

Diazinon—Chemistry and Environmental Fate: A California Perspective

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Contents

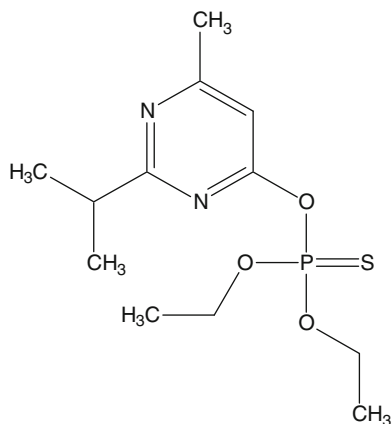
1	Introduction	107
2	Physicochemical Properties	108
3	Use Profile for Diazinon in California	110
4	Environmental Fate	114
4.1	Soil and Sediment.....	114
4.2	Water.....	122
4.3	Air and Precipitation	126
5	Aquatic Toxicology.....	129
5.1	Mode of Action	129
5.2	Bioaccumulation.....	132
5.3	Aquatic Life Benchmarks and Water Quality Criteria	133
6	Summary	134
	References.....	135

1 Introduction

Diazinon (*O,O*-diethyl *O*-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate) was first registered in the USA in 1956 (US EPA 2006) by the Swiss company J.R. Geigy. Diazinon is a broad-spectrum contact organophosphorus pesticide that is used as an insecticide, acaricide, and nematicide. Diazinon has been widely used to control soil and foliage insects and pests on a wide range of crops such as rice, fruits, wine grapes, sugarcane, corn, and potatoes. Diazinon is also used to control mange mites, ticks, lice, biting flies on sheep, cows, pigs, goats, and horses. In California, diazinon has been applied primarily on fruits, vegetables, and for

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Fig. 1 Chemical structure of diazinon



landscape maintenance and structural pest control. In 2010, a total of only 64,122 kg of diazinon was used in California (CDPR 2010a). Diazinon was formerly used in household and garden products for pest control. However, manufacturing of indoor use products was discontinued on June 30, 2001, and production of nonagricultural outdoor use products containing diazinon was discontinued on June 30, 2003. As of December 31, 2004, sales of diazinon-containing products for residential use ceased (US EPA 2000), resulting in diazinon falling to a rank of 94 among the most used pesticides in California by 2010 (CDPR 2010b). Diazinon is formulated as a wettable powder, granules, liquid concentrates, seed dressings, microencapsulations, and impregnated materials (US EPA 2006). Some typical formulations containing diazinon as an active ingredient (a.i.) include the following: Basudin® 10 (10% a.i.), Knoxout® (Pennwalt, 23% a.i.), Nucidol® 60 (60% a.i.), Alfatox®, Gardentox®, and several other trade-named products. Although concentrations have decreased nationwide in urban waters, diazinon is still frequently detected as a residue in agricultural watersheds. In California's agricultural regions with the highest diazinon use, the detection frequencies in 2005–2010 could reach 90% of the monitoring samples; moreover, the exceedance rate vs. the water quality criterion of 0.1 µg/L was 66.7% (Zhang and Starner 2011). This large proportion of detections and exceedance of water quality criteria have led to concerns about diazinon's potential environmental impacts. In this chapter, we provide a review of the environmental fate of diazinon and describe its toxicity to aquatic organisms.

2 Physicochemical Properties

Diazinon (Fig. 1), an organophosphorus pesticide, is a colorless to dark brown liquid, and is denser than water (1.116 g/cm³). Chemical Abstracts Service (CAS) registry number of diazinon is 333-41-5. In addition to the International Union of

Table 1 Physicochemical properties of diazinon

CAS Registry Number	333-41-5
Chemical name (CAS)	<i>O,O</i> -diethyl <i>O</i> -[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate
Chemical name (IUPAC)	<i>O,O</i> -diethyl <i>O</i> -2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate
Chemical formula	C ₁₂ H ₂₁ N ₂ O ₃ PS
Molecular weight	304.35 g/mol
Physical form	Colorless to dark brown liquid
Water solubility	0.06 g/L (20°C) ^a 0.054 and 0.069 g/L (20–40°C) ^b
Density	1.116 g/cm ³ (20°C) ^{c,d} 1.118 (4°C) ^c
Octanol/water partition coefficient, Log <i>K</i> _{ow}	3.69 (pH 7, 20°C) ^a 3.29 ^e 3.3–3.81 ^b
Aqueous photolysis half-life	5.05 days (pH 7, 25°C) ^e 50 days (pH 7) ^a
Hydrolysis half-life	12.4 days (pH 5, 24°C) ^e 43.3 days (pH 7.4, 16°C) ^f 138 days (pH 7, 24°C) ^e
Vapor pressure	8.4 × 10 ⁻⁵ mmHg (20°C) ^b 8.97 × 10 ⁻⁵ mmHg (25°C) ^{a,e} 2.8 × 10 ⁻⁴ mmHg (30°C) ^g
Boiling point	82–84°C (2.0 × 10 ⁻⁴ mmHg) ^h
<i>K</i> _{oc}	40–432 mL/g (mean 191) OC depending on soil type and environmental conditions ^b
Henry's law constant	1.4 × 10 ⁻⁶ atm·m ³ /mol (25°C) 1.13 × 10 ⁻⁷ atm·m ³ /mol depending on the technique used ^b 6.01 × 10 ⁻⁷ atm·m ³ /mol (25°C) ^a

^aIUPAC (2010)^bUS ATSDR (2008)^cBudavari et al. (1989)^dMackay et al. (2006)^eCDPR (2010a)^fMorgan (1976)^gLichtenstein and Schulz (1970)^hGysin and Margot (1958)

Pure and Applied Chemistry (IUPAC) name given in the introduction, the CAS name for diazinon is *O,O*-diethyl *O*-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate. Diazinon has a boiling point of 82–84°C and relatively high water solubility of 60 mg/L. Pesticides with high water solubility may leach below the root zone and at times reach groundwater or can be dispersed by surface runoff far from their application site (Leonard 1990; Wolfe et al. 1990). The major physicochemical properties for diazinon are summarized in Table 1.

3 Use Profile for Diazinon in California

California is the top agricultural state in the USA and grows more than half of the nation’s fruits, vegetables, and nuts. Moreover, California is the only state with an extensive pesticide use reporting system, which was initiated in 1990. Under the pesticides use reporting program, all agricultural pesticide use in all 58 California counties (Fig. 2) must be reported monthly to corresponding county agricultural



Fig. 2 California counties

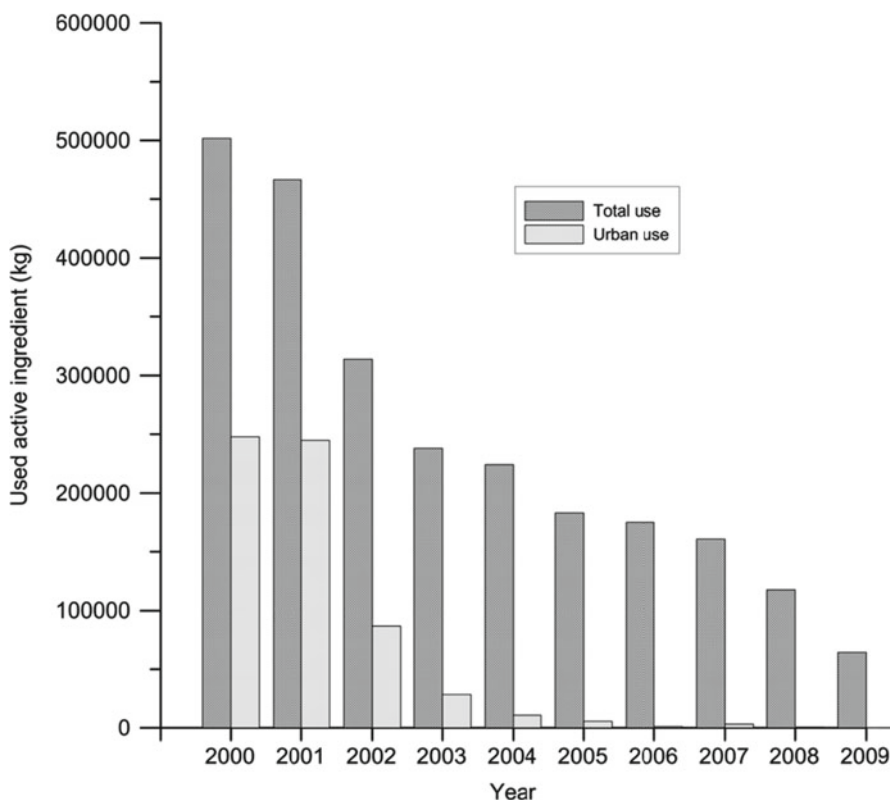


Fig. 3 Reported total and urban use of diazinon active ingredient from 2000 to 2009 in California

commissioners, who, in turn, report their data to Department of Pesticide Regulation (DPR). Consumer home and garden uses are not included in this use profile, but professional landscape maintenance, commercial structures, parks, etc. applications are reported. From 2000 to 2009, a total of 2,445,277 kg of diazinon was reported to have been used in California (CALPIP 2011). There was a significant reduction in urban use (Fig. 3) of diazinon that resulted from a December 2000 agreement between the technical product registrant and the US EPA; this agreement was driven by EPA action to phase out and cancel all indoor and outdoor residential uses of diazinon, to reduce risks to children and others (US EPA 2004).

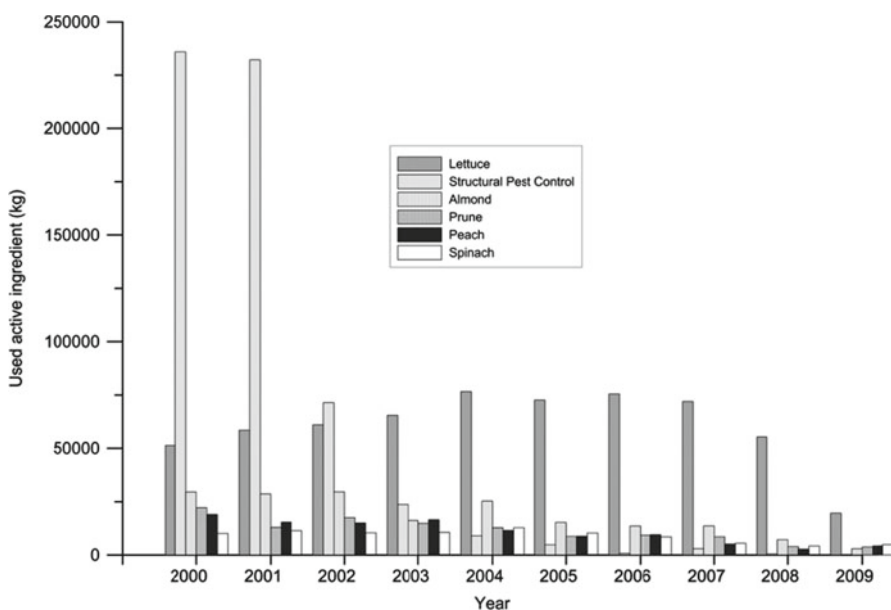
Diazinon use among the top ten counties in California from 2000 to 2009 ranged from 69,648 kg a.i. (San Benito County) to 619,074 kg a.i. (Monterey County) (Table 2). Los Angeles and Stanislaus Counties had the largest decrease in diazinon use, because a majority of their use was for applications to urban areas. The other counties in the diazinon top ten list predominantly used diazinon in agricultural settings (Table 3). Treated acreage remained steady for the period 2000–2007. Although the total amount of diazinon applied (Fig. 3) decreased considerably from the phase out of outdoor and indoor residential uses, the agricultural use of diazinon remained nearly constant until 2008. The effect of phasing diazinon out of agricultural use

Table 2 Total diazinon use (kg a.i.) by the top ten counties in California during the period 2000–2009

County	Year										Total
	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	
Monterey	56,316	64,773	65,061	72,554	78,202	73,552	65,813	65,810	53,673	23,319	619,074
Los Angeles	102,926	113,420	11,891	6,691	2,721	674	2,048	1,010	2,493	683	244,557
Fresno	38,731	32,622	26,598	19,384	19,426	18,894	23,255	19,846	12,674	4,716	216,146
Imperial	21,840	18,472	20,383	19,937	18,796	14,504	13,949	11,592	5,650	2,390	147,513
Stanislaus	33,400	27,998	11,602	6,516	7,293	3,610	3,836	2,710	1,106	1,655	99,727
Kern	17,845	14,396	16,898	7,222	5,122	6,969	6,089	9,383	4,859	2,968	91,751
Sutter	12,897	9,732	13,581	11,747	7,287	6,415	9,805	6,579	4,594	5,371	88,007
Tulare	23,327	19,801	13,728	6,167	4,965	3,511	2,920	1,397	1,008	1,064	77,890
Santa Clara	11,033	13,603	14,020	6,292	7,610	6,269	5,974	6,709	3,363	2,016	76,890
San Benito	10,949	9,058	8,144	6,805	7,633	6,478	6,935	6,478	3,960	3,208	69,648

Table 3 Distribution of urban and agricultural uses (kg a.i.) of diazinon in the top ten California counties between 2000 and 2009

County	Urban	Agricultural	Total
Monterey	4,735	614,339	619,074
Los Angeles	216,426	28,131	244,557
Fresno	20,978	195,169	216,146
Imperial	883	146,630	147,513
Stanislaus	58,258	41,469	99,727
Kern	5,713	86,038	91,751
Sutter	967	87,040	88,007
Tulare	34,144	43,746	77,890
Santa Clara	30,130	46,761	76,890
San Benito	920	68,727	69,648

**Fig. 4** Total diazinon use (kg a.i.) by the top six crop uses in California during the period 2000–2009

was more pronounced in 2009; in 2009, the total treated area was reduced to 56,905 ha, only 55 and 67% of that treated in 2008 and 2007, respectively.

In Fig. 4, we present the total amount of diazinon-active ingredient applied to the top six crops in California. Overall, lettuce had the highest diazinon use (608,265 kg) in the years 2000–2009 (Fig. 4). Although structural pest control had the highest use of diazinon in 2000–2002, this use sharply decreased after 2003, and in 2009, diazinon use for structural pest control was largely phased out (83 kg) (Fig. 4). The other top ranking crops were almond, prune, peach, and spinach. Diazinon was applied primarily by ground equipment from 2000 to 2009, followed by aerial application (Fig. 5).

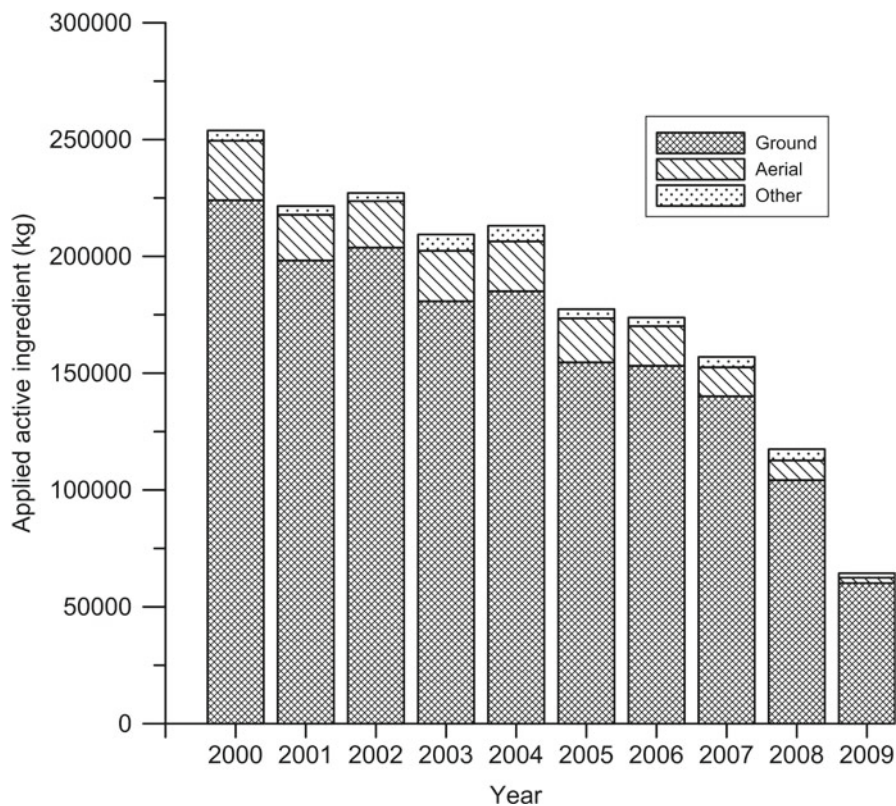


Fig. 5 Total diazinon use (kg a.i.) by application types in California during the period 2000–2009

4 Environmental Fate

4.1 Soil and Sediment

Contamination of surface and groundwater by pesticides is a major concern. Once released to soils, diazinon can be adsorbed by the soil, degraded by several processes, including hydrolysis, photolysis, and microbial degradation, or may move away from the application site by leaching, volatilization, etc. Microbial degradation is generally the major pathway by which diazinon is degraded in soils. Diazinon is moderately mobile as a result of its low to moderate sorption capacity to soils (K_{oc} values range from 40 to 432, mean value 191). Sorption by soil plays an important role in the protection of surface and groundwater from contamination by diazinon, and such studies have been conducted to study the sorption–desorption behavior of diazinon by soils. Below, we present a summary of some of these sorption studies.

4.1.1 Sorption

Diazinon adsorption to soils depends on the soil pH, organic matter (OM) content, and clay content. Adsorption generally increases with increases in OM and clay content (Armstrong et al. 1967). The tendency of a pesticide to bind to soil or sediment particles is often characterized by its organic carbon-normalized soil adsorption coefficient (K_{oc}). Pesticides with relatively high K_{oc} values tend to remain in the soil or attached to soil particles entrained in flowing water, restricting or slowing their movement downstream. Pesticides that have relatively low K_{oc} values tend to bind less tightly to soil particles, and therefore are likely to be leached from the soil and transported by moving water. K_{oc} values have been determined for diazinon in a variety of soil types and have been reported to range between 40 and 432 (mean of 191). The range of these values indicates that diazinon has a low to moderate tendency to remain bound to soil and sediment, and therefore is moderately mobile.

Konrad et al. (1967) equilibrated diazinon with three soils (loamy sand, silty clay loam, and clay) and observed an initial rapid decrease in diazinon concentration from soil adsorption, that was followed by a slow but continual decrease in concentration, which they attributed to degradation. In 24 h, diazinon degradation was 11, 7, and 6% in the silty clay loam, clay, and loamy sand soils, respectively. After 10 h, the release of degradation products approached linearity (measured by release of degradation products), and this release was related to rates of initial soil adsorption. Silty clay loam soil had the highest OM content and the highest diazinon sorption of the three soils studied. Armstrong et al. (1967) reported that adsorption should increase with increasing OM and clay content, but was more closely related to OM than to clay content. Thus, the greater adsorption in the silty clay loam (10.0% OM) over clay (3.8% OM) and loamy sand (1.6% OM) soils was likely caused by the higher OM content of the silty clay loam soil. Konrad et al. (1967) further stated that if the mechanism of diazinon adsorption is mainly through H-bonding, then a decrease in soil pH should increase the extent of adsorption. They observed similar adsorption in both clay and loamy sand soils and concluded that the greater acidity of loamy sand (pH 3.8 vs. 6.4 in clay soil) soil compensated for the slightly greater OM content (3.8% OM in clay vs. 1.6% OM in loamy sand soil) and much greater clay content of the clay soil (18.7% in clay soil and 5.2% in loamy sand soil). They further reported that the effect of higher OM content of the silty clay loam soil could not be compensated for by either the higher clay content of the clay soil or the lower pH of the loamy sand soil.

Arienzo et al. (1994b) observed that more diazinon was sorbed by two soils (loamy sand and sandy loam), when these soils were modified with three organic amendments and with one carbon-rich organic compound, hexadecyltrimethylammonium bromide (HDTMA). HDTMA-modified soil retained the most diazinon amongst all four treatments, retaining as much as 70.5% of the applied diazinon (5 mL of 200 $\mu\text{g/mL}$, equivalent to 5 kg/ha), whereas control soil only retained 25.2% diazinon. The amounts retained by the soils treated with the other three amendments were \sim 30% in sandy loam soil and about 25% in loamy sand soil. These small differences in the amount of retained diazinon can be attributed to small

differences in the clay and OM content of the two soils. The higher sorption by HDTMA-treated soil may be related to the OM content of the treated soils, as HDTMA had the highest organic carbon content of the four amendments. In another study, Arienzo et al. (1994a) studied diazinon adsorption by 25 soils and found soil OM content to be the most important factor in diazinon's sorption in soils containing over 2% OM. They also reported that diazinon adsorbs to soils that have OM content below 2%, and the adsorption was influenced by the silt and clay soil components. Other authors have reported that no correlation existed between soil OM content at content levels below 2% (Calvet et al. 1980; Sanchez-Camazano and Sanchez-Martin 1984; Sanchez-Martin and Sanchez-Camazano 1991). Arienzo et al. (1993) conducted a study on adsorption and mobility of diazinon in soils with aqueous media and mixtures of methanol–water and hexane–water. They reported decreased diazinon adsorption in hexane–water and methanol–water systems, whereas increasing soil OM content increased diazinon adsorption in aqueous media. This shows that diazinon has higher affinity for an organic solvent than soil.

Sarmah et al. (2009) studied diazinon sorption in two New Zealand soils at two depths (0–10 cm and 40–50 cm), and observed that diazinon adsorption in the surface layer (27.7 L/kg) was much higher than in the deeper layer (3.7 L/kg); they attributed this difference to higher organic carbon content of the surface layers. It has been reported that organic matter can bind a substantial proportion of pesticide residues present during the composting process (Frederick et al. 1996; Petruska et al. 1985). For example, after 21 days of composting, a substantial amount of ^{14}C -radiolabeled diazinon was associated with humic and fulvic acids (15%), and with the humin fraction (25%) (Petruska et al. 1985). These results indicate that diazinon mobility in soils is reduced by organic matter, and the nature and composition of organic compounds added to soil, along with the carbon content, have a profound effect on diazinon movement in soils.

Nemeth-Konda et al. (2002) estimated octanol–water partition coefficients (P_{ow}) by using either a computer model or high performance liquid chromatographic parameters, and observed good agreement between experimental and the computer-model estimated data. The octanol–water partition coefficient (P_{ow}) is a useful parameter for predicting the soil adsorption behavior of a chemical. Diazinon had the highest $\log P_{ow}$ (3.86) value among six pesticides studied, namely, acetochlor, atrazine, carbendazim, diazinon, imidacloprid, and isoproturon, indicating that diazinon was the most hydrophobic of the group (Nemeth-Konda et al. 2002). These researchers also conducted sorption studies using Hungarian sandy loam soil and observed that the percentage adsorbed by the soil decreased as the initial concentration of diazinon increased from 0.04 to 5.0 mg/L. These authors further conducted desorption experiments immediately after adsorption to study the intensity of diazinon–soil interaction, and observed that only about 60% of the sorbed amount desorbed, concluding that there is a strong bonding between diazinon and the soil. They also concluded that the higher adsorption capacity of diazinon may be related to diazinon's low water solubility and high hydrophobicity, and thus the rate of diazinon's migration to groundwater will be slower than that of the other six pesticides studied.

4.1.2 Leaching

As previously mentioned, diazinon has a K_{oc} value of 40–432 (mean of 191) (US ATSDR 2008), and is considered to be moderately mobile in soil (US EPA 2006). Among the factors that influence diazinon's leaching potential is soil type (e.g., clay vs. sand), amount of rainfall, depth of the groundwater, and extent of degradation. In laboratory tests of sandy and organic soils, Sharom et al. (1980a) used 10 and 4 g of diazinon-treated (2 ppm) sand and muck, respectively, and found that the amount of diazinon leached from sand decreased with each successive 200-mL wash. They reported that 95% of the added diazinon leached from the sand after ten successive 200-mL washes. However, only 50% leached from the organic soil. Arienzo et al. (1994b) examined the mobility of diazinon in two soils (loamy sand and sandy loam). Each soil was treated with one of four organic amendments (two types of peat, liquid humic amendment, and hexadecyltrimethylammonium bromide (HDTMA)). The authors observed that all four amendments reduced the leaching of diazinon from both soils, with HDTMA being the most effective. The cumulative amount of diazinon in the leachate decreased from 49.5% in the control soil to 18.3% in the HDTMA-treated soil. These results indicate that diazinon mobility in soils is reduced by adding organic materials to soil. The nature and composition of organic compounds added to soil, along with the carbon content, have a profound effect on diazinon movement in soils.

Arienzo et al. (1994a) tested the adsorption and mobility of diazinon in 25 soils having different physicochemical properties. Diazinon movement was correlated to soil organic matter content; diazinon was found to be slightly mobile in soils with organic matter content <3%, and immobile in soils with organic matter content >3%. Levanon et al. (1994) studied the impact of plow tillage on microbial activity in the top 5-cm soil layer, and observed a higher leaching rate for diazinon in plow tillage soils (20.7%) than in no-tillage soils (2.8%), after incubation for 21 days. They attributed the lower diazinon leaching in no-tillage soils to a higher diazinon mineralization rate in these soils. The no-tillage soils were characterized by having a higher organic matter content and higher microbial populations and activity than did plow tillage soils. In another experiment, Arienzo et al. (1993) conducted a soil adsorption and mobility study on diazinon with aqueous media and mixtures of methanol–water and hexane–water. They reported that increasing the soil organic matter content increased diazinon adsorption in aqueous media, whereas an increase in organic solvent concentration decreased diazinon adsorption. For example, the value of the Freundlich adsorption parameter (K) decreased from 8.79 in water to 6.64 and 3.10 in 10 and 20% methanol–water systems, respectively. This decrease was more drastic in the hexane–water system, with K values decreasing to 1.53 and 0.31 in 10 and 20% hexanol–water systems, respectively. The co-presence of such organic solvents with pesticide waste residues, such as at hazardous waste disposal sites, was postulated by the authors to increase the potential for groundwater contamination by increasing the downward movement of diazinon.

Ritter et al. (1973) studied the effect of soil temperature, soil moisture, and soil bulk density on the diffusion of diazinon, atrazine, and propachlor in a silt loam soil

under laboratory conditions. They reported that the greatest movement of diazinon occurred at high soil temperatures, while soil moisture content and soil bulk density had very little effect on diazinon movement.

Leistra et al. (1984), using a computer model of a simplified soil system, simulated the downward flow of water and movement of diazinon through the unsaturated zone in glasshouse soils. They observed that under average situations (irrigation rate, adsorption coefficients, and transformation rate), downward movement of diazinon was restricted and concentrations below 15 cm remained very low. When soils with comparatively low organic matter were used, or the rate of irrigation was increased, diazinon moved deeper in the soil horizon, although most of it was retained in the upper 20 cm soil. Ritter et al. (1973) reported that the degradation of diazinon increased with increased soil temperature and moisture content. They reported that at 43°C, more than 96% of diazinon degraded within 8 days, while 75% of diazinon degraded at 10°C in the same period. They also observed that at 8% soil moisture content, 15.6% diazinon remained in the soils after 8 days, while at 23% soil moisture content, only 12.5% diazinon remained in the soil in the same time period (Ritter et al. 1973). In another study, Ritter et al. (1974) observed only small concentrations (<1.0 ppm) of diazinon in soil samples a few hours after diazinon application, and did not detect any diazinon 21 days after diazinon application. These results show that diazinon degrades rapidly in soil. Consequently, leaching is a relatively unimportant fate process for diazinon.

4.1.3 Mineralization

Mineralization is defined as the process by which organic substances are converted to inorganic substances. Mineralization of a pesticide eventually reduces it to carbon dioxide, water, and other inorganic components. Higher mineralization rates indicate that microorganisms are using an organic substance as a source of carbon and energy. Fenlon et al. (2007) studied diazinon's mineralization in five soils (four organically managed and one conventionally managed) that were aged for 14 weeks. They observed appreciable mineralization of diazinon in two of the organically managed soils. These soils had the highest OM content of the five studied soils. Petruska et al. (1985) used radiolabeled diazinon to study the fate of diazinon under composting systems. Their results indicated that a substantial fraction of diazinon was entrapped within organic matter in a form that resisted extraction by organic solvents. Further, they reported that only 0.2% diazinon mineralized after 3 weeks of composting. Similar results were obtained by Leland et al. (2003), who reported that only 0.2% of the applied ^{14}C -diazinon was mineralized to CO_2 over 30- and 60-day incubation time periods. The low diazinon mineralization rates observed in these studies indicate that diazinon is not used as a carbon and energy source by soil microorganisms.

Levanon et al. (1994) studied the effects of plow tillage on microbial activity and diazinon degradation in the top (0–5 cm) soil layer, and observed higher mineralization rates of diazinon in no-tillage soils (40% mineralization vs. 20% in plow-tillage

soils, after 30 days). They attributed this increase in mineralization rates to higher microbial populations and activity in no-tillage soils, which resulted in decreased leaching from soils with no-tillage vs. plow-tilled soils. Microbial population and activity, measured as biomass, bacterial counts, hyphal length of fungi, and carbon dioxide evolution, were all lower in samples of plow tillage soils.

4.1.4 Dissipation

Dissipation of pesticides relates directly to their persistence (or length of time they reside in the environment). Generally, pesticides remaining in the field for many weeks after application are of concern, and are more prone to move because of their environmental longevity. The field dissipation half-life of a pesticide is a value that expresses the time required for half of a given quantity to degrade or dissipate from the soil. Diazinon has a low persistence in soil, with a half-life of only 34.8 days (Singh and Singh 2005). In a field study conducted to monitor the changes in diazinon concentration over time, Ando et al. (1993) detected the highest diazinon soil residues (17.1 $\mu\text{g/g}$) immediately after the first diazinon application; these amounts decreased to 0.38 $\mu\text{g/g}$ 3 days after the final application. Based on these results, they concluded that diazinon dissipates quickly from the soil. Sarmah et al. (2009) reported that both depth and temperature had an effect on the dissipation half-life (DT_{50}) of diazinon, with lower layers having significantly higher DT_{50} values. They also observed that a decrease in temperature from 20 to 7.5°C caused a threefold increase in the subsoil half-life (25 days—Waikiwi soil; 12 days—Motupiko soil) as compared to surface soil (7 days—Waikiwi soil; 5 days—Motupiko soil). Sattar (1990) incubated silty clay ($\text{OC}=0.6\%$) and sandy clay ($\text{OC}=0.5\%$) soils at 25°C, and reported half-life values for diazinon of 28 days and 36 days, respectively. These soils had lower organic carbon content than the soils used by Sarmah et al. (2009), which may explain the longer half-life values reported by Sattar (1990).

Sarmah et al. (2009) reported that organic carbon content and microbial activity decreases with an increase in soil depth. This decrease reduces soil sorption capacity for organic compounds, which, in turn, slows the degradation rate. Sethunathan and Macrae (1969a) investigated the role of soil microflora on the fate of diazinon in flooded Philippine soils. They reported that diazinon disappeared from both sterilized and nonsterilized submerged soils, and followed first-order kinetics. They obtained half-life values of 8.8 and 33.8 days for nonsterilized and sterilized clay soil, respectively, while the corresponding values for clay loam soil were 17.4 and 43.8 days. Based on these results, the authors concluded that soil microflora are involved in the rapid dissipation of diazinon. Getzin and Rosefield (1966) and Gunner et al. (1966) reported that diazinon persists for more than 160 days in nonflooded soils. Levot et al. (2004), on the other hand, reported that diazinon had a half-life of 64 days under waterlogged conditions, and attributed this to slower biodegradation from oxygen depletion under such soils. In another study, Sethunathan and Yoshida (1969) observed that diazinon degraded faster in nonsterilized than sterilized flooded soil, resulting in greater accumulation of the diazinon hydrolysis

product, 2-isopropyl-6-methyl-4-hydroxy pyrimidine. These differences were more pronounced in the first 10 days. The authors recovered approximately 40% of radioactive-applied material in both soils and concluded that diazinon or its degradation products could possibly have become bound to the soil during incubation. These results indicate that diazinon persists longer under nonflooded and sterilized soil conditions.

Sethunathan and Macrae (1969a) reported that more than 90% of the applied diazinon was lost 70 days after application in three submerged tropical soils. Degradation was more rapid in two of the three nonsterilized soils, indicating that microbes were involved in diazinon's degradation. In the third acidic clay soil (pH 4.7), diazinon degradation was more rapid in the sterilized samples, and the authors attributed this to the compound's instability under acid conditions. These results suggest that microbial activity plays an important role in diazinon's degradation (Schoen and Winterlin 1987). Szeto et al. (1990) reported that diazinon dissipated rapidly from irrigation ditch sediment (pH 4.4) and from sediment in an adjacent reservoir (pH 5.0). They did not detect diazinon in sediment 66 days after the second diazinon application, whereas 120 ppb of diazinon was still present in irrigation ditches.

Diazinon degraded more rapidly in acidic organic soils (pH 5.2) than in neutral mineral soils (pH of 6.8 and 8.0) (Chapman and Cole 1982). Schoen and Winterlin (1987) studied the effects of various soil factors and organic amendments on diazinon degradation. Diazinon degradation was affected by pH, soil type, organic amendments, soil moisture, and pesticide concentration, with soil pH being a major factor affecting the degradation of diazinon. At a soil concentration of 100 ppm of diazinon, and 50% water saturation, estimated half-life values at pH 4, 7, and 10 were 66, 209, and 153 days, respectively, in sandy loam soil; 49, 124, and 90 days, respectively, in clay loam; and 14, 45, and 64 days, respectively, in sandy loam amended with peat. The authors speculated that soil pH was lowered by the addition of acidic peat to the soil, and this could have been responsible for increased diazinon degradation at pH 10. These results indicate that diazinon degrades rapidly in neutral soils. They also showed that diazinon degradation was slower at high diazinon concentrations in neutral or basic mineral soil, and faster when diazinon was present at low concentrations in moist soil that was amended with peat or acidified to a pH of 4 (Schoen and Winterlin 1987). Felsot et al. (2003) reported that there is a critical diazinon level above which soil diazinon dissipation slows significantly, and he attributed this to slowed degradation from diazinon toxicity to the microorganisms.

4.1.5 Photolysis

Photolysis of diazinon on soil surfaces was studied by Burkhard and Guth (1979). They reported 2-isopropyl-6-methylpyrimidin-4-ol as the main breakdown product (Fig. 6). The photolysis rate was only slightly less on dry soil surfaces (viz., 44% of diazinon degraded in 24 h) than on moist soil surfaces (viz., 51% of diazinon degraded

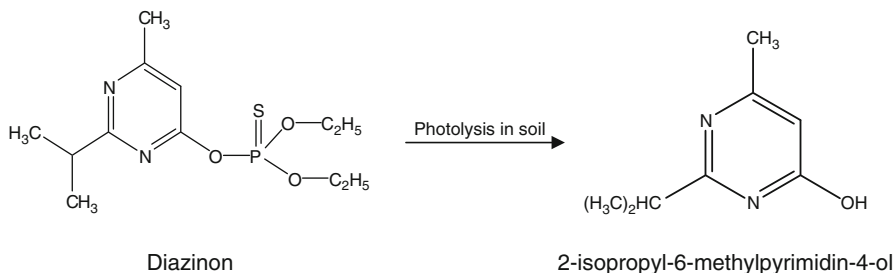


Fig. 6 Photolytic breakdown pathway for diazinon on the soil surface (Burkhard and Guth 1979)

in 24 h). Mansour et al. (1997) reported that diazinon degraded more rapidly in river than in distilled water, and the rate of degradation increased with exposure to sunlight. After 14 days, only 5% of applied diazinon remained in river water exposed to sunlight, while more than 80% was present in distilled water kept in the dark.

4.1.6 Effects on Soil Microorganism Populations

Singh and Singh (2005) reported a significant increase in bacteria (14%, $p < 0.05$) and azotobacter (27%, $p < 0.01$) populations 15 days after diazinon soil treatment. This study was conducted for three consecutive years (diazinon was applied every year), and adverse effects were observed on actinomycetes (10%) and fungal (11%) populations. The authors observed a similar increase in bacteria and azotobacter populations in years 2 and 3 of the study period. The actinomycetes population increased only 60 days after diazinon was applied, by which time initial diazinon residue levels had declined. Sethunathan and Macrae (1969b) also observed a significant increase in the soil actinomycetes population 7 weeks after diazinon soil treatment (two applications, 20 days apart). The actinomycetes population increased from 5,700 (per gram oven dry soil) to 44,800 and 51,100, in soil treated with diazinon at 2 and 20 kg/ha, respectively. Similarly, Gunner et al. (1966) observed an increased actinomycetes population (360,000 vs. 1,000) after diazinon was applied to soil at 3 lb/A. Gunner (1970), in a study with potted bean plants, concluded that the number of microorganisms in the rhizosphere doubled 7 weeks after application of diazinon.

Levanon et al. (1994) studied the effects of plow tillage on microbial activity in the top (0–5 cm) soil layer. Microbial population levels and activity were measured (i.e., biomass, bacterial counts, hyphal length of fungi, and carbon dioxide evolution) and were all higher in no-tillage soil samples. Higher microbial activity resulted in decreased leaching from no-tillage soils, but was associated with a higher rate of diazinon leaching from the plow tillage soils. Further, they observed synergistic effects between fungi and bacteria in the degradation rates of diazinon. The authors noted that almost no mineralization of the compound occurred when either fungi or bacteria were selectively inhibited, demonstrating that synergism existed between the two microbial communities.

Leland et al. (2003) studied the effect of composting on the fate of diazinon and observed that diazinon composted for 30-days was toxic to earthworms; no mortality was observed in earthworms exposed to soil amended with 60-day composted diazinon. The authors reported that 95% of diazinon had degraded after 60-days of composting, and they concluded that composting high concentrations of diazinon greatly reduced the toxicity and amount of diazinon that is bioavailable to soil microorganisms. Ingram et al. (2005) studied the effect of diazinon and imidacloprid on the microbial urease activity in different soils. The studies were conducted with *Proteus vulgaris*, a representative heterotrophic bacteria, and were focused on growth rate. They concluded that increasing the diazinon concentration significantly reduced maximum *P. vulgaris* cell density after 24 h ($p=0.004$). Sethunathan and Macrae (1969b) observed a visible increase in algal populations in the standing water of the diazinon-treated soil. The authors concluded that diazinon generally has a synergistic effect on soil microorganism populations, and quickly dissipates from soil.

4.2 Water

4.2.1 Environmental Monitoring

Diazinon residues in the agricultural environment have been monitored in several studies performed in the USA and Canada. In a national surface water quality monitoring study (1976–1980) performed by Carey and Kutz (1985), diazinon residues were detected in sediment in only 0.5% of samples, with a maximum residue detected of 7.1 ppb. Sapozhnikova et al. (2004) collected sediment samples in 2000 and 2001 from the Salton Sea, an agricultural drainage reservoir in California, and reported diazinon concentrations ranging from 0.5 to 5.4 ppb dry wt in the sediments. Wan et al. (1994) monitored ditch water, soils, and sediments in an agricultural area in the lower Fraser River Valley of British Columbia, Canada. They detected diazinon at five sites in the top 0–5 cm soil layer at an average concentration of 219 ppb, whereas diazinon residues were detected in ditch sediments at three sites at an average concentration of 16 ppb. Further, they reported that diazinon was detected in ditch water at seven locations at an average concentration of 0.07 ppb. Diazinon is of concern as a water contaminant because it may appear in surface or groundwater samples that are slated for drinking purposes.

4.2.2 Groundwater

Diazinon has been detected in irrigated agricultural areas where heavy diazinon applications were made in USA (Cohen 1986) and Canada (Frank et al. 1987, 1990). A groundwater contamination study was performed in 28 of California's 58 counties, in which more than 50 pesticides (from both point and nonpoint sources)

were monitored; diazinon was detected in 12 samples (Cohen 1986). Similarly, between 1979 and 1984, diazinon was detected in rural wells of southern Ontario, Canada (Frank et al. 1987) and in farm wells monitored between 1986 and 1987 (Frank et al. 1990). Holden (1986) reported that diazinon was detected in California's groundwater at a maximum concentration of 9 $\mu\text{g/L}$, and Long (1989) detected diazinon in 5 wells located in the vicinity of agrichemical dealer facilities (total 56 wells studied) at a maximum concentration of 1.1 $\mu\text{g/L}$ (the mean concentration was 0.55 $\mu\text{g/L}$). Similarly, diazinon residues appeared in water from drinking wells in a single south-central Connecticut town that relies on groundwater for its potable water source (Eitzer and Chevalier 1999). Leistra et al. (1984) collected 22 water samples from water courses in areas that had many glasshouses in the Netherlands. They found measurable diazinon concentrations in nine samples, with the two highest values being 8.7 and 21 $\mu\text{g/L}$. A search of California Department of Pesticide Regulation's groundwater database (CDPR 2011) for the period 1985–2011 indicated that only one well tested positive for diazinon residues (2.6 $\mu\text{g/L}$). In a follow-up sampling after 2 months, diazinon was observed at a concentration of 0.2 $\mu\text{g/L}$.

US EPA (2006), using data from the United States Geological Survey National Water Quality Assessment Program (NAWQA), reported diazinon groundwater detections from a variety of sources that included drinking water wells, monitoring wells, and agricultural wells. Many of monitoring studies were conducted in areas that had high pesticide use and agricultural production. Approximately 2% of the ground water samples collected through this program, from 1992 to 1996, had positive detections of diazinon. However, the maximum concentration value was below the limit of quantitation for all wells sampled, and the median value was non-detectable (ND) or <0.002 $\mu\text{g/L}$. Results from the NAWQA database indicate that diazinon was detected more frequently in shallow ground water in urban areas than in agricultural areas. The concentrations of diazinon in ground water (all wells) ranged from ND to 1.0 $\mu\text{g/L}$.

4.2.3 Surface Water

After diazinon's residential use started phasing out in June 2003, and after its retail sales ended in December 2004, the concentrations found in urban watersheds reportedly declined nationwide (Banks et al. 2005; Embrey and Moran 2006; US ATSDR 2008; US EPA 2007; USGS 2007). Similarly, NAWQA monitoring data in California urban watersheds from 1995 to 2005 appeared to show steady declines in annual maximum and average concentrations since 2003 (Table 4). Although the frequency of detection fluctuated during this time period, the annual maximum concentration in 2005 and average concentrations in 2004 and 2005 were below diazinon's chronic water criterion of 0.1 $\mu\text{g/L}$ that was developed by CVRWQCB (2006) for California Central Valley and San Joaquin Estuary. This criterion is more stringent than the water criteria and aquatic life benchmarks proposed by the US EPA (2006, 2011) (Table 3). Although concentrations have decreased in California urban waters, diazinon is frequently detected in California's agricultural watersheds at concentrations

Table 4 Diazinon concentrations detected in California urban surface watersheds from 1995 to 2005. Data sources are from USGS National Water Quality Assessment

Year	Number of detections	Percentage detection	Maximum concentration ($\mu\text{g/L}$)	Mean concentration ($\mu\text{g/L}$)	Standard deviation	90th percentile concentration
1995	16	100	1.100	0.640	0.274	0.915
1996	2	100	0.337	0.277	0.086	0.325
1997	24	100	1.380	0.370	0.285	0.673
1998	5	83.3	0.420	0.223	0.150	0.362
1999	11	52.4	0.198	0.044	0.060	0.095
2000	26	74.3	0.774	0.106	0.204	0.336
2001	29	93.5	0.947	0.342	0.326	0.773
2002	15	88.2	0.430	0.141	0.142	0.347
2003	13	81.3	0.588	0.147	0.164	0.306
2004	15	78.9	0.218	0.056	0.059	0.128
2005	18	100	0.085	0.035	0.021	0.068

Table 5 A summary of statistical results for diazinon monitoring data in California agricultural counties (2005–2010)^a

Region	Number of sites	Number of samples	Maximum concentration ($\mu\text{g/L}$)	Percentage of detection	Number of exceed.	Percentage of exceed.
Sacramento	73	850	2.5	30.2	44	5.2
San Joaquin	121	2,465	1.2	10.0	60	2.4
Salinas	33	244	24.5	91.0	151	61.9
Santa Maria	12	21	0.98	90.5	14	66.7
Imperial	12	58	3.24	51.7	14	24.1

^aA chronic water quality criterion of 0.1 $\mu\text{g/L}$ was used to determine number of exceedances and percent exceedance

exceeding the water quality criterion of 0.1 $\mu\text{g/L}$ (Starner 2009; Zhang and Starner 2011) (Table 5). Sacramento, Salinas, San Joaquin, Santa Maria, and Imperial counties in California are the top five agricultural regions that have the highest diazinon use, highest detection frequencies, and percentages of exceedance to the chronic water criterion from 2005 to 2010 (Table 5). The range of detection frequencies in these areas was 10–91%. The percentages of exceedance to the water quality criterion ranged from 2.4 to 66.7%. Salinas was the county with the highest detection frequency and percentage of samples exceeding the water quality criterion, followed by Santa Maria, Imperil, Sacramento, and San Joaquin counties (Table 5) (Zhang and Starner 2011). The Salinas River watershed receives both urban and agricultural runoff in the region. Hunt et al. (2003) reported significant acute toxicity to *Ceriodaphnia dubia* in 11% of the main river samples, 87% of the samples from a channel receiving urban and agricultural runoff, 13% of the samples from channels draining agricultural tile drain runoff, and 100% of the samples from a channel draining agricultural surface furrow runoff. Toxicity identification evaluations conducted in 12 samples implicated that the organophosphate pesticides diazinon and chlorpyrifos were probable causes of the observed toxicity in 2/3 of the samples. Chemical analyses also confirmed that sufficient diazinon and/or

chlorpyrifos concentrations were detected in samples that caused at least 50% *C. dubia* mortality ($n=31$).

Diazinon can persist in aquatic environments for as long as 6 months. In water, diazinon is subject to both abiotic degradation (i.e., hydrolysis and photolysis) and biotic degradation by microorganisms. The rates of both processes are strongly influenced by pH, temperature, salinity, and the organic content of the water (Larkin and Tjeerdema 2000; US ATSDR 2008). Among the several abiotic transformations that diazinon might undergo in natural waters, hydrolysis and redox reactions are the most common (Brooke and Smith 2005; Wolfe et al. 1990). Frank et al. (1991) observed that temperature had a greater effect on degradation and suggested that hydrolysis was the primary mode of diazinon degradation. Similarly, Garcia-Repetto et al. (1994) and Bondarenko et al. (2004) reported higher diazinon degradation rates under high temperature and more acidic conditions, and reached a similar conclusion. The major diazinon hydrolysis products were 2-isopropyl-4methyl-6-hydroxyprimidine and diethyl thiophosphoric acid or diethyl phosphoric acid (Larkin and Tjeerdema 2000; US EPA 2004). Diazinon undergoes aqueous base-catalyzed and acid-catalyzed hydrolysis and displays the longest hydrolysis half-life near a neutral pH. Morgan (1976) reported a diazinon hydrolysis half-life value as 43.3 days in well water that was between pH 7.4 and 7.7 at 16°C. Rapid diazinon degradation occurred under both higher acidic and basic conditions (Bondarenko et al. 2004; Chapman and Cole 1982; Garcia-Repetto et al. 1994; Frank et al. 1991). Chapman and Cole (1982) reported that pH was the most influential factor on the half-life of diazinon maintained in sterile water–ethanol (99:1) phosphate buffer solutions at $25 \pm 3^\circ\text{C}$. Degradation of diazinon was most rapid under acidic conditions, with half-life values of 3.15, 14, 54.6, 70, and 53.9 days at pH values of 4.5, 5.0, 6.0, 7.0, and 8.0, respectively. There was a similar pH effect on diazinon degradation in work reported by Garcia-Repetto et al. (1994). Bondarenko et al. (2004) investigated the persistence of diazinon in natural waters of various salinities collected from different locations within the Upper Newport Bay-San Diego Creek watershed area located in central Orange County, California. They observed that diazinon degraded fastest in natural water (half-life of 6.3–14.0 days), followed by sea water (half-life of 41.0 days), whereas in sterilized water, diazinon had a half-life of 51.1–54.9 days at 21°C. When the temperature was lowered to 10°C, diazinon persisted much longer, with half-life values of 25.0–28.3 days in natural water; the corresponding half-life value for seawater was 124.0 days. These results suggest that, under similar pH and temperature conditions, diazinon persists the longest in seawater, primarily from lack of microbial degradation in high-saline waters. Diazinon was degraded primarily by abiotic processes in seawater, and any reduction in microbial degradation processes would be expected to produce prolonged persistence. Results also show that sterilization greatly increased diazinon's persistence in freshwater, indicating that as for seawater microbial activity was mainly responsible for its degradation. A comparative study on the degradation of diazinon in sterilized and nonsterilized natural or distilled waters was performed; degradation was more rapid in natural water (12 weeks) than in any other sterilized or distilled

waters (>16 weeks), suggesting that microbial degradation occurred in the natural water (Sharom et al. 1980b).

Photolysis is relatively unimportant for degrading diazinon in aquatic systems (US EPA 1976; US ATSDR 2008). In surface water and groundwater samples, diazinon was degraded at similar rates in the light and dark (0.8 vs. 0.7% loss per day) (Frank et al. 1991). Medina et al. (1999) compared the half-life of diazinon in filtered natural water samples held under light and dark conditions and found that sunlight-exposed samples had a half-life of 31.13 days, only 6 days shorter than samples held in the dark. Frank et al. (1991) and Medina et al. (1999) conducted photolysis studies on diazinon and concluded that the contribution of photolysis to degradation was minor.

Acting either independently or together, temperature, pH, salinity, and microbial content are major factors that affect the persistence of diazinon.

4.3 Air and Precipitation

Diazinon released to the atmosphere is subject to direct photolysis, since it adsorbs light primarily in the ultraviolet (UV) region (10–400 nm) (Bavcon et al. 2003; Feigenbrugel et al. 2005). Muñoz et al. (2011) estimated the vapor phase half-life of diazinon in the troposphere as being approximately 4 h as a result of its reaction with photochemically produced hydroxyl radicals. However, in their experiment at 28°C, Muñoz et al. (2011) observed diazinon's half-life, with respect to direct photolysis, to be greater than 1 day. This indicates that the tropospheric degradation of diazinon is dominantly controlled by reaction with hydroxyl radicals rather than by direct photolysis. The pathway for degradation of diazinon in air is depicted in Fig. 7. Diazinon may be transported to the atmosphere from agricultural air-blast spraying or from post-application volatilization (Glotfelty et al. 1990a; McKinney 2005).

One degradation process for diazinon is photochemical oxidation in air. This process, known as oxidative desulfuration, involves addition of OH radicals to P=S bond, resulting in a P=O bond and eventually diazoxon, which is more toxic than diazinon (Glotfelty et al. 1990a; Raina et al. 2010; US EPA 1999; Zhou et al. 2011). Diazoxon is itself hydrolyzed into IMP (2-isopropyl-6-methyl-4-Pyrimidinol) and diethylphosphate by reactions catalyzed by H⁺ ions. Another diazinon degradation process involves direct hydrolysis to form products of IMP (2-isopropyl-6-methyl-4-Pyrimidinol) and diethylthiophosphate (Bavcon et al. 2003; McKinney 2005).

When diazinon partitions into droplets in accordance with Henry's Law, it may be hydrolyzed in water vapor formed from fog or rain (McKinney 2005). McKinney (2005) indicated that diazinon may be incorporated in fog and rain drops when they collide with diazinon-containing aerosol particles. Since atmospheric diazinon vapor has a longer equilibration time with fog than rain, due to much longer residence time in fog, it is possible that greater concentrations of diazinon vapor will be incorporated into fog.

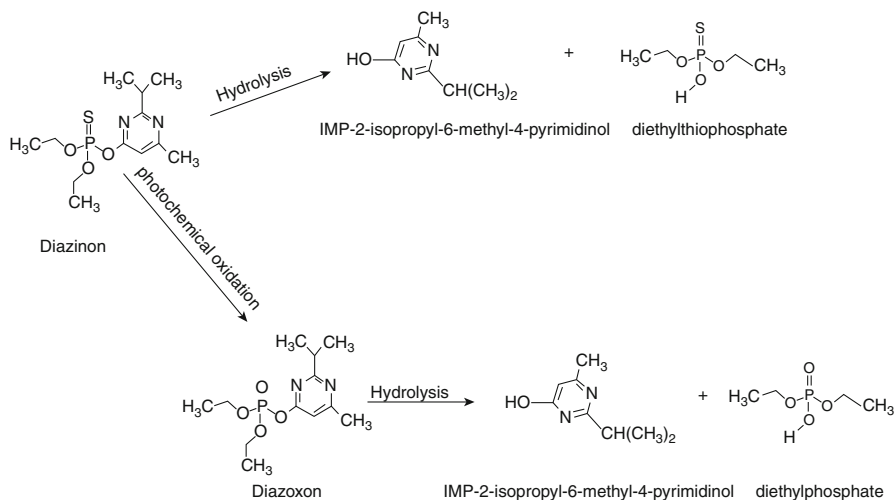


Fig. 7 Diazinon degradation pathways in air

Glotfelty et al. (1990b) studied distribution, drift, and volatilization losses of diazinon to the atmosphere during spray application to a dormant peach orchard. They concluded that distribution and drift losses contributed less diazinon to the atmosphere than the long-term volatilization loss from the soil surface of California's Central Valley. Zabik and Seiber (1993) determined that the organophosphate pesticides, including diazinon, are transported from California's Central Valley to the Sierra Nevada Mountains via several atmospheric processes such as direct air movement, and wet deposition with snow and rain. They observed that pesticide concentrations decreased with distance and elevation from the application site. Diazinon concentrations, which ranged from 13 to 13,000 pg/m^3 at the 114-m elevation, were at times more than a factor of 1,000 greater than those determined (from 1.4 to 83 pg/m^3) at the 533-m elevation. Further, they observed that the concentrations of all compounds appeared to peak during the first 2 weeks of February, within days to weeks after dormant spray applications. At the 1,920-m elevation, the air concentration of diazinon was lower than quantification level (0.7 pg/m^3), whereas the concentration of diazinon in wet-deposition samples was detected at levels up to 48 pg/mL (Zabik and Seiber 1993). McConnell et al. (1998) conducted an extended investigation of atmospheric inputs of pesticides transported from California's Central Valley to the Sierra Nevada Mountains, by collecting winter–spring precipitation (rain and snow) samples from Sequoia National Park (SNP) and from the Lake Tahoe basin. Their study showed that the pesticides currently used in California's Central Valley, including diazinon, were detected in snow and rain samples from two elevations (533 and 1,920 m) in Sequoia National Park in the southern Sierras at much higher levels (<0.21–19 ng/L at 533 m, and <0.057–14 ng/L at 1,920 m) than were samples collected in the Zabik and Seiber (1993) study. The

diazinon concentration in Lake Tahoe basin at 2,200-m elevation was found in the range of 0.057–7 ng/L. This indicated that the Lake Tahoe basin snow generally had lower concentrations than those from SNP. This difference in concentration reflects the proximity of SNP to downwind pesticide usage vs. the Lake Tahoe basin (McConnell et al. 1998).

4.3.1 Air Monitoring in California

The extensive use of pesticides on crops could result in air contamination over a wide area for several weeks because of pesticide volatility and drift from application sites. Sava (1985) conducted a 3-day study (samples collected for 6-h period) in residential areas of Salinas, Monterey County, to determine the level of diazinon in ambient air. Eight samples collected during the period from midnight until pesticides were applied to nearby fields the next day gave positive results (Sava 1985). However, with one exception no diazinon was detected between 12:00 p.m. and 12:00 a.m.; this exception was due to reduced application activity and higher wind speeds.

Seiber et al. (1993) conducted an ambient air monitoring study to assess the air-borne concentrations of diazinon insecticide, when used as dormant sprays on deciduous fruit and nut orchards. For 24-h ambient time-weighted air samples, the maximum diazinon concentration was $0.307 \mu\text{g}/\text{m}^3$ after diazinon was sprayed in orchards 1–100 km from the samplers. Studies conducted in Fresno and Monterey counties for determining aerial movement and deposition of diazinon resulted in the maximum detected concentration of $0.0357 \mu\text{g}/\text{m}^3$ and $0.0004 \mu\text{g}/\text{m}^3$, respectively (Stein and White 1993). Air Resource Board (ARB) (1998a) conducted an ambient air monitoring study to coincide with the use of diazinon as an insecticide on dormant orchards at five different locations in Fresno County during winter of 1997. Of the 121 ambient samples taken, 21.5% were found to exceed the limit of quantitation (LOQ), 47.1% were found to be at a level between the limit of detection (LOD) and LOQ, and 31.4% were found to be below the LOD. The highest concentration reported was $290 \text{ ng}/\text{m}^3$. Segawa et al. (2003) conducted ambient air monitoring for 31 pesticides and their breakdown products in Santa Barbara County, California. They reported maximum diazinon concentrations for the 24 h, 14 day, and 10 week periods as being 0.0021, 0.00087, and $0.00054 \mu\text{g}/\text{m}^3$, respectively. Recently, Wofford et al. (2009) conducted a study to determine whether residents of Parlier, Fresno County, were exposed to pesticides in air by establishing three air-sampling locations. The highest 1-day and highest 14-day average concentration was $0.172 \mu\text{g}/\text{m}^3$, which is above the health screening level of $0.130 \mu\text{g}/\text{m}^3$ and $0.0204 \mu\text{g}/\text{m}^3$, respectively. Recently, ARB conducted an ambient air monitoring study in Monterey, San Benito, and Santa Clara counties of California, to determine whether the level of air emissions of diazinon posed a present or potential exposure hazard (Rider 2010a). They reported that approximately 84% of the 192 ambient samples had concentrations less than the method detection limit (MDL) of $0.00154 \mu\text{g}/\text{m}^3$. The detectable levels found in the study were between 0.00281 and $0.0173 \mu\text{g}/\text{m}^3$.

In addition to the studies cited above, several researchers measured short-term acute air concentrations from individual applications. For example, the Air Resource Board (ARB) (1998b) conducted a diazinon monitoring study on a 40 A dormant peach orchard in Kings County, California, from January 12 to February 2, 1998. They collected 28 samples and found all samples to exceed the Estimated Quantitative Level (EQL) of 44.5 ng/sample, which would be equivalent to 10 ng/m³ for 24-h sampling period at 3 L/min. The highest diazinon concentration was 5,500 ng/m³ and was measured during the third (4 h) sampling period (ARB 1998b). In another diazinon air monitoring study in Glenn County, California, Rider (2010b) reported concentrations ranging from less than the MDL to maximum of 4,261 ng/m³.

Results from the studies conducted in several areas of California indicate that although diazinon is found in ambient air the concentrations of diazinon observed do not warrant immediate regulatory action. However, more research is needed to assess health risks of residue levels found in environmental samples and to determine if exposures should be reduced.

5 Aquatic Toxicology

5.1 Mode of Action

Diazinon shares a common mechanism of toxicity with other organophosphorus insecticides. It inhibits the enzyme acetylcholinesterase, which hydrolyzes the neurotransmitter acetylcholine in cholinergic synapses and neuromuscular junctions. Inhibition of acetylcholinesterase results in accumulation of acetylcholine at neuron synapses causing prolonged stimulation of cholinergic receptors. As a consequence, the prolonged neuron stimulation leads to a suite of intermediate syndromes including anorexia, diarrhea, generalized weakness, muscle tremors, abnormal posturing and behavior, depression, and death (Larkin and Tjeerdema 2000; US EPA 2007).

Diazinon undergoes oxidative desulfurization to form a much more toxic degrade, diazoxon. Diazinon belongs to a chemical subgroup of the organophosphorous pesticides called the organophosphorothiolates. Members of this group are poor inhibitors of cholinesterases. Once absorbed into organisms (target and non-target) the thioates are converted to an oxon form by various cytochrome P450 enzymes. Because animals metabolize the parent compound to the oxon, they are exposed both to the parent thioate residue and the highly toxic oxon form (US EPA 2007).

5.1.1 Aquatic Toxicity

The effects that diazinon has on aquatic life have been extensively tested in numerous species under various conditions. Approximately 250 original toxicological studies that include open literature, testing reports from government agencies and registrants were identified by Palumbo et al. (2010). The aquatic toxicity and environmental fate

of diazinon has been comprehensively reviewed by several authors, including Larkin and Tjeerdema (2000), US EPA Office of Prevention, Pesticides and Toxic Substances (2004), US EPA Office of Pesticide Programs (2007), and US ATSDR (2008). The reviewers had different objectives and used different data evaluation criteria in their individual reviews. Moreover, they relied on different data sets from nonidentical sources, and the result is that discrepancies exist in the range of toxicity values they reported. However, the differences are not significant enough to alter the toxicity ratings for diazinon given for various aquatic taxa. In this review, the toxicity data sets evaluated by Palumbo et al. (2010) in freshwater fish and invertebrates were used to summarize diazinon's toxicity, because the method used by these authors provided an evaluation of toxicity that was more stringent and consistent.

5.1.2 Acute Toxicity

Diazinon toxicity varies widely within and among species, and varies when performed under different testing conditions. Reliable acute toxicity values for diazinon were identified for four fish species and nine invertebrate species (Table 6). The 96-h LC₅₀ values reported ranged from 0.21 µg/L for *C. dubia* to 10,000 µg/L for fathead minnow, *Pimephales promelas*; this level of toxicity was rated by EPA (US EPA 2004) as being very highly to moderately toxic to aquatic organisms. In general, freshwater cladocerans are more sensitive than freshwater teleosts and aquatic plants. The most sensitive organisms tested were members of the family Daphniidae. *C. dubia* had the lowest species mean acute value (SMAV) of 0.36 µg/L, and a similar acute value of 0.52 µg/L was reported for the Daphniidae, *Daphnia magna*. Two amphipods (*Hyalella azteca* and *Gammarus pseudolinaeus*) were tested and had 96-h LC₅₀ values ranging from 4.3 to 16.8 µg/L. Two insects (*Procloeon* sp., *Chironomus tentans*) and one mysid (*Neomysis mercedis*) were tested, and the resulting 96-h LC₅₀ SMAVs ranged from 1.79 to 10.7 µg/L, which is in the range similar as the amphipods. Snails (*Physa* spp. and *Pomacea paludosa*) were the invertebrates that had the lowest sensitivity to diazinon. The SMAVs for snails ranged from 3,198 to 4,441 µg/L. Diazinon is highly or moderately toxic to fish species and displays 96-h LC₅₀s for them ranging from 440 to 10,000 µg/L. The bluegill sunfish *Lepomis microchirus* was the most sensitive fish species tested, and had an SMAV of 460 µg/L. A similar SMAV (723 µg/L) was reported for brook trout *Salvelinus fontinalis*. Flagfish *Jordanella floridae* and fathead minnow were moderately sensitive to diazinon and had SMAVs of 1,643 µg/L and 6,900–9,250 µg/L, respectively. The only available aquatic plant study was performed with green algae (*Pseudokirchneriella subcapitata*) and produced a 7-day EC₅₀ value of 3,700 µg/L (US EPA 2007).

5.1.3 Chronic Toxicity

Two freshwater fish species and one invertebrate species were tested for chronic toxicity (Palumbo et al. 2010; US EPA 2005) (Table 7). The invertebrate, *D. magna*,

Table 6 Acute toxicity of diazinon to freshwater aquatic organisms

Species	Duration hour	Age/size	LC ₅₀ /μg/L-SMAV ^a	References
Flagfish	96	6–7 weeks	1,643	Allison and Hermanutz (1977)
<i>Jordanella floridae</i>				
Bluegill	96	1 year	460	Allison and Hermanutz (1977)
<i>Lepomis macrochirus</i>				
Fathead minnow	96	15–20 weeks	7,656	Allison and Hermanutz (1977)
<i>Pimephales promelas</i>				
Fathead minnow	96	31 days	9,350	Geiger et al. (1988)
<i>P. promelas</i>				
Fathead minnow	96	Newly hatched	6,900	Jarvinen and Tanner (1982)
<i>P. promelas</i>				
Brook trout	96	1 year	723	Allison and Hermanutz (1977)
<i>Salvelinus fontinalis</i>				
Cladocean	96	<24 h	0.36	Bailey et al. (1997, 2000, 2001), Banks et al. (2005), CDFG (1992a, 1998a)
<i>Ceriodaphnia dubia</i>				
Cladocean	96	<24 h	0.52	Ankley and Collyard 1995
<i>Daphnia magna</i>				
Amphipod	96	Mature	16.82	Hall and Anderson (2005)
<i>Gammarus pseudolimnaeus</i>				
Amphipod	96	14–21 days	4.3	Anderson and Lydy (2002)
<i>Hyalella azteca</i>				
Insect	96	3rd instar	10.7	Ankley and Collyard (1995)
<i>Chironomus tentans</i>				
Insect	48	0.5–1 cm	1.79	Anderson et al. (2006)
<i>Procladius</i> sp.				
Mysid	96	<5 days	4.15	CDFG (1992b)
<i>Neomysis mercedis</i>				
Pond snail	96	Juvenile	4,441	CDFG (1998b)
<i>Physa</i> spp.				
Snail	96	1 day, 7 days	3,198	Jarvinen and Tanner (1982)
<i>Pomacea paludosa</i>				

^aSMAV: species mean acute value

Table 7 Chronic toxicity of diazinon to freshwater aquatic organisms

Species	Duration	Age/size	NOEC ^a (µg/L)	References
Cladoceran <i>Daphnia magna</i> .	21 days	<24 h	0.17	Surprenant (1988)
Brook trout <i>Salvelinus fontinalis</i>	173 days	1 year	4.8	Allison and Hermanutz (1977)
Fathead minnow	274 days	5 days	28	Allison and Hermanutz (1977)
<i>Pimephales promelas</i>	32 days	Newly hatched	50	Jarvinen and Tanner (1982)
Fathead minnow <i>P. promela</i>				

^aNOEC: on-observed effect concentration

was most sensitive to the chronic toxicity of diazinon in a 21-days life cycle test. The NOEC and LOEC values in this study, based on a survival endpoint, were 0.17 µg/L and 0.32 µg/L, respectively (Surprenant 1988). A 173-days partial life cycle test with brook trout indicated that the survival of parental stock was unaffected at diazinon concentrations below 4.8 µg/L (Allison and Hermanutz 1977). Fathead minnows tested from 5-day post-hatch to spawning showed a significant higher incidence of scoliosis and reduced hatching rates than did controls at concentrations above 3.2 µg/L (Surprenant 1988). However, according to the US EPA (2007), a chronic NOEC in freshwater fish could not be established because data did not meet test guideline requirements. Currently, the lowest concentration tested using brook trout (<0.55 µg/L) is used as the NOEC for diazinon in freshwater fish.

5.2 Bioaccumulation

Diazinon bioaccumulates, but demonstrates a wide range of accumulation rates and efficiencies among different aquatic organisms (Palumbo et al. 2010; US ATSDR 2008). Its bioconcentration factor (BCF) values ranged from 4 for shrimp (Seguchi and Asaka 1981) to 300 for zebrafish (Keizer et al. 1991). In general, freshwater fish had higher bioconcentration ratios than crustaceans and gastropods (Kanazawa 1978). Differences in metabolism among species and exposure concentrations play a role in determining BCF. For example, guppies ($LC_{50}=0.8$ mg/L) were ten times more sensitive to diazinon than were zebrafish ($LC_{50}=8$ mg/L). Their BCF values also varied greatly from 39 for guppies to >300 for zebrafish (Keizer et al. 1991). In another study, diazinon BCF values for guppies ranged from 148 to 224, depending upon exposure concentrations (Deneer et al. 1999). Diazinon accumulated quickly in most of the tested fish and its BCF values plateaued within a few days. Japanese killifish, exposed to a mixture of pesticides that included diazinon, reached a BCF plateau within 24 h (Tsuda et al. 1995). The BCF values for four fish species (guppy, killifish, goldfish, and white cloud mountain fish) exposed to 2.1–2.9 µg/L diazinon peaked within 120 h in all fish, and ranged from 37.5 in the white cloud mountain fish to 132 in the male guppy (Tsuda et al. 1997). Diazinon is quickly eliminated from tissues of tested animals within a few days (3–8) of exposure, once they are placed in clean water. Sancho

Table 8 Aquatic-life benchmark values and water quality criteria for diazinon

		Benchmark/water quality criteria	
		Acute ($\mu\text{g/L}$)	Chronic ($\mu\text{g/L}$)
Benchmark	Fish	45	<0.55
	Invertebrate	0.11	0.17
	Nonvascular plant	6,700	N/A
	Vascular Plant	N/A	N/A
Water quality criteria	US EPA ^a	0.17	0.17
	CVRWQCB ^b	0.16	0.1
	Palumbo et al. (2010)	0.2	0.07

^aUS EPA: US Environmental Protection Agency

^bCVRWQCB: Central Valley Regional Water Resource Quality Control Board

et al. (1992) observed that >50% diazinon in a freshwater eel was eliminated after 24 h in clean water. El Arab et al. (1990) determined that only 9% of bioaccumulated diazinon was left in perch after 3 days. Kanazawa (1978) treated seven freshwater species, including fish and crustaceans, to 10 and 50 $\mu\text{g/L}$ levels of diazinon for 7 days and found that diazinon was eliminated from tissues within 8 days.

5.3 Aquatic Life Benchmarks and Water Quality Criteria

Aquatic life benchmark and water quality criteria are toxicological reference values developed separately by EPA's Office of Pesticide Program (OPP) and Office of Water (OW) that use different approaches (US EPA 2011). Both EPA offices have responsibilities for evaluating aquatic toxicity data to assess the ecological effects of chemicals in surface water. OPP develops the aquatic life benchmarks for freshwater species based on toxicity values. Each Aquatic Life Benchmark is based on the most sensitive, scientifically acceptable toxicity endpoint for a given taxon (e.g., freshwater fish). OPP uses aquatic toxicity data in ecological risk assessments for large numbers of pesticide registration decisions under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). The diazinon aquatic life benchmarks are available for each taxon and these are shown in Table 8. OW uses aquatic toxicity data to develop ambient water quality criteria that can be adopted by states and Indian tribes on reservation land to establish water quality standards under the Clean Water Act. Based on the procedures described in the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" (Stephan et al. 1985), diazinon water quality criteria were 0.17 $\mu\text{g/L}$ for both of the criteria: continuous concentration and criterion maximum concentration (Table 8) (US EPA 2005, 2011). The California Central Valley Regional Water Resources Control Board (CVRWQCB 2006) developed its own water quality criteria for the control of diazinon runoff into the Sacramento-San Joaquin Delta by using US EPA's methodology, but with slightly different data set. This resulted in an acute water quality criterion for diazinon of 0.16 $\mu\text{g/L}$ and a chronic water

criterion of 0.1 $\mu\text{g/L}$, which are more stringent criteria than those of the US EPA. Palumbo et al. (2010) evaluated all of the existing methodologies worldwide and reported a detailed approach for water quality criteria derivation. Based on their methodology, they recommended diazinon water quality criteria of 0.2 and 0.07 $\mu\text{g/L}$ for acute and chronic exposures, respectively.

6 Summary

Diazinon, first introduced in USA in 1956, is a broad-spectrum contact organophosphate pesticide that has been used as an insecticide, acaricide, and nematicide. It has been one of the most widely used insecticides in the USA for household and agricultural pest control. In 2004, residential use of diazinon was discontinued, and in 2009, diazinon was phased out of all agricultural uses. Consequently, the amounts of diazinon applied have been drastically decreased. For example, in California, the amount of diazinon applied decreased from 501,784 kg in 2000 to 64,122 kg in 2010.

Diazinon has a K_{oc} value of 40–432, and is considered to be moderately mobile in soils. Diazinon residues have been detected in groundwater, drinking water wells, monitoring wells, and agricultural wells. The highest detection frequencies and highest percentages of exceedance of the water quality criterion value of 0.1 $\mu\text{g/L}$ have been reported from the top five agricultural counties in California that had the highest diazinon use. Diazinon is transported in air via atmospheric processes such as direct air movement and wet deposition in snow and rain, although concentrations decrease with distance and elevation from the source. In the environment, diazinon undergoes degradation by several processes, the most important of which is microbial degradation in soils. The rate of diazinon degradation is affected by pH, soil type, organic amendments, soil moisture, and the concentration of diazinon in the soil, with soil pH being a major influencing factor in diazinon degradation rate. Studies indicate that soil organic matter is the most important factor that influences diazinon sorption by soils, although clay content and soil pH also play an important role in diazinon sorption.

Diazinon is very highly to moderately toxic to aquatic organisms. Diazinon inhibits the enzyme acetylcholinesterase, which hydrolyzes the neurotransmitter acetylcholine and leads to a suite of intermediate syndromes including anorexia, diarrhea, generalized weakness, muscle tremors, abnormal posturing and behavior, depression, and death. Differences in metabolism among species and exposure concentrations play a vital role in diazinon's bioaccumulation among different aquatic organisms in a wide range of accumulating rates and efficiencies.

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