CHAPTER I

Introduction

1.1 Problem definition

The need for increased agricultural productivity has led to pesticides residues in natural water. The organophosphorus insecticides (OPs) are currently widely used as most organochlorine insecticides have been withdrawn because of their toxicity, persistence and bioaccumulation in the environment. At least 100 organophosphorus insecticides have been reviewed by World Health Organization (WHO) for consideration as agent for the control of the pests to replace organochlorine insecticides (Edwards, 1987) . Most organophosphate insecticides remain active for a few hours to several months before decomposing and are called nonpersistent insecticides. Although most organophosphate insecticides break down fairly rapidly in the environment, most are much more toxic to aquatic microorganisms, fish, birds, humans and other mammals than chlorinated hydrocarbon pesticides. And because of their nonpersistent activity, farmers usually apply insecticides of regular intervals to help ensure more effective insect control. As a result, these chemicals are often present in the environment almost continuously, like persistent pesticides.There are many different ways of these pesticides distribution in the environment, as summarized in Fig. 1.1 (Prasad, 1992) The aquatic systems take up pesticides from several sources such as direct application, spary drift, aerial spraying, washing from the atmosphere by precipitation, erosion and run off from agricultural land discharge of effluent from factories and sewage. The contamination of these pesticides by running off from agricultural land is considered as the main source of pollution .

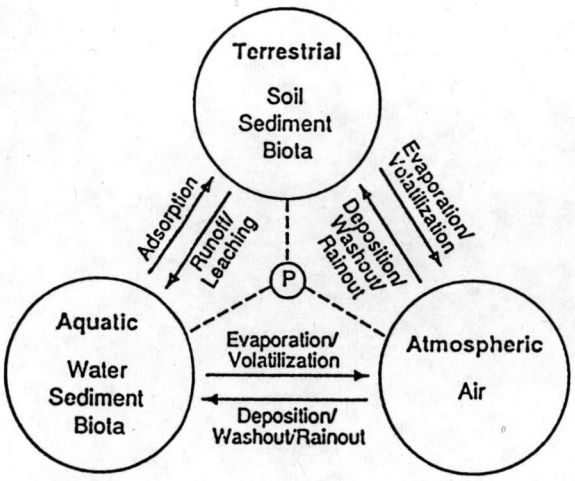

FIGURE 1.1 Environmental distribution and intercompartmental transfer of pesticides (Prasad, 1992).

The organophosphorus insecticides had higher toxicity to fish and aquatic invertebrates than the organochlorine .Toxicity of OPs may be acute and enough to kill the organism relatively quickly. The OPs exert their acute effects in both insects and mammals by inhibiting acetylcholinesterase (AChE) in the nervous systems with subsequent accumulation of acetylcholine (ACh), which is a neurotransmitter. (Cheremisionoff, 1991).

In Thailand, the organophosphorus insecticides have been widely used since the use of organochlorine pesticides was prohibited because of their toxicity. There are many diffrent types of organophosphorus insecticides used on the agricultural land such as malathion, methyl parathion, chlorpyrefos, profenofos and the others. These pesticides could contaminated into surface and ground water and aquatic system during applying in a crop. Recently, there are an increasing quantity of imported pesticides into Thailand that represented in table 1.1.

TABLE 1.1 Quantity of imported pesticides into Thailand in 1994
(Agricultural regluratory division, Department of agriculture, 1994)

No	Insecticides	type	Technica Grade		Finished product		Total	
			Q=Ton	V= mBht.	Q=Ton	V= m.Bht.	Q=Ton	V= mBht.
1.	Organophoaphate	33	3601	324	1751	189	5352	513
2.	Carbamate	12	387	76	580	158	967	234
3.	Organochlorine	3	401	76	61	9	462	85
4.	Pyrethroid	10	85	97	263	55	348	152
5.	Bio-insecticide	2	-	-	115	53	115	53
6.	fumigant	3	-	-	345	30	345	30
7.	Other Group	11	91	19	330	67	421	86
	Total	78	4565	592	3488	585	8053	1180

Remark: Q= Quantity = Ton V = Value = million baht (m.Bht)

Most of these pesticides are the organophosphate. Since, there are many application to use these pesticides, they could be accumulated in the environment. Many people have become concern about the risk and danger rising from the use of there pesticides on large areas of agricultural land. Several methods have been developed to monitor the pesticides in water.The analysis of the organophosphorus pesticides residue in water usually requires a preconcentration step before the determination by gas chromatography (GC) or liquid chromatography (LC). The sample preconcentration step of analytical method is the most important process. The use of a solid sorbent for the extraction and preconcentration of pesticides from water has been widely investigated. In comparison to the conventional liquid-liquid extraction, this technique offers the advantages of a shorter analysis time, lower cost and lower organic solvents volumes consumtion (Vinuesa, 1989).

Solid-phase extraction has become popular over the last ten years and some procedures have been validated by the U.S. Environmental Protection Agency (EPA) (Bidlingmeyer, 1984). This technique has already been applied to a variety of pesticides such as organochlorine, organophosphorus and carbamate pesticides.

The aim of this study is to develop a practical method for the determination of the organophosphorus insecticides in water using solid-phase extraction and reverse phase high performance liquid chromatography (HPLC). The study involves the performance of Sep-Pak C_{18} cartridge for the extraction and preconcentration of four selected organophosphorus insecticides from agricultural water drain and the determination by reverse phase HPLC. Octadecyl bonded porus silica has become the most popular packing in chromatographic columns (Foster and Synovec, 1996). This four insecticides namely methyl-paration, malathion, profenofos and chlorpyrifos were chosen as they are among the organophosphorus insecticides of most concerning in agriculture area.

The investigated parameters are as followed :

- The quantity of sorbent needed in the cartridge to adequately retain the analysis (100-500 mg C_{18} cartridge)
- Optimum volume of solutions needed in cartridge (100-500 ml)
- Ratio of elution solvents such as methanol/water and acetonitrile/water (in a range of 10-90 %)
- Volume of elution sovent (1-10 ml)
- SPE vacuum pressure (3.0-22.0 in. Hg)

At each stage of the solid-phase extraction procedure, the variable operating parameters were investigated to the optimized conditions.

1.2 Hypothesis

The trace organophosphorus insecticides can be detected under the SPE optimum condition of various parameters such as sorbent mass of C_{18} cartridge , ratio of elution solvents, volume of elution solvents, pressure of SPE pump and volume of sample then following HPLC analysis. The use of solid-phase extraction provides a rapid, efficient and reproducible method for the determination of various pesticides in water samples.

1.3 The Purpose of the study

1.3.1 To examine the performance of Sep-pak C_{18} cartridges for the optimum extraction and concentration of methly-parathion, malathion, profenofos and chlopyrefos from water.

1.3.2 To determine the organophosphorus pesticides in water samples by using the high performance liquid chromatography (HPLC) analysis.

1.4 Anticipated Benefits

The optimum condition of various parameters for solid-phase extraction can be applied in other trace pesticides determinations. Furthermore, this project has developed the optimum conditions of organophosphorus insecticides separation for including HPLC analysis which can be used in other related studies and mornitoring works.