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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). 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 to 45-fold. The difference in diazinon FWM concentrations among storms at the same site ranged from 1.25 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, but this was not always a predictable temporal trend. Additional sources of variability likely include pesticide usage within the catchment.

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 (DPR 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.

OP pesticides are toxic to a wide variety of non-target aquatic organisms including fish and invertebrates (Menconi et al. 1994a, 1994b). OP pesticide usage in agricultural watersheds of California has migrated into 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). The consistent toxicity measured in urban wet weather discharges has 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 < 1 cfs to > 10,000 cfs 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 from different land uses to assess their relative contributions of OP pesticides during storm events. However, flow and water quality are highly variable within storms in southern California and understanding these dynamic relationships in flow and concentration may help water quality mangers determine the most effective actions for controlling OP pesticide in urban stormwater runoff. Therefore, the goal of this study was to generate pollutagraphs that facilitate the evaluation of flow and concentration dynamics during storm events.

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 land uses, ranging in size from 0.5 to 2.6 km^2, were sampled throughout the Los Angeles region (Fig 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-NU) 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-BC) and Santa Monica Canyon (ME-SM), each drain separate basins comprised of multiple land uses in varying proportions (Table 1). The sampling sites, referred to mass emission (ME) sites, are located just upstream of where the creeks discharge to Santa Monica Bay.

Flow at the land use sites was measured at 15 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 the 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 the work of Leecaster et al (2001). All samples were collected with one of three methods: 1) peristaltic pumps with intakes 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 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 1ml 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 min; 50-100 °C at 25 °C/min; 100-310 °C at 10 °C/min for 7 min.

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

Data Analysis

There were three 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:

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

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

Samples below the detection limit 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, within replicate land use categories, and 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, the pollutagraphs from individual storm events were examined to determine the presence of runoff characteristics such as first flush or tail flush. Pollutagraphs 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.

RESULTS

Five of seven possible rain events, ranging in size from 0.16 to 1.05 in, 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 hours. Mean flow ranged from 0.1 to 60.8 cfs in the land use sites, and peak flows ranged from 0.3 to 134 cfs. 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 3.1 to 1346 cfs, with peak flows of 3780 cfs recorded in Ballona Creek.

Comparison Among Land Use Types

Diazinon was detected in 93% of all samples including 12 of 13 site-events. Concentrations of diazinon were highly variable among the various land uses, with a FWM concentration range from < 20 to 4,076 ng/L; 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 two 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. Therefore, the remainder of the results 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. 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 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 (p-value < 0.05; 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.

Temporal Variability Within Storm Events

There was no clear and consistent pattern of within storm variability at each of the land use sites (Fig 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. Concentration maxima were 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 ME sites had an array of pollutagraphs similar to the patterns observed at the land use sites (Fig 2). Three of the four ME site-events had peak diazinon concentrations prior to peak flow.

DISCUSSION

Of all the sources evaluated, the agricultural land use generated the greatest concentrations of diazinon in stormwater runoff. Others have supported this finding when concentrations of diazinon in ambient surface waters significantly increased after storm events that followed field or orchard applications (deVlaming et al 2000). 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 predominately residential subwatersheds generated higher runoff concentrations of diazinon than predominately 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 personal communication).

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 et al 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 the diazinon TMDL (URS 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 toxicity to aquatic organisms (Menconi et al 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 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.

One way the current data can be used to assist stormwater managers in difficult decision-making is to develop a dynamic water quality model. The dynamic model can be used to identify locations (i.e. important subwatersheds) where the most effective reductions should be tested and implemented. Furthermore, the model could be used to identify the most efficient use of best management practices (BMPs) within that subwatershed. For example, this study observed that a first flush often occurred during most storm events. A dynamic water quality model could be used to identify the optimum conditions that a structural BMP would be most effective including amount of volume treated, amount of diazinon reduction necessary to meet targets, etc. The model development, however, is hindered by the lack of understanding about the effectiveness of the different BMPs that currently exist for reducing OP pesticide concentrations.

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REFERENCES

Bailey, H., C. DiGiorgio, K. Kroll, J. Miller, D. Hinton, G. Starrett. 1996. Development of procedures for identifying pesticide toxicity in ambient waters; carbofuran, diazinon and chlorpyrifos. *Environmental Toxicology and Chemistry* 15:837-845.

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 vs volume in stormwater discharges and the first flush phenomenon. *Water Research* 32:2341-2356.

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

DPR. 2000. Summary of Pesticide Use Report Data 1999. California Department of Pesticide Regulation. Sacramento, CA.

Leecaster, M., K. Schiff, and L. Tiefenthaler. 2001. Assessment of efficient sampling designs for urban stormwater monitoring. Pp 45-51 *in*: Weisberg, S. and D. Elmore (eds), Southern California Coastal Water Research Project Annual Report 1999-2000. Southern California Coastal Water Research Project. Westminster, CA.

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

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

Teifenthaler, L., K. Schiff, and M. Leecaster. 2001a. Temporal variability in patterns of stormwater concentrations in urban runoff. Pp 52-62 *in*: Weisberg, S. 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. 2000. Report of wet weather monitoring for the City of San Diego and co-permittees, 1999-2000. URS Greiner Woodward Clyde. San Diego, CA.

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

	Percent 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

Table 2. Land use and mass emission site sampling dates, duration of sampling, and mean and peak flow measured.

	Date of Storm Event	Rainfall (in)	Sampling Duration (hrs)	Mean Flow (cfs)	Peak Flow (cfs)
LAND USE SITES					
High Density Residential	2/10/2001	0.16	11	2.89	19.87
	2/19/2001	0.17	10	2.16	8.24
Low Density Residential	2/19/2001	0.44	4	2.39	3.41
	3/4/2001	1.05	8	0.66	2.52
Commercial	2/19/2001	0.44	4	0.14	0.28
	4/7/2001	0.73	6	0.28	0.64
Industrial	2/10/2001	0.30	23	8.94	63.60
	2/19/2001	0.16	11	7.25	27.32
Agriculture (Mixed)	2/19/2001	0.20	5	0.91	1.50
	3/4/2001	0.58	8	0.76	1.88
Agriculture (Nursery)	4/7/2001	0.81	7	60.83	134.22
Recreational	2/19/2001	0.17	5	0.59	1.55
Open Space	2/10/2001	0.16	6	<0.01[a]	<0.01
MASS EMISSION SITES					
Ballona Creek	2/19/2001	0.40	9	1345.51	3779.70
	4/7/2001	0.54	20	1151.26	3561.20
Santa Monica Canyon	2/19/2001	0.44	9	3.11	40.00
	4/7/2001	0.73	8	22.87	106.69

[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 Residential	2/10/2001	10	125.3 ± 6.1	99.2 ± 12.6
	2/19/2001	10	90.1 ± 6.9	
Low Density Residential	2/19/2001	10	55.9 ± 5.9	67.6 ± 4.4
	3/4/2001	11	94.6 ± 5.5	
Commercial	2/19/2001	10	66.2 ± 8.9	324.0 ± 57.0
	4/7/2001	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
	3/4/2001	10	219.6 ± 49.5	
Agriculture (Nursery)	4/7/2001	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

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
	4/7/2001	10	252.3 ± 57.9	
Santa Monica Canyon	2/19/2001	10	239.1 ± 49.3	452.3 ± 205.3
	4/7/2001	10	505.3 ± 255.9	

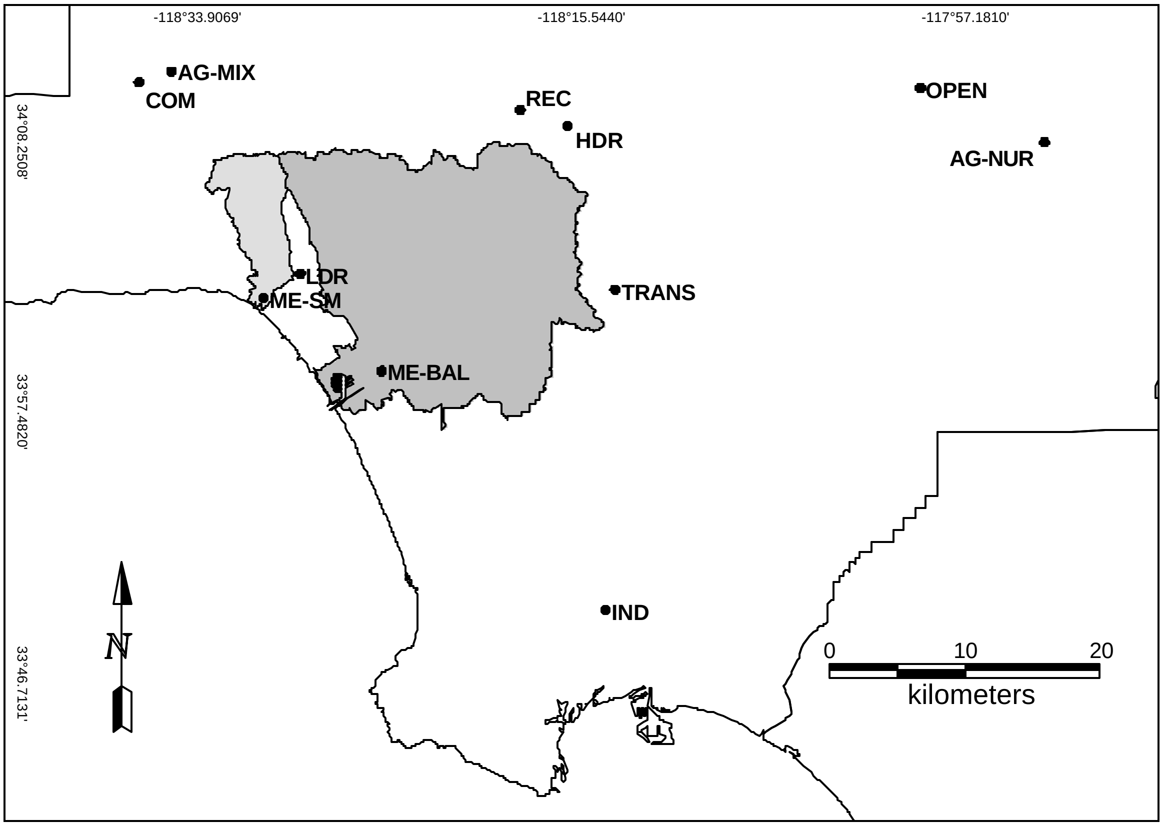


Figure 1. Map of land use and mass emission sites throughout the Los Angeles region (see text for abbreviations). Mass emission watersheds are highlighted

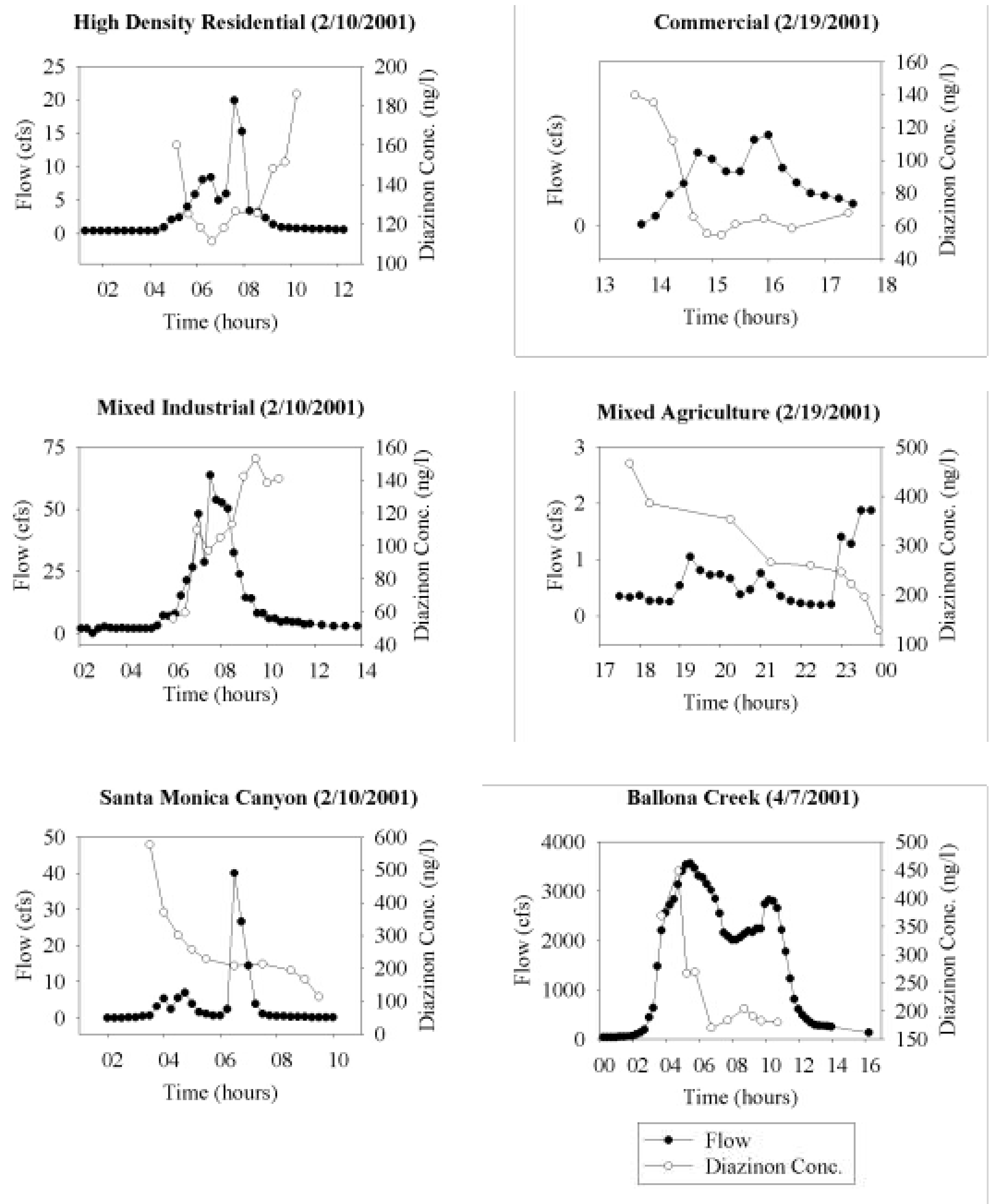
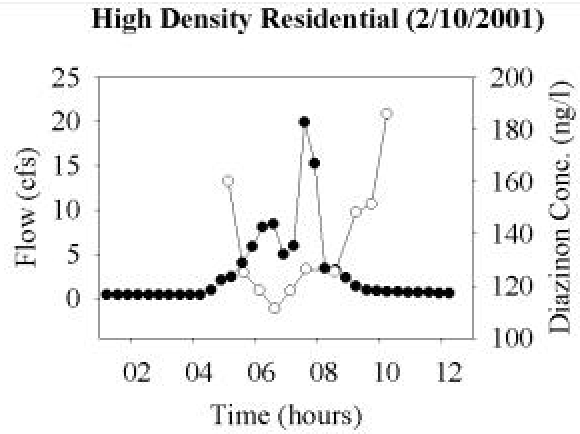
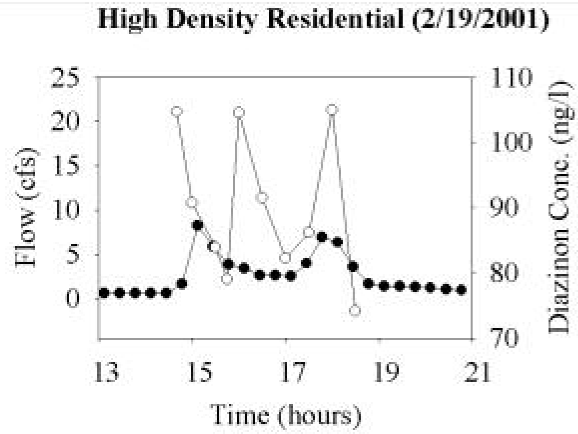


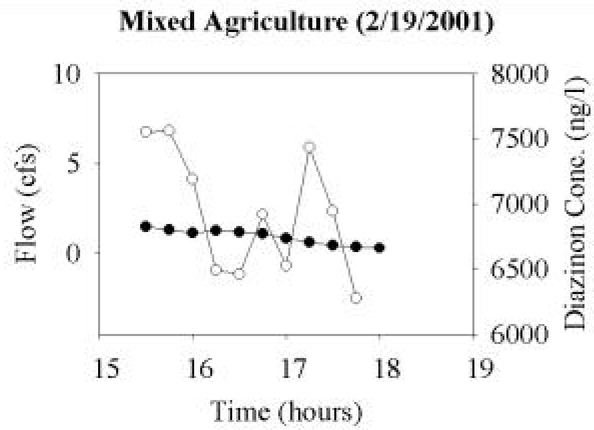
Figure 2. Pollutagraphs of storm events for various land use and mass emission sites.

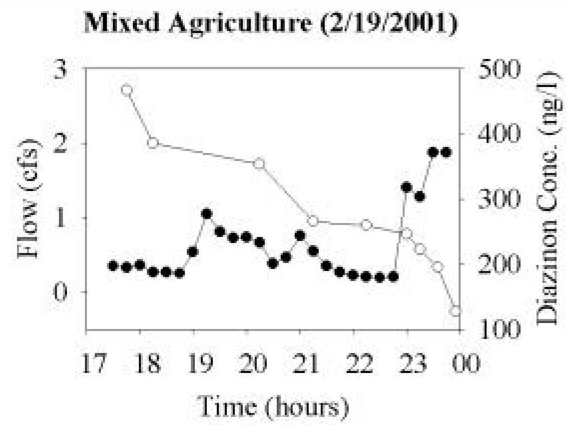
Appendix A

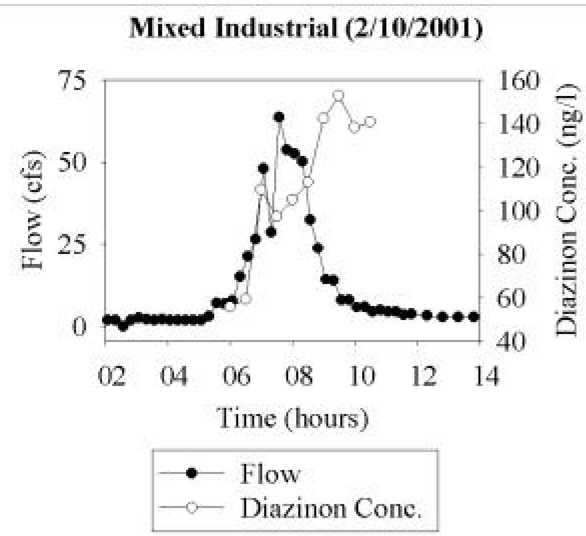
Pollutographs

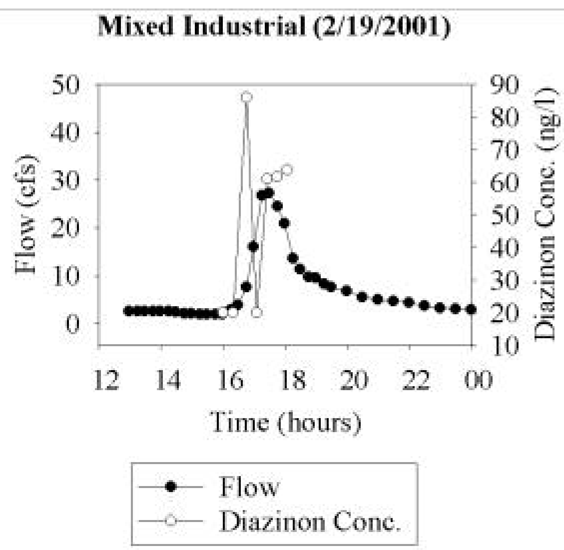

High Density Residential (2/10/2001)
Flow (cfs)
Diazinon Conc. (ng/l)
Time (hours)
25
20
15
10
5
0
200
180
160
140
120
100
02
04
06
08
10
12


High Density Residential (2/19/2001)
Flow (cfs)
Diazinon Conc. (ng/l)
Time (hours)
25
20
15
10
5
0
110
100
90
80
70
13
15
17
19
21

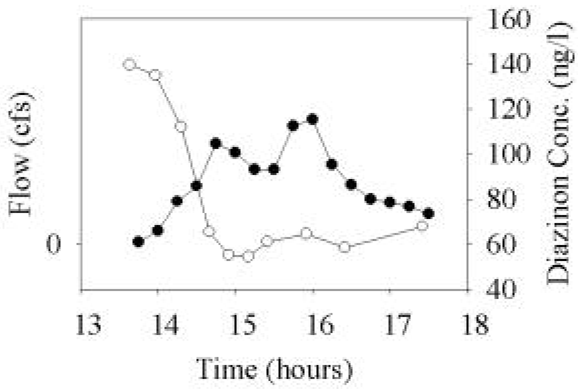

Mixed Agriculture (2/19/2001)
Flow (cfs)
Diazinon Conc. (ng/l)
Time (hours)
10
5
0
8000
7500
7000
6500
6000
15
16
17
18
19


Mixed Agriculture (2/19/2001)
Flow (cfs)
Diazinon Conc. (ng/l)
Time (hours)
3
2
1
0
500
400
300
200
100
17
18
19
20
21
22
23
00

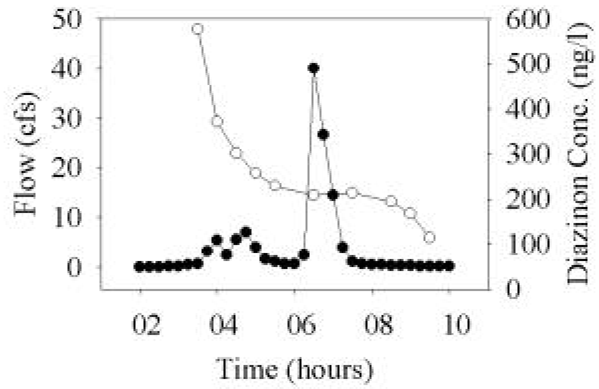

Mixed Industrial (2/10/2001)
Flow (cfs)
Diazinon Conc. (ng/l)
Time (hours)
75
50
25
0
160
140
120
100
80
60
40
02
04
06
08
10
12
14
Flow
Diazinon Conc.


Mixed Industrial (2/19/2001)
Flow (cfs)
Diazinon Conc. (ng/l)
Time (hours)
50
40
30
20
10
0
90
80
70
60
50
40
30
20
10
12
14
16
18
20
22
00
Flow
Diazinon Conc.

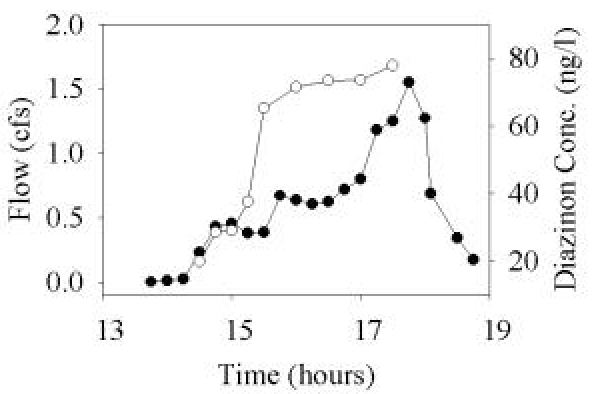
Commercial (2/19/2001)



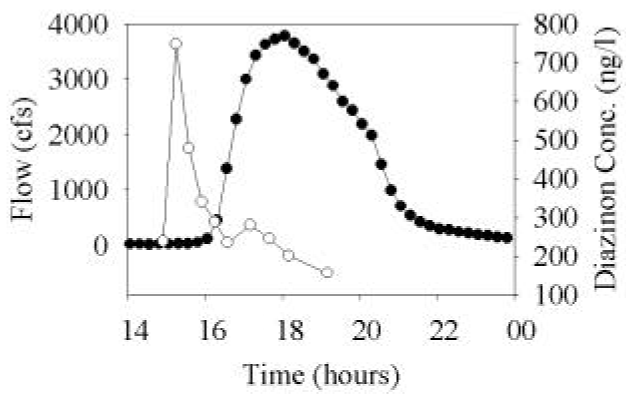
Santa Monica Canyon (2/10/2001)



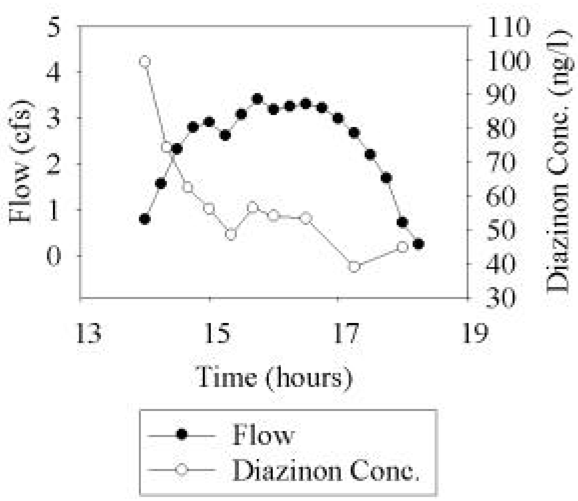
Recreation-Horse Stables (2/19/2001)



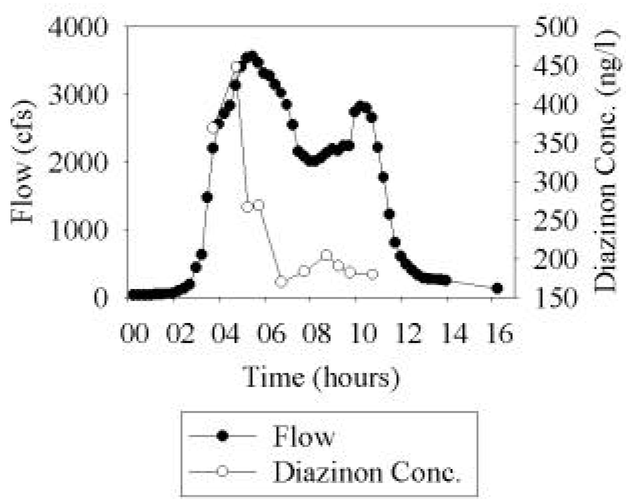
Ballona Creek (2/19/2001)



Low Density Residential (2/19/2001)



Ballona Creek (4/7/2001)



Appendix B

Raw Data

Site ID	Land Use Description
LU01	High Density Residential (HDR) Mixed
LU03	Low Density Residential (LDR) Sewer
LU08	Commercial Without Homeless
LU09	Industrial Mixed
LU14	Agriculture (Ag) Mixed
LU15	Agriculture (Ag) Nursery
LU17	Recreation (Rec) Horse
LU21	Open Space
ME05	Ballona Creek
ME06	Santa Monica Canyon

LU01 - HDR Mixed

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
02/10/2001	5:10	2.45	160.1	<20
02/10/2001	5:40	5.86	125.1	<20
02/10/2001	6:10	8.05	118.4	<20
02/10/2001	6:40	8.35	111.1	<20
02/10/2001	7:10	5.96	118.2	<20
02/10/2001	7:40	19.87	126.4	<20
02/10/2001	8:35	3.23	125.5	<20
02/10/2001	9:15	1.34	148.0	<20
02/10/2001	9:45	0.84	151.4	<20
02/10/2001	10:15	0.74	186.1	<20

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
02/19/2001	14:40	1.64	104.7	<20
02/19/2001	15:00	8.24	90.6	<20
02/19/2001	15:15	7.05	-	-
02/19/2001	15:30	5.87	83.9	<20
02/19/2001	15:45	3.78	79.0	<20
02/19/2001	16:00	3.36	104.5	<20
02/19/2001	16:15	3.36	-	-
02/19/2001	16:30	2.55	91.5	<20
02/19/2001	17:00	2.49	82.2	<20
02/19/2001	17:30	3.95	86.1	<20
02/19/2001	18:00	6.32	105.0	<20
02/19/2001	18:30	3.55	74.1	<20

LU03 - LDR Sewer

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
02/19/2001	14:00	0.80	99.5	<20
02/19/2001	14:20	1.95	74.3	<20
02/19/2001	14:40	2.81	62.3	<20
02/19/2001	15:00	2.92	56.3	<20
02/19/2001	15:20	2.63	48.5	<20
02/19/2001	15:40	3.41	56.4	<20
02/19/2001	16:00	3.20	54.0	<20
02/19/2001	16:30	3.32	53.3	<20
02/19/2001	17:15	2.68	39.1	<20
02/19/2001	18:00	0.74	44.8	<20

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
03/04/2001	18:30	0.11	86.3	<20
03/04/2001	19:00	0.04	-	-
03/04/2001	19:30	0.15	74.4	<20
03/04/2001	20:00	0.05	-	-
03/04/2001	21:00	0.01	86.4	<20
03/04/2001	23:10	0.00	67.6	<20
03/04/2001	23:25	0.39	73.8	<20
03/04/2001	23:40	1.47	92.5	<20
03/04/2001	23:55	1.78	85.3	<20
03/05/2001	0:10	2.25	95.1	<20
03/05/2001	0:40	2.14	97.7	<20
03/05/2001	1:10	0.61	90.1	<20
03/05/2001	1:40	2.13	105.4	<20

LU08 - Commercial Without Homeless

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
02/19/2001	13:38	0.01	139.6	<20
02/19/2001	13:58	0.03	134.8	<20
02/19/2001	14:18	0.10	112.0	<20
02/19/2001	14:40	0.22	65.4	<20
02/19/2001	14:55	0.20	55.1	<20
02/19/2001	15:10	0.17	54.4	<20
02/19/2001	15:25	0.17	61.1	<20
02/19/2001	15:55	0.28	64.5	<20
02/19/2001	16:25	0.13	58.4	<20
02/19/2001	17:25	0.07	67.9	<20

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
04/07/2001	3:15	0.33	315.1	<20
04/07/2001	3:45	0.28	643.7	<20
04/07/2001	4:15	0.20	414.4	<20
04/07/2001	4:45	0.16	-	-
04/07/2001	5:15	0.17	263.6	<20
04/07/2001	6:00	0.29	346.4	<20
04/07/2001	6:45	0.17	-	-
04/07/2001	7:30	0.09	326.0	<20
04/07/2001	8:00	0.47	620.2	<20
04/07/2001	8:30	0.64	456.2	<20
04/07/2001	9:00	0.43	374.1	<20
04/07/2001	9:30	0.13	370.2	<20

LU09 - Industrial Mixed

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
02/10/2001	6:00	7.88	55.6	<20
02/10/2001	6:30	21.20	59.4	<20
02/10/2001	7:00	48.00	109.5	<20
02/10/2001	7:30	63.60	97.1	<20
02/10/2001	8:00	52.40	105.0	<20
02/10/2001	8:30	32.40	113.0	<20
02/10/2001	9:00	14.30	142.1	<20
02/10/2001	9:30	8.02	153.0	<20
02/10/2001	10:00	5.78	138.1	<20
02/10/2001	10:30	4.42	140.6	<20

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
02/19/2001	16:00	2.03	20.0	<20
02/19/2001	16:20	2.87	20.0	<20
02/19/2001	16:45	7.68	85.9	<20
02/19/2001	17:05	21.47	20.0	<20
02/19/2001	17:25	27.32	61.0	<20
02/19/2001	17:45	24.50	61.7	<20
02/19/2001	18:05	17.28	63.7	<20

LU14 - Ag Mixed

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
02/19/2001	15:30	1.50	7549.9	50.4
02/19/2001	15:45	1.30	7560.1	42.7
02/19/2001	16:00	1.13	7190.0	47.5
02/19/2001	16:15	1.25	6491.9	51.6
02/19/2001	16:30	1.20	6463.7	51.1
02/19/2001	16:45	1.10	6918.0	51.2
02/19/2001	17:00	0.84	6530.2	51.5
02/19/2001	17:15	0.63	7433.2	47.1
02/19/2001	17:30	0.46	6945.1	50.7
02/19/2001	17:45	0.35	6275.6	52.4

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
03/04/2001	17:45	0.33	466.1	<20
03/04/2001	18:15	0.27	386.0	<20
03/04/2001	19:15	No Data	-	-
03/04/2001	20:15	0.67	352.9	22.1
03/04/2001	21:15	0.55	265.8	<20
03/04/2001	22:15	0.27	259.8	24.5
03/04/2001	22:45	No Data	-	-
03/04/2001	23:00	1.40	245.6	24.5
03/04/2001	23:15	1.28	221.8	24.9
03/04/2001	23:35	1.88	195.4	25.5
03/04/2001	23:55	1.50	127.6	<20
03/05/2001	0:15	No Data	-	-
03/05/2001	1:30	0.82	88.2	<20

LU15 - Ag Nursery

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
4/7/01	5:00	7.84	294.4	-
4/7/01	5:30	39.49	179.4	-
4/7/01	6:00	94.24	141.5	-
4/7/01	6:30	113.83	126.6	-
4/7/01	7:00	44.36	160.6	-
4/7/01	8:00	24.55	145.2	-
4/7/01	8:45	98.29	162.2	-
4/7/01	9:30	59.86	163.2	-
4/7/01	10:15	134.22	142.4	-
4/7/01	11:30	34.80	109.2	-

LU17 - Rec Horse

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
02/19/2001	14:30	0.23	20.0	-
02/19/2001	14:45	0.43	28.5	-
02/19/2001	15:00	0.46	29.0	-
02/19/2001	15:15	0.38	37.5	-
02/19/2001	15:30	0.39	65.1	-
02/19/2001	16:00	0.63	71.3	-
02/19/2001	16:30	0.62	73.3	-
02/19/2001	17:00	0.80	73.5	-
02/19/2001	17:30	1.25	77.9	-
02/19/2001	18:15	0.69	79.4	-

LU21 - Open Space

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
02/10/2001	4:50	<0.01	<20	<20
02/10/2001	5:45	<0.01	<20	<20
02/10/2001	6:15	<0.01	<20	<20
02/10/2001	7:00	<0.01	<20	<20
02/10/2001	7:30	<0.01	<20	<20
02/10/2001	8:30	<0.01	<20	<20
02/10/2001	9:15	<0.01	<20	<20
02/10/2001	9:45	<0.01	<20	<20
02/10/2001	10:15	<0.01	<20	<20
02/10/2001	11:10	<0.01	<20	<20

ME05 - Ballona Creek

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
02/19/2001	14:55	21.24	240.0	<20
02/19/2001	15:15	23.12	748.4	<20
02/19/2001	15:35	29.41	477.9	<20
02/19/2001	15:55	51.58	341.1	<20
02/19/2001	16:15	454.00	288.8	<20
02/19/2001	16:35	1387.40	235.0	<20
02/19/2001	17:10	3427.60	281.0	<20
02/19/2001	17:40	3716.10	245.8	<20
02/19/2001	18:10	3644.30	201.9	<20
02/19/2001	19:10	2882.10	156.7	<20

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
4/7/01	3:45	2205.70	368.7	<20
4/7/01	4:45	3133.00	447.8	<20
4/7/01	5:15	3534.20	266.3	<20
4/7/01	5:45	3468.20	269.1	<20
4/7/01	6:45	3017.40	169.8	<20
4/7/01	7:45	2079.30	183.4	<20
4/7/01	8:45	2128.20	204.5	<20
4/7/01	9:15	2170.10	190.6	<20
4/7/01	9:45	2238.40	182.6	<20
4/7/01	10:45	2653.40	179.7	<20

ME06 - Santa Monica Canyon

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
02/10/2001	3:30	0.62	576.8	<20
02/10/2001	4:00	5.28	371.3	<20
02/10/2001	4:30	5.50	301.3	22.9
02/10/2001	5:00	3.88	257.6	<20
02/10/2001	5:30	1.14	228.9	<20
02/10/2001	6:30	40.00	208.5	<20
02/10/2001	7:30	1.13	214.1	32.2
02/10/2001	8:30	0.38	194.9	25.6
02/10/2001	9:00	0.26	168.1	<20
02/10/2001	9:30	0.18	114.4	<20

Date	Time	Flow (cfs)	Diazinon (ng/L)	Chlorpyrifos (ng/L)
4/7/01	4:30	54.38	300.7	<20
4/7/01	5:00	25.23	257.3	15.3
4/7/01	5:30	25.35	271.8	17.8
4/7/01	6:00	15.54	282.7	<20
4/7/01	6:30	8.72	254.4	19.5
4/7/01	7:30	6.27	248.9	<20
4/7/01	8:30	6.21	219.6	<20
4/7/01	9:00	67.42	891.6	<20
4/7/01	9:30	18.99	851.6	<20
4/7/01	10:30	6.98	462.7	<20