Chapter 10

Degradation of Fenamiphos, Chlorpyrifos and Pirimiphos-Methyl in the Aquatic Environment: A Proposed Enzymatic Kinetic Model That Takes Into Account Adsorption/Desorption of the Pesticide by Colloidal and Sediment Particles

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/46841

1. Introduction

Organophosphate compounds are among the most common chemical classes used in crop and livestock protection, and account for an estimated 34% of world sales (Singh and Walker, 2006; Caceres et al., 2010). Fenamiphos (*N*-[Ethoxy-(3-methyl-4-methylsulfanylphenoxy)phosphoryl] propan-2-amine, [CAS number 22224-92-6]), chlorpyrifos (o,o-diethyl-o-3,5,6-trichloro-2-pyridyl phosphorothioate, [CAS Number 2921-88-2]) and pirimiphos-methyl (o-2-diethylamino-6-methyl pyrimidin-4-yl-o,o-dimethyl phosphorothioate, [CAS number 29232-93-7]) are among some of the commonly used organophosphate pesticides. Fenamiphos is a systematic nematicide used for the control of ecto and endo parasitic free living nematodes. Fenamiphos is applied to the soil before planting or at planting time. It can also be applied to established plants. Fenamiphos is toxic to mammals (LD_{50} = 8 mg/kg body weight male rats (USEPA, 1984)), and to fish at concentrations above 3 mg/litre. It is moderately persistent in soil, and half-life ranges of 10 to 67 days and 12 to 87 days, and an average half-life of 30 days, have been reported (Nicholls, 1994; Simon et al., 1992).

Chlorpyrifos is a non-systemic insecticide, with broad spectrum insecticidal activity (Rackie, 1993). It is used in a wide range of agricultural and specialty pest control scenarios to control insects and other arthropod pests, e.g., corn and cotton agriculture, termite control, citrus horticulture. Chlorpyrifos is toxic to mammals (LD_{50} = 163 mg/kg body weight male rats (USEPA, 1984)), and acts as a cholinesterase inhibitor. Chlorpyrifos is a very persistent

pesticide, and a half-life range of 30 to 120 days has been reported (Nicholls, 1994). Murray et al. (2001) studied the persistence of chlorpyrifos applied for termite control on six Australian soils at initial chlorpyrifos concentrations of 1000, 100 and 10 mg/kg and reported half-lives of 385, 155, and 41 days for the three concentrations respectively for all six soils. Soil pH had no effect on the rate of degradation at all concentrations studied. Hui-ming and Guo-nian (2003) reported half-lives of 278, 91.8 and 79.2 days for similar experiments with chlorpyrifos. Bondarenko and Gan (2004) studied the degradation and sorption of chlorpyrifos in urban stream sediments from southern California, USA, and reported half-lives of 14 - 24 days and 58 – 223 days under aerobic and anaerobic conditions respectively. Half-lives of 4.28, 0.58 and 1.35 days were reported by Zhang et al. (2011) for the dissipation of chlorpyrifos from rice plants, water and soil respectively under paddy field conditions. Gilani et al. (2010) reported 100% recovery of chlorpyrifos after 6 months and 1 year from tap water and irrigation water treated with different fertilizers.

Pirimiphos-methyl is a post-harvest insecticide used on stored corn and sorghum grain and seed, and incorporated into cattle ear tags. It is used for the control of various insects, e.g., mealy bugs and mites, various types of beetles, grain weevils, grain borers and moths. Pirimiphos-methyl can cause cholinesterase inhibition in humans (USEPA, 2002a). Use of pirimiphos-methyl as an insecticide for warehouses, stored grain, and vegetable crops will results in its release into the environment. If released into water, pirimiphos-methyl is expected to adsorb to suspended solids and sediments. Pirimiphos methyl hydrolyses rapidly at acidic pH, with half-lives of 7.3 days at pH 5, 79.0 days at pH 7, and 54.0 - 62.0 days at pH 9 (USEPA, 2002b). Patakioutas et al. (2002) studied the degradation of pirimiphos-methyl in top soils of untilled and tilled soil, and reported half-lives of 16.7 and 9.2 days respectively.

Pesticides find their way into surface and ground water as a result of agricultural land drainage or industrial waste discharges. Organophosphate pesticides are highly toxic to fresh water invertebrates (Caceres et al., 2007), hence there is need to understand the factors that determine the persistence of these pesticides in the aquatic environment. The persistence of pesticides in the aquatic environment is usually expressed in terms of the half-lives of the pesticides in the environment, in accordance with the conventional pseudo first order kinetics approach to the study of pesticide persistence in the environment. Half-life data that have been obtained for fenamiphos, chlorpyrifos and pirimiphos-methyl under different environmental conditions are summarized in Table 1. It is apparent from this brief survey that half-life data reported in the literature are highly variable, whereas in true first order kinetics, a constant value should be obtained for the half-life, irrespective of the actual environmental conditions prevailing. Wania and Mackay (1999) suggested that techniques for modeling the persistence of pesticides should take into account spatial, temporal and climatic variability, as well as concepts such as equilibrium partitioning. It is apparent therefore that more studies are required to elucidate further the kinetics of the degradation of pesticides in the aquatic environment.

Pesticide	Environment	Half-life (days)	Reference
Fenamiphos	Soil	10 - 67	Nicholls, 1994
	Soil	12 - 87	Simon et al., 1992
Chlorpyrifos	Soil	385, 155, 41[a]	Murray et al., 2001
	Soil	30 - 120	Nicholls, 1994
	Soil	278, 91.8, 79.2[a]	Hui-ming & Guonian, 2004.
	Sediment	14 – 24 (aerobic)	Bondarenko & Gan, 2004
	Sediment	58 -223 (anaerobic)	Bondarenko & Gan, 2004
	Rice plants	4.28	Zhang et al., 2011
	Water	0.58	Zhang et al., 2011
	Soil	1.35	Zhang et al., 2011
	Tap water	>180	Gilani et al., 2010.
	Irrigation water	>365	Gilani et al., 2010.
Pirimiphos-methyl	Water	7.5, 79.0,59 – 62[a]	USEPA, 2002.
	Soil (untilled)	16.7	Patakioutas et al., 2002.
	Soil (tilled)	9.2	Patakioutas et al., 2002.

[a]Depending on pH.

Table 1. Persistence data for Fenamiphos, Chlorpyrifos and Pirimiphos-methyl from the literature.

Zaranyika and Nyandoro (1993) studied the kinetics of the degradation of glyphosate [N-(phosphonomethyl) glycine] in the aquatic environment and observed two linear rates of degradation. The results were explained in terms of a steady state enzymatic kinetic model, which takes into account microbial degradation of both free and colloidal-particle-adsorbed glyphosate. According to this model the rate of degradation of glyphosate was given by

$$dP/dt = k_2[G_B] + k_6[GC_B] \quad (1)$$

where G denotes glyphosate, GC denotes glyphosate-colloidal-particle complex, the subscript B denotes microbial bound, and k_6 and k_2 are the rate constants for the degradation of the colloidal-particle adsorbed and unadsorbed glyphosate respectively, and P denotes products. It was further shown that, provided the concentration of glyphosate in the medium was in excess of the microflora that can bind the pesticide, then a steady state obtains and the rate equation becomes:

$$dP/dt = k_2' + k_6' \quad (2)$$

These experiments were conducted using river water and sediment in order to simulate as closely as possible conditions to be found in the natural aquatic environment. Biphasic linear degradation rates have also been observed for the degradation of endosulfan I and endosulfan II in experimental microcosm aquatic ecosystems (Zaranyika et al., 2010).

The aim of the present work was to carry out similar semi-field experiments with pirimiphos-methyl, chlorpyrifos and fenamiphos in order to determine whether the degradation of the pesticide in the aquatic environment can be interpreted in terms of steady state kinetics. The

experiments were conducted using river water and sediment contained in a plastic drums covered with clear perforated plastic and exposed to sunlight. The rate of degradation of the pesticide was monitored in the water as well as the sediment phase of the experiment.

2. Experimental methodology

2.1. Equipment

A microprocessor controlled Perkin Elmer Autosystem Gas Chromatograph equipped with a built-in Auto sampler, a split/splitless injector, and a nitrogen-phosphorus detector (NPD) (Perkin Elmer, Norwalk, CT, USA), was used in conjunction with a BPX-5- 95% phenyl polydiphenylene-silicone capillary column 30m x 0.25 mm id , film thickness 0.25 μm (SGE Analytical Science, Melbourne, Australia); white plastic tanks, 200 L capacity; 3.7 mL Pyrex glass sample vials with hollow caps and Teflon-lined septa (Supelco SA, Switzerland); A Buchi Rotary Evaporator Model R-124 (Buchi Labortechnik AG, Switzerland), equipped with a water bath was used to concentrate the sample extracts to near dryness; and a Stuart Scientific model SF1 flask mechanical shaker (Stuart Scientific, Redhill, UK).

2.2. Materials

The following were used: pesticide residue analysis grade diethyl ether, ethyl acetate, hexane and acetone (Fischer Scientific, Loughorough, U.K.). Other materials used include glass wool, Florisil (60 – 100 mesh, [Fluka Chemie AG, Switzerland]); anhydrous sodium sulphate (99.8% purity, Acros Organics, New Jersey, USA); Whatman 541 filter paper; double distilled water; river water and sediment collected from Kutsaga Dam on the Hunyani river near the Tobacco Research Board Kutsaga Research Station, Harare, Zimbabwe; high purity nitrogen carrier gas; fenamiphos (99.5% pure), chlorpyrifos and pirimiphos-methyl (99.8% pure) reference standards, supplied by Dr. Ehrenstnfer, D86 199, Ausberg, Germany; Nemacur (containing 400 g/L fenamiphos), Dursban (containing 480 g/L chlorpyrifos), and Shumba (containing 40 g/100mL pirimiphos methyl) (Agricura (Pvt) Ltd., Zimbabwe).

2.3. Procedure

Volumes of 100 L each of Kutsaga dam and distilled water were charged into two separate 200 L tanks and the levels were marked. About 1.93 kg of sediment was added into the tank containing dam water. Volumes of 37. 5 mL of nemacur, 31.25 mL of dursban, and 37. 5 mL of Shumba, meant to give 150 μg/mL each fenamiphos, chlorpyrifos and pirimiphos-methyl respectively, were added into each of the tanks. The contents were thoroughly mixed. Samples were taken at zero time immediately after the system had settled. The tanks were covered with transparent perforated polyethylene and left exposed to sunlight at the roof of the Pesticide Analysis Laboratory Building, Kutsaga Research Station. Thereafter samples of water and sediment were collected periodically for a period of 90 days, each time compensating for evaporation 24 hours prior to sampling. Water and sediment samples were taken with minimal disturbance of the system. The new level was marked after each sampling, then the system was stirred and left to settle.

Once collected all samples were stored in the freezer in plastic bottles with screw caps until required for analysis. All the samples were thawed and mixed thoroughly prior to analysis.

2.4. Extraction, cleanup and concentration

Water samples were analysed by GC-NPD using a BPX-5, phenyl-polydiphenylene silicon capillary column following liquid-liquid extraction (Greeve and Goewie, 1985; Mansour et al., 1998). Water samples were analyzed in duplicate. 100ml of water samples were extracted 3 times with 50 ml portions of diethyl ether using a separatory funnel, and collected over anhydrous sodium sulphate. The combined extracts were concentrated to near dryness using the rotary evaporator maintained at 40^0C in the water bath, and then redissolved in 2.0 ml acetone for subsequent clean-up prior to analysis by GC-NPD.

Sediment samples were analysed following liquid-solid extraction (Mansour et al., 1998). Sediment samples were extracted after the excess water in the sample had been removed by suction from a Buchner funnel through a Whatman No. 1 filter paper, and then air dried for three hours. The moisture content of the air dried sediment samples was determined after thoroughly mixing the sample. About 20 g accurately weighed of dried sediment sample was weighed and placed in a 250ml flask, and 100 ml of acetone were added and the flask stoppered. The mixture was then shaken on the mechanical shaker for 30 min., and then filtered through anhydrous sodium sulphate. The sample was then quantitatively transferred to the rotary evaporator maintained at 40^oC, and the crude extract was concentrated to near dryness and then redissolved in 2 ml acetone for subsequent clean-up prior to GC-NPD analysis.

For clean-up the concentrated extract was transferred to a chromatographic column plugged with glass wool and containing 5g of Florisil and 1g of anhydrous Na_2SO_4 pre-cleaned by eluting with 10% diethyl ether in hexane. Care was taken not let the column run dry. The column was then eluted twice using 100 mL each of 5% diethyl ether in hexane and 10% diethyl ether in hexane. The two fractions were collected and concentrated to near dryness and then redissolved in 2 ml acetone for subsequent GC-NPD analysis (Tse et al., 2004).

2.5. Gas chromatography

Gas chromatographic conditions employed are given in Table 2. One microliter of the concentrated extract was injected each time. Pirimiphos-methyl, chlorpyrifos and fenamiphos eluted at 3.37, 3.70 and 5.19 min. respectively in the GC-NPD chromatogram, see Fig. 1. Quantification was done by the external standard technique. Recoveries of 85±1 %, 86±2 and 87±2% , and of 95±2 %, 95±2 and 70±2% were obtained when dam water and sediment samples spiked with 5 ng/g and 20 ng/g respectively pirimiphos-methyl, chlorpyrifos and fenamiphos respectively, were extracted and determined as described above. Pirimiphos-methyl, chlorpyrifos and fenamiphos were not detected when blank determinations were done on the sediment and dam water samples. The results obtained are shown in Table 3. Table 4 shows the material balance calculations for the initial and final distribution of chlorpyrifos, pirimiphos-methyl and fenamiphos in the microcosm.

GC compartment	Parameter	Setting
Column	Initial temperature	195°C
	Initial hold time	2.0 min.
	Final temperature	235°C
	Temperature program	10°C/min.
	Final hold time	9.0 min
	N_2 carrier gas flow rate	5.2 ml/min.
Injector	Temperature	230°C
	Mode	Splitless
Detector	Type	NPD
	Temperature	300°C
	Range	1
	Auto zero	on
	Time constant	200
Detector gas flows	Air	179.0 ml/min.
	Hydrogen	4.4 ml/min.

Table 2. Gas chromatographic conditions employed.

t (days)	Chlorpyrifos			Pirimiphos-methyl		Fenamiphos		
	$C_{t(DW)}$	$C_{t(LW)}$	$C_{t(LS)}$	$C_{t(LW)}$	$C_{t(LS)}$	$C_{t(DW)}$	$C_{t(LW)}$	$C_{t(LS)}$
BC	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0	149.8	117.7	1280	117.0	930	156.0	80.1	108
3	149.9	115.5	930	116.1	740	156.0	67.1	99
6	149.1	113.3	680	101.6	nr	155.1	63.0	67
9	149.0	111.3	710	94.7	560	150.4	42.9	59
15	148.9	109.2	360	85.4	374	149.3	32.0	42
21	148.0	106.3	180	75.1	260	149.1	15.9	43
26	147.0	106.3	172	72.1	255	149.1	16.0	29
34	147.0	105.4	173	68.2	240	148.0	14.8	21
50	147.0	106.4	168	66.6	220	148.0	12.9	18
64	145.9	105.2	164	64.9	190	147.9	11.0	12
72	145.9	105.1	163	60.6	187	147.8	10.7	11
90	145.9	105.1	164	60.2	191	147.8	10.7	10

Table 3. Concentration (μg/g) of chlorpyrifos, pirimiphos-methyl and fenamiphos in distilled waster, Kutsaga dam water and sediment phases of the experiment as a function of time, t (C_t = concentration (μg/g) at time t; DW = distilled water; LW = lake water; LS = Lake sediment; BC = before charging; nr = no result).

Pesticide	Phase	Initial concentration		Final concentration	
		Analysis[a]	Total[b]	Analysis[a]	Total[b]
Chlorpyrifos	Water	117.7	11.77	105.1	10.1
	Sediment	1280	2.27	164	0.317
	Container[c]		0.76		0.76
	Deg. loss[d]				3.623
	Total		14.90		14.80
Pirimiphos-methyl	Water	117.0	11.70	60.2	6.02
	Sediment	930	1.79	191	0.369
	Container[c]		1.51		1.51
	Deg. Loss[d]				7.101
	Total		15.0		15.0
Fenamiphos	Water	80.1	8.01	10.7	1.070
	Sediment	108	0.21	10	0.019
	Container[c]		6.78		6.78
	Deg. Loss[d]				7.131
	Total		15.0		15.0

[a]μg/g/day (see Table 2); [b]g/vol (or mass) of phase; [c]Adsorbed to walls of the container; no change assumed during period of the experiment. [d]Loss due degradation (see Table 5).

Table 4. Material balance calculations: Initial and final distribution of chlorpyrifos, pirimiphos-methyl and fenamiphos in the microcosm.

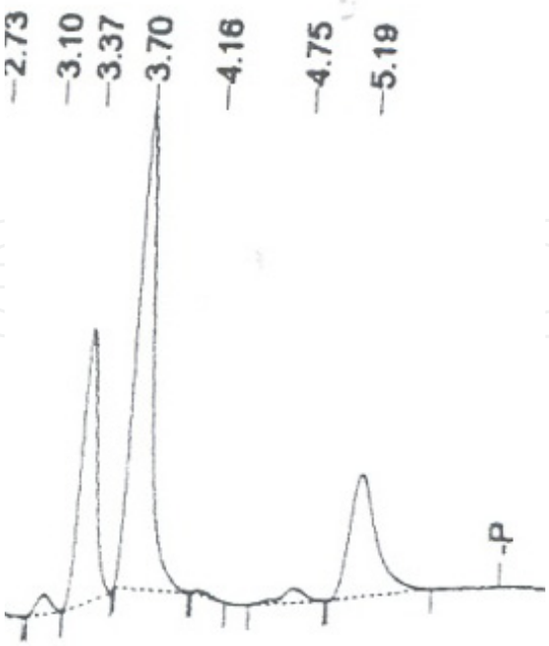

Figure 1. Typical chromatogram for the sediment sample collected on day 9 showing the retention time for pirimiphos methyl, chlorpyrifos and fenamiphos at 3.37, 3.70 and 5.19 min. respectively.

Figure 2 shows the persistence curves for chlorpyrifos and fenamiphos in the water phase of the experiment and control. The loss in the pesticide after a given time period t in days, i.e., $C_t - C_o$, was calculated and plotted as a function of t in Figs. 3 to 5. The slopes of the linear portions of the curves in Fig. 3 to 5 were obtained using regression analysis, and give the respective rates of degradation, which are summarized in Tables 5.

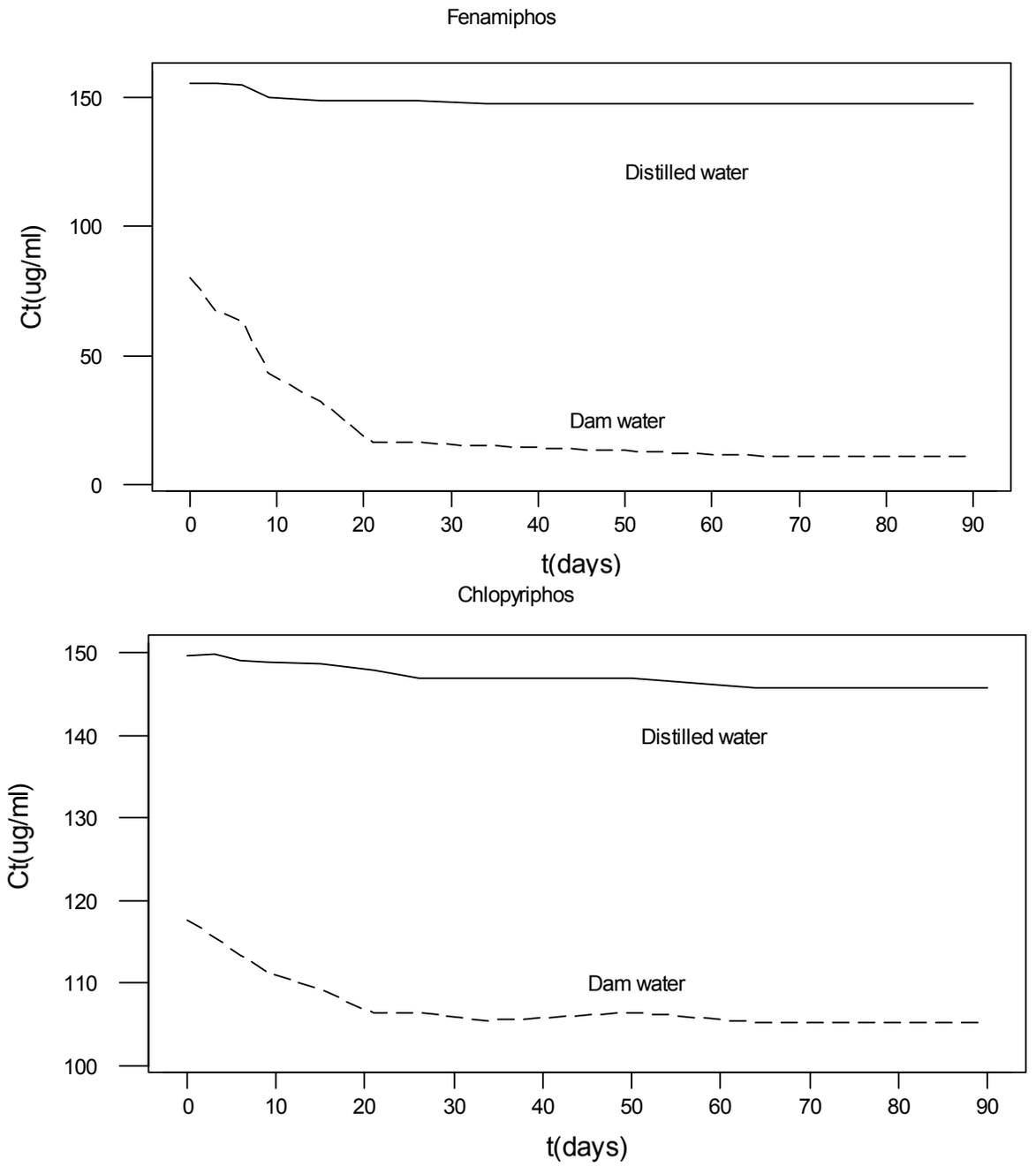

Figure 2. Persistence of chlorpyrifos and fenamiphos in distilled water and Kutsaga dam water

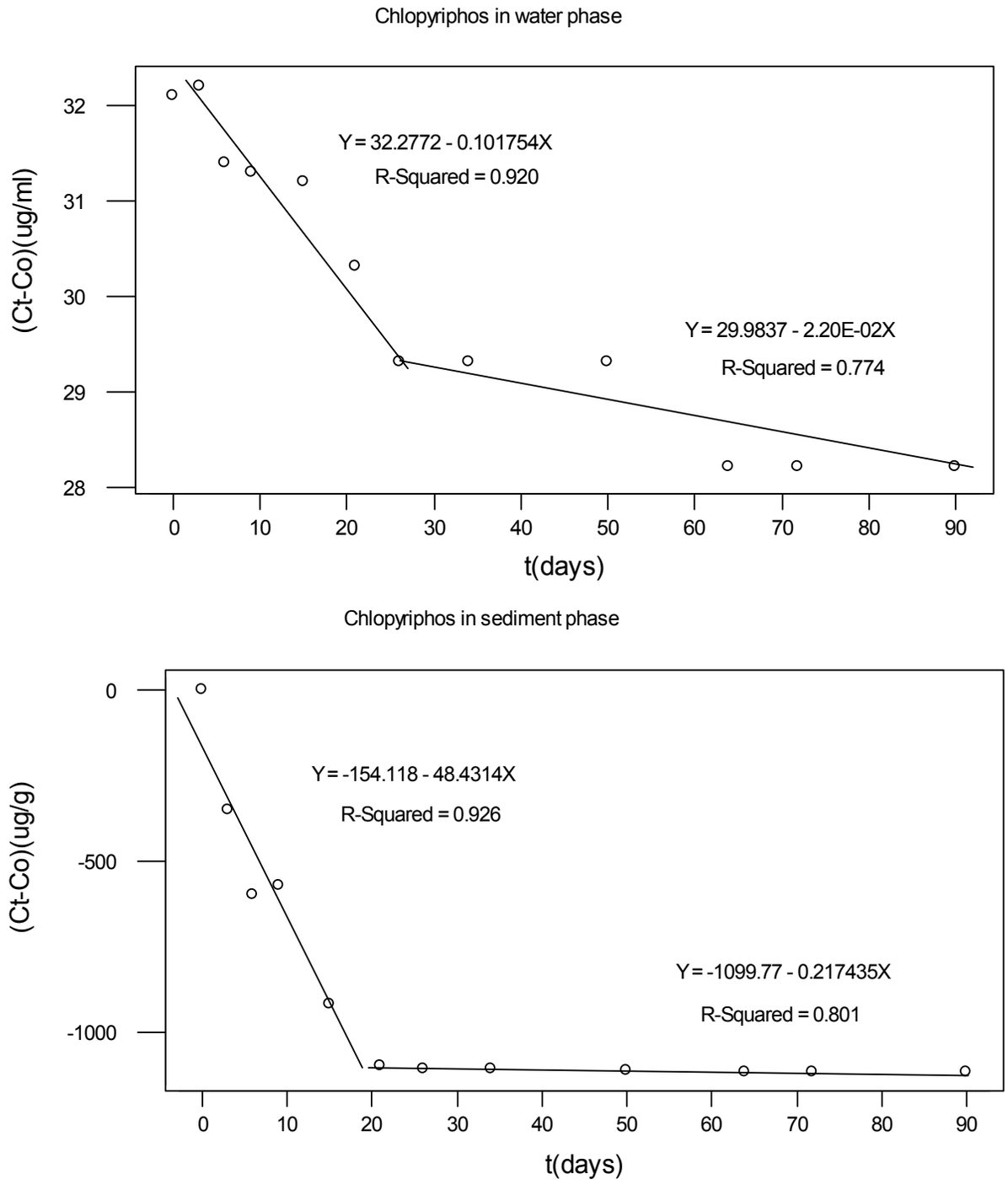

Figure 3. Rates of degradation of chlorpyrifos in the water phase and sediment phase of Kutsaga dam

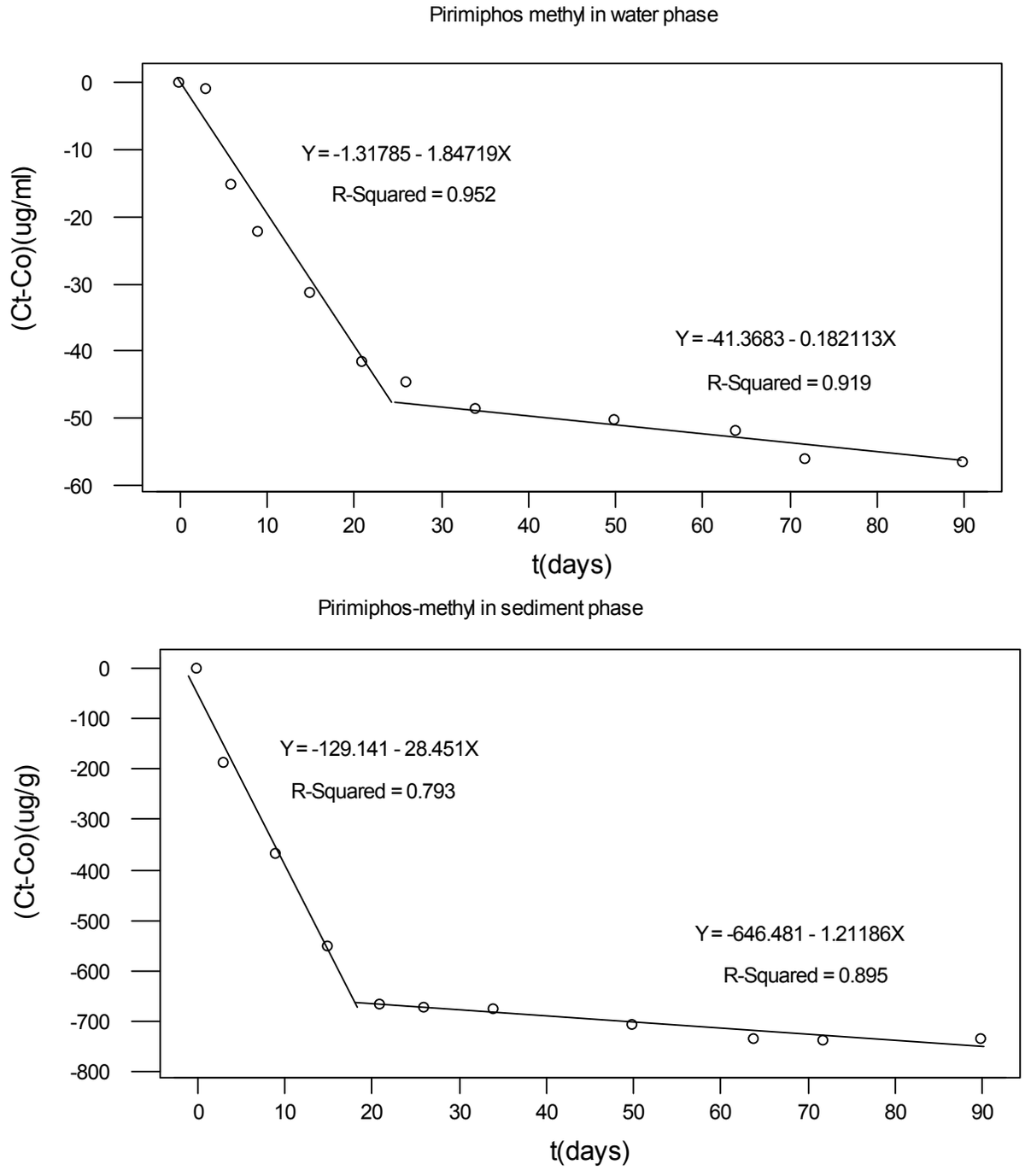

Figure 4. Rates of degradation of pirimiphos-methyl in the water phase and sediment phase of Kutsaga dam

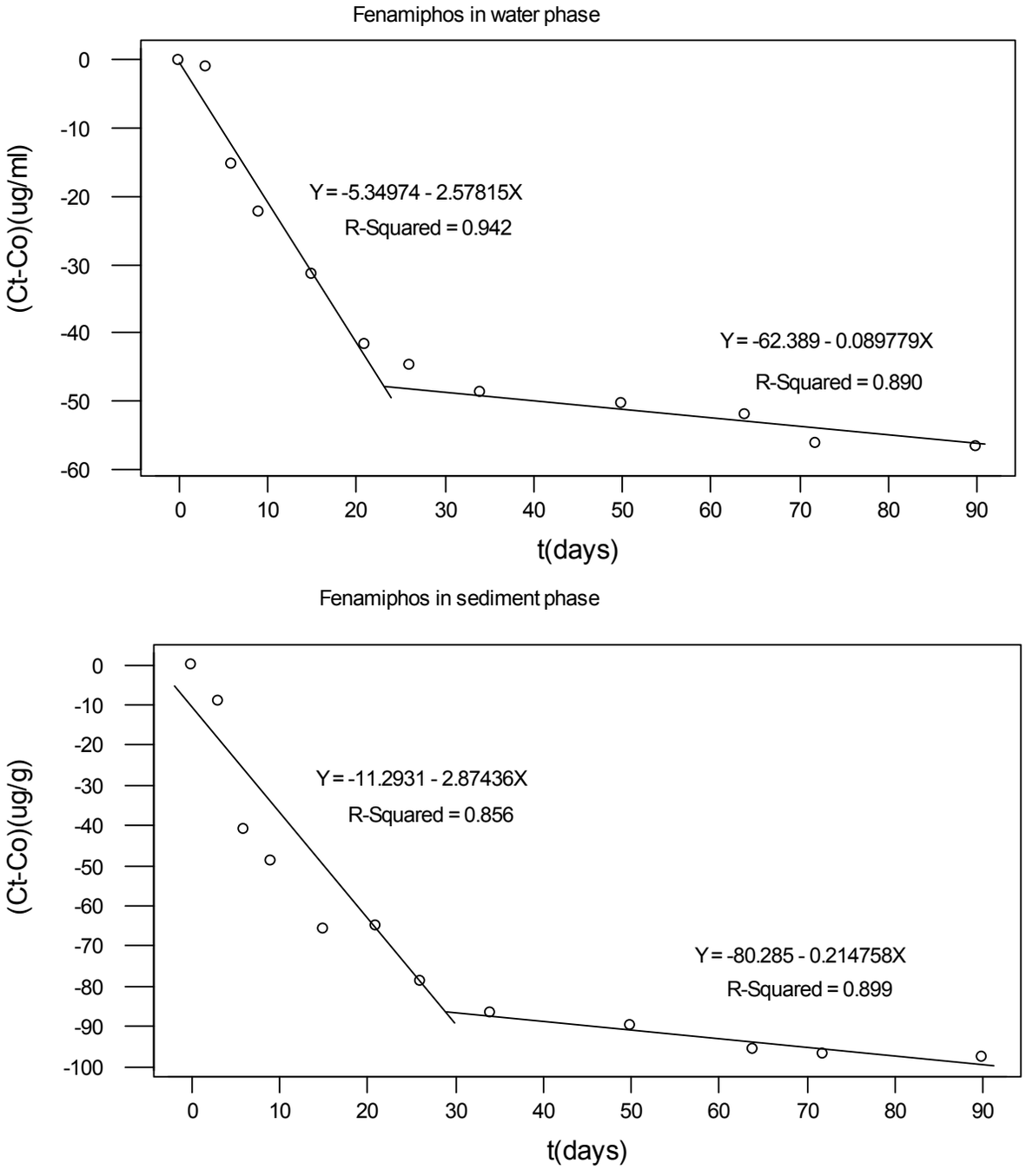

Figure 5. Rates of degradation of fenamiphos in the water phase and sediment phase of Kutsaga dam

Rate of degradation (μg/g / day)				Inference
Description	Chorpyrifos	Pirimiphos-methyl	Fenamiphos	
Fast, water phase	0.102	1.847	2.578	Free, in solution
Slow, water phase	0.022	0.182	0.098	Adsobed, in solution
Fast, sediment phase	48.43	28.48	2.874	Adsorbed onto sediment particle surface
Slow, sediment phase	0.217	1.212	0.215	Adsorbed onto sediment colloidal particles.

Table 5. Rates of degradation (μg/g / day) of chlorpyrifos, pirimiphos-methyl and fenamiphos in the sediment and water phases of the dam-water-and-sediment experiment.

3. Results and discussion

A heavy green algal growth developed in the Dam water plus sediment experiment after 6 days. The algal growth disappeared after 64 days. No algal growth was observed in the distilled water experiment. The results of material balance calculations based on day zero analysis data for the dam water-plus-sediment experiments in Table 4 show that (a) of the 14.9g chlorpyrifos charged into the experimental container, 11.77g and 2.27g respectively were found in the water and sediment phases, while the balance of 0.76g is attributed to adsorption by the walls of the container, (b) of the 15g pirimiphos-methyl charged into the experimental container, 11.7g and 1.79g respectively were found in the water and sediment phases, while the balance of 1.51g is attributed to adsorption by the walls of the container, and (c) of the 15g fenamiphos charged into the experimental container, 8.01g and 0.21g respectively were found in the water and sediment phases, while the balance of 6.78g is attributed to adsorption by the walls of the container. The amount of each pesticide lost by degradation over the 90 day period of study is shown in Table 6.

3.1. Contribution from chemical and photochemical degradation

Comparison of the data for the degradation of chlorpyrifos and fenamiphos in distilled water and the water phase of the river water plus sediment experiment, in Table 3 and Fig. 2 shows that, whereas in the distilled water experiment 2.6% and 5.3% degradation is achieved in 90 days respectively for chlorpyrifos and fenamiphos, in the water phase of the dam water plus sediment experiment 25.8% and 86.75% degradation respectively is obtained in the same period. This suggests that chemical degradation and photochemical degradation are minor routes for the degradation of chlorpyrifos and fenamiphos, if cognizance is taken of the fact that the 2.6% and 5.3% degradation observed in the distilled water experiments also contain a contribution from microbial degradation as a result of microbial contamination from the atmosphere, as no preservative was added to the distilled water control.

Pesticide	Speciation[a]	Rate of degradation (μg/g/day)	Persistence (days)	Phase volume/mass	Pesticide mass in speciation form (g).
Chlorpyrifos	Free, in solution (WP)	0.102	26	100 000 L	0.265
	CP adsorbed (WP)	0.022	>90	100 000 L	0.198
	SPS adsorbed (SP)	48.43	20	1930 g	1.869
	CP adsorbed (SP)	0.217	>90	1930 g	0.038
	Total				2.371
Pirimiphos-methyl	Free, in WP	1.847	25	100 000 L	4.618
	CP adsorbed (WP)	0.182	>90	100 000 L	1.638
	SPS adsorbed (SP)	28.48	20	1930 g	1.099
	CP adsorbed (SP)	1.212	>90	1930 g	0.211
	Total				7.565
Fenamiphos	Free, in WP	2.578	24	100 000 L	6.187
	CP adsorbed (WP)	0.098	>90	100 000 L	0.882
	SPS adsorbed (SP)	2.874	30	1930 g	0.111
	CP adsorbed (SP)	0.215	>90	1930 g	0.037
	Total				7.238

[a]WP = water phase; SP = sediment phase; CP = colloidal particle; SPS = sediment particle surface.

Table 6. Speciation and mass of the different speciation forms of chlorpyrifos, pirimiphos methyl and fenamiphos detected by the experiment.

3.2. Microbial degradation

From Table 3, it is apparent that 52.6%, 25.8% and 86.75% degradation was achieved in 90 days respectively for pirimiphos-methyl, chlorpyrifos and fenamiphos in the experiment. As explained above, most of this degradation is attributed to microbial degradation. From Figures 3 to 5, it is apparent that the degradation of the three insecticides in the water and sediment phases, can be resolved into two linear rates: an initial fast rate of degradation, followed by a slower rate. The rapid degradation in the water phase lasted for about 25, 26 and 24 days respectively for pirimiphos-methyl, chlorpyrifos and fenamiphos. In the sediment phase, the rapid degradation lasted for about 20 days for pirimiphos-methyl and

chlorpyrifos, and 30 days for fenamiphos. The slower rate of degradation lasted up to the end of the experiment period for all three pesticides.

The fact that both the fast and the slower rates of degradation of pirimiphos-methyl, chlorpyrifos and fenamiphos in the water phase, as well as the sediment phase, of the experiment are linear, points to steady state kinetics, and hence microbial degradation, whereby the observed rates correspond to the plateau in the Michelis-Menten curve (Zaranyika and Nyandoro, 1993; Zaranyika et al., 2010). The difference between the fast linear rate and the slow linear rate of degradation in the water phase of the experiment is attributed to adsorption of the pesticide by colloidal particles (Nomura and Hilton, 1977; Zaranyika and Nyandoro, 1993; Zaranyika et al., 2010).

Linear rates for biodegradation were reported previously by Siddique et al. (2003) when the biodegradation of α- and β-endosulfan by Fusanium ventricosum and a Pandoraea species was studied using zero order kinetics.

Table 4 summarizes the different rates of degradation obtained in the experimental ecosystem. The fast and slow rates of degradation in the water phase are attributed to degradation of free and colloidal particle adsorbed insecticide respectively, as has been discussed above. The existence of free and particle bound insecticide in water samples was previously demonstrated by Lee and Skemitt (1998). These workers developed a small-volume filtration method for the filtration of small volumes of water for separation of dissolved pesticide residues, with which they were able to demonstrate the existence of free and particle bound insecticide in water samples of moderate or low turbidity, using immunoanalysis. These workers were also able to show that in highly turbid water, antibodies were unable to recognize particle bound endosulfan as well as other pesticides. This is consistent with the microbial degradation mechanism being proposed above. If we assume that microorganisms will only bind the pesticide in the desorbed state, then the rate of insecticide desorption will be rate limiting for the colloidal particle adsorbed pesticide (Briggs, 1981; Nicholls, 1994).

3.3. Speciation trends of pirimiphos-methyl, chlorpyrifos and fenamiphos in the microcosm

Persistence data in Table 4 are presented in Fig. 6 in bar graph form. Comparison of the slow rates in the water phase and the slow rates in the sediment phase in Fig. 6 (B), shows that the slow rates in the water and sediment phases follow a similar pattern, i.e., degradation rates follow the order: chlorpyrifos < pirimiphos-methyl > fenamiphos. The similarity in the pattern of the slow rates in the water phase and sediment phase, suggests that the slow rates arise from the degradation of similar speciation forms. For the water phase, the slow rate can only be attributed to degradation of pesticide molecules adsorbed by colloidal particles within the water phase of the experiment, hence we conclude that the slow rate in the sediment also results from degradation of colloidal particle adsorbed pesticide.

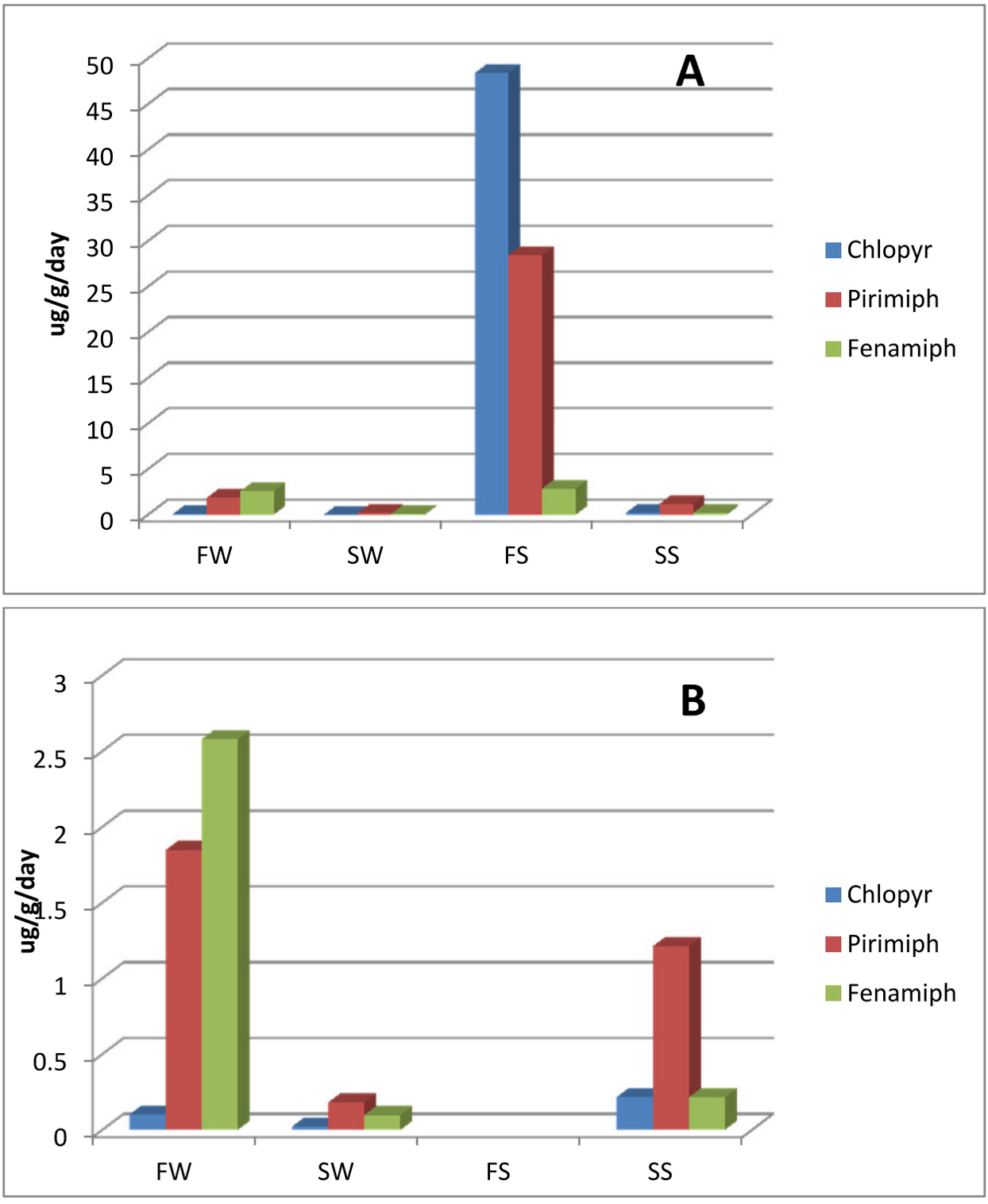

Figure 6. Persistence pattern of free and colloidal and/or sediment particle adsorbed insecticide: (Chlorpyr = chlorpyrifos; Pirimiph = pirimiphos-methyl; Fenamiph = fenamiphos; FW = fast degradation in water phase; SW = slow degradation in water phase; FS = fast degradation in sediment phase; SS = slow degradation in sediment phase; A: All 4 speciation forms; B: FS speciation form removed)..

It is recognized that the major adsorption interactions which bind small molecules in soil environments involve soil particles of colloidal dimensions (Burchill et al., 1981). Zaranyika and Mandizha (1998) proposed an adsorption/desorption equilibrium model whereby each colloidal particle, C, is associated with n pesticide molecules, X, thus:

$$nX + C \rightleftharpoons CX_n \quad (3)$$

and used a modified Freundlich isotherm to determine the value of n for the adsorption of amitraz [N'-(2,4-dimethylphenyl)-N-(((2,4,-dimethylphenyl)imino)methyl)-N-methyl-methanimidamide][33089-61-1] by a river sediment. A value of n of 0.26±0.03 was obtained, suggesting that a single molecule of amitraz was associated with 4 colloidal particles. The most likely structure of the adsorption complex in this case is one in which each phenyl ring of amitraz is sandwiched between two colloidal particles, and can be represented by XC_n, where n is the number of colloidal particles associated with each amitraz molecule. Different structures of such pesticide-colloidal particle complexes are expected, depending on the nature of the pesticide molecule and nature of the colloidal particles encountered in the ecosystem. Although equation 3 assumes a single-step desorption, in practice desorption of a pesticide molecule from such XC_n pesticide-colloidal-particle adsorption complexes in which $n > 1$ involves several steps, hence degradation of the pesticide should be very slow. Such adsorption complexes are to be expected in the bulk water phase, as well as in the sediment phase pore water.

A comparison of the pattern of fast rates in the water phase in Fig. 6(B), and the pattern of fast rates in the sediment in Fig. 6(A), shows that the pattern of rates is reversed in the sediment phase. This suggests a difference in the speciation of the pesticide in the water phase and sediment phase. Whereas the fast rate in the water phase is attributed to degradation of free pesticide molecules in solution, the degradation of the free pesticide in the pore water of the sediment appears to be influenced by the sediment. The pore water is in close contact with sediment particles, and a plausible explanation for the apparent difference in speciation of pirimiphos-methyl, chlorpyrifos and fenamiphos in sediment pore water is that molecules of pesticide in the pore water are involved in surface adsorption equilibria involving sediment particles, thus:

$$\vdash S + X \rightleftharpoons \vdash S\text{-}X \quad (4)$$

where $\vdash S$ is a surface adsorption site on a sediment particle. The rate of degradation will be limited by the rate of desorption of pesticide molecules from such surface adsorption complexes. These surface adsorption complexes are essentially 1:1 monolayer complexes, hence desorption is very fast. However we would expect rates of degradation to be slower than in the water phase because of these sediment particle adsorption equilibria. The much higher rates of degradation of the free pesticide in the sediment pore water has been attributed to greater microbial populations in the sediment. (Zaranyika and Nyandoro, 1993; Zaranyika et al., 2010).

3.4. Proposed degradation kinetic model

The degradation trends above are similar to those obtained by Zaranyika and Nyandoro (1993) for glyphosate , and Zaranyika et al. (2010) for endosulfan I and endosulfan II, as explained above. In terms of the speciation forms discussed above, data in Table 4 suggest that the degradation of pirimiphos-methyl, chlorpyrifos and fenamiphos occurs according to the steps shown in Table 7.

3.4.1. Fast degradation in water phase.

From Steps 2, it can be shown that

$$\frac{dP}{dt} = \frac{k_2 k_3 [X_B][E]}{k_{-2} + k_3} = k_E [X_B] \tag{5}$$

where k_E is the apparent rate constant for the enzymatic degradation of the microbial bound insecticide.

Step	Water phase		Sediment phase	
	Reaction[a]	Rate constant	Reaction[a]	Rate constant
1(a)	$X + M \rightarrow X_B$	k_1	$X + M \rightarrow X_B$	k_1
	$X_B \rightarrow X + M$	k_{-1}	$X_B \rightarrow X + M$	k_{-1}
2	$X_B + E \rightarrow XE$	k_2	$X_B + E \rightarrow XE$	k_2
	$XE \rightarrow X_B + E$	k_{-2}	$XE \rightarrow X_B + E$	k_{-2}
	$XE \rightarrow P + E$	k_3	$XE \rightarrow P + E$	k_3
1(b)	$X + nC \rightarrow XC_n$	k_4	$X + nC \rightarrow XC_n$	k_4
	$XC_n \rightarrow X + nC$	k_{-4}	$XC_n \rightarrow X + nC$	k_{-4}
1(c)			$X + S \rightarrow XS$	k_5
			$XS \rightarrow X + S$	k_{-5}

[a]X = insecticide; M = microorganism; X**E** = insecticide-enzyme complex; **E** = enzyme;
P = products; Subscript B = "microbial-bound"; C = colloidal particle; XC = insecticide-colloidal particle complex; S = sediment particle; XS= insecticide sediment particle complex.

Table 7. Degradation of chlorpyrifos, pirimiphos-methyl and fenamiphos in the aquatic environment: Proposed kinetic model.

From steps 1(a) , it can be shown that

$$[X_B] = \frac{k_1}{k_{-1}} [X][M] \tag{6}$$

Within the organism [E] >> [X_B], hence [E] = 1, and when [X] is in large excess of [M], [X] = 1, hence eq. 5 reduces to eq. 7:

$$\frac{dP}{dt} = k_E\left(\frac{k_1}{k_{-1}}\right)[M] = k'_E \tag{7}$$

where k'_E is the apparent linear rate of degradation of the pesticide in the water solution phase of the experiment. It is apparent from eq. 7 that k'_E is a function of the pesticide-micro-organism binding equilibrium constant, $K_B = k_1/k_{-1}$. The value of K_B will depend on the structure and properties of the pesticide, and micro organism type.

3.4.2. Slow degradation in water phase and sediment phase

From Steps 1(a) and 2, assuming [E] = 1, it can be shown that

$$\frac{dP}{dt} = \frac{k_1 k_2 k_3 [X][M]}{k_{-1}(k_{-2} + k_3)} \tag{8}$$

From Step 1(b)

$$[X] = \frac{k_{-4}[XC_n]}{k_4[C]^n}$$

hence eq. 8 becomes

$$\frac{dP}{dt} = \frac{k_1 k_2 k_3 k_{-4}[XC_n]_w[M]_w}{(k_{-2} + k_3)k_{-1}k_4[C]_w^n} = k_{Cw}[XC_n]_w \tag{9}$$

and

$$\frac{dP}{dt} = \frac{k_1 k_2 k_3 k_{-4}[XC_n]_s[M]_s}{(k_{-2} + k_3)k_{-1}k_4[C]_s^n} = k_{Cs}[XC_n]_s \tag{10}$$

where the subscripts w and s denote concentrations in the water phase and sediment phase respectively, and k_C is the apparent rate constant for the degradation of colloidal particle adsorbed pesticide. When [C] is in large excess of [X], [XC_n] is constant and assuming [M] is constant, Eqs. 9 and 10 reduce to

$$\frac{dP}{dt} = k'_{Cw} \tag{11}$$

and

$$\frac{dP}{dt} = k'_{Cs} \tag{12}$$

where k'_{Cw} and k'_{Cs} are the linear rates of degradation of the colloidal particle adsorbed pesticide in the water phase and sediment phase, respectively, of the experiment.

3.4.3. Fast degradation in sediment phase

From Step 1(c)

$$[X] = \frac{k_{-5}[XS]}{k_5[S]}$$

hence eq. 8 becomes

$$\frac{dP}{dt} = \frac{k_1 k_2 k_3 k_{-5}[XS][M]}{(k_{-2} + k_3)k_{-1}k_5[S]} = k_S[XS] \tag{13}$$

where ks is the apparent rate constant for the degradation of sediment particle adsorbed pesticide. When [S] is in large excess of [X], [XS] is constant and assuming [M] is constant, Eq. 13 reduces to

$$\frac{dP}{dt} = k'_S \tag{14}$$

where k'_S is the linear rate of degradation of the sediment particle adsorbed pesticide in the sediment phase of the experiment.

3.4.4. Overall rates of degradation in the water phase and sediment phase

From Table 4, the overall rate of degradation in the water phase of the experiment is given by the sum of Eq. 5 and Eq. 9, or Eq. 7 and Eq. 11, i.e.,

$$\frac{dP}{dt} = k_E[X_B]_w + k_C[XC_n]_w \tag{15}$$

or

$$\frac{dP}{dt} = k'_{E(W)} + k'_{C(W)} \tag{16}$$

whereas the overall rate of degradation in the sediment phase of the experiment is given by Eq. 13 and Eq. 10 or Eq. 14 and Eq. 12, i.e.,

$$\frac{dP}{dt} = k_S[XS] \ + k_C[XC_n]_{(S)} \tag{17}$$

or

$$\frac{dP}{dt} = k'_S + k'_{C(S)} \tag{18}$$

In the Introduction section we noted that persistence data for pesticides in the aquatic environment reported in the literature in terms of half-lives of the pesticide, in accordance with the conventional pseudo first order kinetics approach, are highly variable, whereas in true first order kinetics, a constant value should be obtained for the half-life irrespective of the actual environmental conditions prevailing. It is apparent from Eqs. 8, 9, 10 and 13 above that the linear rates of degradation obtained in terms of the steady state kinetic model presented above, depend on the type and density of the microbial organisms responsible for the degradation. The actual rates of degradation observed will also depend on the composition of the water and sediment, temperature and pH, in as much as these will affect the populations of the different microorganisms in the study medium. Thus variable rates of degradation are expected depending on the specific environmental conditions prevailing.

3.5. Possible pollution remediation strategies

Equations 8, 9 and 11 define the factors that affect the rate of degradation of pirimiphos-methyl, chlorpyrifos and fenamiphos in the aquatic environment. Any remediation measures for the abatement of pirimiphos-methyl, chlorpyrifos and fenamiphos pollution of aquatic ecosystems, must be designed to (a) maximize k_1, k_2, k_3, k_{-4}, k_{-5} and the density of microorganisms capable of degrading the pesticide, and (b) minimize k_4 and k_5, the rate constants for the adsorption of the pesticide by colloidal and sediment particles in the ecosystem. The rate constants k_1, k_2 and k_3 can be maximized by proper selection of the microorganism(s). Under such conditions, $k_3 \gg k_{-2}$, and assuming C and S are in large excess, eqs. 9 and 13 reduce to:

$$k_{C(\max)} = k_2 \left(\frac{k_1}{k_{-1}} \right) \left(\frac{k_{-4}}{k_4} \right) [M] \tag{19}$$

And

$$k_{S(\max)} = k_2 \left(\frac{k_1}{k_{-1}} \right) \left(\frac{k_{-5}}{k_5} \right) [M] \tag{20}$$

Many attempts are being made to find the optimal pH and the best microorganisms for the degradation of specific pesticides (Singh BK et al., 2003, 2006, Megharaj et al., 2003; Caceres et al., 2008; Cabrera et al., 2010; Yang et al., 2005; Salama et al., 1999). Equations 19 and 20 suggest that even after k_1, k_2, k_3 and [M] have been maximized, the rate of desorption of the pesticide can still be rate limiting.

Figures 3 to 5 show that the degradation of pirimiphos-methyl, chlorpyrifos and fenamiphos in the aquatic environment proceeds via biphasic linear rates in the water phase as well as the sediment phase. Similar results were reported previously for endosulfan I, endosulfan II and glyphosate, although only one linear rate was obtained for glyphosate in the sediment phase. This suggests that the kinetic model proposed above will also apply in the cases of endosulfan I, endosulfan II and glyphosate, and the comments made above regarding possible remediation strategies for pollution of aquatic ecosystem with pirimiphos-methyl, chlorpyrifos and fenamiphos, should also apply in the case of pollution of aquatic ecosystems with endosulfan and glyphosate.

4. Conclusions

From the foregoing discussion, we conclude that pirimiphos-methyl, chlorpyrifos and fenamiphos exist in two adsorption speciation forms in the aquatic environment. The adsorption forms consist of (a) a sediment particle surface adsorbed form which is highly labile, and in equilibrium with pirimiphos-methyl, chlorpyrifos and fenamiphos in solution in the sediment phase pore water; and (b) a slow degradation colloidal particle adsorbed form, found in the water phase as well as the sediment phase. The degradation of all speciation forms proceeds via linear rates, and is primarily due to microbial decomposition.

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Acknowledgement

This work was supported by a grant from the Research Board of the University of Zimbabwe. The support of one of us (J. Mlilo) by the Zimbabwe Tobacco Research Board is gratefully acknowledged.

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