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Oxadiazon Residue Concentrations in Sediment, Fish, and Shellfish from a Combined Residential/Agricultural Area in Southern California

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The occurrence of organochlorine pesticides in California has been monitored statewide in fresh, estuarine, and coastal waters by the California State Water Resources Control Board for over ten years (Phillips 1988; Rasmussen and Blethrow 1990). The Toxic Substances Monitoring Program and the California State Mussel Watch Program utilize the results of fish, mussel, and clam tissue analyses to determine the presence of approximately fifty pesticides thought to be persistent in the environment. One objective of the monitoring programs is to determine the composition of unidentified chromatographic peaks from sample extracts using gas chromatography-mass spectrometry (GC-MS).

An unidentified chromatographic peak from an extract of a composite sample of fish from San Diego Creek near Irvine, Orange County, California was identified as oxadiazon by GC-MS. Further investigation resulted in the identification of oxadiazon in sediment and clams from San Diego Creek and in mussels from Newport Bay.

Sold as Ronstar®, oxadiazon [3-{2,4-Dichloro-5-(methylethoxy)phenyl}-5-(1,1-dimethylethyl)-1,3,4-oxadiazol-2-(3H)-one] is a herbicide manufactured by the *Societe Rhône-Poulenc, France*. It has been used for 20 years as a pre-emergent herbicide on a wide range of annual dicotyledons and as a post-emergent herbicide on annual broad-leaved weeds. It is used, selectively, on a number of crops and grasses such as rice, soybeans, ornamentals, potatoes, onion, sunflowers, turf, and perennial orchard and vineyard crops (Guardigli et al. 1976; Ambrosi et al. 1978). It is insoluble in water but soluble in solvents. It is considered toxic to fish (Farm Chemicals Handbook 1991) and moderately persistent in soil with a half life of three to six months (Thomson 1987).

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MATERIALS AND METHODS

In 1989 Red Shiners (*Notropis lutrensis*) were collected using a seine from two locations in the San Diego Creek drainage, Peters Canyon Channel and San Diego Creek at Michelson Drive. These two locations were sampled again in 1990 with an additional site at Barranca Parkway on San Diego Creek. The fish were immediately frozen on dry ice and remained frozen until they were prepared for analysis.

Sediment samples were collected in 1988 using methods modeled after those used by the Southern California Coastal Water Research Project (SCCWRP) for marine sediment (Scherfig and Phillips 1989).

Mussels (*Mytilus californianus*) and freshwater clams (*Corbicula fluminea*) were collected from Bodega Head in northern California and the American River in Sacramento, CA respectively for transplantation. Mussels were deployed into Newport Bay on September 2, 1989 and collected on December 27, 1989 for analysis. Clams were collected on January 11, 1990 and depurated in Aptos Creek from January 11 to February 1, 1990. They were then deployed into the San Diego Creek drainage on February 1, 1990 and collected on March 14, 1990 for analysis. Mussel and clam samples were immediately frozen after collection and remained frozen until processed in the laboratory.

Tissue samples were homogenized using a Brinkman Polytron (Model PT10-35) equipped with an all titanium and Teflon generator (Model PTA-20).

The extraction method used for tissue samples was from the U.S. Food and Drug Administration Pesticide Analytical Manual (PAM) section 212: General Methods For Nonfatty Foods (US Food and Drug Administration 1989). Sediments were extracted using EPA Method 3550: Sonication Extraction (US Environmental Protection Agency 1986). All extracts were cleaned up using Florisil according to PAM method 211.14d (US Food and Drug Administration 1989).

Sediment samples were extracted using a Heat Systems Model W-375 sonicator cell disrupter equipped with a No. 207 3/4 in. tapped disrupter horn. Pulsed sonication was used with the output set at 10 and the duty cycle set at 50 percent.

All solvents were pesticide residue grade distilled in glass. All chemicals and reagents used were reagent grade or better. Florisil was pesticide residue grade, 60/100 mesh.

A reference standard of oxadiazon was obtained from Accustandard Inc., New Haven, CT., 06511.

Sample extracts analyzed at the Water Pollution Control Laboratory were chromatographed using a Varian model 3500 gas chromatograph equipped with dual nickel 63 electron capture detectors, temperature programmable on-column injector, and model 8035 autosampler. A 30 meter J&W Scientific DB1 fused silica capillary column was connected to the injector, the column effluent was split using a J&W press-fit "Y" connector and 30 meter J&W Scientific DB5 and DB17 columns. Helium was used as the carrier gas and nitrogen was used as the detector make-up gas.

Sample extracts analyzed at the Long Marine Laboratory were chromatographed using a Hewlett-Packard model 5890A gas chromatograph equipped with a model 7673 autosampler, a splitless capillary inlet system, and dual nickel 63 electron capture detectors. Dual column verification was provided through the use of 30 meter J&W Scientific DB5 and DB17 columns. Helium was used as the carrier gas and argon-methane was used as the detector make-up gas.

Gas chromatographic/mass spectrometric (GC/MS) analyses were performed using a Hewlett-Packard model 5890A gas chromatograph equipped with a model 7673A autosampler and a Finnigan ITD 800 ion trap detector. The column used was a J&W Scientific 30 meter DB5. Sample mass spectra were compared with spectra in the National Institute of Standards and Technology (NIST) library which provided the first indications that the unidentified peak was due to oxadiazon.

RESULTS AND DISCUSSION

Oxadiazon was identified in Red Shiners collected from two locations in the San Diego Creek drainage in 1989 and at similar concentrations from three locations in 1990.

Three sediment samples collected from San Diego Creek in 1988 contained oxadiazon. All three transplanted clam samples and six transplanted mussel samples collected from the San Diego Creek drainage and Newport Bay in 1989 contained detectable levels of oxadiazon.

The concentrations of oxadiazon found in Red Shiners from the San Diego Creek drainage are given in Table 1 and Figure 1. All of the samples of Red Shiners collected contained levels of oxadiazon that substantially exceeded the concentrations of the other pesticides and herbicides identified in these samples.

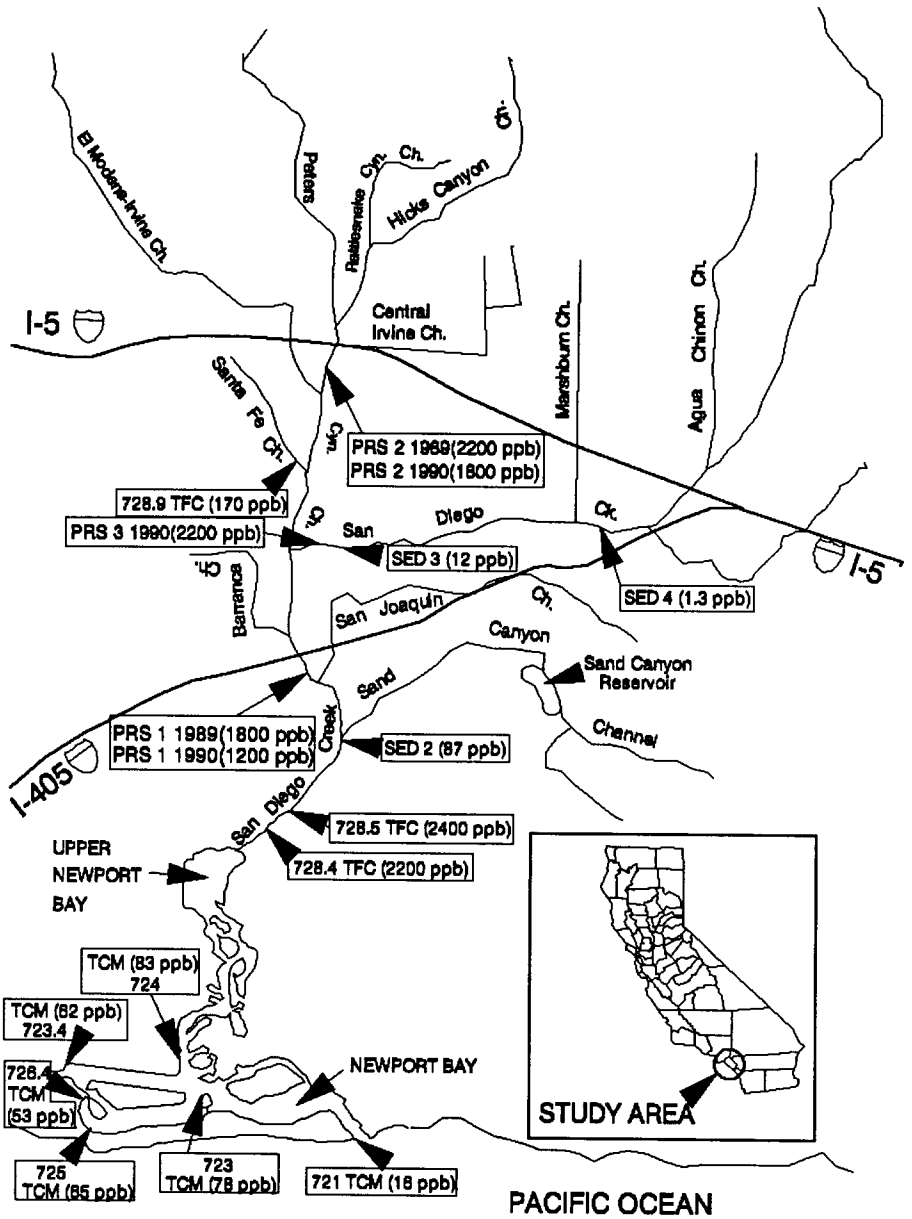

Figure 1. Study area with sampling sites and oxadiazon concentrations found in red shiners (PRS), transplanted *Corbicula* (TFC), transplanted *Mytilus* (TCM), and sediment (SED).

Concentrations of oxadiazon found in sediment samples from San Diego Creek were between 1.3 and 87 ng/g. As shown in Figure 1, oxadiazon levels increased the further downstream the samples were collected. Concentrations of oxadiazon in the three sediment samples are given in Table 2 and Figure 1. Correlations between the sediment concentrations and the concentrations in fish taken from the same site cannot be made since the sediments were collected in the year prior to the collection of fish.

Table 1. Oxadiazon concentrations in Red Shiners (PRS) from San Diego Creek.

Site No.	Location	Oxadiazon (ng/g) fresh weight 1989-90	1990-91
PRS 1	Michelson Drive	1800.	1200.
PRS 2	Peters Canyon Channel	2200.	1800.
PRS 3	Barranca Parkway	--	2200.

Table 2. Oxadiazon concentrations in San Diego Creek sediment.

Site No.	%Water	Oxadiazon (ng/g) dry weight
SED 2	42.0	87.
SED 3	20.7	12.
SED 4	10.3	1.3

Corbicula samples transplanted to San Diego Creek near Upper Newport Bay contained over 2000 ng/g of oxadiazon. *Corbicula* samples transplanted to the Santa Fe Channel near where the fish and sediment samples were collected contained 170 ng/g of oxadiazon. Mussels transplanted into Newport Bay contained oxadiazon at concentrations from 16 ng/g to 83 ng/g decreasing in concentration with increasing distance from San Diego Creek. Concentrations of oxadiazon in clams and mussels are given in Table 3 and Figure 1.

The data indicate that the source of the oxadiazon in Newport Bay is San Diego Creek and its tributaries. Oxadiazon is probably used by parks, golf courses, and nurseries in the area.

The reported use of oxadiazon in California has increased steadily since 1979 and doubled between 1986 and 1987, Table 4 (*CDFA Pesticide Use Report Summary*).

Oxadiazon use in 1988 according to type of application indicates that its primary uses in California are maintenance of landscape and rights of way, Table 5 (*CDFA Pesticide Use Report Summary*).

Table 3. Oxadiazon concentrations in transplanted *Mytilis*(TCM) and *Corbicula* (TFC).

Site No.	Type	%Water	Oxadiazon (ng/g) dry weight
721.0	TCM	84.2	16.
723.0	TCM	84.7	78.
723.4	TCM	88.1	62.
724.0	TCM	85.5	83.
725.0	TCM	87.2	65.
726.4	TCM	88.3	53.
728.4	TFC	88.1	2200.
728.5	TFC	86.9	2400.
728.9	TFC	89.5	170.

Table 4. Oxadiazon use in California 1979-88 reported by the California Department of Food and Agriculture (CDFA).

Year	Total Pounds
1979	600.96
1980	704.06
1981	1173.95
1982	1666.5
1983	2991.
1984	2286.6
1985	2945.6
1986	3702.4
1987	7728.
1988	10995.1

Table 5. Number of applications and total number of pounds of oxadiazon active ingredient used in California in 1988 reported by CDFA.

Application	No. of Applications	Pounds Applied
Landscape Maint.	1594	5886.09
Rights of Way	248	5102.82
Ornamentals	1	0.24
Struct. Pest Control	9	5.53
Turf	1	0.40
Total	1853	10995.08

Table 6 reveals that several other California counties report the use of similar quantities of oxadiazon to that of Orange county, the county of the study area (*Personal Communication with Muffit Wilkerson, CDFA*).

The toxicity of oxadiazon to selected aquatic animals based on 48-hour LC-50 data has been reported to be: carp (32 ppm); Daphnia (>40 ppm); Physa (8.7 ppm); and tadpole (2.5 ppm) (Hashimoto and Nishiuchi 1982).

Toxicological data for fish and wildlife indicate an acute LD_{50} of greater than 1000 mg/kg for mallard ducks and 6000 mg/kg for bobwhite quail. The LC_{50} in fresh water fish was greater than 2 ppm for all species tested (Herbicide Handbook 1989).

Table 6. Total number of pounds of oxadiazon used in top ten California counties in 1988.

County	Pounds Applied
Los Angeles	2539
Orange (county of study area)	1427
Contra Costa	1374
San Diego	1043
Solano	759
Santa Clara	755
Ventura	692
San Bernardino	558
Sonoma	293
Sacramento	290

Oxadiazon has been added to the list of compounds routinely analyzed statewide by both the Toxic Substances Monitoring Program and the State Mussel Watch Program.

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