Memorandum

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Date : January 9, 1991

Place : Sacramento

From : Department of Food and Agriculture — Clarice Ando, Env. Res. Scientist
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Subject: Literature Review of the Environmental Fate of Oxadiazon

Recently, the State Water Resources Control Board's (SWRCB) Monitoring and Assessment Unit reported the detection of high levels of the herbicide oxadiazon in red shiner fish collected through their Toxic Substances Monitoring Program (TSMP). This memorandum provides a summary on the oxadiazon detection in Orange County and a literature review of the environmental fate of oxadiazon.

Oxadiazon (2-tert-butyl-4-(2,4-dichloro-5-isopropoxyphenyl)Δ^2-1,3,4-oxadiazolin-5-one) (Figure 1) is a selective preemergent herbicide registered for use on woody ornamentals (i.e. shrubs and trees) and turf areas to control annual grasses and broadleaf weeds.

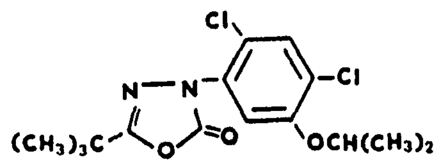

Figure 1. Structural formula of oxadiazon herbicide.

Two formulations are currently available for use and include the wettable powder 50% active ingredient (ai) and the granular material (1-2% ai). Chemical and physical properties of oxadiazon (Rhone-Poulenc, 1986 and 1989) are listed in Table 1.

Table 1. Chemical and physical properties of oxadiazon

Molecular Weight	345.23 g/mole
Vapor Pressure	2.0E-07 mm Hg at 25° C
Solubility in Distilled Water	1.0E-04 g/100ml at 25° C
Octanol-Water Partition Coefficient	8.1E+04 at 25° C
Henry's Law Constant	3.5E-07 atm m^3 g/mol at 25° C

Adsorption Values (cm^3/g) for four soils:

Soil Type	Koc	Kd
silt loam	1409	16.91
clay	1903	22.83
sandy loam	2848	11.39
sand	3268	8.17

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In 1989 and 1990, the TSMP reported unusually high levels of oxadiazon ranging from 960 to 2,200 ng/g (Table 2) in red shiner fish (Notropis lutrensis) collected in Orange County near the city of Irvine. Whole fish samples were gathered at three sites along an approximate three mile segment of the San Diego Creek drain (Figure 2) and analyzed for oxadiazon on a wet weight basis. This was the first time that oxadiazon had been detected in the monitoring program, although in other years, this pesticide may have gone unidentified.

Table 2. Oxadiazon levels in red shiner fish (wet weight)*

Sample Location	Sample Date	Oxadiazon Concentration (ng/g)
San Diego Creek/Michelson Drive	5/23/89	1,800
San Diego Creek/Michelson Drive	5/23/90	1,200
San Diego Creek/Barranca Parkway	5/23/90	2,200
Peters Canyon Channel	5/23/89	960
Peters Canyon Channel	5/23/89	2,200
Peters Canyon Channel	5/23/90	1,800

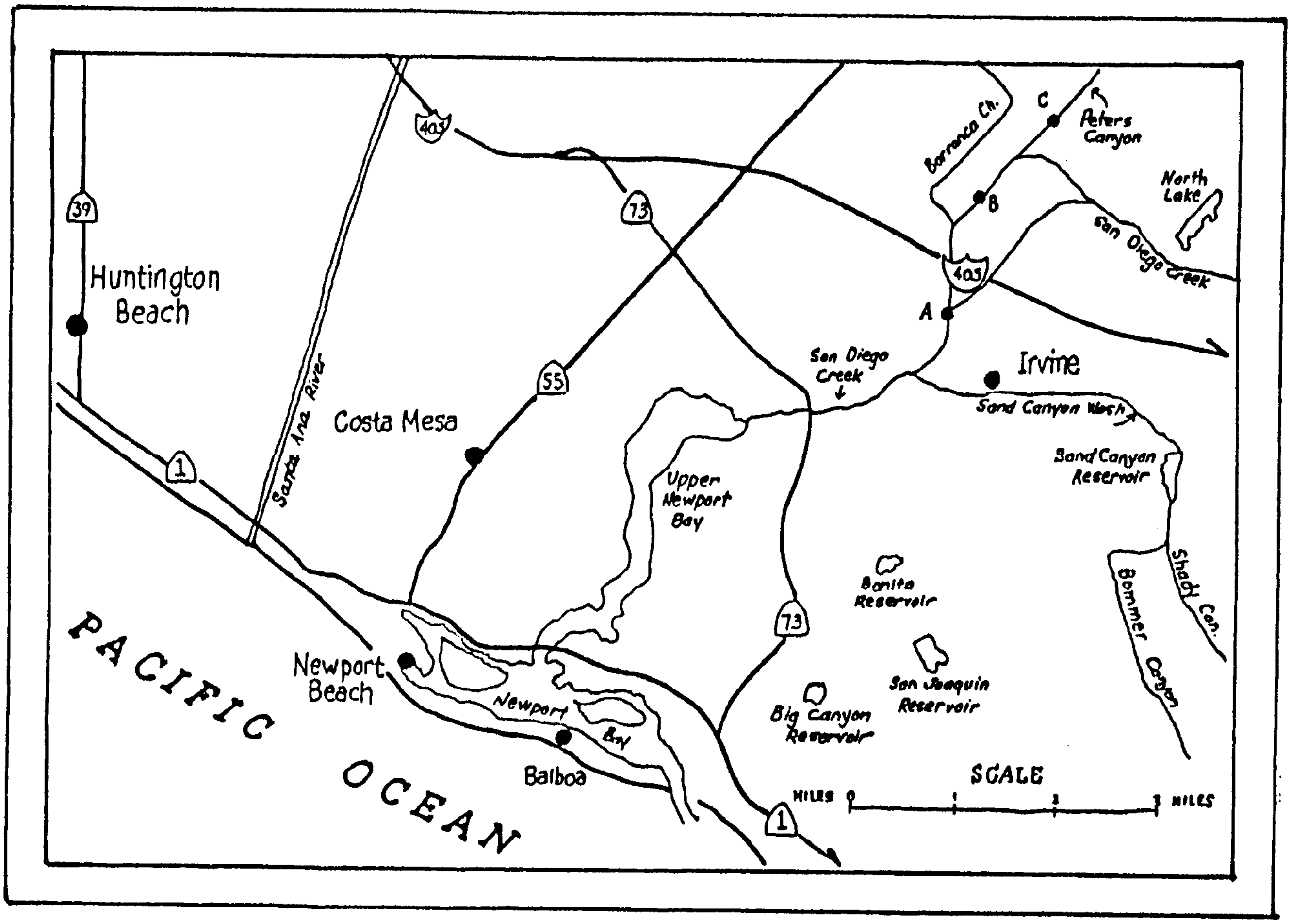
* Source: October 29, 1990 Memorandum from Walter G. Pettit, Chief of Division of Standards and Assessment (SWRCB) to Rex Magee, Associate Director, Division of Pest Management (CDFA).

Oxadiazon use in Orange County for the first quarter of 1990 indicates that 385 pounds ai was applied during January through March (CDFA, 1990). The distribution of the applications are as follows: 45% applied to containerized plants or field grown plants located in outdoor nurseries, 34% used for landscape maintenance, 13% applied to rights-of-way, and the remainder was used on greenhouse grown containerized plants and outdoor nursery grown transplants or propagative material. This distribution only characterizes use for the first three months of the year and may not represent annual use.

AIR

Volatilization

Ambrosi et al. (1977) examined the distribution of volatile products of radiolabeled oxadiazon incorporated in loam and sandy loam soils under two soil moisture conditions. Treatments were maintained at either 75% field-water capacity or were flooded under 2.5 cm of water for 25 weeks. Losses through volatilization were reported to



LEGEND

A - San Diego Creek/Michelson drive site
B - San Diego Creek/Barranca Parkway site
C - Peters Canyon Channel site

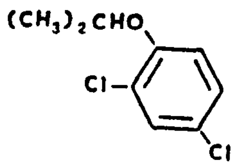
Figure 2. Sampling sites for red shiner fish in Orange County. Shaded portion on the inset map shows the area of California represented by the larger map.

be negligible (0.5-1.1%) for soils held at either soil moisture condition. Rhone-Poulenc (1986) showed that the distribution of volatile compounds released during photodecomposition of oxadiazon (0.45 ppm) in an aqueous solution at pH 5 with 2% acetone was also negligible (< 0.005 ppm).

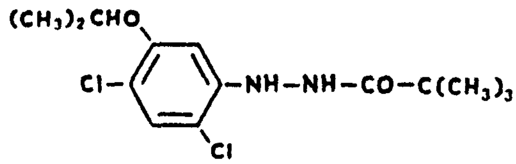
WATER

Hydrolysis

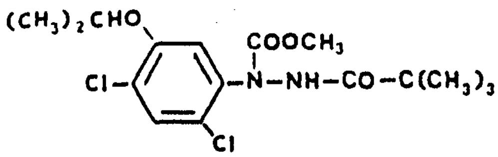
Hydrolysis studies by Rhone-Poulenc (1986) determined that oxadiazon at 23° C is stable at pH 5 and 7 in water containing 1% methanol. At pH 9, the chemical is unstable and the half-life is approximately 14 days. The degradation pathway is the opening of the oxadiazole ring to form three major degradates (Figure 3): 2,4-dichloroisopropyloxybenzene, 1-(2,4-dichloro-5-isopropyloxyphenyl)-2-trimethylacetyl hydrazine, and 1-(2,4-dichloro-5-isopropyloxyphenyl)-1-methoxycarbonyl-2-trimethylacetylhydrazine.



2,4-dichloroisopropyloxybenzene



1-(2,4-dichloro-5-isopropyloxyphenyl)-2-trimethylacetyl hydrazine



1-(2,4-dichloro-5-isopropyloxyphenyl)-1-methoxycarbonyl-2-trimethylacetylhydrazine

Figure 3. Three major oxadiazon degradation products identified at pH 9.

Photodegradation

Photodegradation of an aqueous buffered solution of oxadiazon (0.45 ppm), exposed to natural light for a period of 11 hours, resulted in the reduction of the initial oxadiazon concentration by 40%. When oxadiazon was exposed to artificial light, only 20 minutes were required to reach 40% decomposition. In both conditions, degradation products were similar and numbered more than fifteen. All compounds were detected below 0.01 ppm with the exception of three products identified as N-aminobenzoxazolone derivatives found at higher levels, ranging from 0.01 to 0.06 ppm (Rhone-Poulenc, 1986).

SOILS

Photodegradation

Oxadiazon appears to be very persistent in the soil. Photodegradation of oxadiazon incorporated in sterile and non-sterile loam soil, maintained between 40-70% field-water capacity, were kept in the dark or exposed to light emitted from a fluorescent lamp (300-700 nm) for 68 days (Rhone-Poulenc, 1986). It was reported that light had little effect on oxadiazon degradation in either sterile or non-sterile soil. Degradation was highest in the non-sterile soil exposed to light, resulting in degradation of 15% of the applied oxadiazon.

Aerobic/Anaerobic Degradation

Rhone-Poulenc (1988) conducted laboratory studies on radiolabeled oxadiazon applied to clay loam and silty clay soils maintained under aerobic and anaerobic conditions for a year. In aerobic conditions, the half-life of oxadiazon (10 ppm) in clay loam soil was 604 days while in silty clay, the half-life was determined to be 159 days. The primary degradates were dichlorisopopoxybenzene, monochloro-oxadiazon, oxadiazon-phenol, methoxy-oxadiazon, and oxadiazon acid, all of which represented about 10% of the overall radioactivity.

Under anaerobic soil conditions, 85% of the applied oxadiazon remained in the soil after one year. The half-life was determined to fall between 1111 to 2018 days for a clay loam soil, and the major degradation products were oxadiazon-phenol and an unidentified compound, both found below 3% of the total radioactivity.

It was observed that the binding of oxadiazon was greater and the degradation rate lower in the clay loam soil than the silty clay soil. This was due to the higher organic matter content found in the clay loam soil. Carringer et al. (1975) also reported oxadiazon to be strongly bound to organic matter: adsorbed to the hydrophobic regions of the organic molecules. Osgerby (1973) suggested that the binding process would remove a chemical from solution and possibly decrease the degradation rate. Carringer et al. (1975) noted that oxadiazon was not adsorbed by montmorillonite, an expanding clay mineral.

Desorption From Soil to Water

Laboratory studies of radiolabeled oxadiazon (Ambrosi et al., 1978) incorporated into 400 g of silt loam soil (1.5% organic matter) at 1 and 10 ppm were placed into large tanks with 16 L of water per tank for a period of 48 days. Oxadiazon was found to partition from the soil to the water very rapidly within the first week of treatment. Desorption continued slowly thereafter, never reaching equilibrium and it was concluded that oxadiazon was strongly bound, but slowly released in an aqueous environment. Final herbicide concentrations were approximately 20% of the total applied for both treatments.

Leaching

Leaching studies were carried out on four soils: loamy sand, sandy loam, clay loam, and silt loam placed into 40-cm long columns. Labeled oxadiazon was dissolved in acetone and distributed to the top of the column. The solvent was evaporated and a $CaSO_4$ solution was added to the column. Column segments were analyzed four days after treatment. Ninety-five percent of the oxadiazon was found in the first 5 cm of soil. The remainder was detected in the lower soil segments and also in the gravitational water (water not retained in the column).

Ambrosi and Helling (1977) applied radiolabeled oxadiazon on soil thin-layer chromatographic plates of Sterling loam, Norfork sandy loam, Lakeland sandy loam, Hagerstown silty clay loam, and Benevola silty clay. The Rf values obtained (0.02-0.29), indicated that oxadiazon was not very mobile in any of the soils examined. It was observed that as the soil organic matter increased, the Rf values decreased, with the exception of the value obtained for the Lakeland soil (0.29).

AQUATIC BIOTA

Daphnids, Mosquito Fish, Snails, and Algae/Bioaccumulation Ratio

Crustaceans (*Daphnia magna*) exposed to oxadiazon for 96 hours at rates of 0.5 , 1.0, 2.0, 4.0, 8.0, and 16.0 ppm were examined at 24 hr intervals (Rhone-Poulenc, 1990a). At the 96 hour observation period, 60% mortality was observed at the lowest pesticide concentration, which increased to 90, 100, 100, 100, and 100%, respectively.

Conversely, Ambrosi et al. (1978) found the daphnid population to increase within a 48 day period when exposed to 1 or 10 ppm radiolabeled oxadiazon treated soil, placed in a tank with 16 L of water. Snails (Helisoma sp.), mosquito fish, (Gambusia affinis) and algae and were also introduced to the model ecosystem. The snails and mosquito fish did not appear to be affected by oxadiazon, although algae growth was greatly curtailed by the herbicide. The distribution of the recovered C in the form of oxadiazon for each variable at day 48 showed 35, 50, 57, and 63% for snails, fish, water, and algae, respectively. Although snails contained a lower level of oxadiazon, higher levels of the phenol compound and polar materials were detected, suggesting that snails were capable of degrading accumulated oxadiazon to a greater degree than the algae or fish. Imanaka et al. (1981) reported that oxadiazon appeared to have a long persistence in crucian carp (Cyprinus carpio) which were collected in Lake Kojima, Japan, at 2, 4, and 9 months after herbicide application.

Bioaccumulation ratios (herbicide concentration in tissue/herbicide concentration in water) for the tank study (Ambrosi et al., 1978) were 42, 25, and 180 for algae, snails, and fish at the 1 ppm level and 65, 34, and 212 at the 10 ppm level, respectively. The ratios were fairly similar, indicating that the oxadiazon levels accumulated by the organisms were controlled by the oxadiazon levels available in the water.

Rainbow Trout Egg and Fry Life Stage

Rhone Poulenc (1990b) conducted preliminary studies on rainbow trout (Oncorhynchus mykiss) at varying life stages. Oxadiazon levels of 0.005, 0.05, and 0.5 ppm were toxic to trout eggs at 29 days post fertilization resulting in mortality rates of 61.5, 74.5, and 65.0%, respectively. At 42 days, (8 days post-hatch), mortality rates were also high, and were measured at 76.5, 94.0, and 95.5%, respectively. Hiroaka and Okuda (1983) reported signs of vertebrae damage to fry and fry developed from eggs of Oryzias latipes var. medaka exposed to aqueous solutions ranging from 2 to 16 ppm of Oxa (5-t-butyl-3(2,4-dichloro-5-isopropoxyphenyl)-3,4-oxadiazol-2-one), a form of oxadiazon herbicide used in Japan.

Adult Bluegill Sunfish and Rainbow Trout

Rhone-Poulenc (1990a) evaluated Bluegill sunfish (Lepomis macrochirus) and rainbow trout (Salmo gairdneri) for potential toxicity to oxadiazon. Herbicide levels of 5.0 and 10.0 ppm produced no abnormal behavior on bluegill sunfish. Higher levels of oxadiazon (12.0 to 55.0 ppm), however, did result in loss of equilibrium and death. Trout were susceptible to oxadiazon concentrations ranging between 1.0 and 5.5 ppm, displaying loss of equilibrium, distended ventral surface, and death. The LC50 (96 hr) for bluegill sunfish and rainbow trout were 12.5 and 2.0 ppm, respectively.

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