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Full Length Research Paper

Degradation Dynamics of Malathion and Phorate in Different Environmental Systems

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The degradation of Malathion and Phorate was studied in four soil samples under different laboratory-controlled and environmental conditions. Soil and water samples were collected from different sites. Soil samples, having been contaminated with malathion and phorate and were poured in different water samples like well water, river water and sea water so as to understand the leaching and degradation ability of malathion and phorate in different environmental matrices. These matrices were selected on the basis of their different physico-chemical characteristics and chemical composition. The investigation results showed that the malathion and phorate were hydrolyzed and degraded faster at basic environments with high salinity, whereas it was observed that they were extremely slower in the neutral and acidic environments. It was considered that it was due to the physico-chemical characteristics of soil, water and salinity. The type of soil and its organic carbon content along with other microbiological degradation had also influenced the degradation of malathion and phorate. It was observed that the degradation of Malathion and Phorate was faster in sea water with high salinity. Limited degradation was observed in distilled water followed by river water and ground water. The degradation was pH dependent. Malathion and phorate were degraded more rapidly at basic media.

Key words: Malathion, phorate, degradation, environmental matrices.

INTRODUCTION

Several hundreds of pesticides of diverse chemical nature are widely used worldwide for agricultural and non-agricultural purposes (Andres et al., 2006). In the last century, the development and use of pesticides have played an immensely important role in the increase of agricultural productivity, because of their effectiveness, low cost and acute toxicity. Pesticides applied to soil, crops and animals may be adsorbed by, or degraded in soil. They may reach streams or ground water through leaching, spillage, aerial transport or attached to eroding soil, and be adsorbed by soil, plants and eatable vegetables that begin the introduction of pesticides in living organisms (Mohamed et al., 2009). Among newly developed pesticides, organophosphorous pesticides (OPPs) are most commonly used (Akhtar et al., 2007). To protect crops and improve agricultural production by controlling insects, diseases, fungi and other pests, organophosphorus pesticides are used worldwide. The usage of organophosphorus pesticides (OPPs) is preferred to the usage of other pesticides such as, for example, organochlorine compounds, for organo-phosphorus pesticides degrade much faster in the environment (Schellin et al., 2004). OPPs are widely found in water resources. They are released into the environment from manufacturing, transportation and agricultural applications. OPPs affect human health by attacking the system of neural transmission and may cause permanent neurological damage, such as, paralysis of the legs (Ziming and James, 2000). Organic phosphate pesticides are of great environmental importance primarily because they are toxic to mammals and birds and are soluble in water, to contaminate surface water and ground water (Ku et al., 2007).

Malathion [O,O dimethyl-S-(1-2 dicarbethoxy ethyl) phosphorodithioate] is an organophosphorous insecticide

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widely used in both domestic and agricultural contexts. Malathion is a nonsystemic, wide-spectrum organophosphorous pesticide and suited for the control of sucking and chewing insects on fruits and vegetables, and is also used to control mosquitoes, flies, household insects, animal parasites. Malathion has also been used to control the Mediterranean fruit fly in Australia. Malathion itself is of low toxicity; however, absorption or ingestion into the human body readily results in its metabolism to malaxon, which is substantially more toxic. Malathion is toxic and carcinogenic in nature (Senthilkumaar et al., 2010). Malathion has several chemical bonds that are potentially labile under anticipated environmental reaction conditions (Wolfe et al., 1975).

Phorate [O,O-diethyl S-ethylthiomethyl phosphorodithioate] is an organophosphorous insecticide and acaricide used for the control of sucking and biting insects, mites and certain nematodes on root and feed crops, cotton, brassicas and coffee (Pesticide Registrant Survey Report, 1986). Phorate released to the soil is rapidly oxidized to the sulphoxide and sulphone forms and their phosphorothioate analogues, which are then, hydrolyzed (Agrochemicals Hand Book, 2nd edition, 1988).

Analysis of organophosphorus (OPs) and assessment of their impact on the aquatic environment are complicated because OPs are decomposed by various natural conditions in the environment: by hydrolysis, photo degradation, and bacterial degradation. Relatively little research in the identification of a comprehensive list of OP degradation products has been carried out. In some cases, the degradation products show higher toxicity than the parent compound. Therefore, identification of degradation products of pesticides after their release into the environment is necessary for the evaluation of the toxicity of OPs. The extensive use of OPs makes them common environmental pollutants in aqueous environments including ground water, surface water and drinking water. Most of the pesticides fail in natural degradation. The rapidly growing use of pesticides, often accompanied with insufficient technical research or advice, has unfortunately generated many environmental problems. As a result, human beings are exposed indirectly under pesticides, which are usually in small amount of certain foodstuff. There is now an increasing environmental grave concern with regard to these compounds because of their potential and deleterious side effects on the aquatic organisms and humans (Zhao et al., 2009).

In this study, the degradation of Malathion and Phorate has been investigated in the contaminated soil samples poured in river, well and sea water samples and analyzed spectrophotometrically with an established method.

MATERIALS AND METHODS

All reagents used were of analytical reagent grade and double distilled water was used throughout the experiment. Malathion (technical grade 95.50%) and phorate (technical grade 93.20%) were obtained from Hyderabad Chemicals Ltd., Hyderabad, India. N-bromosuccinimide is obtained from Sigma Aldrich. Rhodamine B was obtained from National Laboratories, Pune, India. Acetic acid was obtained from Merck, India.

Sample collection

Soil Samples

Soil samples were collected from agricultural site, industrial site, residential area and dumping yard in Tirupati and sieved using 2000 µm mesh and stored in polyethylene bags. The bags were sealed air tight after filling with the soil samples and immediately carried to the laboratory for the measurement of pH, electric conductivity, redox potential, cation exchange capacity and organic carbon content and other parameters.

Water samples

Well water (Indira Nagar, Nellore), River water (Penna River, Nellore), and Sea water (Bay of Bengal, Nellore) samples were collected in polyethylene containers and immediately transported to the laboratory. For the ground water sample, more than 30 L of water was flushed before collection. The containers were carefully filled to overflowing without passing air bubbles through sample or trapping air bubbles in sealed containers. Sample containers were washed with detergent, rinsed with tap water, double distilled water and air dried before sampling. Water samples were filtered using 0.4 µm filter paper and stored for further studies.

Degradation of malathion and phorate in different environmental matrices

Degradation of malathion and phorate at the concentration of 20 µg g^{-1} in soil was carried out in 200 ml conical flasks. 10 g of soil was well mixed with 20 µg ml^{-1} of malathion and phorate and to it, 50 ml of river, well and sea water were added separately in different conical flasks. Control samples were prepared in the same manner by adding double distilled water instead of river, well and sea water. Then they were stirred continuously for 30 to 45 min with the magnetic stirrer and kept for settlement. About 8 to 12 h time had been taken by the soil water system for the full settlement. Then the concentration of the malathion and phorate in the aliquots (concentration range in between 0.1 and 1.0 µg/ml for malathion and 0.1 to 0.8 µg/ml for phorate) was determined spectrophotometrically by adding 1.5 ml (0.01%) of N-Bromosuccinimide, 1 ml of acetic acid, 0.5 ml (0.4 ml^{-1}) and 0.7 ml (0.02%) rhodamine B. A time gap of 10 min was maintained before the addition of rhodamine B (0.02%) to the aliquots. At the same time, sodium chloride and sodium acetate was added to the river, well and sea water samples to check the affinity of the salinity towards the malathion and phorate degradation.

The oxidation of the organophosphorous pesticide occurs with the addition of slight excess N-bromosuccinimide (NBS) to form oxidation products. The remaining unconsumed NBS is then estimated with the decrease in the colour intensity of rhodamine (Sunitha et al., 2007).

RESULTS AND DISCUSSION

This study selects various soil and water samples to

Table 1. Physicochemical properties and acute toxicity of the malathion and phorate (Druzina et al., 2007).

Insecticide	M (gmol^{-1})	Solubility (water mg $^{-1}$)	Vapour pressure (MPa)	Octanol/water partition coefficient (Log K_{ow})	Soil sorbtion coefficient (log Koc)	Acute toxicity LD50 (mg kg^{-1} rat)
Malathion	330	125 to 145	5.3	2.8 to 2.9	3.3	1000
Phorate	260	50	110	3.9	3	1.1 to 3.7

Table 2. Range of physicochemical parameters observed in case of four different soils.

Physico-chemical parameter	Value
pH (1:25)	5.4 to 6.5
Clay minerals	1 : 1 (kaolinite)
Moisture equivalent (%)	24 to 34
Total soluble salts (mm/cm)	1.16 to 1.26
CEC (meq %)	11.15 to 12.85
Exchange Ca (meq %)	3.55 to 4.10
Exchange K (meq %)	0.13 to 0.16
Organic Carbon (%)	1.5 to 0.9
Coarse sand (%)	9 to 11
Fine sand (%)	20 to 32
Silt (%)	24 to 28
Clay (%)	28 to 34
Na^{+} (mg kg^{-1})	10000 to 22000
Mg^{++} (mg kg^{-1})	5600 to 15000
K^{+} (mg kg^{-1})	900 to 4000
Ca^{++} (mg kg^{-1})	9000 to 67000
Fe^{+++} (mg kg^{-1})	28000 to 117000
Cu^{++} (mg kg^{-1})	4 to 160
Ni^{++} (mg kg^{-1})	1.8 to 135
Co++ (mg kg^{-1})	2 to 20
Mn++ (mg kg^{-1})	50 to 1200

Table 3. Water sample properties.

Water Sample	pH	Electrical Conductivity (m)
Sea Water	8.54	0.550
Well water	7.20	0.422
River water	5.70	0.414

check the leachability and degradation of malathion and phorate at various environmental conditions. Physico-chemical parameters of the Pesticides are shown in Table 1. Physicochemical characteristics of both soil and water may affect the degradation of the organic compounds. Organic content of Soil will also affect the degradation of the pesticides. Physicochemical charac-teristics of both soil and water samples were studied and shown in Tables 2 and 3.

Malathion, once deposited to the water, could undergo chemical, photochemical and biological processes. These degradation pathways depend on the presence of light, temperature, alkali, ionic, or enzymatic activity (Menzie et al., 1966; Paris et al., 1975; Walker, 1976; Wolfe, 1977). Hydrolysis occurs at several reactive centers in a given OPs molecule, where H_2O and OH^- act as nucleophiles. Thus, phosphorothioates are the major products after hydrolysis (Zhao et al., 2009).

Effect of pH on the degradation of malathion

Hydrolysis of organophosphates proceeds at higher rates under alkaline conditions, indicating that hydroxide-catalyzed hydrolysis is more effective than hydronium- or water-catalyzed hydrolysis. Control samples were prepared and degradation of Malathion was studied at different pHs. It is observed that the Malathion is more stable at acidic pH. At pH 8.5 the degradation rate of malathion is more. The results show that alkaline hydrolysis was the most competitive pathway for malathion degradation which was similar to other reports (Guerrand et al., 1970; Walker et al., 1972). At pH 6, 30% of the initial malathion was still present after 30 days. At pH 7, 7% was present after 30 days, while at pH 8.16, malathion was almost completely degraded in 15 days.

However, malathion is rapidly degraded *in vitro* by salt-marsh bacteria to malathion monocarboxylic acid, malathion dicarboxylic acid and various phosphorthionates as a result of carboxyesterase cleavage in sea water. Besides these, phosphatase activity produces desmethyl malathion, phosphomono- and dithionates, 4-carbon dicarboxylic acid and the corresponding ethyl esters (http://ces.iisc.ernet.in/energy/HC270799/HDL/ENV/enven/vol347.htm). Malathion had a half-life of 2.0 days in the seawater/sediment system (pH 7.3 to 7.7). If only the chemical hydrolysis were taking place, the half-life for malathion in the seawater / sediment experiment should be longer than that observed in the seawater at pH 8.0 to 8.5. The fact that malathion has such a short half-life at the lower pH indicates that microbial activity and/or interaction with the sediments may play a role in malathion degradation (William et al., 1989). Decomposition of malathion in river waters involves oxidation and hydrolysis as the main transformation routes. Hydrolysis occurs at several reactive centers in a given OPs molecule, where H_2O and OH^- act as

Degradation of malathion in water is pH dependant and degrades quickly in water with pH > 7.0. Hydrolysis is the main route of degradation in alkaline aerobic conditions. The half-life range of malathion is 0.2 weeks at pH 8.0 compared to 21 weeks at pH 6.0. Metabolites resulting from hydrolysis include; malaoxon, malathion alpha and beta monoacid, diethyl fumarate, diethyl thiomalate, O, O-dimethylphosphorodithioic acid, diethylthiomalate and O, O-dimethylphosphorothionic acid. Biodegradation also plays a role when pH < 7.0 and the rate of hydrolysis is slow relative to the rate of biodegradation. Breakdown constituents of biodegradation include beta monocaboxylic acid dicarboxylic acid and diethyl thiomalate. Malathion is not persistent under anaerobic conditions (Wang, 1991).

Effect of pH on the degradation of phorate

Under basic conditions, OH^- ions promote the rate of hydrolysis as a catalyst. Phorate was not degraded more effectively at the acidic pH. At pH range of 8 to 9, the degradation was observed at higher rates. At pH 5 and 6, the phorate was stable and any degradation in all the matrices was not observed. At pH 9, it had been totally degraded from the sample matrices within 4 days (http://sitem.herts.ac.uk/aeru/footprint/en/Reports/519.htm).

Effect of Sodium chloride and Sodium acetate on the degradation of malathion and phorate

Sodium chloride and sodium acetate were added to the soil-water systems so as to increase the salinity of the system. Significant change was not observed in the degradation of Malathion when sodium chloride was added; but the degradation of malathion and phorate was more when sodium acetate was added as the salinity had increased.

Effect of type of soil in the degradation of malathion and phorate

The type of soil may also affect the degradation of pesticides. Soil texture, porosity and organic carbon content play a prominent role in the degradation of any contaminant in the soil. It was observed that the malathion and phorate had degraded at faster rates in agricultural soil and sea water system. This may be due to the more organic carbon content and porosity of the agricultural soil.

It was observed that there is no significant effect of temperature on the degradation of malathion. Malathion was thermostable at 21°C temperature and rapidly dissipates at the temperature between 27 and 32°C (Bourquin, 1977), whereas, the Phorate degradation was more when the temperature rose above 50°C.

Conclusion

It has been concluded that the malathion and phorate are degrading at faster rates in agricultural soil and sea water system. These pesticides had degraded at faster rates in sea water compared to river and well water. This indicates that the hydroxide-catalyzed hydrolysis is a major pathway for the degradation in marine systems. Higher temperatures increased the degradation rates and pH is the most dominant factor influencing the hydrolysis.

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