticide use can also have an affect on runoff water quality. In San Diego, a telephone survey was conducted in support of their diazinon TMDL (URS Greiner Woodward-Clyde 2000). Results showed that most homeowners apply OP pesticides throughout the year, often without regard to subsequent irrigation or precipitation.

Most of the diazinon concentrations found during this study exceeded thresholds of concern established by the State of California. The California Department of Fish and Game has established water quality guidelines of 80 ng/L based upon expected acute toxicity to aquatic organisms (Menconi and Cox 1994b). All of the samples collected at the ME sites exceeded this threshold. At least 8 of the 13 FWMs collected at land use sites during this study exceeded this threshold; every storm had at least one sample

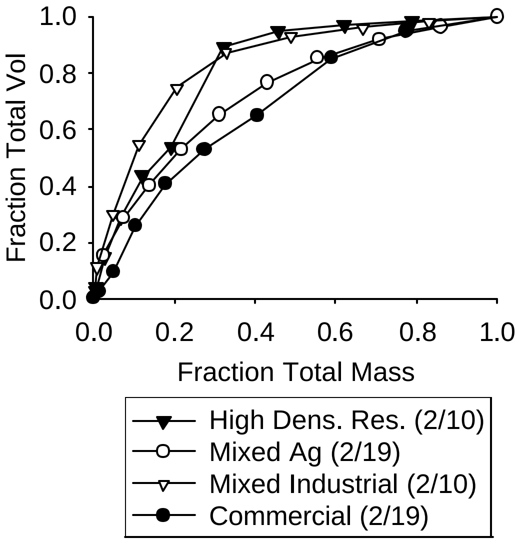

Figure 3. Cumulative mass emissions versus cumulative discharge volume for four site events in southern California.

that exceeded these guidelines. Therefore, even the land uses that contributed relatively lower concentrations of diazinon could be considered a risk to aquatic life by the State of California.

Time-concentration series plots in this study frequently identified a first flush of diazinon. However, these early storm maxima did not affect loading from any of the individual land use catchments. This was a reflection of the imperviousness of urban watersheds, where most of the runoff surfaces have been paved and much of the rainfall results in runoff rather than soaking into the ground (Ackerman *et al.* 2003). In this study, flow rates typically varied by three orders of magnitude whereas diazinon concentration typically varied 2-fold to 5-fold. Therefore, flow variability overwhelms concentration variability and loading is a function of flow. If environmental managers are concerned about concentrations, then targeting management actions early in the storm event might be a serious consideration. Conversely, if loading is the management endpoint of concern, managers will be better served by attenuating peak flows where proportionately greater emissions occur. Managers can use the FWM concentration data generated by this study to estimate loading in their respective watersheds, but caution should be exercised since we found large storm-to-storm and site-to-site variability.

LITERATURE CITED

Ackerman, D., K. Schiff and S. Weisberg. 2003. Evaluating HSPF in an arid, urbanized watershed. pp. *in:* S. Weisberg, and D. Elmore (eds.), Southern California Coastal Water Research Project Biennial Report 2001-2002. Southern California Coastal Water Research Project. Westminster, CA.

Bailey, H., L. Deanovic, E. Reyes, T. Kimball, K. Larson, K. Cortright, V. Conner and D. Hinton. 2000. Diazinon and chlorpyrifos in urban waterways in northern California, USA. *Environmental Toxicology and Chemistry* 19: 82-87.

Bertrand-Krajewski, J., G. Chebbo and A. Saget. 1998. Distribution of pollutant mass versus volume in stormwater discharges and the first flush phenomenon. *Water Research* 32: 2341-2356.

Denton, D. 2001. Ph.D. dissertation. University of California, Davis. Davis CA.

Department of Pesticide Regulation. 2000. Summary of pesticide use report data 1999. California Department of Pesticide Regulation. Sacramento, CA.

DeVlaming, V., V. Connor, C. DiGiorgio, H. Bailey, J. Deanovic and D. Hinton. 2000. Application of whole effluent toxicity test procedures to ambient water quality assessment. *Environmental Toxicology and Chemistry* 19: 42-62.

Leecaster, M., K. Schiff and L. Tiefenthaler. 2001. Assessment of efficient sampling designs for urban stormwater monitoring. *Water Research* 36: 1556-1564.

Menconi, M. and C. Cox. 1994a. Hazard assessment of the insecticide chlorpyrifos to aquatic organisms in the Sacramento-San Joaquin River system. Report 94-1. California Department of Fish and Game. Sacramento, CA.

Menconi, M. and C. Cox. 1994b. Hazard assessment of the insecticide diazinon to aquatic organisms in the Sacramento-San Joaquin River system. Report 94-2. California Department of Fish and Game. Sacramento, CA.

San Diego Regional Water Quality Control Board (SDRWQCB). 2000. Total maximum daily load (TMDL) for the pesticide diazinon on Chollas Creek, San Diego County, California. San Diego Regional Water Quality Control Board. San Diego, CA.

Sansalone, J. and S. Buchberger. 1997. Partitioning and first flush of metals in urban roadway storm water. *Journal of Environmental Engineering* 123: 134-143.

Schiff, K., S. Bay and C. Stransky. 2002. Characterization of stormwater toxicants from an urban watershed to freshwater and marine organisms. *Urban Water* 4: 215-227.

Tiefenthaler, L., K. Schiff and M. Leecaster. 2001a. Temporal variability in patterns of stormwater concentrations in urban runoff. pp. 52-62 *in*: S. Weisberg and D. Elmore (eds.), Southern California Coastal Water Research Project Annual Report 1999-2000. Southern California Coastal Water Research Project. Westminster, CA.

Tiefenthaler, L., K. Schiff, S. Bay, D. Diehl. 2001b. Characteristics of parking lot runoff produced by simulated rain. Technical Report 343. Southern California Coastal Water Research Project. Westminster, CA.

URS Greiner Woodward Clyde. 2000. Report of wet-weather monitoring for the City of San Diego and co-permittees, 1999-2000. URS Greiner Woodward Clyde. San Diego, CA.

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