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Levels of the Organophosphorus Pesticide Diazinon in the Chollas Creek Watershed, San Diego CA, since Its Phase-Out in 2004

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Abstract.—In 2004, the organophosphorus pesticide, diazinon, was phased-out for all residential uses in the United States. The objective of this study was to determine the temporal trend of diazinon levels in the Chollas Creek, CA watershed since the phase-out of this pesticide. Stormwater samples from Chollas Creek were collected during seven storm events in 2006–2007. The median diazinon level for all samples was 0.13 µg/L. Statistical analysis using the Kruskal-Wallis test revealed no statistically significant ($p=0.765$) spatial difference among any of the sampling sites. Correlational analysis (using the Spearman's rho test) revealed that there was no significant association between antecedent dry days and median diazinon levels ($p=0.383$, rho=0.393). Additionally, no association between storm event precipitation ($p=0.355$, rho=−0.414), median storm event intensity ($p=0.585$, rho=−0.252), or annual cumulative precipitation ($p=0.760$, rho=0.143) was observed. Trend analysis of diazinon levels (1998–2005) showed that levels in this watershed have declined with a negative slope of 0.0002 µg/L per year, and statistical analysis (using the Mann-Whitney U test) showed there was a significant decline in levels after the pesticide's phase-out in 2004 ($p<0.05$).

Chollas Creek is located within a highly urbanized area of San Diego County, CA and drains into San Diego Bay, San Diego, California. The drainage area is 6585.4 hectares (3753.9 hectares in North fork, 2831.6 hectares in South fork) (San Diego Region Water Quality Control Board [SDRWQCB] 2002a). It has highly variable flows, the highest of which are associated with storm events. Toxicity tests using the water flea *Ceriodaphnia dubia* have indicated that stormwater flows in Chollas Creek are toxic to aquatic life, and toxicity identification evaluations (TIEs) showed that diazinon was responsible for this toxicity (Southern California Coastal Water Research Project [SCCWRP] 1999). Such consistent toxicity, and levels of organophosphorus pesticides in urban runoff in the state California, has led regulators to add at least 32 California streams to their list of impaired water bodies (303 d list) (Schiff and Sutula 2004).

Diazinon is an organophosphorus insecticide that until recently was common in indoor, residential, landscape and agricultural applications. Although, the breakdown rate of diazinon in the aqueous phase is pH dependent, with rapid degradation occurring under increasingly acidic conditions, its average half-life in neutral waters is about six months (EXTOXNET, 2003). Diazinon concentrations in Chollas Creek during storm events have caused violations of the ''toxicity'' and ''pesticide'' water quality objectives

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(SDRWQCB 2002a). Accordingly, Chollas Creek was placed onto the List of Water Quality Limited Segments in 1996 (commonly referred to as the 303(d) List) (SDRWQCB 2002a). Clean Water Act Section 303 (d) requires the Regional Board to develop a Total Maximum Daily Load (TMDL) for waters on this list (SDRWQCB 2002b). The SDRWQCB has since developed the Chollas Creek TMDL to begin to address water quality impairment due to diazinon (SDRWQCB 2002b).

On December 31, 2002, the United States Environment Protection Agency (USEPA) started to impose restrictions on many uses of diazinon in the United States under the revised risk assessment and agreement between the USEPA and diazinon registrants. The agreement included indoor uses and all uses on lawns gardens, and turf (USEPA 2001). The agreement mandated that technical registrants reduce the amount of diazinon produced for outdoor non- agricultural uses by 50% or more by the start of 2003, and sales to retailers were stopped on August 31, 2003. Any remaining diazinon at retailers was returned to manufacturers beginning on December 31, 2004. The overall objective of this study was to determine the temporal trend of diazinon levels in the Chollas Creek watershed since the phase-out of this pesticide in 2004, in order to determine if this regulatory strategy has been effective in this urban watershed.

Materials and Methods

Sampling Method

Stormwater samples from Chollas Creek watershed were collected as grab samples during storm events on March 2, March 29, April 14, May 22, and December 16 of 2006, and February 19, and April 20 of 2007 from four sites (Fig. 1). Sampling times varied in relation to both the start and duration of the storm event as shown in Table 1. The samples, collected using one liter amber glass containers, were transported on ice to the laboratory after collection, and were stored at 4°C until testing. Samples were then analyzed using enzyme-linked immunosorbent assay (ELISA) (Sullivan and Goh 2000) within seven days of collection.

ELISA Analytical Chemistry

A diazinon EnviroGard Kit (Strategic Diagnostics, Newark, Delaware) was used for the ELISA analyses performed in this study. Concentrations of diazinon in samples were derived by reading optical densities of the calibration standards using a spectrophotometer at 450 nm (Spectra max PLUS 384 Molecular Devices). The method has a limit of detection of 0.022 μg/L for diazinon (Strategic Diagnostics, Newark, Delaware).

Precipitation Data

Precipitation data from San Diego Lindbergh international airport were taken from National Oceanic and Atmospheric Administration (NOAA, Retrieved June 6, 2007, from: http://www.ncdc.noaa.gov/oa/mpp/).

Data Analysis

For present study (2006–2007), lab duplicates for each sample site were analyzed. SPSS Version14.0 was performed for statistical analysis. The median diazinon level at each site was calculated and Kruskal-Wallis test (Kruskal and Wallis 1958) was used for spatial trend analysis. The Spearman's rho test (Spearman 1904) was used to determine correlation between a single median diazinon level of all sites for each storm event, and the number of antecedent dry days (the number of days without rain or with less than

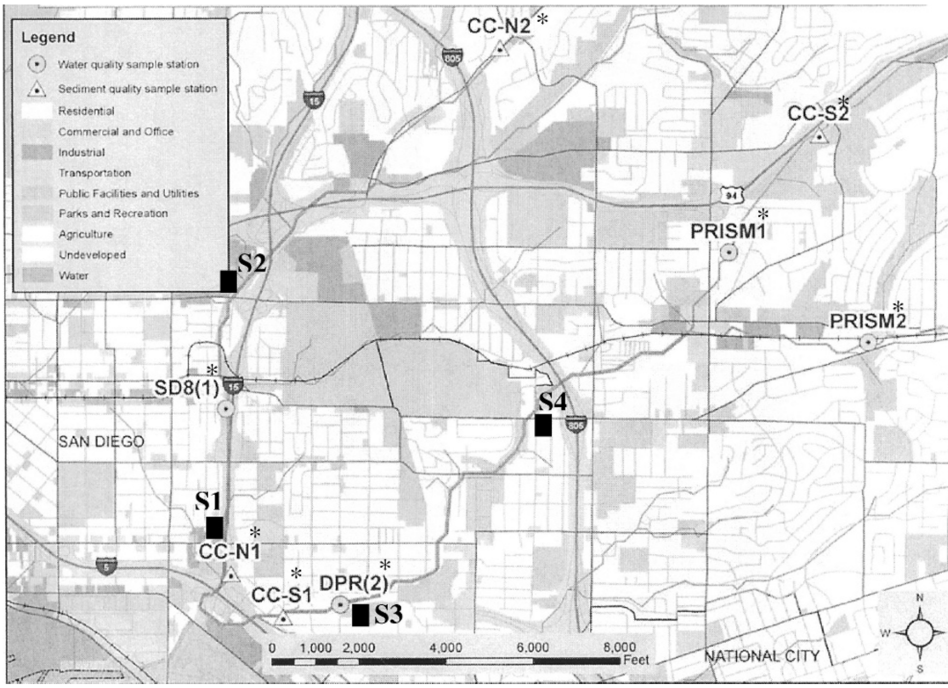

Fig. 1. Sampling sites on Chollas Creek, and associated land use of the Chollas Creek watershed. Note. *DPR(2), PRISM1, PRISM2, SD8(1) CC-N1, CC-N2, CC-S1, CC-S2 were sampling sites from Weston Solutions, Inc., 2006.

0.1 inch in water year), storm event precipitation, intensity (the amount of precipitation in centimeters per hour during storm event), and annual cumulative precipitation. Annual cumulative precipitation was calculated based on a water year, from October to September of the following year. Flow measurements for Chollas Creek during this study were not available.

A Mann-Whitney U test (Mann and Whitney 1947) was performed to compare diazinon levels before the pesticide's phase-out period (1998–2004) to levels after the phase-out was completed (2005), and a Kendall's test (Kendall 1955) was performed to determine if the declining trend in levels of diazinon from 1998 through 2005, has been significant.

Quality Assurance (QA) and Quality Control (QC) Procedures

Quality control samples consisted of field blanks, field duplicate samples, and lab duplicate samples. Precision for all samples were within the objective for diazinon of 25% which was previously established (San Diego Baykeeper 2005), except for a single sample (Site 4 on March 29, 2006) which showed precision of 26%. Overall precision was 4.96% for all tests. Additionally, QA/QC procedures consisted of enrichment of natural Chollas Creek waters at each sampling site, with at least two different levels (100 ppt and 200 ppt or 500 ppt) of diazinon spiked into these samples, in order to determine the accuracy of the ELISA method. Accuracy of the ELISA test for diazinon-spiked samples for each rain event ranged from 67.8% to 204.2%, with a median value of 115.0% for all diazinon-enriched samples. This indicated that there was no significant inhibition by materials in the river water which could significantly mask the ELISA results.

Table 1. Correlations between diazinon levels and rainfall parameters.

Start of rain event (Time)	Site	Date sampled	Time	Median diazinon (ug/L)	Anteced-ent dry days	Precipita-tion (cm)	Intensity (cm/hour)	Cumulative precipitation (cm)
27 Feb, 2006 (18:00)	S1	2 Mar, 2006	11:55	0.052	2	2	0.076	2.2
	S2		12:47					
28 Mar, 2006 (20:00)	S1	29 Mar, 2006	9:24	<0.022	8	0.99	0.1	5.8
	S2		8:40					
	S3		9:00					
	S4		9:46					
14 Apr, 2006 (6:00)	S1	14 Apr, 2006	15:45	0.12	10	0.58	0.17	7.7
	S2		14:50					
	S3		16:00					
	S4		15:26					
22 May, 2006 (3:00)	S1	22 May, 2006	10:06	0.042	38	2	0.2	9.9
	S2		9:25					
	S3		10:17					
	S4		9:50					
16 Dec, 2006 (7:00)	S1	16 Dec, 2006	21:52	0.19	6	0.41	0.076	3.2
	S2		21:40					
	S3		22:08					
	S4		21:04					
17 Feb, 2007 (10:00)	S1	19 Feb, 2007	11:36	0.23	19	1.8	0.11	7.6
	S2		11:00					
	S3		11:48					
	S4		11:15					
20 Apr, 2007 (4:00)	S1	20 Apr, 2007	17:20	0.39	57	0.76	0.089	9.6
	S2		16:44					
	S3		17:27					
	S4		17:00					

Results

Overall, seven storm events were sampled at sites S1 and S2, and six were sampled at sites S3 and S4. No hydrograph data was available, and sample times varied among the storm events, but our study showed that significant levels of diazinon may still be found in the Chollas Creek watershed even several years after the complete phase-out of the pesticide in 2004. Median levels of diazinon at sample sites in the Chollas Creek Watershed, from March 2, 2006 to April 20, 2007 are shown in Table 2. Diazinon levels ranged from as low as the detection limit (0.022 μg/L) at S1 (National Ave), S2 (Market

Table 2. Diazinon levels at each sample site for the study period from March 2006 through April 2007.

Sample site	N	Mean	Standard Deviation	Median	Minimum	Maximum	% of acute criterion exceedance	% of chronic criterion exceedance
S1	7	0.13	0.13	0.08	<0.022	0.4	43	71
S2	7	0.15	0.15	0.12	<0.022	0.42	57	57
S3	6	0.15	0.13	0.14	<0.022	0.38	57	71
S4	6	0.19	0.12	0.19	0.042	0.36	71	71
All Sites				0.13				

Note: Acute criterion 0.08 μg/L; Chronic criterion 0.05 μg/L

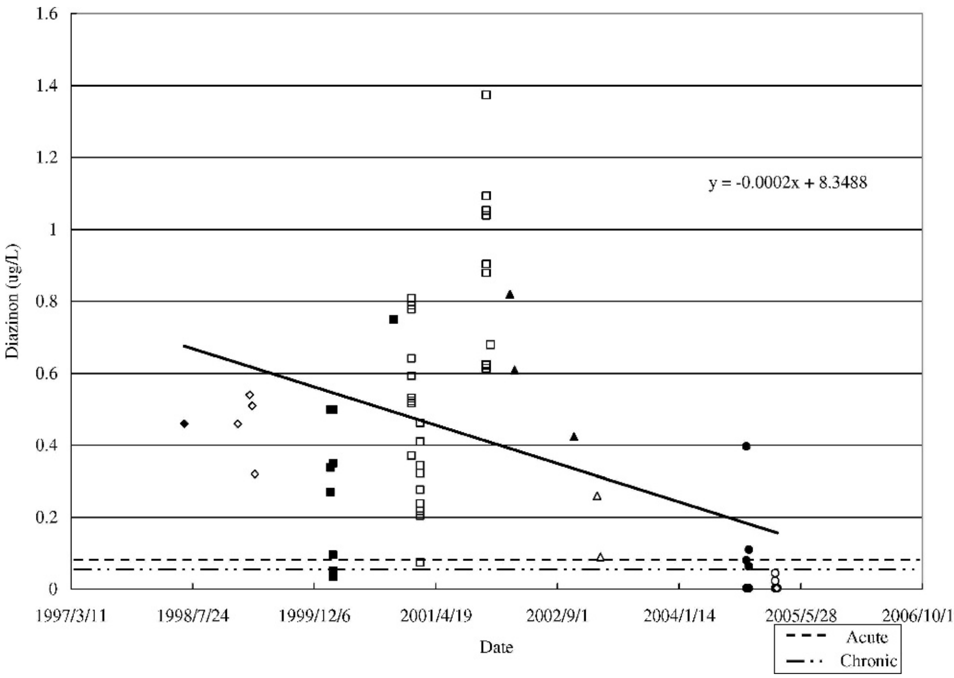

Fig. 2. Trend analysis between diazinon level (μg/L) and year between 1998 and 2005. Note. Each data point represents the mean for all samples and all sites for that particular study. ◆ URS Greiner Woodward Clyde 1999; ◇ URS Greiner Woodward Clyde 1999 and Southern California Coastal Project, 1999; ■ MEC Analytical Systems Inc. 2002, and Project Clean Water 2004; □ MEC Analytical Systems Inc. 2002, Project Clean Water 2004; ▲ Project Clean Water 2004; △ Project Clean Water 2004; ● Weston Solutions Inc. 2006; ○ Weston Solutions Inc. 2006; * present study, – present study. Kendall's Test $p=0<0.05$ tau$=-0.352$.

St), and S3 (38th St) on March 29, 2006, to 0.42 μg/L at S2 (Imperial Ave) on April 20, 2007. The median level of all sites and dates combined was 0.13 μg/L. This value exceeded both the chronic (0.050 μg/L) and acute (0.080 μg/L) criteria listed by SDRWQCB (2002a). The acute criterion was exceeded 43% to 71% of the 26 total times sampled, and the chronic criterion was exceeded 57% to 71%of the total times sampled.

S4 had the highest median concentration of diazinon (0.19 μg/L) (Table 2). However, statistical analysis using Kruskal-Wallis test revealed no statistically significant ($p=0.765$) difference among any of the sampling sites. In order to test whether buildup and wash off of diazinon in the Chollas Creek watershed could account for the temporal pattern of diazinon observed in total seven storm events, correlational analysis between the number of antecedent dry days and median diazinon level of all sites for each storm events was performed (Table 1). No significant association between antecedent dry days (2–57 days) and the median diazinon levels (<0.022–0.39 μg/L) ($p=0.383$, rho$=0.393$) was found. Additionally, no association between storm event precipitation (0.41–2.0 cm) ($p=0.355$, rho$=-0.414$), median storm event intensity (0.076–0.20 cm/hour) ($p=0.585$, rho$=-0.252$), or annual cumulative precipitation (2.2–9.9 cm) ($p=0.760$, rho$=0.143$) was observed (Table 1).

This historical diazinon data for Chollas Creek, as represented by the diazinon levels at all sites sampled for each past study, is shown in Figure 2. Since flow-associated variability may complicate the analysis, only studies based on flow-weighted composite sampling in the Chollas Creek watershed were plotted. Between 1998 and 2005, diazinon levels significantly declined with a negative slope of 0.0002 µg/L per year (Kendall's test, $p<0.05$, tau$=-0.352$). Moreover, a Mann-Whitney U test of the temporal data showed that there has been a significant ($p<0.05$) decline in diazinon levels when levels before the phase-out (1998–2004), were compared to levels after the phase-out (2005).

Discussion

Our study found that the median level of diazinon in 2006–2007 (three years after the phase-out) for all sites and dates combined was 0.13 µg/L, and this value still exceeded both the chronic (0.050 µg/L) and acute (0.080 µg/L) criteria listed by SDRWQCB (2002a). Diazinon has been shown to exert acute and chronic toxicity in aquatic ecosystems (Menconi & Cox 1994; USEPA 2005). A study based on *Ceriodaphnia* survival was done in Chollas Creek and TIEs showed that diazinon was the principal cause of toxicity in this watershed (SCCWRP 1999). Apparently, despite the phase-out in the 2004, diazinon is still at levels that may exert adverse ecological effects, although studies conducted in the watershed since 2004 using *Ceripdaphnia*, showed no evidence of persistent toxicity (Project Clean Water 2007).

After the complete phase-out of the use of diazinon in 2004, a study on the Chollas Creek watershed showed that median diazinon levels were 0.16 µg/L, but by 2005, they had been reduced to levels below the diazinon criteria for both acute (0.080 µg/L) and chronic (0.050 µg/L) exposure (Weston Solutions Inc. 2006). However, the present study on Chollas Creek found that the acute and chronic criteria were still exceeded by 43%–71%, and 57%–71%, respectively, in 2006 and 2007. This might reflect the fact that the shelf life of diazinon is five to seven years (Missouri Environment and Garden 2003), and consumers might have continued to use purchased quantities of diazinon in the Chollas Creek watershed despite its complete phase-out in 2004.

Statistical analysis using Kruskal-Wallis test revealed no statistically significant ($p=0.765$) difference among any of the sampling sites in Chollas Creek Watershed. This may be due to the fact that levels of diazinon in the Chollas Creek watershed were somewhat variable both spatially and as a function of the particular characteristics of a given rain event. A more robust data set may be necessary to reveal significant spatial differences. The specific relationship of land use to levels of diazinon in urbanized watersheds has not been well assessed. Although Hoffman et al. (2000) found that the insecticide use was similar in urban and agricultural areas based on water samples from eight urban streams from across the United States, Schiff and Sutula (2004) found that diazinon levels in a mixed agricultural land use exceeded the residential and commercial land use categories by one to two orders of magnitude in an urbanized watershed of southern California. A study using toxicity identification evaluations in the Salinas River, CA, between 1998 and 2000, found significant *Ceriodaphnia dubia* mortality in 87% of the samples from a channel draining an urban/agricultural watershed, and 100% of the sample from a channel agricultural surface furrow runoff (Hunt et al. 2003), suggesting that both land use types may be major contributors. The fact that the Chollas Creek watershed is located in an urban area where nearly 70% of the land use is residential (Woodward-Clyde International-Americas 1998), as opposed to the Salinas River watershed composed of mostly agricultural lands, suggests that residential land uses may continue to be a significant and major source of diazinon.

Bumgardner et al. (1994) showed that build-up and wash off effects of pollutants could be identified by linear regression analyses, and found that for certain pollutants, wash off by rainfall does deplete the pollutant supply (accumulated by build-up processes) available for wash-off in subsequent rain events. The fact that there was no statistically significant association between antecedent dry days and diazinon levels (Table 1) may reflect the limited number of rain events we sampled or that levels in stormwater do not follow a simple buildup-wash off model.

Trend analysis (Fig. 2) showed that diazinon levels have been decreasing since 1998 to 2005, with negative slope of 0.0002 μg/L per year (Kendall's test, $p<0.05$, tau$=-0.352$), and statistical analysis (Mann-Whitney U test) showed there has been a significant decline in diazinon levels since the pesticide's phase-out in 2004 ($p<0.05$). A study on diazinon in surface waters in the City of Denton, Texas (Banks et al. 2005) showed a similar statistically significant ($p<0.0001$) decrease during the years (from 2001 and 2004) spanning the USEPA phase-out period. The National Water Quality Assessment (NAWQA) done by the United States Geological Survey between 1997 through 2004 found that diazinon concentrations decreased significantly ($p<0.05$) in five of seven in urban and mixed land use streams in the northeastern U.S. by the end of its phase-out period in 2004, with a median decrease in these NAWQA streams of 28% (Philips et al. 2006). Our analysis of historical diazinon data for the Chollas Creek watershed (Fig. 2) showed that a decline of 93% was observed over the same period (1998–2004). Apparently, the decline of diazinon levels since the start of the phase-out has been greater in the Chollas Creek Watershed than in northeastern U.S. (Philips et al. 2006), but levels of diazinon still persist that may exert ecotoxicity.

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