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Organophosphorous Pesticides and Natural Water

G.Viswanathan, Mayuri
EISD Division,
National Environmental Engineering Research Institute, Nagpur.

Abstract:-The use of pesticides (such as herbicides, insecticides, and fungicides) increases crop yields and is beneficial in controlling weeds and nuisance organisms, but pesticides can adversely affect the environment (Larson and others, 1997a) and human health. Many pesticides are soluble in water and may enter a surface-water body in a dissolved state. Other pesticides bind to soil particles and can be transported to surface-water bodies through soil erosion. Pesticides bound to soil particles can remain suspended in the water column or can become entrained in the bed sediment. The transport of pesticides from their application areas by water is recognized as a source of contamination, and elevated levels of pesticides in surface water can render the water unfit for human consumption. Pesticides released into the environment can have adverse effects on ecological and human health. Many pesticides are known or suspected carcinogens and can be toxic to humans and aquatic species. Many of the known health effects, however, require exposure to concentrations higher than those typically found in the environment; the health effects of chronic, long-term exposure to low or trace concentrations of pesticides are generally unknown. Other concerns include synergistic effects of multiple pesticides as well as the processes of bioaccumulation, bioconcentration, and biomagnification, which entail the uptake and accumulation of chemical substances by organisms through the food chain: Organophosphorus pesticides (OPs) have been widely used throughout the world since1960. This review discusses the fate of organophosphorus pesticides in the aquatic environment via processes such as adsorption, hydrolysis, oxidation, and photochemical degradation. Further-more, the breakdown products of OPs are discussed, as new research has indicated that the products of degradation can be very harmful as well and because relatively little research has been carried out on comprehensive product identification. Recommended future research areas are highlighted.

I. INTRODUCTION

A. Pesticide Scenoria in the India and in the World

Pesticide consumption in world has reached to 2 million tones as per Abhilash and Nandita and from these 2 million tones Europe utilizes 45% followed by USA 24% and rest 25% in rest of the world. Pesticide consumption in Asia is also alarming. China uses highest percentage followed by Korea, Japan and India. In India use of pesticide is about 0.5 kg/hectare and large contribution is from organochlorine pesticides. The usage is because of warm humid climatic conditions . The concept of green revolution has played a important role for utilization of variety of pesticides for high yield varieties. Presently India is largest producer of pesticides in Asia and ranks 12th in world. Pesticide residue in several crops has also affected the export of agricultural commodities in the last few years. In this context, pesticide safety, regulation of pesticide use, proper application technologies, and integrated pest management are some of the key strategies for minimizing human exposure to pesticides and to maintain the fertility of the soils for proper productivity. There is a dearth of studies related to these issues in India Uttar Pradesh is the largest consumer followed by Punjab, Haryana and Maharashtra. Regarding the pesticide share across agricultural crops, cotton account for 45% followed by rice (25%), chillies/vegetables/fruits (13-24%), plantations (7-8%), cereals/ millets/oil seeds (6-7%), sugarcane (2-3%) and other (1-2%) .

II. PESTICIDE

Classification Pesticides encompass a variety of different types of chemicals including herbicides, insecticides, fungicides and rodenticides. Pesticides are usually classified on the basis of structure (Table). The structural classification include organochlorine, organophosphorus, carbamates, nitrogen based pesticides

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PESTICIDES	TARGET	PESTICIDES	TARGET
Algicides	Algae	Mollucides	Snails
Avicides	Birdes	Nematicides	Nematode
Bactericides	Bacteria	Viricides	Virusus
Fungicides	Fungi	Rodenticides	Rodents
Incecticides	Insect	Miticides or agarcides	Mites

Table1: Classification of Pesticides According To Their Targets.

Recently, the USEPA has reconsidered its regulations on the use and the residual concentrations of OPs allowed in food products. This renewed interest toward OPs stems from a larger concern on compounds, which may alter (even if incrementally) the human nervous system or affect the hormonal balance in humans (e.g., testosterone). The proper development of the central nervous system is very important, particularly in children, because theirs is undergoing rapid development, and thus the impact of OPs should be known better. Based on the molecular structures, OPs are typically categorized into four subgroups: phosphates, phosphorothioates, phosphorodithioates, and phosphorothiolates. Many of the OPs are considered controlled substances and have very strict application instructions for the workers; others may be controlled indirectly by the governmental bodies in developed countries, who set maximum allowable concentration standards of OPs in drinking water, for instance. The OPs that have been restricted in their use in the USA are listed in Table 2 together with the estimated usage amount, the main crops and the primary usage states as reported by the USDA . As can be seen, several OPs are still allowed and widely used for the protection of a variety of crops against pests. Table 3 lists the structures, names, and selected physical properties of the most common OPs (Howard and Meylan, 1997), categorized into the subgroups of Figure 1.

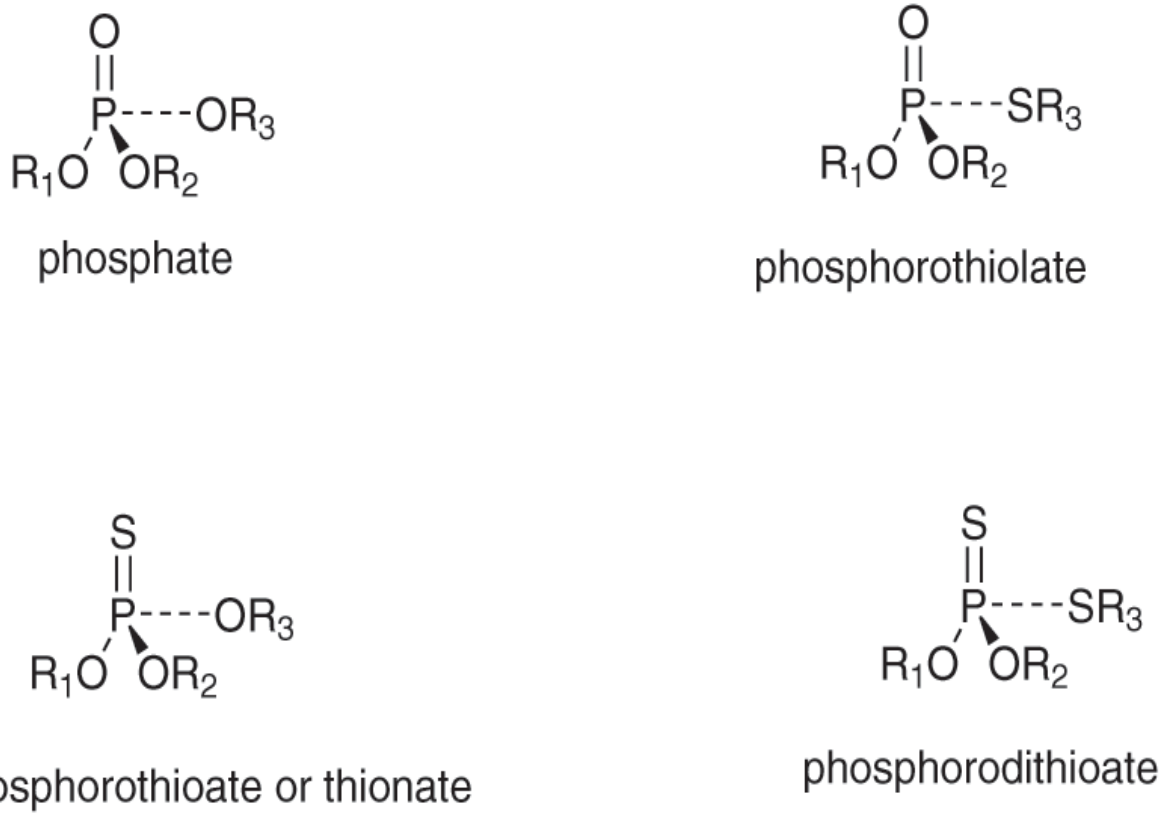

Fig 1: Classification of Pesticides According To Their Structure

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		Annual Amount Applied (10^3 lbs)	States Surveyed
Azinphos-Me	Upland cotton	293	AL, AZ, AR, CA, LA, MS, MO, NC, SC, TN and TX
	Apples	699.7	CA, GA, MI, NJ, NY, NC, OR, PA, SC and WA
	Blueberries	15.2	GA, MI, NJ, NC and OR
	Peaches	61.3	CA, GA, MI, NJ, NY, NC, PA, SC and WA
	Pears	138.6	CA, MI, OR and MA
	Sweet cherries	26	CA, MI, OR and MA
	Tart cherries	34.0	MI, NY, OR and PA
Chlorpyrifos	Winter wheat	289	CO, ID, IL, KS, MO, MT, NE, OH, OK, OR, PA, SK, TX and WA
Diazinon	Black berries	1.1	OR
	Blue berries	3.5	GA, MI, NJ, NC and OR
	Grapes	5.3	CA, MI, NY, OR, PA and WA
	Raspberries	11.6	OR and WA
Disulfoton	Upland cotton	282	AL, AZ, AR, CA, LA, MS, MO, NC, SC, TN and TX
Ethoprop	Fall potatoes	222	ID, ME, MN, MT, ND, OR, WA and WI
Fenamiphos	Lemons	13.9	CA
	Raspberries	4.2	OR and WA
Fonofos	Fall potatoes	123	ID, ME, MN, MT, ND, OR, WA and WI
	Corn	213	IL, IN, IA, MI, MN, MO, NE, OH, SD and WI
Methamidphos	Fall potatoes	410	ID, ME, MN, MT, ND, OR, WA and

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			WI
Methyl Parathion	Corn	1517	IL, IN, IA, MI, MN, MO, NE, OH, SD and WI
	Soybeans	293	AR, DE, IL, IN, IA, KS, KY, LA, MI, MN, MS, MO, NE, NC, OH, PA, SK, TN and WI
	Upland cotton	1996	AL, AZ, AR, CA, LA, MS, MO, NC, SC, TN and TX
	Winter wheat	228	CO, ID, IL, KS, MO, MT, NE, OH, OK, OR, PA, SK, TX and WA
	Apples	279.6	CA, GA, MI, NJ, NY, NC, OR, PA, SC and WA
	Grapes	13.6	CA, MI, NY, OR, PA and WA
	Nectarines	23.7	CA
	Peaches	92.1	CA, GA, MI, NJ, NY, NC, PA, SC and WA
	Pears	27.6	CA, MI, OR and MA
	Plums	31.1	CA
Phorate	Corn	444	IL, IN, IA, MI, MN, MO, NE, OH, SD and WI
	Fall potatoes	584	ID, ME, MN, MT, ND, OR, WA and WI
	Upland cotton	667	AL, AZ, AR, CA, LA, MS, MO, NC, SC, TN and TX
Profenofos	Upland cotton	558	AL, AZ, AR, CA, LA, MS, MO, NC, SC, TN and TX
Terbufos	Corn	3200	IL, IN, IA, MI, MN, MO, NE, OH, SD and WI

Table 2: Structures of 48 Widely Applied Organ phosphorus Pesticides and Related Parameters

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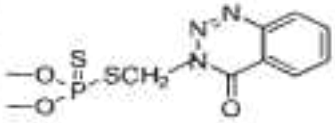
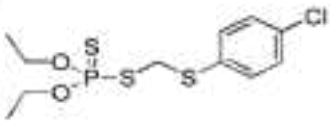
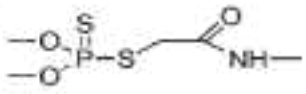
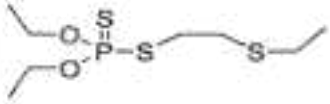
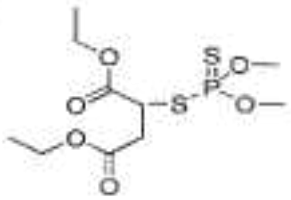
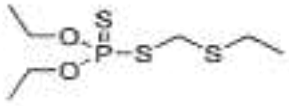
A. USDA Usage

I. Phosphorodithioate

Name and Structure	log K_{ow}	Vapor Pressure (mm Hg)	Water Solubility at 20 ^{0}C (mg/L)
Azinphos-Me 	2.6	2.03×10^{-7}	3.3×10^{1}
Carbophenothion 	5.33	3.0×10^{-7}	6.3×10^{-1}
Dimethoate 	0.78	8.25×10^{-6}	2.38×10^{4}
Disulfoton 	4.02	1.8×10^{-4}	1.63×10^{1}
Malathion 	2.36	7.9×10^{-6}	1.43×10^{2}
Phorate 	3.56	8.4×10^{-4}	5.0×10^{1}

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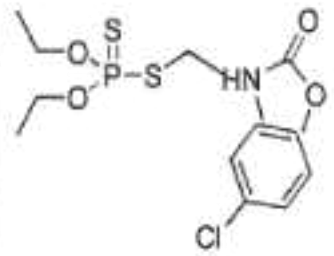
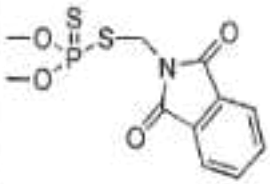
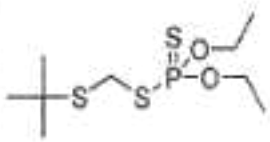
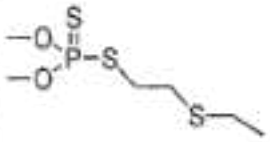
Phosalone 	4.38	4.54×10^{-8}	2.15×10^{0}
Phosmet 	2.78	4.9×10^{-7}	2.44×10^{1}
Terbufos 	4.48	3.20×10^{-4}	5.07×10^{0}
Thiometon 	2.88	1.70×10^{-5}	2.0×10^{2}

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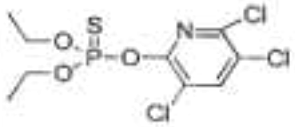
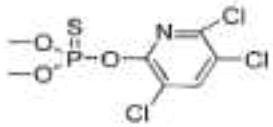
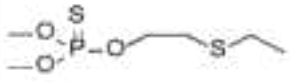
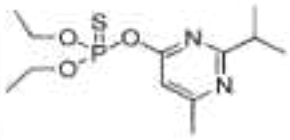
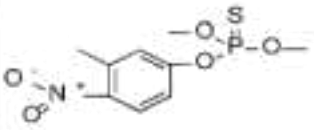
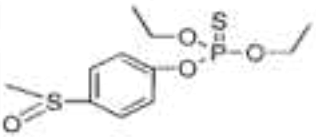
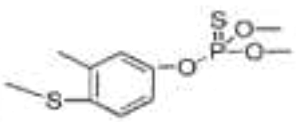
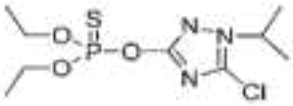
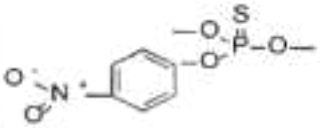
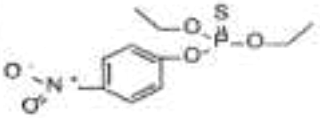
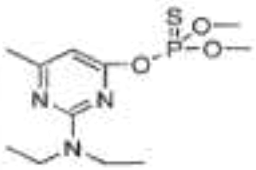
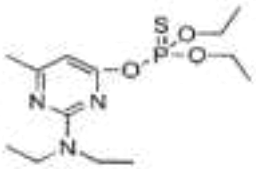
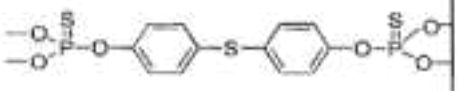
II. Phosphorothioate

Name and Structure	log K_{ow}	Vapor Pressure (mm Hg)	Water Solubility at 20 °C (mg/L)
Chlorpyrifos 	NA	1.85×10^{-5}	$2.0E \times 10^{0}$
Chlorpyrifos-Me 	4.24	4.2×10^{-5}	4.0×10^{0}
Demeton-O 	NA	3.0×10^{-4}	6.0×10^{1}
Diazinon 	3.81	1.12×10^{-2}	$4.0E \times 10^{1}$
Fenitrothion 	3.30	5.4×10^{-5}	3.0×10^{1}
Fensulfothion 	2.23	5.0×10^{-5}	$2.0E \times 10^{3}$

Fenthion 	4.09	3.0×10^{-5}	7.5×10^{0}
Isazofos 	3.82	8.7×10^{-5}	$1.5E \times 10^{-2}$
Methyl Parathion 	NA	1.5×10^{-5}	5.7×10^{1}
Parathion 	3.83	9.65×10^{-6}	6.54×10^{0}
Pirimiphos-Me 	4.20	8.99×10^{-6}	2.25×10^{1}
Pirimiphos-Ethyl 	4.85	2.90×10^{-4}	3.96×10^{0}
Temephos 	4.0	NA	3.0×10^{-2}

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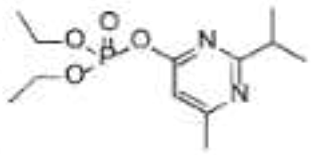
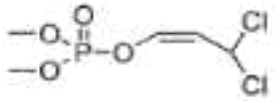
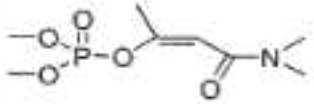
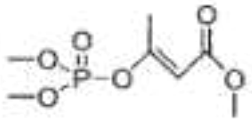
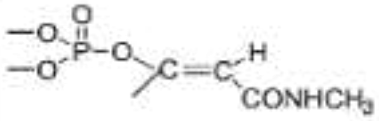
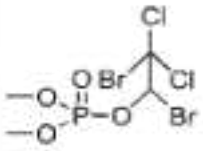
III. Phosphate

Name and Structure	log K_{ow}	Vapor Pressure (mm Hg)	Water Solubility at 20 ^{0}C (mg/L)
Diazoxon 	2.07	1.1×10^{-5}	2.45×10^{2}
Dichlorvos (DDVP) 	1.16	5.3×10^{-2}	1.0×10^{4}
Dicrotophos 	-0.49	8.63×10^{-5}	1.0×10^{6}
Mevinphos 	0.13	1.3×10^{-4}	6.0×10^{5}
Monocrotophos 	-0.22	7.0×10^{0}	1.0×10^{6}
Naled 	1.38	2.0×10^{-3}	2.0×10^{3}

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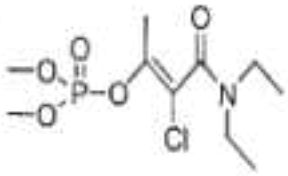
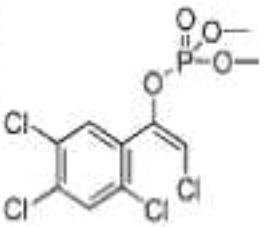
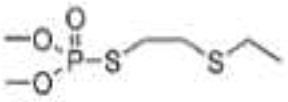
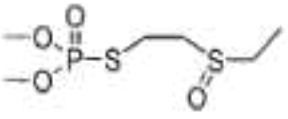
Phosphamidon 	0.38	1.65×10^{-5}	1.0×10^{6}
Tetrachlorvinphos 	3.53	4.20×10^{-8}	1.1×10^{1}

IV. Phosphorothiolate

Name and Structure	log K_{ow}	Vapor Pressure (mm Hg)	Water Solubility at 20 ^{0}C (mg/L)
Demeton-S 	1.2	3.0×10^{-4}	3.3×10^{3}
Oxydemeton-Me 	-0.75	2.85×10^{-5}	1.0×10^{6}

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OPs are applied to the protectedcrops via a variety of methods. Malathion is frequently applied from low-flyingairplanes in agricultural as well as urban areas. For instance, in Southern Californiathe nighttime sprayings of Malathion from airplanes to control the Mediterranean Fruitfly were common .

Phorate is an example of a soil pesticide that is applied as granules on soil where the protected crop is cultivated (e.g., corn and potatoes). Chlorpyrifos belongs to a group of OPs that is applied directly to the fruit and/or leaves of the crop to be protected. For example, in the Central and South American banana plantations, Chlorpyrifos containing bags often cover the banana bunches from their inception.

Research focusing on the fate of OPs in the aquatic environment dates back to the 1950s and 1960s. For example, Muhlmann and Schrader (1957) and Faust and Gomaa (1972) studied the hydrolytic degradation of OPs and related the rate of hydrolysis with the OP molecular structure. In another study, Mortland and Raman (1967) investigated the influence of selected metal ions (e.g.cu+) on the hydrolysis of half-life of Diazinon and other OPs. Wolfe and co-workers carried out a comprehensive study on the degradation of Malathion in water (Wolfe et al., 1977). In particular, the thermodynamic and product studies were very thorough along with several proposed mechanisms (Figure 2). Wanner and co-workers (Wanner et al., 1989) studied the fate of select OPs in the Rhine river ecosystem after a chemical fire at Sandoz Corp. in Basel, Switzerland, in November 1986, and the subsequent release of a variety of chemicals into the Rhine river (e.g., Disulfoton and Thiometon).

They concluded that biotransformation and oxidation by singlet oxygen were important processes for the reduction of the OP load in Rhine river. The degradation of OPs in water can occur via a variety of pathways. Oxidation of OPs to the corresponding oxons, sulfones, and sulfoxides has been reported widely (Figure 3). Oxidation can occur either biotically via specific enzymes or abiotically by radical mechanisms, ozone, dissolved oxygen, or aqueous chlorine. Photodegradation can occur either by a direct photolysis of OPs, which have an absorption spectrum overlap with the solar spectrum or by indirect photodegradation, whereby dissolved humic and fulvic acids can act as a sensitizer or when particles can lead to semiconductor promoted photodegradation. Hydrolysis of OPs is perhaps the most thoroughly studied process. It can occur by a homogeneous mechanism, where H2O and OH–(H+ catalysis is less common) act as nucleophiles in an SN2 mechanism. Alternatively, it can take place when dissolved metal ions enhance the rate of hydrolysis by catalysis (e.g., Cu2+ for Diazinon [Mortland and Raman, 1967] or Hg2+for Malathion, Fenitrothion, Fenthion and Parathion-methyl [Wan et al., 1994]). Finally, heterogeneous surfaces such as Fe and Al oxides and different clays can enhance the rate of hydrolysis by providing surface sites atwhich the nucleophile and the OP can react (Sanchezcamazano and Sanchezmartin, 1991; Racke et al., 1996; Dannenberg and Pehkonen, 1998; Smolen and Stone, 1998).

The mechanism of surface catalyzed hydrolysis of OPs remains largely uncertain at this time, although many mechanisms have been proposed (Stone and Torrents, 1995; Smolen and Stone, 1998. An important area of any degradation and/or fate studies of compounds in the environment must be the identification and quantification of the products. This is particularly important for OPs, because their structures are relatively complex and contain numerous moieties that are prone to attack by nucleophiles. Thus, a variety of products can be expected depending on which mechanism dominates under a given set of environmental conditions. A classic example of the complexities involved in the product identification was the study of Malathion degradation by

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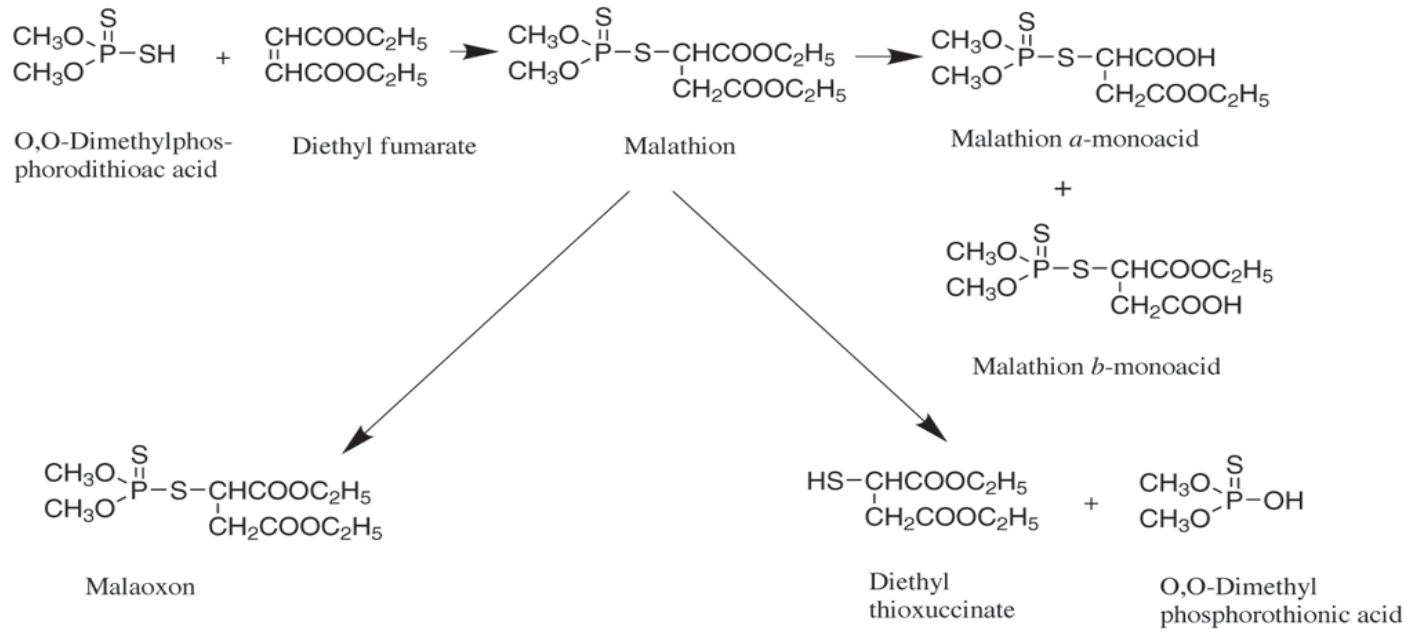
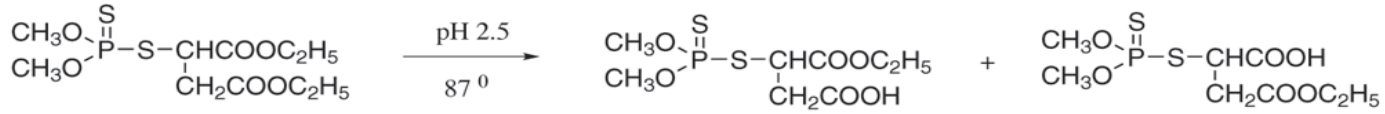
Scheme I



Scheme II



Scheme III

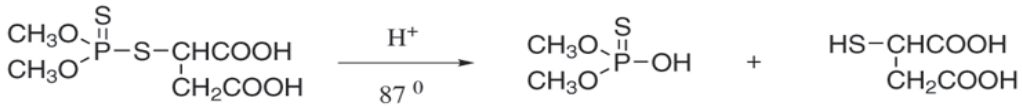


Fig. 2 : Degradation Way of Malathion

Wolfe and co-workers (Wolfe et al., 1977). Unexpected products such as HCHO and dialkyl sulfides can also be formed as reported by Hong and Pehkonen (1998) and Hong et al. (2000 and 2001), due to reactions in the ester side chains of OPs. A large body of research exists that has probed the toxicity of OPs toward a variety of common aquatic organisms, including Daphnia, killifish, and many birds (Blaise et al., 1988; Munkittrick et al., 1991; Feffando et al., 1996; Corson et al., 1998; and Wolfe and Kendall, 1998). The toxic effect of OPs in synergy with selected xenobiotic compounds has also been studied (Agyeman and Sultatos, 1998). However, in light of recent studies showing surprising, not previously detected degradation products such as formaldehyde and alkyl disulfides (Dannenberg and Pehkonen, 1998; Hong and Pehkonen, 1998), research that probes the overall toxicity and the ecological impact of OPs from their initial application to the final degradation products is critically needed.

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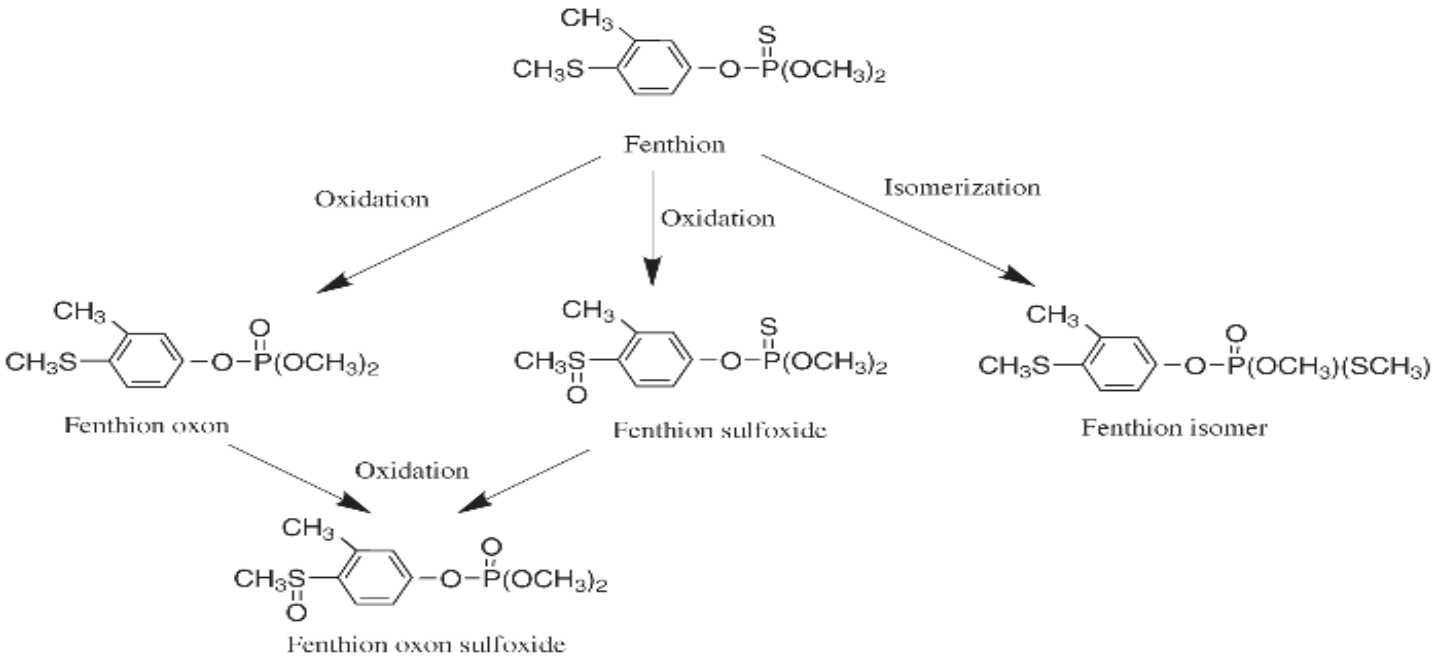

Fig. 3: Oxidation and Isomerization of Fenthion

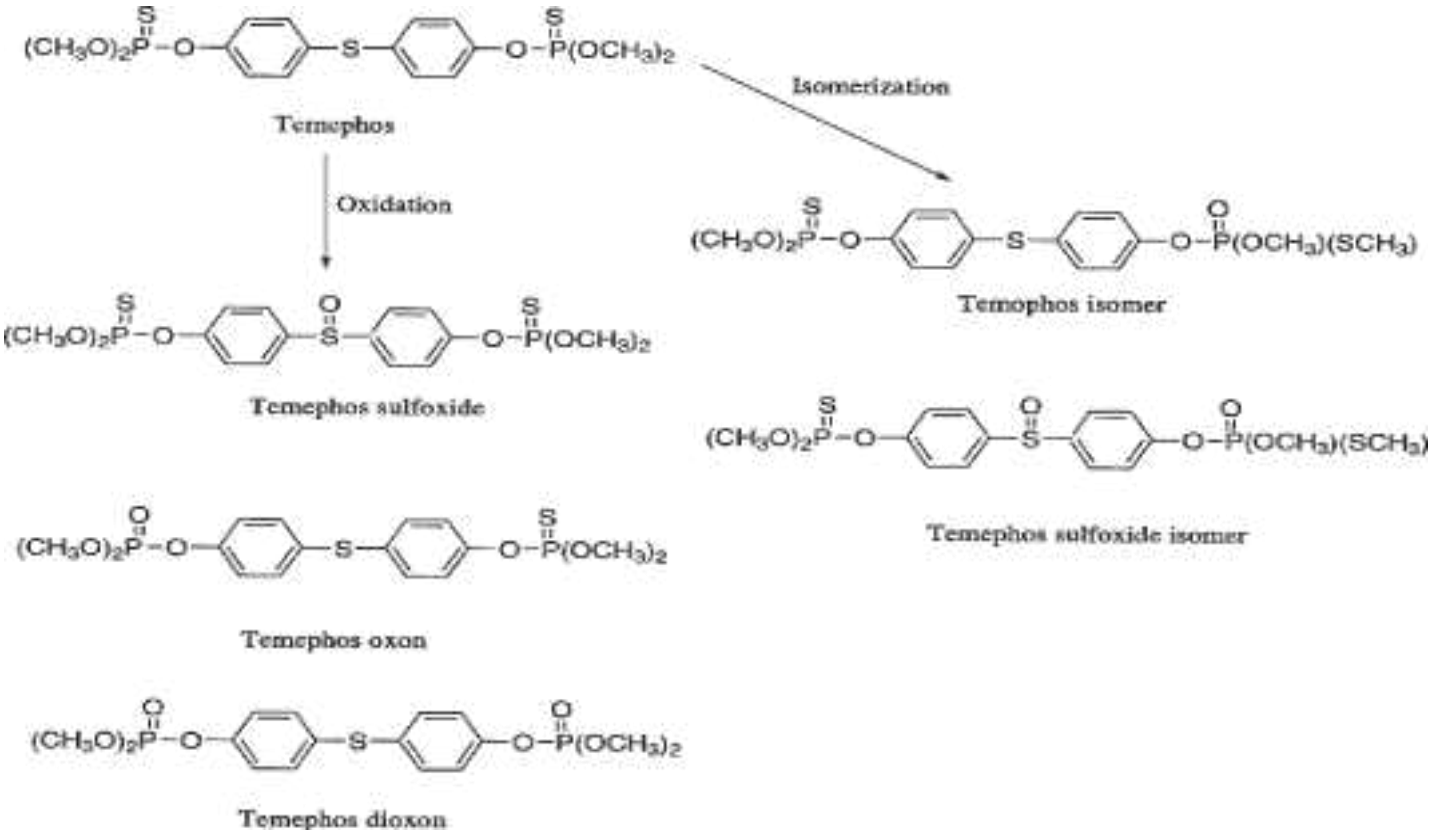

Fig. 4: Oxidation and Isomezation of Temophos

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It is very important to try to predict and assess the ultimate fate of OPs in the environment by considering all the aforementioned degradation pathways, the conditions at which each pathway is dominant and the way by which the degradation products are formed. Additionally, it is imperative that toxicity studies focus on the entire lifespan of the pesticides in the environment, including the degradation products and any synergism between the parent OPs and degradation products that may amplify the overall toxicity even higher. The purpose of this critical review is many fold. It describes the current scope of knowledge with regard to OP degradation in aquatic systems. It discusses the different degradation pathways and the characteristics of each pathway that will determine which might dominate under specific environmental conditions. It describes the degradation products that have been detected. Finally, the review provides suggestions for future research that is critically needed so that governmental regulators will have a more thorough reference point from which to determine the future of this widely applied pesticide.

III. ADSORPTION

Adsorption by soil can be a key step in the degradation of an OP in many aquatic environments. The degree of adsorption and the rate and extent of ultimate degradation are influenced by a number of factors. These include solubility, volatility, charge, polarity, molecular structure, and the size of the pesticides. The adsorption of an OP by soil components may have several effects. Under some conditions it can retard degradation of OPs by separating the pesticide from the enzymes that degrade it, while at other conditions, an enhancement may occur. Abiotic hydrolytic degradation may also be enhanced by adsorption (Smolen and Stone, 1998). Furthermore, the loss of OPs by volatilization or leaching is diminished after adsorption. The forces holding a pesticide to soil particles may be of several types. Physical adsorption via van der Waals forces arises from dipole-dipole interactions between the pesticide and soil particles. Ion exchange is especially effective for cationic pesticides adsorbed to negatively charged soil particles. Protonation of neutral OPs can also result in the ion exchange mechanism of adsorption. Hydrogen bonding is another mechanism by which OPs can adsorb to soils. Finally, a metal-ligand chelate can form between soil mineral ions such as Fe3+and Al3+and oxygen, nitrogen, or sulfur atoms of OPs (Stone and Torrents, 1995; Dannenberg and Pehkonen, 1998; Smolen and Stone, 1998). Adsorption and the resulting reduced mobility of OPs in soils are important factors affecting their behavior in nature. From an environmental point of view, it is of great importance to assess the sorption of pesticides by soil, because these phenomena affect other processes that determine the compounds' final fate, such as chemical, pincreasingly frequent occurrence of OPs in the surface and groundwater worldwide, has drawn the attention of environmental researchers. The adsorption of a pesticide to soil is experimentally determined by shaking an aqueous solution of the pesticide of known concentration with a known mass of soil until equilibrium is reached (Beltran et al., 1995). Two parameters are frequently used to describe the degree of adsorption: soil sorption coefficient (Kd) and organic-carbon-normalized partition coefficient (Koc). In general Kd values vary considerably according to the properties of the soils tested. Therefore, the sorption characteristics of a pesticide are often normalized to obtain Koc based on the organic carbon content. Kd and Koc

are definedµgpesticide/ gsoil

Kd=
µgpesticide /gwater

Koc = Kd* 100/ organiccarboninsoil(%)

Kd and Koc of different OPs in various soils have been reported (Table 3) (Sanchez-Martin and Sanchez-Camazano, 1991; Domagalski and Kuivila, 1993; Rodrfguez-Gonzalo et al., 1993; Arienzo et al., 1994; Sanchez-Camazano and Sanchez-Martin, 1994; Beltran et al., 1995; Kile et al., 1995; Baskaran et al., 1996; Mandal and Adhikari, 1997).

Adsorption of OPs in soils is best described by adsorption isotherms, which may be obtained by measuring adsorption at a number of different concentrations. Frequently, such isotherms are nonlinear, and it is found that they may be described by the empirical Freundlich equation

Cs= KCwn

lnCs = lnK + nlnCw

Where Cs

is the amount of adsorbed pesticide on 1 g of soil (g/g soil), Cw is the concentration of the pesticide in the solution at equilibrium (g/mL of aqueous phase), K and n are constants. K is the amount adsorbed for an equilibrium concentration of 1 g mL–1 soil, and therefore it represents the adsorption at low levels of adsorbate concentration and n is a measurement of the intensity of adsorption and reflects the degree to which adsorption is a function of concentration. Several researchers confirmed this conclusion and determined K and n values for various pesticides (Table 3) (Rodrfguez-Gonzalo et al., 1993; Arienzo et al.,

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pesticide	log K	1/n	Kd	Koc	log Kom	log Kd	log Kdom	Remarks (conditions)	Reference
Diazinon	1.30	0.9524	18		3.4			Marismas (silty clay, OM%=0.82)	Arienzo et al., 1994
Diazinon	0.68	0.9804	4.6		2.6			Marismas (clayed, OM%=1.1)	Arienzo et al., 1994
Diazinon	0.85	0.885	5.6		2.7			Marismas (clayed, OM%=1.55)	Arienzo et al., 1994
Diazinon	0.73	0.9434	4.45		3			Marismas (clayed, OM%=0.57)	Arienzo et al., 1994
Diazinon	0.80	0.885	4.9		2.5			Marismas (sandy clay loam, OM%=2.16)	Arienzo et al., 1994
Diazinon	0.20	1.0309	1.66		2.5			Marismas (sandy clay loam, OM%=0.55)	Arienzo et al., 1994
Diazinon	1.36	0.9346	19.7		2.35			Salamanca (sandy loam, OM%=10.2)	Arienzo et al., 1994
Diazinon	1.41	0.8475	18.5		2.46			Salamanca (sandy loam, OM%=8.9)	Arienzo et al., 1994
Diazinon	1.30	0.7874	12.6		2.52			Salamanca (loamy sand, OM%=6.0)	Arienzo et al., 1994
Azinphosmethyl	2.17	1.18						montmorillonite	Sanchez-Camazano & Sanchez-Martin, 1994
Dichlorvos	2.95	0.88						montmorillonite	Sanchez-Camazano & Sanchez-Martin, 1994
Azinphosmethyl	1.63	0.72			2.91			soil 1 (OM%=5.3)	Sanchez-Camazano & Sanchez-Martin, 1994
Azinphosmethyl	1.69	0.065			2.93			soil 2 (OM%=5.7)	Sanchez-Camazano & Sanchez-Martin, 1994
Azinphosmethyl	1.84	0.64			2.71			soil 3 (OM%=13.1)	Sanchez-Camazano & Sanchez-Martin, 1994
Azinphosmethyl	1.79	0.46			3.02			soil 4 (OM%=5.6)	Sanchez-Camazano & Sanchez-Martin, 1994
Azinphosmethyl	1.87	0.57			2.82			soil 5 (OM%=11)	Sanchez-Camazano & Sanchez-Martin, 1994
Azinphosmethyl	3.46	0.78			3.46			humic acid	Sanchez-Camazano & Sanchez-Martin, 1994
Dimethoate	0.23	1.14	1.1	50				Soil 1(OM%=2.2)	Beltran et al., 1995
Fenitrothion	1.33	0.85	25.95	1174				Soil 1(OM%=2.2)	Beltran et al., 1995
Methidathion	1.65	1.64	16.82	761				Soil 1(OM%=2.2)	Beltran et al., 1995
Dimethoate	0.00	1.08	0.77	192				Soil 2(OM%=0.4)	Beltran et al., 1995
Fenitrothion	0.81	1.15	4.28	1069				Soil 2(OM%=0.4)	Beltran et al., 1995
Methidathion	0.28	1.13	1.24	311				Soil 2(OM%=0.4)	Beltran et al., 1995
Parathion						3.41	3.43	humic acid	Rodriquez-Gonzalo et al., 1993
Paraoxon						2.59	2.62	humic acid	Rodriquez-Gonzalo et al., 1993
Parathion						2.67		natural montmorillonite	Rodriquez-Gonzalo et al., 1993
Paraoxon						1.83		natural montmorillonite	Rodriquez-Gonzalo et al., 1993
Parathion						1.26	2.9	soil 1(OM%=5.3)	Rodriquez-Gonzalo et al., 1993
Paraoxon						0.41	1.69	soil 1(OM%=5.3)	Rodriquez-Gonzalo et al., 1993
Parathion						1.28	2.92	soil 2(OM%=7.1)	Rodriquez-Gonzalo et al., 1993
Paraoxon						0.65	1.8	soil 2(OM%=7.1)	Rodriquez-Gonzalo et al., 1993
Parathion						1.23	2.93	soil 3(OM%=2.4)	Rodriquez-Gonzalo et al., 1993
Paraoxon						1.86	1.53	soil 3(OM%=2.4)	Rodriquez-Gonzalo et al., 1993
Parathion						2.2	3.01	soil 4(OM%=10.2)	Rodriquez-Gonzalo et al., 1993
Paraoxon						0.94	1.93	soil 4(OM%=10.2)	Rodriquez-Gonzalo et al., 1993
Methyl parathion			17.3					soil 1 (Mollic Solonetz), OM%=4	Sanchez-Martin & Sanchez-Camazano, 1991
Ethyl parathion			52.3					soil 1 (Mollic Solonetz), OM%=4	Sanchez-Martin & Sanchez-Camazano, 1991

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Methyl paraoxon		14.3		
Ethyl paraoxon		23.6		
Methyl parathion		9.2		
Ethyl parathion		42.3		
Methyl paraoxon		9.21		
Ethyl paraoxon		49.4		
Methyl parathion		12.1		
Ethyl parathion		42.3		
Methyl paraoxon		3.02		
Ethyl paraoxon		2.57		
Methyl parathion		16.3		
Ethyl parathion		59.2		
Methyl paraoxon		5.98		
Ethyl paraoxon		4.51		
Methyl parathion		3.61		
Ethyl parathion		16.7		
Methyl paraoxon		7.92		
Ethyl paraoxon		7.98		
Methyl parathion		3.2		
Ethyl parathion		8.11		
Methyl paraoxon		0.8		
Ethyl paraoxon		2.94		
Methyl parathion		5.46		
Ethyl parathion		20.3		
Methyl paraoxon		1.55		
Ethyl paraoxon		0.82		
Methyl parathion		27.6		
Ethyl parathion		104		
Methyl paraoxon		7.89		
Ethyl paraoxon		8.76		
Phorate		17.4		
Terbufos		18.5		
Phorate		30.3		
Terbufos		33.5		
Methyl parathion	10 (in µg/g)	0.6		
Fenitrothion	7 (in µg/g)	0.62		
Methyl parathion	32 (in µg/g)	0.39		
Fenitrothion	16 (in µg/g)	0.57		

soil 1 (Mollic Solonetz), OM%=4	Sanchez-Martin & Sanchez-Camazano, 1991
soil 1 (Mollic Solonetz), OM%=4	Sanchez-Martin & Sanchez-Camazano, 1991
soil 2 (Mollic Solonetz), OM%=1.2	Sanchez-Martin & Sanchez-Camazano, 1991
soil 2 (Mollic Solonetz), OM%=1.2	Sanchez-Martin & Sanchez-Camazano, 1991
soil 2 (Mollic Solonetz), OM%=1.2	Sanchez-Martin & Sanchez-Camazano, 1991
soil 2 (Mollic Solonetz), OM%=1.2	Sanchez-Martin & Sanchez-Camazano, 1991
soil 3 (Humic cambisol), OM%=5.3	Sanchez-Martin & Sanchez-Camazano, 1991
soil 3 (Humic cambisol), OM%=5.3	Sanchez-Martin & Sanchez-Camazano, 1991
soil 3 (Humic cambisol), OM%=5.3	Sanchez-Martin & Sanchez-Camazano, 1991
soil 3 (Humic cambisol), OM%=5.3	Sanchez-Martin & Sanchez-Camazano, 1991
soil 4 (Humic cambisol), OM%=7.1	Sanchez-Martin & Sanchez-Camazano, 1991
soil 4 (Humic cambisol), OM%=7.1	Sanchez-Martin & Sanchez-Camazano, 1991
soil 4 (Humic cambisol), OM%=7.1	Sanchez-Martin & Sanchez-Camazano, 1991
soil 4 (Humic cambisol), OM%=7.1	Sanchez-Martin & Sanchez-Camazano, 1991
soil 5 (Pellic Vertisol), OM%=0.8	Sanchez-Martin & Sanchez-Camazano, 1991
soil 5 (Pellic Vertisol), OM%=0.8	Sanchez-Martin & Sanchez-Camazano, 1991
soil 5 (Pellic Vertisol), OM%=0.8	Sanchez-Martin & Sanchez-Camazano, 1991
soil 5 (Pellic Vertisol), OM%=0.8	Sanchez-Martin & Sanchez-Camazano, 1991
soil 6 (Chromic luvisol), OM%=0.4	Sanchez-Martin & Sanchez-Camazano, 1991
soil 6 (Chromic luvisol), OM%=0.4	Sanchez-Martin & Sanchez-Camazano, 1991
soil 6 (Chromic luvisol), OM%=0.4	Sanchez-Martin & Sanchez-Camazano, 1991
soil 6 (Chromic luvisol), OM%=0.4	Sanchez-Martin & Sanchez-Camazano, 1991
soil 7 (Humic cambisol), OM%=2.4	Sanchez-Martin & Sanchez-Camazano, 1991
soil 7 (Humic cambisol), OM%=2.4	Sanchez-Martin & Sanchez-Camazano, 1991
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soil 7 (Humic cambisol), OM%=2.4	Sanchez-Martin & Sanchez-Camazano, 1991
soil 8 (Humic cambisol), OM%=10.2	Sanchez-Martin & Sanchez-Camazano, 1991
soil 8 (Humic cambisol), OM%=10.2	Sanchez-Martin & Sanchez-Camazano, 1991
soil 8 (Humic cambisol), OM%=10.2	Sanchez-Martin & Sanchez-Camazano, 1991
soil 8 (Humic cambisol), OM%=10.2	Sanchez-Martin & Sanchez-Camazano, 1991
Tokomaru Soil (OC%=3.2)	Baskaran et al., 1996
Tokomaru Soil (OC%=3.2)	Baskaran et al., 1996
Patua Soil (OC%=8.2)	Baskaran et al., 1996
Patua Soil (OC%=8.2)	Baskaran et al., 1996
Burdwan soil (OM%=0.65)	Mandal and Adhikari, 1997
Burdwan soil (OM%=0.65)	Mandal and Adhikari, 1997
Kakdwip soil (OM%=1.52)	Mandal and Adhikari, 1997
Kakdwip soil (OM%=1.52)	Mandal and Adhikari, 1997

Methyl parathion	28 (in µg/g)	0.42	Krishnagar soil (OM%=1.07)	Mandal and Adhikari, 1997
Fenitrothion	10 (in µg/g)	0.56	Krishnagar soil (OM%=1.07)	Mandal and Adhikari, 1997
Methyl parathion	40 (in µg/g)	0.32	Mohitnagar soil (OM%=3.19)	Mandal and Adhikari, 1997
Fenitrothion	18 (in µg/g)	0.5	Mohitnagar soil (OM%=3.19)	Mandal and Adhikari, 1997
Methyl parathion	25 (in µg/g)	0.52	Purulia soil (OM%=0.89)	Mandal and Adhikari, 1997
Fenitrothion	9 (in µg/g)	0.69	Purulia soil (OM%=0.89)	Mandal and Adhikari, 1997

Major factors that affect the adsorption of a given pesticide in soil include the organic matter content in soils (OMC), the characteristics of soil (i.e., clay content, moisture content, porosity, permeability, pH of soil, etc.), the temperature of soil, the cation exchange capacity (CEC), and the structure of pesticides. Among these factors, OMC has been proven to be the most important one. Data from previous studies indicate a good correlation between Kd or Koc.

and OMC: the higher theOMC is, the larger Kd and Koc are (Sanchez-Martin and Sanchez-Camazano, 1991;Somasundaram et al., 1991; Domagalski and Kuivila, 1993; Rodrfguez-Gonzalo et al., 1993; Arienzo et al., 1994; Sanchez-Camazano and Sanchez-Martin, 1994; Beltran et al., 1995; Baskaran et al., 1996; Mandal and Adhikari, 1997). The capacity of OMC to retain the pesticides varies depend on where the soil arederived. The molecular structure of OPs has an important influence on adsorption, because it determines the physical and chemical properties. Mandal and Adhikari (1997) determined Kd values for methyl parathion and fenitrothion on soil samples collected from different state agricultural farms in India. They observed that Kd values of methyl parathion are higher than those of fenitrothion for all the adsorbent-adsorbate interactions considered (Table 3). They explained that the presensce of the CH3 group instead of H in fenitrothion is causing steric hindrance and resulting in lower adsorption and lower Kd values. Their results also showed that the interaction of polar functional groups (P-O, P=S, NO2) as well as the conjugated ring structure of methyl parathion and fenitrothion with polar functional groups of organic matter and charged clay surfaces in soil favor higher adsorption. Beltran et al. (1995) studied the adsorption of fenitrothion, methidathion, and dimethoate on soil samples collected at depths of 0 to 20 cm and around 100 cm from an experimental citrus crop field (Table 3). Their data showed that the most strongly adsorbed pesticide is fenitrothion, followed by methidation and dimethoate. They also found that the Kd for dimethoate was not affected by the organic matter content of the soil. This can be explained by the higher polarity and water solubility of dimethoate. Rodfguez-Gonzalo et al. (1993) investigated the sorption of parathion and its oxidized metabolite paraoxon by natural montmorillonite in water. Larger Kd values for parathion than those for paraoxon showed a clear influence of the hydrophobic nature of the two pesticides on adsorption. Sanchez-Martin and Sanchez-Camazano (1991) studied the adsorption of methyl parathion, ethyl parathion, methyl paraoxon, and ethyl paraoxon by eight soils with a broad range of clay and organic matter content. They observed that phosphate (Table 2) adsorption is related to clay content, while organic matter governs the adsorption of thiophosphates (Table 2). Finally, Baskaran et al. (1996) studied the sorption of ionic and nonionic pesticides in soil. Their Kd values indicated that, in general, sorption of nonionic pesticides (e.g., Terbufos and Phorate) is greater than that of ionic pesticides (e.g., 2,4-D and atrazine).

Few studies have investigated the kinetics of OP adsorption in soils. Sujatha and Chacko (1992) studied the adsorption of malathion and methyl parathion to three different estuarine sediment types. They observed that the kinetics of pesticide adsorption follows a first-order pattern. Data from Baskaran et al. (1996) showed sorption to be a two-stage process with a short initial phase of rapid sorption, followed by an extended period of slower sorption. They concluded that the initial rapid sorption appears to be on the external surface of the sorbents and, as sorption proceeds, rates slow and sorption is by diffusion onto internal sites.

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IV. LABORATORY DEGRADATION STUDIES

A. Homogeneous Photodegradation

The quantum yields (QYs) for direct photolysis of 16 OPs and their phenolic products in aqueous solutions were determined (Wan et al., 1994). A good correlation between the QYs at 254 nm and those at 313 nm was obtained. A highly significant correlation between the QYs of the OPs and those of their phenolic products was also found (Wan et al., 1994). Wan and co-workers (1994) also investigated the relationship between the QYs and the OP molecular structure. QYs of for most OPs and their phenolic products were found to be higher at 254 nm than at 313 nm, with the exception of chlorpyrifos and chlorpyrifos-methyl (Wan et al., 1994). OPs with strongly electron-withdrawing groups attached to the aromatic rings had lower QYs when compared with those that had alkyl or chloro groups attached to the rings (Wan et al., 1994). The phenolic products have much higher rate constants than their parents due to their greater absorption of sunlight The degradation of fenitrothion, an OP, under environmental conditions was studied (Lacorte and Barcelo, 1994). Fenitrothion was applied in the irrigation ditches of the Ebre Delta in Spain at ~ 200 and 20 µg/L to eliminate the American crab. Fenitrothion levels and its transformation products (TPs) were recorded for 4 days after its application (Lacorte and Barcelo, 1994). The TPs were 3-methyl- 4-nitrophenol, fenitrooxon, and S-methyl isomer of fenitrothion (Lacorte and Barcelo, 1994). The concentration of fenitrothion decayed sharply in 2 h to less than 10% of the initial amount and reached a steady state within 10 h, while TPs were at a very low 0.01 µg/L level. The half-life of fenitrothion was 13 h, with a rate of 0.053 h–1 primarily via photolysis. The degradation of fenitrothion and the formation of TPs are closely related to environmental factors, such as wind (Lacorte and Barcelo, 1994). The overall Fenitrothion degradation is shown in Figure 5. In another study, Durand and co-workers (1994) studied the photodegradation of fenitrothion in a mixture of distilled water/methanol (5:1). For the identification of final products, fenitrooxon and carboxyfenitrothion were also irradiated under identical conditions (Durand et al., 1994). A total of 21 products of oxidation, isomerization, denitration, and solvolysis were identified.

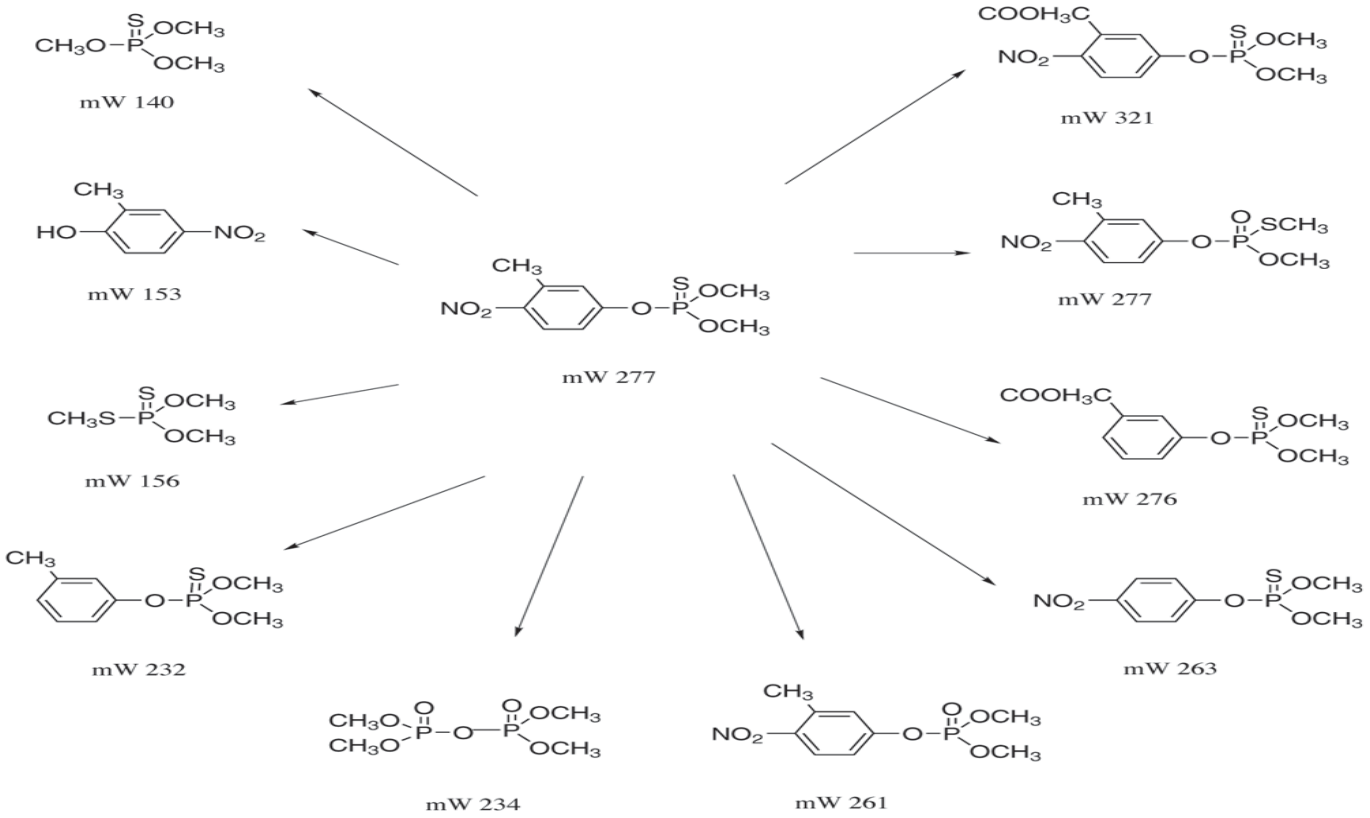

Fig. 5 : Fenithrothion Degradation

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41Sharma and Gupta (1994) studied the photolysis of Phorate as a thin film on a glass surface and in a solution of methanol-water (60:40) by UV light. The rate of disappearance of Phorate showed first order kinetics with a rate constant of 4.9×10–5s–1(Sharma and Gupta, 1994). The structures of the major photoproducts were characterized utilizing H-NMR and mass spectroscopy (Sharma and Gupta, 1994) and were found to be phorate sulfone, phorate sulfoxide, phorate oxon, and other more complex products.

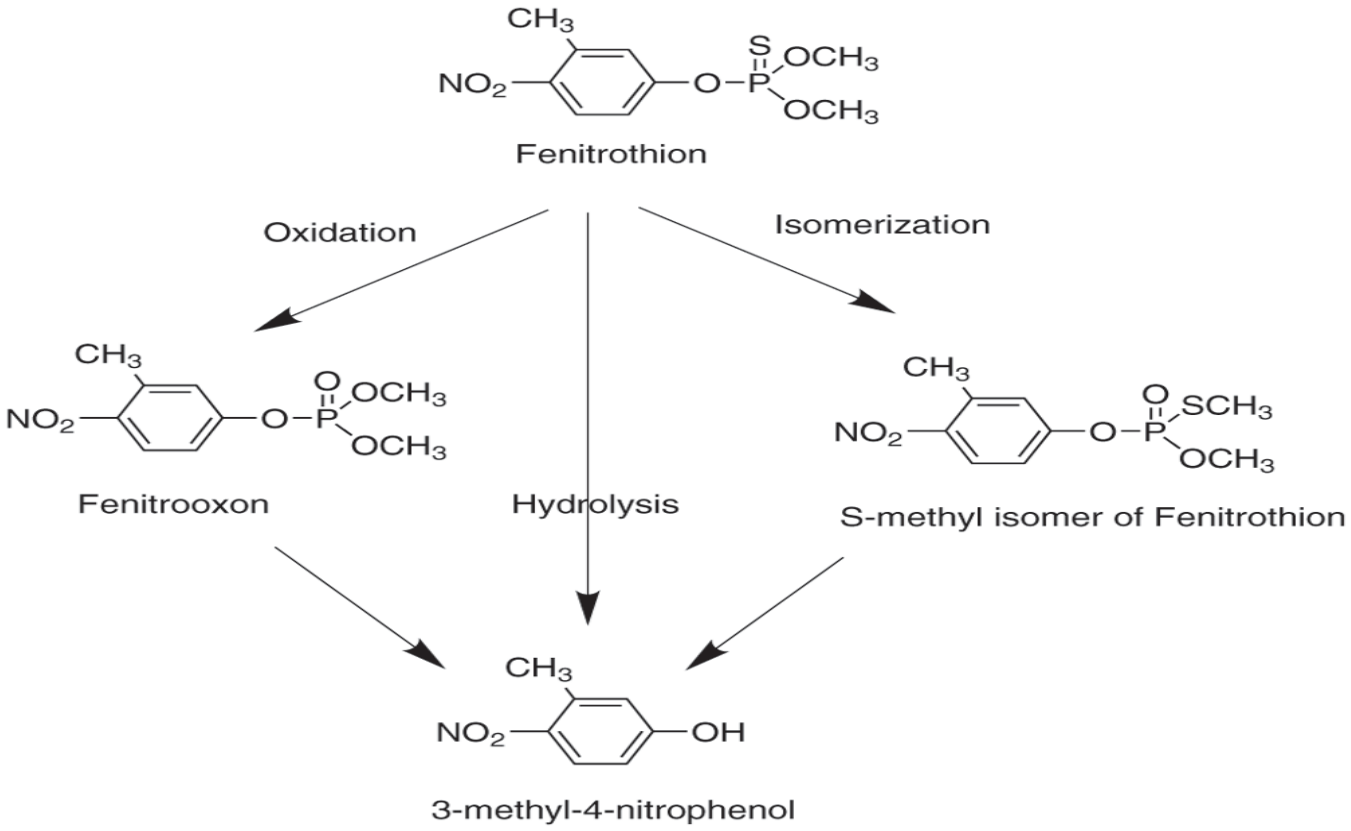

Fig. 6:Methyl-4-Nitrophenol

Kamiya and Nakamura (1995) studied the inclusion effects of several cyclodextrins (CyDs) on the photodegradation of parathion and paraoxon. CyDs are cyclic oligosaccharides produced by microbially induced breakdown of starch and have doughnut-shaped cavities that are able to form inclusion complexes with many chemicals (Kamiya and Nakamura, 1995). The inclusion effect of beta-CyD waparaoxon. Basic properties of the CyD inclusion effects were explained in terms of the difference in the degree of proximity between the catalytic sites of the CyD host cavities and the reaction centers of the OP guests (Kamiya and Nakamura, 1995). The inclusion effect of β-CyD is environmentally notable, because it inhibits the photolysis of parathion under sunlight and promotes the photolysis of paraoxon, which a more toxic oxidation product of parathion (Kamiya and Nakamura, 1995).

B. Heterogeneous Photodegradation

Doong and Chang (1997) investigated the photooxidation of OPs such as methamidophos, phorate, malathion, diazinon, and EPN in UV-TiO2, UV-H2O2 and UV-TiO2-H2O2 systems. Although it is unlikely that these combinations are often available in ambient waters, they can provide a useful framework and a reference point for the importance of iron oxide catalyzed photodegradation in sunlit surface waters. Apparent first-order rate constants were used to describe the degradation. Batch results demonstrate that the degradation of OPs increased in the order of phorate > methamidophos > malathion ~ diazinon > EPN. The photooxidation of methamidophos and phorate was primarily due to direct photolysis (Doong and Chang, 1997), while TiO2 promoted

the degradation of diazinon,malathion, and EPN. H2O2 was found as an intermediate in UV-TiO2 system (Doong and Chang, 1997). Longer irradiation decreased H2O2 due to the high electron-hole recombination rate on TiO2 surface. The addition of H2O2 is more effective on the photooxidation of OPs than the addition of TiO2 (Doong and Chang, 1997). It is important to realize that H2O2 has also been detected in sunlit surface waters around the world (Zika et al., 1985; Moffett and Zafiriou, 1990; Moffett and Zafiriou, 1993). Thus, processes that can produce H2O2 in sunlit waters may also affect the loss rates of OPs.

The photocatalytic degradation of OPs, such as methamidophos, malathion, diazinon, phorate, and EPN, was studied using UV radiation in combination with H2O2 (Doong and Chang, 1998). Iron species (e.g., Fe(0), Fe2+) can enhance the degradation of OPs (Doong and Chang, 1998). A nearly complete removal of OPs was observed when the system was amended with iron. The degradation of OPs in the UV/Fe/H2O2 system was more effective than that of OPs in the UV/H2O2 system. The Fe2+ , which was produced from the surface oxidation of Fe(0), reached a maximum of 21.6 μM at 160 min and rapidly converted to Fe3+ within 25 min (Doong and Chang, 1998). The degradation was pseudo-first-order with rate constants from 0.004 to 0.026 min–1. The order of reactivity was phorate > methamidophos > EPN > diazinon > malathion (Doong and Chang, 1998). The pesticides carbofuran, diazinon, isoproturon, metamitron, terbuthylazine, and pendimethalin were irradiated with UV light of different wavelengths in water or water/soil suspensions (Scheunert et al., 1993; Mansour et al., 1997). Compared with pure distilled water, photodegradation was increased in the presence of TiO2, H2O2, or ozone, or by using river or lake water (Scheunert et al., 1993; Mansour et al., 1997). In water/soil suspensions, diazinon was converted to its isomer: isodiazinon (Figure 6) as well as other unidentified products (Scheunert et al., 1993; Mansour et al., 1997).

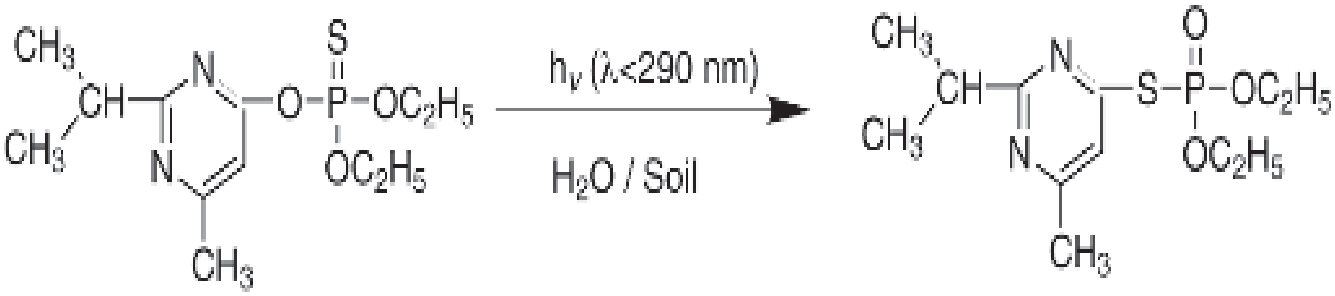

Fig. 7: Conversion of Diazinon

Heterogeneous photodegradation of OPs can occur in natural waters due to the presence of semiconductor solids such as iron oxides and oxidants such as hydrogen peroxide. The key question is how important is heterogeneous photodegradation of OPs in the overall degradation scheme. First of all, the photodegradation is limited to the surface waters receiving sufficient sunlight and containing heterogeneous surfaces, secondly other substrates (present at higher concentrations when compared with OPs) may adsorb to the surfaces of semiconducting solids and thus be preferentially photodegraded. No studies in ambient waters have been carried out in order to pinpoint the importance of heterogeneous photodegradation pathways, although in controlled laboratory studies the degradation of OPs occurs quite rapidly.

C. Sensitized Photodegradation

Barcelo and co-workers (1993) studied the aqueous photodegradation of chlorpyrifos, fenamiphos, and vamidothion. Acetone (5%) was added as a photosensitizer in the photolysis of vamidothion. A suntest apparatus with a Xe arc lamp-simulating radiation of ambient sunlight was utilized (Barcelo et al., 1993). With an array of advanced spectroscopic tools, 3,5,6-trichloro-2-pyridinol, fenamiphos sulfoxide, and vamidothion sulfoxide were found to be the major products of chlorpyrifos, fenamiphos, and vamidothion, respectively (Barcelo et al., 1993).

With a series of substituted anilines, a series of substituted phenols as well as diazinon and tetrabromobisphenol-A, alterations of short-term acute toxicity to the water flea Daphnia magna were studied in the presence of dissolved humic material (DHM) and sunlight (Steinberg et al., 1992). Toxicity decreased significantly with diazinon, 4-chloroaniline, and 4-nitrophenol (Steinberg et al., 1992). As demonstrated for diazinon in the presence of DHM and light, the chemical speciation of this chemical is altered and products are formed probably via photoactive species of DHM (Steinberg et al., 1992). Alterations in acute toxicity of species may be attributed to adsorption to DHM as well as to the

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photoactive species mediated formation of products having toxicity different from that of the parent OP (Steinberg et al., 1992).

Kamiya and Kameyama (1998) studied the effects of humic substances on the degradation of OPs (Kamiya and Kameyama, 1998). The degradation was enhanced depending on the radical generation abilities of humics (Kamiya and Kameyama, 1998). Also, the degree of the sensitization effects of humic acids tended to increase with a decrease in the inherent direct photolysis rates of OPs in the humin-less system (Kamiya and Kameyama, 1998).

In conclusion, just like the heterogeneous photodegradation of OPs, the sensitized photodegradation has been shown to be important in laboratory studies. Factors that will determine its importance in natural waters include sunlight intensity, the sources and the concentrations of humic and fulvic acids, the concentration of nitrate (a common source of OH radicals) in natural waters, and the presence of other compounds in water (e.g., carbonate and bicarbonate ions), which can scavenge the photoactive species of DHM or OH radicals. Finally, as mentioned before, certain OPs photolyze quite readily via a direct absorption of sunlight and would be less likely to undergo significant sensitized photodegradation.

D. Photodegradation Products

During photodegradation of OPs, several types of products are typically formed. For instance, during photodegradation of Fenitrothion (Figures 4 and 5), the oxidation of P=S to P=O was observed, in addition to the formation of S-methyl isomer of Fenitrothion (Figures 4 and 5). A cleavage of the P-O bond (similar to what is expected during hydrolysis) was also observed with the concomitant production of 3-methyl-4-nitrophenol. Some of the initial photodegradation products may be considered to be only short-lived intermediates as can be seen in Figure 5. Mansour et al. (1997) studied the photodegradation of Diazinon under UV irradiation in a water/ soil suspension and found Diazinon's isomer, isodiazinon (Figure 6), as one of the products. This product is again formed by internal rearrangement, similar to the case of the aforementioned S-methyl isomer of Fenitrothion. In photodegradation studies of several OPs, Mak and Hung (1992) found several simple ionic products including PO43–, SO42–, NH3, NO3–, and Cl–. These products can be considered to be the final, stable products formed via several short-lived intermediates. Finally, it is important to realize that depending on the hydrolytic half-life of the OP, it is entirely plausible that both photodegradation and hydrolysis occur simultaneously. Therefore, the product identities obtained in many "photodegradation studies" may not be due to photodegradation, but also due to hydrolysis.

E. Hydrolysis

Muhlmann and Schrader (1957) studied the hydrolysis of Demeton-S, DemetonS sulfone, and Demeton-S sulfoxide. They found that Demeton-S hydrolysis was not dependent on pH, while for Demeton-S sulfone and Demeton-S sulfoxide, the pH had a strong effect. The hydrolysis half-lives at 70°C and pH of 7 were 10 days for Demeton-S, 30 days for Demeton-S sulfoxide, and 1 day for Demeton-S sulfone (Muhlmann and Schrader, 1957). They speculate that Demeton-S hydrolyzes by an SNi mechanism, while the other two compounds cannot due to their molecular structure and may instead undergo β-elimination (Muhlmann and Schrader, 1957). However, no product identification was carried out; therefore, the proposed mechanisms remain speculative.

Acid-catalyzed hydrolysis of Malathion is too slow to be important under most environmental conditions (Wolfe et al., 1977). However, alkaline hydrolysis is fast enough to be a very important degradation pathway in the aquatic environment. The second-order alkaline hydrolysis rate constant of Malathion at 27° C is 5.5M–1s–1 (Wolfe et al., 1977). At pH of 8.5, the above will result in a hydrolytic halflife of 11 h. The products of alkaline hydrolysis are temperature dependent. The products of Malathion hydrolysis (i.e., Malathion monoacids and Malathion diacid) hydrolyze at much lower rates (i.e., with k values between 2 × 10–2 and 3 ×10–1M–1s–1) (Wolfe et al., 1977).

Abiotic hydrolysis of simazine, atrazine, diazinon, methylparathion, and chlorpyrifos was studied in three natural waters and buffered Milli-Q water (Noblet et al., 1996). The rates for diazinon and methylparathion were similar in all waters (Noblet et al., 1996), while chlorpyrifos exhibited ~ 32% decrease in rate in the presence of a high concentration of dissolved organic matter (DOM) (34.5 mg/L DOC) (Noblet et al., 1996). The activation energies are larger, and thus the predicted hydrolysis rates are much slower (Table 4) than those previously reported (Noblet et al., 1996). The results suggest that uncatalyzed abiotic hydrolysis is quite slow for these OPs (Table 4) at the ambient temperatures and pH values and confirm the need for a greater understanding of the relative influence of DOM, catalysis, and biodegradation on the fate of OPs (Noblet et al., 1996).

Michel and co-workers (1997) investigated the fate of diazinon, the most widely used lawn care pesticide, during the composting of leaves and grass. The yard trimmings were amended with [Delta-2-C-14] labeled diazinon (10 mg kg –1 wet wt.) and composted in a laboratory-scale compost system for 54 days (Michel et al., 1997). During composting, 11% of the C-14-diazinon was mineralized to (CO2)-C-14 (Michel et al., 1997). Initially, most of the added C-14-diazinon was ether extractable (83%), but Inclusion effects of beta-cyclodextrin

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(beta-CyD) and its methyl derivatives on the hydrolysis of OPs, such as parathion, methyl parathion, and fenitrothion, were investigated in a humin-rich alkaline medium (Kamiya et al., 1995). The inclusion effects of beta-CyDs were characterized by the multiple linear regression analysis using as descriptors the inclusion depth and orientation of OPs, the dissociation constant of CyD-OP inclusion complexes and the degree of the methylation of the catalytically active secondary hydroxyl groups of the CyDs' host cavity (Kamiya et al., 1995). The inhibition of hydrolysis caused by beta-CyD for both parathion and methyl-parathion is significant, while for fenitrothion the inhibition is smaller. The inhibition effect of beta-CyD is believed to stem from the protection of the pesticide reactive site (i.e., the ester group) from interaction with OH–.

Pesticide	k	half life	Reference	Notes
Fenitrothion	0.036 hr^{-1}	19 hrs	Oubina et al., 1996	by ELISA method
Fenitrothion	0.063 hr^{-1}	11 hrs	Oubina et al., 1996	by HPLC/DAD
P-O bonds in 5 OPs	67 - 5000 s^{-1}	0.010 - 0.00014 s	Lai et al., 1995	Acephate, Azinophos-ethyl, Demeton-S, Malathion and Phosalone by OPH (Organophosphorus Hydrolase)
P-F bonds in 5 OPs	0.01 - 500 s^{-1}	69 - 0.0014 s	Lai et al., 1995	Acephate, Azinophos-ethyl, Demeton-S, Malathion and Phosalone by OPH (Organophosphorus Hydrolase)
P-S bonds in 5 OPs	0.0067 - 167 s^{-1}	103 - 0.0042 s	Lai et al., 1995	Acephate, Azinophos-ethyl, Demeton-S, Malathion and Phosalone by OPH (Organophosphorus Hydrolase)
Chlorpyrifos	0.002 - 0.0075 day^{-1}	347 - 92 days	Racke et al., 1996	in acidic soils
Chlorpyrifos	0.0035 - 0.063 day^{-1}	198 - 11 days	Racke et al., 1996	in alkaline soils
Chlorpyrifos		5 - 141 days	Racke et al., 1996	aerobic soil degradation
Chlorpyrifos		≤3 week	Racke et al., 1996	dry soils
Chlorpyrifos		1 - 2 weeks	Racke et al., 1996	on soil surfaces
Chlorpyrifos		1 - 2 months	Racke et al., 1996	soil profile
Chlorpyrifos/copper(II)	43(±3) $mol^{-1} h^{-1}$		Blanchet & St-George, 1982	at 25 C (depends on conc. of copper)
Chlorpyrifos/copper(II)	21(±2) $mol^{-1} h^{-1}$		Blanchet & St-George, 1982	at 15 C (depends on conc. of copper)
Chlorpyrifos/copper(II)	10.5(±5) $mol^{-1} h^{-1}$		Blanchet & St-George, 1982	at 35 C (depends on conc. of copper)
Chlorpyrifos-methyl thionate	1.4 x 10-5 min^{-1}	825 hours	Smolen and Stone, 1998	homogeneous hydrolysis at pH of 7
Chlorpyrifos-methyl thionate	1.6 x 10-5 min^{-1}	722 hours	Smolen and Stone, 1998	hydrolysis with 10 g/L TiO2 at pH of 7
Chlorpyrifos-methyl thionate	1.7 x 10-5 min^{-1}	680 hours	Smolen and Stone, 1998	hydrolysis with 10 g/L Al2O3 at pH of 7
Chlorpyrifos-methyl oxonate	4 x 10-5 min^{-1}	289 hours	Smolen and Stone, 1998	homogeneous hydrolysis at pH of 7
Chlorpyrifos-methyl oxonate	2.8 x 10-4 min^{-1}	41 hours	Smolen and Stone, 1998	hydrolysis with 10 g/L TiO2 at pH of 7
Chlorpyrifos-methyl oxonate	3.4 x 10-4 min^{-1}	34 hours	Smolen and Stone, 1998	hydrolysis with 10 g/L Al2O3 at pH of 7
Methamidophos	0.024 min^{-1}	28.9 min	Doong & Chang, 1998	photodecomposition with a 100 W lamp
Methamidophos	0.115 min^{-1}	6.1 min	Doong & Chang, 1998	photodecomposition with a 450 W lamp
Malathion	0.011 min^{-1}	63 min	Doong & Chang, 1998	photodecomposition with a 100 W lamp
Malathion	0.057 min^{-1}	12.2 min	Doong & Chang, 1998	photodecomposition with a 450 W lamp
Diazinon	0.012 min^{-1}	57.8 min	Doong & Chang, 1998	photodecomposition with a 100 W lamp
Diazinon	0.054 min^{-1}	12.8 min	Doong & Chang, 1998	photodecomposition with a 450 W lamp
Phorate	0.039 min^{-1}	17.8 min	Doong & Chang, 1998	photodecomposition with a 100 W lamp
Phorate	0.099 min^{-1}	7.0 min	Doong & Chang, 1998	photodecomposition with a 450 W lamp
EPN	0.012 min^{-1}	57.8 min	Doong & Chang, 1998	photodecomposition with a 100 W lamp
EPN	0.053 min^{-1}	13.1 min	Doong & Chang, 1998	photodecomposition with a 450 W lamp
Methamidophos	0.051 min^{-1}	13.6 min	Doong & Chang, 1997	UV-H_2O_2 system with a 100 W lamp
Methamidophos	0.054 min^{-1}	12.8 min	Doong & Chang, 1997	UV-H_2O_2-TiO_2 system with a 100 W lamp
Malathion	0.017 min^{-1}	40.8 min	Doong & Chang, 1997	UV-H_2O_2 system with a 100 W lamp
Malathion	0.026 min^{-1}	26.7 min	Doong & Chang, 1997	UV-H_2O_2-TiO_2 system with a 100 W lamp

Diazinon	0.024 min^{-1}	28.9 min	Doong & Chang, 1997	UV-H_2O_2 system with a 100 W lamp
Diazinon	0.025 min^{-1}	27.7 min	Doong & Chang, 1997	UV-H_2O_2-TiO_2 system with a 100 W lamp
Phorate	0.054 min^{-1}	12.8 min	Doong & Chang, 1997	UV-H_2O_2 system with a 100 W lamp
Phorate	0.055 min^{-1}	12.6 min	Doong & Chang, 1997	UV-H_2O_2-TiO_2 system with a 100 W lamp
EPN	0.008 min^{-1}	86.6 min	Doong & Chang, 1997	UV-H_2O_2 system with a 100 W lamp
EPN	0.011 min^{-1}	63 min	Doong & Chang, 1997	UV-H_2O_2-TiO_2 system with a 100 W lamp
Malathion		18.5 days	Wang & Hoffman, 1991	pH 6, 28 degree C, sterile water
Malathion		17.4 days	Wang & Hoffman, 1991	pH 6, 28 degree C, non-sterile water
Malathion		8.96 days	Wang & Hoffman, 1991	pH 7, 28 degree C, sterile water
Malathion		8.78 days	Wang & Hoffman, 1991	pH 7, 28 degree C, non-sterile water
Malathion		1.96 days	Wang & Hoffman, 1991	pH 8.16, 28 degree C, sterile water
Malathion		1.65 days	Wang & Hoffman, 1991	pH 8.16, 28 degree C, non-sterile water
Parathion		46.5 days	Wang & Hoffman, 1991	pH 6, 28 degree C, sterile water
Parathion		12.6 days	Wang & Hoffman, 1991	pH 6, 28 degree C, non-sterile water
Parathion		37.8 days	Wang & Hoffman, 1991	pH 7, 28 degree C, sterile water
Parathion		10.3 days	Wang & Hoffman, 1991	pH 7, 28 degree C, non-sterile water
Parathion		30.8 days	Wang & Hoffman, 1991	pH 8.16, 28 degree C, sterile water
Parathion		7.84 days	Wang & Hoffman, 1991	pH 8.16, 28 degree C, non-sterile water
Diazinon	0.041 d^{-1}	17 days	Noblet et al., 1996	hydrolysis at 40 C and pH of 8 in Milli-Q water
Methyl parathion	0.068 d^{-1}	10 days	Noblet et al., 1996	hydrolysis at 40 C and pH of 8 in Milli-Q water
Chlorpyrifos	0.062 d^{-1}	11 days	Noblet et al., 1996	hydrolysis at 40 C and pH of 8 in Milli-Q water
Diazinon	0.036 d^{-1}	19 days	Noblet et al., 1996	hydrolysis at 40 C and pH of 8 in natural waters
Methyl parathion	0.054 to 0.058 d^{-1}	12-13 days	Noblet et al., 1996	hydrolysis at 40 C and pH of 8 in natural waters
Chlorpyrifos	0.042 to 0.057 d^{-1}	12-17 days	Noblet et al., 1996	hydrolysis at 40 C and pH of 8 in natural waters
Parathion		170 days	Lartiges & Garrigues, 1995	pH 6.1, 20 degree C
Parathion		200 days	Lartiges & Garrigues, 1995	pH 7.8, room temp, estuarine water
Chlorpyrifos		120 days	Lartiges & Garrigues, 1995	pH 6.1, 20 C
Azinphos-methyl		11 days	Lartiges & Garrigues, 1995	seawater at pH 8.1 and 22 C
Azinphos-ethyl		11 days	Lartiges & Garrigues, 1995	seawater at pH 8.1 and 22 C
bromophos		2 days	Lartiges & Garrigues, 1995	seawater at pH 8.1 and 22 C
coumaphos		8 days	Lartiges & Garrigues, 1995	seawater at pH 8.1 and 22 C
diazinon		47 days	Lartiges & Garrigues, 1995	seawater at pH 8.1 and 22 C
dimethoate		74 days	Lartiges & Garrigues, 1995	seawater at pH 8.1 and 22 C
fenitrothion		3 days	Lartiges & Garrigues, 1995	seawater at pH 8.1 and 22 C
fenthion		5 days	Lartiges & Garrigues, 1995	seawater at pH 8.1 and 22 C
isofenphos		19 days	Lartiges & Garrigues, 1995	seawater at pH 8.1 and 22 C
malathion		14 days	Lartiges & Garrigues, 1995	seawater at pH 8.1 and 22 C
ethyl parathion		18 days	Lartiges & Garrigues, 1995	seawater at pH 8.1 and 22 C

methyl parathion	34 days	Lartiges & Garrigues, 1995	seawater at pH 8.1 and 22 C
phosmet	very fast	Lartiges & Garrigues, 1995	seawater at pH 8.1 and 22 C
triazophos	67 days	Lartiges & Garrigues, 1995	seawater at pH 8.1 and 22 C
chlormephos	< 34 days	Lartiges & Garrigues, 1995	seawater at pH 8.1 and 22 C
dichlorvos	< 81 days	Lartiges & Garrigues, 1995	seawater at pH 8.1 and 22 C
			the conditions below for November
Disulfoton	170 days	Warmer et al., 1989	by abiotic hydrolysis (Rhine River)
Thiometon	230 days	Warmer et al., 1989	by abiotic hydrolysis (Rhine River)
Disulfoton	1000 days	Warmer et al., 1989	by photochemical transformation (Rhine River)
Thiometon	1000 days	Warmer et al., 1989	by photochemical transformation (Rhine River)
Disulfoton	7-41 days	Warmer et al., 1989	by primary biodegradation (Rhine River)
Thiometon	5-29 days	Warmer et al., 1989	by primary biodegradation (Rhine River)
		Warmer et al., 1989	the conditions below for Summer
Disulfoton	62 days	Warmer et al., 1989	by abiotic hydrolysis (Rhine River)
Thiometon	73 days	Warmer et al., 1989	by abiotic hydrolysis (Rhine River)
Disulfoton	100 days	Warmer et al., 1989	by photochemical transformation (Rhine River)
Thiometon	100 days	Warmer et al., 1989	by photochemical transformation (Rhine River)
Disulfoton	4-28 days	Warmer et al., 1989	by primary biodegradation (Rhine River)
Thiometon	3-20 days	Warmer et al., 1989	by primary biodegradation (Rhine River)

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F. Enzymatic Hydrolysis

Role of enzymes Enzymes take part in key role in Biodegradation of any xenobiotics and are able to renovate pollutants to a noticeable rate and have prospective to restore polluted environment [18]. Enzymes are also involved in the degradation of pesticide compounds, both in the target organism, through intrinsic detoxification mechanisms and evolved metabolic resistance, and in the wider environment, via biodegradation by soil and water microorganisms. P. putida theoretical oxygen demand (TOD) enzyme is a representative of a much larger family of enzymes with application in the biocatalysis of environmentally relevant reactions. Fungal enzymes especially, oxidoreductases, laccase and peroxidases have prominent application in removal of polyaromatic hydrocarbons (PAHs) contaminants either in fresh, marine water or terrestrial [19]. The enzymes play a key role in the biodegradation of any xenobiotics compounds.

ENZYME	SOURCE	Degradation
Aryl acylamidase	Bacilus sphaericus	Herbicides and fungicides
Organophosphorous hydrolase	B.diminuta and Flavobacterium sp	Xenobiotic compounds
Organophosphorous acid hydrolase	Alteromonas undina and Alteromonas haloplanktis	Xenobiotic compounds

Enzymes that are able to hydrolyze many OPs are known from a large number of aquatic species (i.e., from fish to bacteria) (Landis, 1991). These enzymes are currently called the organophosphorus acid anhydrases, although they have also been referred to as A esterase, DFPase, phosphotriesterase, somanase, parathion hydrolase, and paraoxonase (Landis, 1991). The natural substrates for the OPA anhydrases are not known. However, these enzymes are capable of hydrolyzing a wide variety of organophosphorus acetylcholinesterase inhibitors (Landis, 1991). In aquatic species, the enzymes have been identified and partially characterized from squid, fish, invertebrates such as Rangia cuneata, the protist Tetrahymena thermophila, and various thermophilic and other bacteria (Landis, 1991). The enzymes have evolved in response to the metabolism of naturally occurring organophosphates and halogenated organic compounds (Landis, 1991).

An enzyme derived from an overproducing strain of Pseudomonas diminuta, called parathion hydrolase (PH), carries out hydrolysis of the phosphate ester bond in the OP molecule, resulting in an as much as 100-fold decrease in toxicity (Havens and Rase, 1991). Partially purified PH was covalently immobilized after several rigid supports and retained a large degree of its activity and subsequently was used to degrade a variety of OPs (Havens and Rase, 1991).

A recombinant baculovirus, Autographa californica nuclear polyhedrosis vi-rus (AcNPV), was utilized to express the opd (organophosphate-degrading) gene from Pseudomonas diminuta in insect tissue-culture cells (Sf9) of the fall army-worm (Spodoptera frugiperda) (Dave et al., 1994). The broad-spectrum organo-phosphate hydrolase (EC 3.1.8.1) encoded by this gene is a member of a class of enzymes [organophosphate (OP) anhydrolases] that include parathion hydrolyses.di isopropyl-flurophosphates,somanasaes, and op phosphotriesterases. (Dave et al., 1994). This particular enzyme possesses the ability to hydrolyze paraoxon (P-O bond), DFP, sarin (P-F bond), VX (P-S bond), and tabun (P-CN bond), as well as a number of other widely used OPs (Dave et al., 1994).

Of 13 Rhizobium and Bradyrhizobium strains investigated for the production of cellular and extracellular phosphodiesterase and phosphotriesterase, all were found to produce both enzymes (Abdalla, 1994). Phosphodiesterase was produced at a much higher level than phosphotriesterase (Abdalla, 1994).

Rhizobium meliloti TAL 1373 was the most productive. The extracellular enzymes were activated by inclusion of Ca2+ or Mg2+ in the assay mixture. The enzymes were inhibited by Zn 2+, but not greatly affected by Cu2+, Co2+, or Mn2+ (Abdalla, 1994). Both hydrolases were inhibited by dithiothreitol but not by thiol-directed inhibitors,indicating that sulfhydryl groups are not directly involved in catalysis (Abdalla,1994). The enzymes have the ability to hydrolyze some OPs, thus Rhizobium AndBradyrhizobium strains play an important role in OP degradation (Abdalla, 1994).

Pseudomonas putida utilized methyl parathion as the sole C and/or P source (Rani and Lalithakumari, 1994). The bacterium elaborated the enzyme organo- phosphorus acid anhydrase, which hydrolyzed methyl parathion to p-nitrophenol. P-Nitrophenol was further degraded to hydroquinone and 1,2,4- benzenetriol, which was in turn

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cleaved by benzenetriol oxygenase to maleyl acetate (Rani and Lalithakumari, 1994).

OPH is capable of hydrolyzing the P-X bond of various organophosphorus compounds at quite different catalytic rates: P-O bonds (k cat= 67-5000 s–1), P-Fbonds (kcat= 0.01-500 s–1), and P-S bondskcat= 0.0067 to 167 s–1) (Lai et al.1995). P-S bond cleavage was readily demonstrated by quantifying the released free thiol groups using 5,5'-dithio-bis-2-nitrobenzoic acid or by monitoring an upfield shift of approximately 31 ppm by P-31 NMR (Lai et al., 1995).

A decrease in the toxicity of hydrolyzed products was demonstrated by directly quantifying the loss of inhibition of acetylcholinesterase activity (Lai et al., 1995).

Phosphorothiolates (e.g., demeton-S) provided noncompetitive inhibition for paraoxon (a P-O triester) hydrolysis; thus, the binding of the two classes of OPs was not identical (Lai et al., 1995).

Several OP-degrading bacteria were isolated from test turf green soil using clear zones formed around their colonies on plates supplemented with isoxathion (Ohshiro et al., 1996). The degrading activity of the isolates for isoxathion was tested by incubation in liquid cultures and evaluated by GC (Ohshiro et al., 1996). Strain B-5 exhibited the highest isoxathion-degrading ability in the isolates and it was identified as an Arthrobacter sp. A high concentration of nutrients in the media affected the isoxathion-degrading activity of strain B-5. The bacterium could not utilize isoxathion as a sole source of C and P (Ohshiro et al., 1996). The degradation products of isoxathion were 3-hydroxy-5- phenylisoxazole and diethylthiophosphoric acid, suggesting that the strain hydrolyzes the heterocycle ester bond in isoxathion (Ohshiro et al., 1996). Arthrobacter sp. strain B-5 also hydrolyzed other OPs: diazinon, parathion, EPN,fenitrothion, isofenphos, chlorpyrifos, and ethoprophos (Ohshiro et al., 1996). Isofenphos was affected most by the hydrolytic activity of the bacterium (com- pletely removed 10 mg/l within 1 h of incubation) (Ohshiro et al., 1996).

OP hydrolase has high efficiency in hydrolysis of different phosphotriester and phosphothiolester pesticides (P-O bond) such as paraoxon (kcat> 3800 s-1) and coumaphos (kcat= 800 s-1) or phosphonate (P-F) neurotoxins such as DFP (kcat =350 s-1) and the chemical warfare agent sarin (kcat= 56 s-1) (Kolakowski et al.,1997) (Table 4).

In contrast, the enzyme has much lower catalytic capabilities for phosphonothioates, such as acephate (kcat= 2.8 s-1) or the warfare agent VX (kcat= 0.3 s-1) (Kolakowski et al., 1997). The P-S bond hydrolysis was determined by detecting free -SH groups and the cleavage of the P-S bond by 31P-NMR (Kolakowski et al., 1997).

Organophosphorus hydrolase (OPH) was displayed and anchored onto the surface of Escherichia coliusing an Lpp-OmpA fusion system (Richins et al., 1997). The production of the fusion proteins in membrane fractions was verified by immunoblotting with OmpA antisera. Inclusion of the organophosphorus hydrolase signal sequence was necessary for achieving enzymatic activity on the surface. More than 80% of the OPH activity was located on the cell surface as determined by protease accessibility experiments (Richins et al., 1997). Whole cells expressing OPH on the cell surface degraded parathion and paraoxon very effectively without any diffusional limitation, resulting in sevenfold higher rates of parathion degradation compared with whole cells with similar levels of intracellular OPH (Richins et al., 1997).

An improved whole-cell technology for degrading organophosphates was developed recently based on genetically engineered Escherichia coli with organophosphorus hydrolase anchored on the surface (Mulchandani et al., 1999. An improved whole-cell technology for degrading organophosphates was developed recently based on genetically engineered Escherichia coli with organophosphorus hydrolase anchored on the surface (Mulchandani et al., 1999).

Mulchandani et al. (1999) report the immobilization of these novel biocatalysts on nonwoven polypropylene fabric and their applications in detoxifying contaminated wastewaters. The best cell loading (256 mg cell dry weight/g of support or 50 mg cell dry weight/cm(2) of support), and subsequent hydrolysis of organophosphate nerve agents were achieved by immobilizing nongrowing cells in a pH 8, 150 mM citrate-phosphate buffer supplemented with 1 mM Co2+for 48 h via simple adsorption, followed by organophosphate hydrolysis in a pH 8, 50 mMcitrate-phosphate buffer supplemented with 0.05 mM Co2+and 20%methanol at 37 degrees C (Mulchandani et al., 1999). In batch operations, the immobilized cells degraded 100% of 0.8 mM paraoxon, a model organophosphate, in approximately 100 min, at a specific rate of 0.160 mM min(-1) m(celldry wt)(-1). The immobilized cells retained almost 100% activity during the initial six repeated cycles and close to 90% activity even after 12 repeated cycles, extending over a period of 19 days without any nutrient addition (Mulchandani et al., 1999). Besides paraoxon, other commonly used organophosphates, such as diazinon, coumaphos, and methylparathion were hydrolyzed efficiently (Mulchandani et al., 1999).

Enzymatically mediated hydrolysis is clearly an important and rapid degradation pathway for many OPs. It can be considered a catalytic process whereby the enzyme acts as a catalyst. The

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mechanism of enzymatic hydrolysis has not been thoroughly investigated, although it is likely that it is similar to hydroxide ion induced SN2 abiotic hydrolysis. Enzymatic hydrolysis may also result in somewhat different products compared with abiotic hydrolysis. An example of this is the ease of P-S cleavage for many OPs as observed by Lai et al. (1995), while Hong et al. (2000) did not observe the cleavage of the P-S bond in the case of Phorate, although it should occur readily based on thermodynamic considerations. The importance of these pathways to the overall OP fate is unknown, although Wanner et al. (1989) found that "biotransformation" was one of the most important processes for Disulfoton and Thiometon transformation in the Rhine river. The main question is whether the "biotransformation" as described by Wanner et al. (1989) was enzymatic hydrolysis or biotic oxidation (vide infra). Finally, it is not clear how ubiquitous OPH is in most natural waters and thus how important its role is in the overall OP fate.

G. Metal Ion Catalyzed Hydrolysis

Wan and co-workers (1994) investigated the catalyzed hydrolysis of some Opsby Hg(II) ion. The presence of HgCl2at 20 ppm increased the initial hydrolysis rates of malathion, fenitrothion, fenthion, and parathion-methyl in a pH 5.5 buffer by two to three orders of magnitude, while Hg(II) ion had little effect on dichlorvos hydrolysis. The hydrolysis was found to be first order with respect to both the mercury(II) ion and the OP (Wan et al., 1994). The main hydrolysis product was 3-methyl-4-nitrophenol for fenitrothion, and 4-nitrophenol for parathion-methyl. The proposed scheme involves the formation of a 1:1 complex, followed by a very slow regeneration of Hg(II) from it (Wan et al., 1994).

The divalent metal ion-catalyzed hydrolysis of thionate (P=S) and oxonate (P=O) OPs has been examined with three proposed mechanisms: (1) metal ion coordination of the thionate sulfur or oxonate oxygen to enhance the electrophilicity of P; (2) metal ion coordination and induced deprotonation of H2 O to create areactive nucleophile; and (3) metal ion coordination of the leaving group to facilitate its leaving (Smolen and Stone, 1997). The effect of Co(II), Ni(II), Cu(II), Zn(II) and Pb(II), each at 1 mM, was examined. These metal ions were selected for their ability to bind with organic ligands and inorganic nucleophiles (Smolen and Stone, 1997), as well as their use in earlier studies (Mortland and Raman, 1967).

Pb(II) nearly matched Cu(II) as a catalyst for oxonate esters, but is a less effective catalyst for thionate esters. Catalysis by Co(II), Ni(II), and Zn(II) was found to be negligible (Smolen and Stone, 1997). Product analysis indicates that metal catalysis in some cases shifts hydrolysis from alkyl carbon-centered to P-centered pathways (Smolen and Stone, 1997).

Earlier studies on metal-promoted hydrolysis (Wan et al., 1994) have reported overall rate constants simply as a function of the total metal concentration (Zeinali and Torrents, 1998). There are three advantages in reporting the relative importance of the different species: (1) results can be extrapolated from one situation to another, (2) rates can be predicted for specific conditions, and (3) a better understanding of the catalysis mechanism can be obtained. In a study by Zeinali and Torrents (1998), Hg-promoted hydrolysis of an OP, parathion-methyl (Table 2) was studied as a function of Hg(II) speciation (Zeinali and Torrents, 1998). The observed rate of hydrolysis was a function of specific Hg species rather than of the total Hgaq (Zeinali and Torrents, 1998). A pH-dependent kinetic expression was developed: kobs = αHg2+k1+ αHgOH+k2+ αHgOH2k3. In the above equation, ki= KiKir, with Ki representing the Hg:OP equilibrium constant, ki the rate constantfor Hg:OP hydrolysis for the different Hg(II) species, and α is the fraction of thetotal Hg(II) present as specific species, provides a plausible interpretation of thesystem (Zeinali and Torrents, 1998). Mercury-chloride species proved to have little catalytic power, while the contributions of Hg2+and HgOH+ were significant. Theresults also suggest that a mixed mechanism (electrophilic and nucleophilic) may have to be considered for metal-promoted hydrolysis of OPs (Zeinali and Torrents, 1998).

The important question to answer whether metal ion-catalyzed hydrolysis of OPs is an important process focuses on the speciation of the metal ion and its concentration. In ambient waters, many chelating agents are present, and although some of the above studies probed the effect of metal ion speciation, it is still unknown how effective these metal ions are in the presence of strong chelating agents such as siderophores and components of humic and fulvic acids. No studies to date have really addressed this important issue. A second important consideration is whether some of the aforementioned metal ions are going to be present at high enough concentrations in natural waters to effect catalysis. For example, Hg(II) is not usually present even at submicromolar levels, and therefore its influence may be very limited. Some of the other ions are more abundant, yet the aforementioned speciation may reduce the overall catalytic ability.

H. Heterogeneous Hydrolysis

Soils contained in pots were treated with methyl parathion, fenitrothion, or *p*-nitrophenol at 15-day intervals under flooded or nonflooded (60% WHC) con- ditions (Misra et al., 1992). Nonsterile and sterile suspensions of these treated and untreated soils were tested for their ability to degrade methyl parathion, parathion, fenitrothion, and diazinon (Misra et al.,

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1992). Only nonsterile suspensions of methyl parathion- and *p*-nitrophenol-enriched soils distinctly accelerated hydroly- sis of methyl parathion, parathion, and fenitrothion, while diazinon was not hydro- lyzed by the suspension of methyl parathion-enriched soils (Misra et al., 1992). *P*-Nitrophenol, which was formed from methyl-parathion or parathion, was me- tabolized to nitrite, while 3-methyl-4-nitrophenol, which was formed from fenitrothion, resisted further degradation (Misra et al., 1992). As in soil enrichment cultures, two bacterial isolates, one each from methyl parathion-enriched flooded alluvial and laterite soils, effected rapid hydrolysis of methyl parathion, parathion, and fenitrothion and further metabolized *p*-nitrophenol to nitrite (Misra et al., 1992).

In a follow-up study, fenitrothion or its hydrolysis product, 3-methyl-4-nitrophenol, was applied three times to three soils under flooded or nonflooded conditions at 15-day intervals (Misra et al., 1993). After the After the third application,suspensions of treated and untreated soils were tested for their ability to degradefenitrothion or 3-methyl-4-nitrophenol added to a mineral salt medium (Misra etal., 1993). Repeated additions of fenitrothion or 3-methyl-4-nitrophenol conditioned the three soils for accelerated hydrolysis of fenitrothion as a function of soiltype, moisture regime, and the applied substrate (fenitrothion or 3-methyl-4-nitrophenol). Some enrichment cultures degraded fenitrothion past 3-methyl-4-nitrophenol to nitrite (Misra et al., 1993).

The abiotic hydrolysis of the OP, chlorpyrifos, was examined in 37 different soils, which were chosen to represent a variety of physicochemical characteristics (e.g., pH 3.8 to 8.5) (Racke et al., 1996). Samples of soil were sterilized by γ-irradiation, treated with 14C-chlorpyrifos at 10 µg/g, and incubated for up to 4months. Chlorpyrifos hydrolysis proceeded at a slow rate (.OPs may be degraded into compounds that also have pesticidal activity against target and/or non-target pests (Felsot and Pedersen, 1991). Relatively few studies have documented the level of product pesticidal activity. However, the few studies indicate that the products may be more, less, or similar in activity to the parent pesticide (Felsot and Pedersen, 1991). The prolonged efficiency of many insecticides against foliar feeding insects depends on OP absorption from soil by plants and their metabolism into water-soluble but equally toxic anticholinesterase agents (Felsot and Pedersen, 1991). In the soil, the more watersoluble products of OPs are less toxic to insect larvae than the parent OPs, although when these compounds are topically applied toxicity is similar. For example, the hydrolysis of chlorpyrifos to 3,5,6-trichloro-2-pyridinol results in a total loss of insecticidal activity, but the product is bioactive against several fungal pathogens (Felsot and Pedersen, 1991).

Organic pollutant degradation may be affected via interaction with the surfaces of oxides and other soil minerals (Torrents and Stone, 1994). Torrents and Stone (1994) studied oxide surface-catalyzed hydrolysis of carboxylate and phosphorothioate esters. Esters and hydrolysis products were monitored in acetate-buffered suspensions of 10 g L–1 oxide. Methyl chlorpyrifos is the most susceptible of the phosphorothioate esters to oxide-catalyzed hydrolysis, because it possesses a good auxiliary ligand donor (Tor- rents and Stone, 1994). Methyl parathion and ronnel, which do not possess a suitable auxiliary ligand donor, are also susceptible to oxide-catalyzed hydrolysis, indicating that chelate formation is not required for surface catalysis (Torrents and Stone, 1994). The presence of methanol and acetonitrile co-solvents reduces catalysis; the wide- spread use of co-solvents in laboratory fate studies may have underestimated hetero-geneous hydrolysis (Torrents and Stone, 1994).The susceptibility of OPs and their transformation products to mineral-surface- catalyzed hydrolysis was studied (Smolen and Stone, 1998). Experiments were performed in an aqueous-buffered, constant ionic strength medium with 0 to 25% of methanol (Smolen and Stone, 1998). The addition of 10 g L–1 TiO2, a-FeOOH, and Al2O3 catalyzes the hydrolysis of the thionate (P=S) and oxonate (P=O) forms of chlorpyrifos-methyl (Table 2) (Smolen and Stone, 1998). Paraoxon is also subject to surface-catalyzed hydrolysis, while zinophos is not (Smolen and Stone, 1998). The influence of pH and the identity of the metal (hydr)oxide were discussed in light of the previously proposed catalysis mechanisms (Smolen and Stone, 1997).

Heterogeneous hydrolysis is another difficult pathway to assess carefully. Factors such as the presence of other chemicals that may preferentially adsorb to the surface of metal oxides or clay particles must be considered. Secondly, the hydrolysis products may also adsorb to the clay particles or metal oxides, slowing down the further hydrolysis of OPs themselves. Other factors that have been shown to play an important role in heterogeneous OP hydrolysis include the nature of the clay material, the identity of the exchangeable cations, soil moisture content, and soil pH.

I. Hydrolysis Products

Although the ultimate degradation product of OPs is phosphate, it is seldom formed at a fast enough rate to be of consequence in most environmental systems.

The di- and monoesters of OPs typically hydrolyze at much lower rates when compared with the triesters. Moreover, it is very likely that the most environmen- tally relevant degradation products originate from the thioester side chain of OPs, because the thioester side chain is usually the leaving group after the initial hydrolysis step (i.e., the cleavage of the P-S bond in phosphorodithioates, Figure 1). Furthermore, it contains the most complicated and varied structural moieties (see phosphorodithioates in Table 2 and Figures 7 and 8). As the sulfur-containing ester group is usually a much better leaving group than the alkoxy groups (either methoxy or

ethoxy in most cases, Table 2), the initial phosphorus containing hydrolysis product is either (RO)2P(S)OH or (RO)2P(S)SH. Evidence for both exists. For instance, Lai and co-workers (Lai et al., 1995) and Kolakowski and co- workers (Kolakowski et al., 1997) have established the formation of the former (by 31P-NMR) inexperiments, where hydrolase-mediated enzymatic hydrolysis of severof Phorate. It is interesting to note that the formation of a P-O bond is very favorable from a thermodynamic point of view (i.e., P-O bond is ~40% stronger than P-S bond), particularly in H2O. It seems that in the case of Phorate, kinetic factors dominate and the less thermodynamically stable product is observed (Hong et al., 2000). Finally, it is noteworthy that one of Terbufos hydrolysis products, di- *t*-butyl disulfide, is much more toxic than Terbufos itself, at least according to microtax screening test.

The hydrolysis products of OPs can be numerous and usually involve the cleavage of the P-S bond (in the case of phosphorodithioates and phosphorothiolates [Table 2]) or the P-O bond (in the case of phosphorothioates) that results in the best leaving group. A good

Fig: A summary of phorate hydrolysis pathways yielding HCHO (Hong et al., 2000).

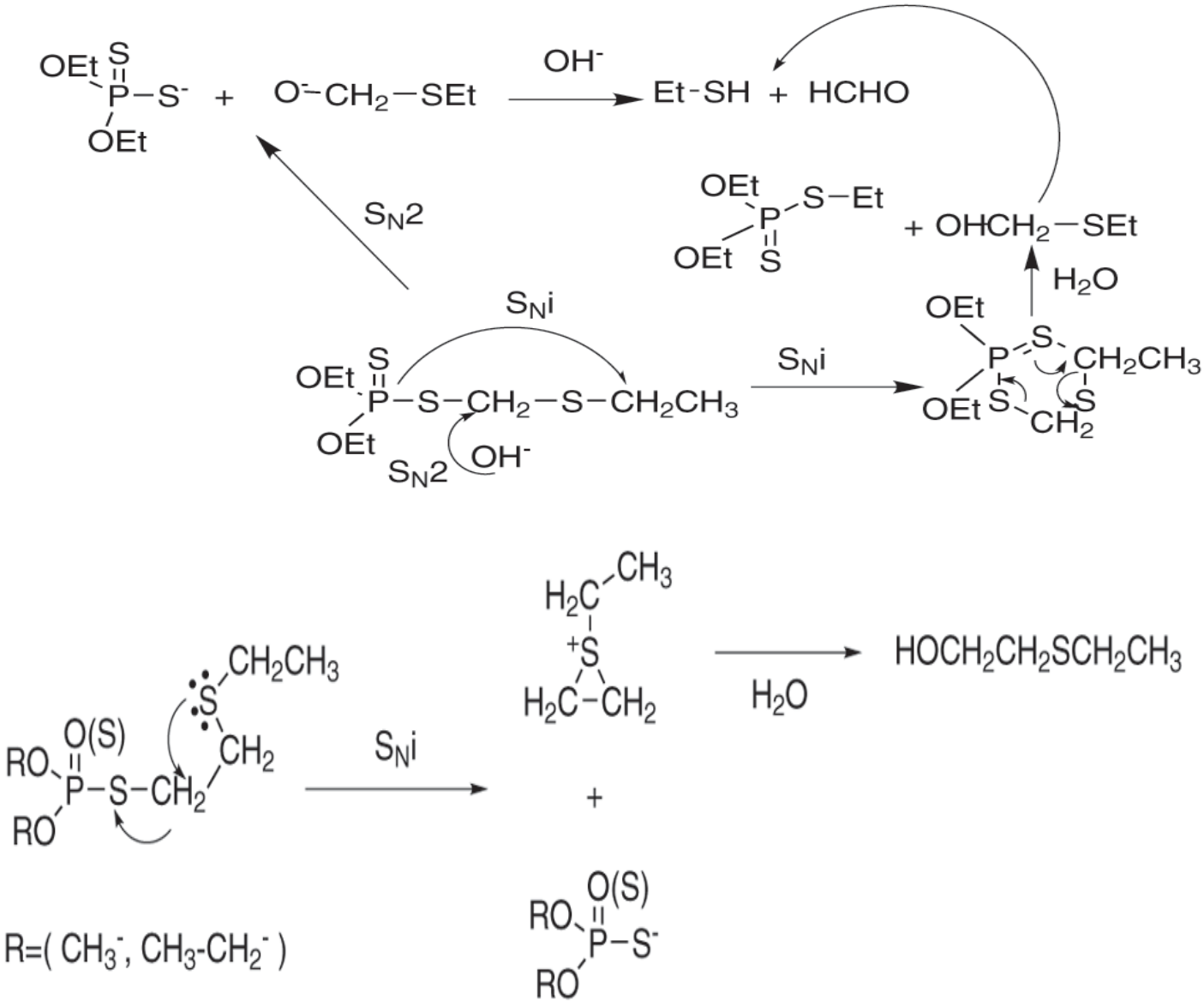

Fig. 8: An SNi Mechanism for Demeton-S Hydrolysis (Schwarzenbach et al., 1993)

behavior can be found for the other phosphorothioates (Table 3). The same argument regarding the leaving groups can also be made for phosphates (Table 3). Thus, during the hydrolysis of Dichlorvos, the likely initial hydrolytic cleavage is between the P and the O atom attached to the carbon of the double bond (Table 3). Once the initial cleavage has occurred, the ester (or thioester) fragment can undergo additional reactions, as can be easily observed for Phorate (Figure 7). It is particularly noteworthy that when a single carbon atom exists between two heteroatoms (e.g., sulfur in the case of Phorate or Terbufos) in the ester side chain, the degradation chemistry can turn out to be very interesting. The instability of any carbon atom possessing two functional groups is well known. Therefore, it is not difficult to predict the sequence of reaction steps described in Figure 7 for Phorate. Similar reaction sequences have been determined to occur during the hydrolysis of Terbufos (Hong et al., 2001). Formaldehyde was initially detected from certain OPs as early as the late 1950s. However, it was produced from OPs under harsh conditions of high temperatures and/or high or low pH values (Giang and Schechter, 1958; Giang and Schechter, 1960). The liberation of HCHO was actually used as an analytical technique to detect certain OPs (Giang and Schechter, 1958; Giang and Schechter, 1960). HCHO production from OP hydrolysis was reported in simulated ambient waters much later (Hong and Pehkonen, 1998) .

OPs may be degraded into compounds that also have pesticidal activity against target and/or non-target pests (Felsot and Pedersen, 1991). Relatively few studies have documented the level of product pesticidal activity. However, the few studies indicate that the products may be more, less, or similar in activity to the parent pesticide (Felsot and Pedersen, 1991). The prolonged efficiency of many insecticides against foliar feeding insects depends on OP absorption from soil by plants and their metabolism into water-soluble but equally toxic anticho- linesterase agents (Felsot and Pedersen, 1991). In the soil, the more water- soluble products of OPs are less toxic to insect larvae than the parent OPs, although when these compounds are topically applied toxicity is similar. For example, the hydrolysis of chlorpyrifos to 3,5,6-trichloro-2-pyridinol results in a total loss of insecticidal activity, but the product is bioactive against several fungal pathogens (Felsot and Pedersen, 1991)

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J. Hydrolysis Mechanisms

Hydrolysis is the most thoroughly studied degradation pathway of OPs. For that reason, this section focuses on some of the intriguing findings regarding the hydrolysis mechanisms of OPs. Dannenberg and Pehkonen (1998) have attempted to use the activation enthalpy and entropy approach to gain insight into the mechanisms of OP hydrolysis. Both homogeneous and heterogeneous studies were carried out at a variety of different temperatures and the activation enthalpy and entropy were determined for four OPs: Demeton S, Disulfoton, Thiometon, and Diazinon (Dannenberg and Pehkonen, 1998). The oxide phases utilized in the study were amorphous aluminum hydroxide, goethite, hematite, and ferrihydrite.

Some useful insight can be gained following this type of treatment, although there are still too many experimental variables to pinpoint the mechanism by which oxide surfaces can alter the hydrolysis of OPs. Hong et al. (2000) used this approach again to try to differentiate between SNi and SN2 (and even SN1) hydrolysis pathways of Phorate. Because SNi and SN2 mechanisms can result in very different degradation products and should also exhibit very different pH dependencies in ambient waters, it is useful to be able to distinguish between them (Figure 7). Again, the difficulties in interpreting the activation parameter values that one would expect for each mechanism are very obvious. Ab initio calculations using advanced software may allow theoretical calculations to determine the theoretical activation parameter values (Katagi,1992), which could then in turn be compared to experimentally obtained values.This approach has not yet been attempted by researchers, but it can be a very *useful tool to differentiate the various hydrolysis mechanism*

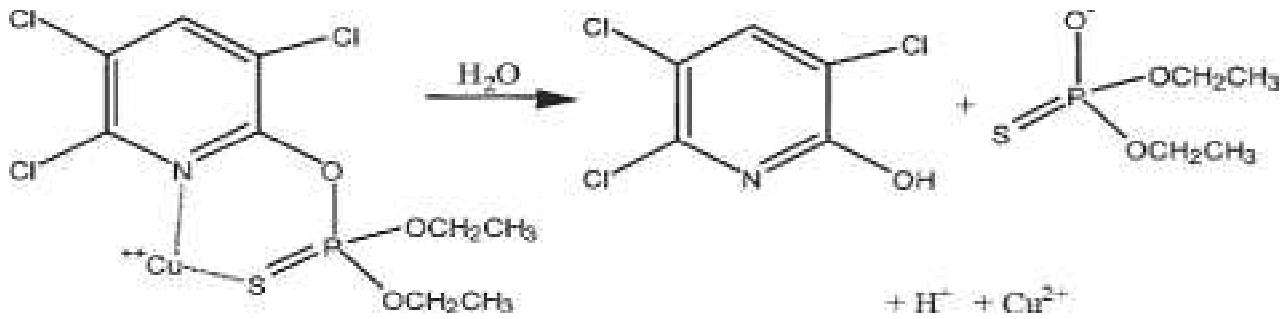

Fig. 9: Copper Catalyzed Hydrolysis Mechanism of Chlorpyrifos (Mortland And Raman,1967; Blanchet And St-George, 1982)

Stone and co-workers have also studied the mechanistic details of OP hydrolysis by selecting several structurally similar OPs and investigating the effect of dissolved metal ions and metal oxide surfaces on the hydrolysis rates of OPs (Torrents and Stone, 1994; Stone and Torrents, 1995; Smolen and Stone, 1998). Stone and co-workers (Smolen and Stone, 1998) and earlier researchers have concluded that the role of the metal ions is complex, perhaps a combination of several distinct mechanisms. One mechanism of the metal-catalyzed hydrolysis of Chlorpyrifos (Mortland and Raman, 1967; Blanchet and St-George, 1982) has been proposed to occur via a chelate formation between Cu2+ and the OP (Figure 9).

K. Distinguish Between Various Hydrolysis Mechanisms.

Stone and co-workers have also studied the mechanistic details of OP hydrolysis by selecting several structurally similar OPs and investigating the effect of dissolved metal ions and metal oxide surfaces on the hydrolysis rates of OPs (Torrents and Stone, 1994; Stone and Torrents, 1995; Smolen and Stone, 1998). Stone and co-workers (Smolen and Stone, 1998) and earlier researchers have concluded that the role of the metal ions is complex, perhaps a combination of several distinct mechanisms. One mechanism of the metal-catalyzed hydrolysis of Chlorpyrifos (Mortland and Raman, 1967; Blanchet and St-George, 1982) has been proposed to occur via a chelate formation between Cu2+and the OP (Figure9). Other studies with structurally very similar OPs have led to very insightful conclusions. For example, based on the insensitivity of Demeton-S hydrolysis halflife on pH, as originally reported by Muhlmann and Schrader (1957), Schwarzenbach et al. (1993) proposed an intriguing SNi mechanism to explain the experimental data (Figure 8). Unfortunately, no product studies were carried out (Muhlmann and Schrader, 1957) to more conclusively prove the presence of the SNi mechanism In situ spectroscopic tools can be very powerful in monitoring the appearance of certain degradation products and deducing the reaction mechanism from product dentities (Lai et al., 1995, Hong et al., 2000). In particular, 31P-NMR can be a useful analytical tool for this purpose, as several investigators have reported on its use to identify either parent OPs (Mortimer and Dawson, 1991) or OP degradation products (Lai et al., 1995; Kolakowski et al., 1997; Hong et al., 2000). The main drawback of NMR is still its relatively low sensitivity, thus requiring the use of organic co-solvents.

L. Abiotic Oxidation

Primary degradation products and the oxidation pathways of diazinon, fenthion (MPP), and edifenphos (EDDP) by ozone in water were studied by GC-MS (Ohashi et al., 1994). Mass-spectra of ozonation products of the 17 OPs suggested that they were oxons (Ohashi et al., 1994). Sulfate was also produced, as their thiophosphorile bonds were oxidized by ozone into phosphorile bonds (Ohashi et al., 1994). Although oxons were stable against ozonation, they were further hydrolyzed into trialkyl phosphate and other products. However, in the case of MPP, thiomethyl radicals were oxidized prior to thiophosphorile bonds and MPP-sulfoxide was produced (Ohashi et al., 1994). MPP-sulfone, MPP-sulfoxide-oxon and MPP-sulfone-oxon, were also generated from MPP (Figure 3a). Two major products were obtained from bis-dithio type ethion (Ohashi et al., 1994). EDDP of the phosphate type was resistant to ozonation, but its oxidation products were detected after hydrolysis. As oxons are resistant to ozonation and are also toxic, they should be monitored. The decomposition of monocrotophos (Table 2) in aqueous solution by ozonation was studied under various solution pH values, gaseous ozone dosages, and alkalinity levels (Ku et al., 1998). The decomposition rate increased with a decreasing solution pH and an increasing ozone dosage (Ku et al., 1998). The presence of HCO3–and CO32– inhibited the decomposition of monocrotophos to a certain extent, but severely retarded the mineralization of the intermediates (Ku et al., 1998). The presence of Fe2+ and Mn2+ions interfered with the decomposition in acidic solutions (Ku et al., 1998). A pathway was proposed and the breakage of the C=C bond by ozonation was found to occur first to form various N and p containing produtcs which further degraded to H2O, CO2, NO3–, and PO43–.

(Ku et al., 1998 Zhang and Pehkonen (1999) studied the oxidation of Diazinon by aqueous chlorine. Because Diazinon has been detected at a variety of wastewater treatment plants (Jop et al., 1991; Amato et al., 1992; Bukhard and Jenson, 1993), its fate visa vis oxidation by aqueous chlorine should be evaluated. The results of Zhang andPehkonen (1999) indicated that the half-life of Diazinon oxidation by aqueouschlorine is only for several minutes at typical chlorine concentrations found inwastewater treatment plants. Zhang and Pehkonen (1999) further found a very strongpH dependence on the rate of oxidation, with HOCl being a much more potentoxidant when compared with OCl–. The oxidation products of Diazinon by aqueouschlorine were found to be SO42–and Diazoxon (Zhang and Pehkonen, 1999).

Although the oxidation of OPs by aqueous chlorine or ozone may not initially seem to fall under the classification of ambient water systems, one has to consider that many of the more persistent OPs can easily find their way into water treatment facilities, where they may interact with either ozone or aqueous chlorine. If the degradation products of these abiotic oxidation reactions are more harmful than the starting OPs, then scientific attention to these reactions is warranted. Furthermore, both ozone and chlorine are very powerful oxidizing agents, and thus their interaction with OPs can reduce the otherwise rather long lifetime of some of the more persistent OPs, such as Diazinon.

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M. Enzymatic Oxidation

Chloroperoxidase from Caldariomyces fumagowas tested for the oxidation of10 OPs (Hernandez et al., 1998). OPs from the phosphorothioates: azinphos-methyl,chlorpyrifos, dichlorofenthion, dimethoate, parathion, phosmet, and terbufos were oxidized by chloroperoxidase in the presence of H2O2and Cl– (Hernandez et al.,1998). The products were identified as oxon derivatives (phosphates), where anS atom from the thioate group is substituted by an O atom (Figure 3). No hydrolysisproducts were detected after the enzymatic oxidation, and no halogenation of substrates was detected (Hernandez et al., 1998). Chloroperoxidase oxidation of relatively toxic OPs produces metabolites similar to those formed by cytochrome P450during the metabolic activation of pesticides (Hernandez et al., 1998). The maindifference between the two biocatalysts is that a further cleavage of oxons (commonwith P450) was not observed with chloroperoxidase (Hernandez et al., 1998).

N. Oxidation Products

The oxidation of OPs can occur by a direct absorption of light, by an attack of photoproduced radicals, or by aqueous oxidants such as dissolved oxygen, aqueous chlorine, or by enzymatic reagents such as oxygenases. In Figure 3, two OPs (Temephos and Fenthion) and their oxidation products are shown. The oxidation schemes shown in Figure 3 are quite typical for other OPs as well, and thus can be used as an example of the types of products expected during OP oxidation. In the case of Fenthion (Figure 3a), four products were found after oxidation with NBS. These products are Fenthion oxon (from the replacement of the doubly bonded S with O), Fenthion sulfoxide (from the oxidation of the S in one of the ester sidechains), Fenthion oxon sulfoxide (from the combination of the above two), and finally the S-methyl isomer of Fenthion (by an internal rearrangement). In the case of Temephos (Figure 3b), similar products to the aforementioned Fenthion were found. The main difference is that Temephos has two P=S bonds, thus dioxon can also be formed. An oxidation product that is not shown in Figure 3, but whose formation is possible during the oxidation of OPs, is sulfone. Sulfone is formed when sulfoxide in the ester side chain is further oxidized to yield two S=O bonds on a single sulfur atom. Demeton S and Phorate are two examples of OPs, whose oxidative degradation has yielded both sulfoxides and sulfones.

V. BIOREMEDIATION HISTORY AND USE

Bioremediation from it root meaning means to use microorganisms to remediate/ destroy or to immobilize pollutant from environment [15]. Natural Bioremediation has been used by civilizations for the treatment of waste water but intentional use for reduction of hazardous waste is more recent development. Modern bioremediation and use of microbes to consume pollutants are credited in part to George Robinson He used microbes to consume an oil spill along the coast of Santa Barbara, Calfornia in the Tale 1960.

VI. PESTICIDE BIOREMEDIATION METHODS

The level of toxicity caused by the pesticides leads to the great need for bioremediation. No doubt in some cases intrinsic bioremediation occurs because of microbes that are already present in polluted ecosystems, but it is also true that in some cases intrinsic bioremediation is not adequate. The requirements for the process of bioremediation of pesticides given by Ref. are summarized in Table.

Factor	Conditions required
Micro organism	Aerobic anaerobic
Natural biological processes of microorganismm	Catabolism anabolism
Environmental factor	Oxygen content, temperature, Ph,electron acceptor and donor
Nutrients	Carbon, nitrogen, oxygen etc
Soil moisture	25-28% water holding capacity
Type of the soil	Low clay or slit content

VII. FIELD STUDIES

Model calculations and laboratory experiments were carried out to assess the dynamic behavior of two insecticides (Disulfoton and Thiometon) in the Rhine River (Wanner et al., 1989). Dilution, longitudinal dispersion, and biotransformation were found to be the dominant processes in determining the concentrationtime profile of the two compounds after their accidental release into the Rhine River at Schweizerhalle in November 1986. Biotransformation and, for summer conditions, also abiotic hydrolysis and oxidation by singlet oxygen are the dominant processes for reduction of the total load of the studied OPs in the Rhine River (Table 4) (Wanner et al., 1989). For the conditions prevailing after the accident and a flow distance of 700 km (i.e., a travel time of 8 days), a reduction of the peak concentration of 97 to 98%, but a reduction of the total load of only ~50% is predicted for both (Wanner et al., 1989). Model predictions of the concentrationtime courses of disulfoton and thiometon show good agreement with field measurements carried out at various sampling stations after the accident at Schweizerhalle (Wanner et al., 1989).

Pesticides were analyzed in air and fog in several fog events sampled near Monterey, CA, to determine whether the uptake of pesticides in advected oceanic fog was different from uptake in fog formed under stagnant atmospheric inversion in California's Central Valley in the winter (Schomburg et al., 1991). Data for several pesticides common to both areas showed that the pesticide content and distribution were remarkably similar at the two locations. The conversion of OPs to their corresponding oxons (Figure 3) and aqueous-phase enrichment factors were also very similar (Schomburg et al., 1991). Enhanced pesticide levels in ogwater are caused by sorptive nonfilterable particles in fogwater that are derived from atmospheric aerosol (Schomburg et al., 1991).

Air sampling was conducted at Parlier (CA) in the winter of 1989 to assess the airborne concentrations of OPs used as dormant sprays on deciduous fruit and nut orchards (Seiber et al., 1993). For 24-h air samples, concentrations ranged to above 100 ng/m3for parathion, chlorpyrifos, and diazinon, and less (~ 30 ng/m3) for methidathion (Seiber et al., 1993). Nighttime air residues were generally higher than daytime, perhaps reflecting a lowered inversion boundary layer and calmer winds (Seiber et al., 1993). Oxons of the four OPs tended to be in larger amounts relative to the parent thions in day vs. night samples, indicating photooxidation as their source (Seiber et al., 1993). Concurrently collected fogwater contained traces of all four OPs and their oxons (Seiber et al., 1993). Oxons tended to be higher in the tree drip, indicating involvement of the tree surface in their formation. The OP residue content of red-tailed hawks collected in the area indicated deposition to non-target wildlife (Seiber et al., 1993).

Organophosphate (OP) pesticide residues have been found in rain, snow, fog, and air samples collected in the Sierra Nevada mountains (Aston and Sieber, 1996). A major component of the Sierra Nevada ecosystem is the varied plant biomass. Interaction between chemical vapors and plant material has been demonstrated for various semivolatile organic compounds (Aston and Sieber, 1996). The study by Aston and Sieber (1996) addresses the hypothesis that the extensive forests of the western slopes of the Sierra Nevada mountains, which lie in the predominant downwind direction from the agricultural Central Valley of California, might serve as sinks for airborne OPs (Aston and Sieber, 1996). The main paths of vapor-leaf interaction are cuticular and stomatal. More specifically interactions may include sorption of residues to surface dust particles, or to the needle surface, solubilization in the cuticular wax of the needle, and penetration to the interior of the needle either by absorption through the stomata or migration through the cuticle (Aston and Sieber, 1996). Analytical methods, which can separately assess surface, cuticle adsorbed, cuticle dissolved, and intemal needle tissue residues, have been applied in two cases. One involved measuring the vapor-needle distribution coefficient for several OPs exposed as vapors to pine branches in a laboratory chamber (Aston and Sieber, 1996). A second, involving air and needle analyses for trees placed in and downwind from a diazinon-treated orchard, provided outdoor distribution coefficients for a comparison with chamber data (Aston and Sieber, 1996). The results support the hypothesis that forests act as sinks for airbome pesticide vapors (Aston and Sieber, 1996).

Wang and Hoffman (1991) determined the persistence and degradation of both Malathion and Parathion in the Indian River estuary on Florida's East Coast. The proton concentration, temperature, salinity, and microorganisms affected the persistence of both OPs. Alkaline hydrolysis was the most dominant pathway for Malathion (Wang and Hoffman, 1991), consistent with an earlier laboratory study (Wolfe et al., 1977). Only slow biological and photochemical degradation of Malathion was observed, while biological degradation was found to be significant for Parathion. Alkaline hydrolysis and photolysis were only secondary pathways for Parathion degradation. The half-lives for Parathion and Malathion in the Indian River (24-ppt salinity and pH 8.16) were 7.84 and 1.65 days, respectively (Table 4) (Wang and Hoffman, 1991).

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The disappearance of fenitrothion was studied in the rice crop field of the Ebre Delta (Tarragona, Spain) during July 1995 by helicopter spraying at a rate of 148 mL/ha Tionfos 50 LE (50% of pure fenitrothion) (Oubina et al., 1996). For monitoring fenitrothion residues in water, two different analytical techniques were used: enzyme-linked immunosorbent assay (ELISA) and automated on-line solidphase extraction (Prospekt) and HPLC/diode array detection (Oubina et al., 1996). The unequivocal identification of fenitrothion, fenitrooxon, 3-methyl-4-nitrophenol, and S-methyl isomer of fenitrothion was achieved by LC/MS (Oubina et al., 1996). Fenitrothion residuals in the rice crop field waters varied from 119 to 178 µg/Ldown to 3.8 to 1.5 µg/L after 48 h of application. The half-lives were 19.3 h (ELISA) and 11 h (HPLC/DAD) (Oubina et al., 1996) (Table 4).

The evolution of a mixture containing 19 OP and organonitrogen pesticides at ppb levels was studied over a 6-month period in different waters (i.e., ultrapure water, natural seawater, river water, and filtered river water) under a variety of conditions (Lartiges and Garrigues, 1995) (Table 4). The degradation kinetics were monitored in dark, closed bottles at 6 and 22°C and in a system exposed to natural sunlight. Activation energies (Ea) and half-lives (t1/2) were determined (Lartiges and Garrigues, 1995). Very different degradation behavior with respect to physicochemical conditions and molecular structures of the pesticides was observed. For instance, photodegradation in river water was much faster than in natural seawater for Dimethoate (likely due to humic matter sensitized photodegradation), while for Diazinon the rate was very similar (likely due to direct photolysis). Half-lives of OPs can be more than several months and therefore can lead to long-term environ- mental pollution (Table 4) (Lartiges and Garrigues, 1995) A nested surface water monitoring network was designed to measure variability in pesticide concentrations in the San Joaquin River (SJR) and selected tributaries during the irrigation season (Domagalski, 1997). The SJR Basin, CA, was sampled from April to August 1992, with no rainfall (Domagalski, 1997). Orestimba Creek, which drains a part of the western San Joaquin Valley, was sampled three times per week for 6 weeks, followed by a once per week sampling for six weeks, and then three times per week sampling for 6 weeks. A site on the SJR near the mouth of the basin, and an irrigation drain of the eastern San Joaquin Valley, were sampled weekly during the entire campaign (Domagalski, 1997). Pesticides were most often detected in samples collected from Orestimba Creek, suggesting that the western valley irrigation drainage was the primary source during the irrigation season. Pesticide levels of Orestimba Creek showed greater temporal variability when sampled three times per week than when sampled once a week, likely due to variations in field management and irrigation (Domagalski, 1997) in a related study, pesticides in stormwater runoff within the Sacramento River Basin, CA, were assessed during a storm in January 1994 (Domagalski, 1996). Two OPs (diazinon and methidathion) were detected and their levels increased with the rising stage of the hydrographs; maximum concentrations were measured near the peak discharge (Domagalski, 1996). Diazoxon, a toxic product of Diazinon, constituted approximately 1 to 3% of the total Diazinon load (Domagalski, 1996).

It is clear from the field studies that various OP pesticide degradation mechanisms are concurrently reducing their load in the aquatic environment. As hydrolysis, photodegradation, and microbial degradation all have large seasonal fluctuations, their relative importance in OP fate also varies from one season to the next (Wanner et al., 1989). Some of the field studies have identified OP degradation products, while others have not. Without the proper monitoring for OP degradation products, it is difficult to ascertain which degradation pathway is the most dominant one, more importantly it also makes it difficult to assess the overall ecological impact of OPs in ambient waters. Furthermore, multiple pathways are simultaneously degrading the OPs (e.g., the hydrolysis of OP oxons), and therefore it is very desirable to characterize the stable final products of OP degradation. In order to isolate and assess the relative importance of various degradation pathways in field studies, it may be useful to manipulate the ambient water samples and carry out additional experiments in the laboratory (e.g., the addition of biocide followed by OP spiking can aid in the determination of abiotic degradation rate). The addition of radiolabeled OPs to collected ambient water samples may be another way to assess their degradation in a simple, robust way. Finally, it should be noted that the molecular structure of the OP plays a very important role in determining the degradation rate (Lartiges and Garrigues, 1995); therefore generalizations regarding degradation rates must be made with extreme caution.

VIII. RECOMMENDATIONS FOR FUTURE RESEARCH AND CONCLUSIONS

No doubt the pesticides have caused serious impact on the soil fertility. Soils contaminated with pesticides have attracted high attention because it impacts human health and natural ecosystem. Bioremediations has a tremendous potential for remediation of the soils that are affected by pesticides. Microorganisms that are present in the soils can remove pesticides from the environment. Biopesticide enzymatic degradation of polluted environment represents most important strategy for pollutant removal and degradation of persistent chemical substances by enzymatic reactions have been found high bioremediation potential. Hence

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bioremediation is much promising approach to overcome the pesticide pollution that can surely solve the problem of pesticide pollution of soils. This technology has proved again and again its potential to degrade not only pesticides but also the various in organic compounds. So time is to utilize this eco-friendly technology for better and safe future.

Although much research has been carried out in the area of organophosphorus pesticide degradation, additional research is required in order to estimate the environmental impact of these ubiquitous pesticides. For example, many of the photodegradation studies have been carried out in the presence of significant quantities of co-solvents (e.g., methanol) that may sensitize the photolysis of the OPs significantly and lead to erroneous direct photolysis rate constants. Also, systematic adsorption studies to assess whether soils or sediments exhibit markedly different Kdvalues for OPs should be carried out; the impact of aging of the soil or sediment sorbent material should also be studied. Furthermore, it is not clear how oxidation and hydrolysis interact. Very few studies that have probed the rate of hydrolysis of oxidized OPs (e.g., oxons, sulfones, and sulfoxides, Figure 3) exist in the scientific literature. In particular, studies with sulfones and sulfoxides are almost nonexistent, with one exception, a 40-year-old study dealing with the hydrolysis of oxidized Phorate (Bowman and Casida, 1957). As aquatic environments can easily support both degradation pathways, it would be valuable to assess the above. Few studies to date have isolated the conditions sufficiently well to really pinpoint whether the degradation products originate from oxidation, hydrolysis, photolysis or a combination of the above. One may argue that this separation is not necessary, as long as one knows the identity of the degradation products. Although the product identity is important, it also matters which pathway produced them, if we want to thoroughly understand the fate of OPs as a function of changing environmental conditions, such as lake water acidification. Degradation pathways that may be independent of ambient pH, such as the intramolecular nucleophilic attack, SNi (Schwarzenbach et al., 1993; Hong et al., 2000), are examples that require further research. The toxicity of OP degradation products has also received scant attention. For instance, hydrolysis of Phorate and Terbufos produce formaldehyde, hydrogen sulfide, and quite toxic (based on Microtox assay) dialkyl disulfides. None of these products have been considered in comprehensive toxicity assays such as Daphnia, etc. Only data based on the screening test utilizing Microtox exists (Hong and Pehkonen, 1998; Hong et al., 2001). Furthermore, it is possible that the toxicity of the parent OP in the presence of its degradation products may be enhanced due to synergism. No studies exist to report on this intriguing aspect.

Following the isolation and identification of some of the unusual ester side chain hydrolysis products of Phorate and Terbufos, it would be useful to carry out studies in the field to try to isolate and confirm whether the laboratory findings can be extended to natural water conditions. More importantly, the levels of formaldehyde, hydrogen sulfide, and dialkyl disulfides that may be formed under ambient conditions should be known. For example, are the degradation product levels significant enough to impact the non-target organisms near the pesticide application sites?

Finally, recent advances in molecular orbital (MO) calculations provide an opportunity to examine electronic properties of compounds and their reaction mechanisms at a molecular level (Katagi, 1992). The semiempirical and ab initio MO methods have been applied to theoretically estimate the various pesticide transformations in the ambient environment (Katagi, 1992). The electron distribution in the frontier MOs was used as the most convenient index to explain the reactivity of pesticides along with their regioselectivity (Katagi, 1992), and electronic properties in the excited states were useful to estimate photooxidation and photosensitization of pesticides (Katagi, 1992).

Because the regulatory agencies, such as the USEPA, are reconsidering the wide use of OPs and the resulting exposure and environmental impact, it is necessary to broaden the research objectives with some of the aforementioned suggestions. Without a more thorough understanding of the fate of OPs, a proper regulatory decision based on the best available science cannot be made.Because very few good alternative products exist for the phase-out of OPs, this becomeseven more important.