

**Landwirtschaftliche Fakultät -  
Rheinische Friedrich-Wilhelms-Universität Bonn  
Institute for Environment and Human Security -  
United Nations University in Bonn**

# **PESTICIDE USE AND MANAGEMENT IN THE MEKONG DELTA AND THEIR RESIDUES IN SURFACE AND DRINKING WATER**

**Inaugural – Dissertation**

Zur

Erlangung des Grades

Doktor der Agrarwissenschaften

(Dr. agr.)

der

Hohen Landwirtschaftlichen Fakultät

der

Rheinischen Friedrich-Wilhelms-Universität

zu Bonn

Vorgelegt am 10. October 2011

von

**PHAM VAN TOAN**

aus Can Tho, Vietnam



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Korreferent: Prof. Dr. Richard A. Sikora

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## **ERKLÄRUNG (DECLARATION)**

Ich versichere, dass ich diese Arbeit selbständig verfaßt habe, keine anderen Quellen und Hilfsmaterialien als die angegebenen benutzt und die Stellen der Arbeit, die anderen Werken dem Wortlaut oder dem Sinn nach entnommen sind, kenntlich gemacht habe. Die Arbeit hat in gleicher oder ähnlicher Form keiner anderen Prüfungsbehörde vorgelegen.

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## **DEDICATION**

**This dissertation is dedicated to my parents!**



## ABSTRACT

Pesticides are essential inputs in agricultural production to control target pests and thus to improve crop yields. Appropriate use and management of these chemicals and reduction of its negative influences on human health and the environment are global concerns. In the Mekong Delta, Vietnam, an area which contributes more than 90% to the country's rice exports, pesticides have been increasingly applied since the so called Doi Moi (renovation). In this present study, two representative areas were selected to conduct different studies related to 1) pesticide use and management at household level, 2) resulting residue concentrations in surface water in fields and irrigation canals, 3) treatment practices of surface water for the purpose of drinking, and 4) pesticide concentrations in drinking water derived from surface water. One study area is characterized by intensive rice cultivation in Tam Nong District, Dong Thap Province, while the second area was selected as a representative for a peri-urban site mixed agricultural production pattern in Cai Rang District, Can Tho City. Surveys and monitoring campaign were carried out from August 2008 to August 2009. Survey results indicated that a majority of respondent farmers improperly used and managed pesticides. The study found that organochlorine and organophosphorus pesticides were less used while several pesticide groups such as pyrethroid, conazole, biopesticide and amide were being frequently applied. Half of investigated pesticides belong to moderately and slightly hazardous categories according to WHO hazard classification. 12 out of 15 studied pesticides (buprofezin, butachlor, cypermethrin, difenozonazole,  $\alpha$ -endosulfan,  $\beta$ -endosulfan, endosulfan-sulfate, fenobucarb, fipronil, hexaconazole, isoprothiolane, pretilachlor, profenofos, propanil and propiconazole) were quantified in surface water in fields and irrigation canals, with average concentrations ranging from 0.02 to 3.34  $\mu\text{g/L}$  and from 0.01 to 0.37  $\mu\text{g/L}$  at the intensive rice cultivation and mixed agricultural production areas, respectively. Monitoring of pesticide residues in drinking water quantified seven out of 15 studied pesticides, with average concentrations ranging from 0.01 to 0.47  $\mu\text{g/L}$ . The study also revealed that aluminium sulfate and boiling practice, frequently applied to treat surface water for drinking by respondent farmers, unfortunately could not remove the most of studied pesticides from drinking water. Consequently, as compared to European Commission guideline values for drinking water local people were exposed to several pesticides which might pose their health at risk. The present study provides and discusses possibly measures in order to improve pesticide management practices as well as to decrease pesticide inputs into water ecosystems and thus reduce the exposure of (rural) people to these potentially harmful chemicals..

## ABSTRAKT

Pestizide sind essentielle Elemente in der landwirtschaftlichen Produktion um Schädlinge zu bekämpfen und damit die Ernteerträge zu verbessern. Ein angemessener Einsatz und Management dieser Chemikalien, sowie die Reduzierung der negativen Einflüsse auf die menschliche Gesundheit und die Umwelt sind ein globales Anliegen. Im Mekong Delta, Vietnam, einem Gebiet, das mehr als 90% des exportierten Reis der ganzen Landes produziert, werden seit der sogenannten Doi Moi (Erneuerung) zunehmend Pestizide eingesetzt. In der vorliegenden Studie wurden zwei repräsentative Gebiete ausgewählt, um verschiedene Studien im Zusammenhang mit 1) der Verwendung von Pestiziden und deren Management auf Ebene der Privathaushalte, 2) den daraus resultierenden Konzentration von Rückstand im Oberflächenwasser in Feldern und Bewässerungskanälen, 3) den Aufbereitungs-Praktiken von Oberflächenwasser zum Trinken, und 4) der Pestizid-Konzentrationen im aus Oberflächenwasser gewonnen Trinkwasser. Das erste Forschungsgebiet im Tam Nong District, Dong Thap Provinz, wird durch intensive Reisanbau charakterisiert, während das zweite Gebiet als Vertreter für einen peri-urbanen Standort mit gemischten landwirtschaftlichen Produktions-Mustern im Cai Rang District, Can Tho City, gewählt wurde. Von August 2008 bis August 2009 wurden Umfragen und Monitoring Kampagnen durchgeführt. Die Umfrageergebnisse zeigten, dass die Mehrheit der Befragten Bauern Pestizide unsachgemäß anwendeten und verwalteten. Die Studie ergab zudem, dass Chlororganische- und Organophosphor-Pestizide weniger eingesetzt wurden, während mehrere Pestizid-Gruppen wie Pyrethroide, Conazol, Biopestizids und Amid häufig angewendet wurden. Die Hälfte der untersuchten Pestizide gehören in die moderat und schwach gefährlichen Kategorien der WHO Einstufung. 12 von 15 untersuchten Pestiziden (Buprofezin, Butachlor, Cypermethrin, Difenoazonazole,  $\alpha$ -Endosulfan,  $\beta$ -Endosulfan, Endosulfan-Sulfat, Fenobucarb, Fipronil, Hexaconazol, Isoprothiolane, Pretilachlor, Profenofos, Propanil und Propiconazol) wurden im Oberflächenwässer in Feldern und Bewässerungskanälen quantifiziert, mit durchschnittlichen Konzentrationen von 0,01 bis 0,37  $\mu\text{g/L}$  von 0,02 bis 3,34  $\mu\text{g/L}$  in den Intensivs-Reisanbau Gebieten und den gemischten landwirtschaftlichen Produktions Gebiete. Das Monitoring von Pestizidrückständen im Trinkwasser quantifizierte sieben von 15 untersuchten Pestiziden, mit durchschnittlichen Konzentrationen im Bereich von 0,01 bis 0,47  $\mu\text{g/L}$ . Die Studie ergab auch, dass Aluminiumsulfat und Kochen die häufigst angewandten Praktiken der befragten Landwirte waren, um Oberflächenwasser als Trinkwasser nutzen zu können; jedoch konnten diese leider nicht die meisten der untersuchten Pestizide aus dem Trinkwasser entfernen. Folglich ist, im Vergleich zu den

Richtwerte für Trinkwasser der europäischen Kommission, die lokalen Bevölkerung mehreren gesundheitsgefährdenden Pestiziden ausgesetzt. Die vorliegende Studie liefert und bespricht mögliche Maßnahmen zur Verbesserung der Pestizid-Management-Praktiken, sowie die reduzierte Einbringen von Pestiziden in Wasser-Ökosysteme und damit auch die reduzierte Exposition der (ländlichen) Bevölkerung auf diese potenziell schädlichen Chemikalien.

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## LIST OF ABBREVIATIONS

ACS	American Chemical Society
Bt	Bacillus thuringiensis
COD	Chemical oxygen demand
CTC	Can Tho City
CERWASS	Center for Rural Water Supply and Sanitation
DAS	Days After Sowing
DLR	German Aerospace Centre
DO	Dissolved oxygen
EC	European Commission
ECD	Electron Capture Detector
ELISA	Enzyme-linked immunosorbent assay
FFS	Farmer Field School
GC	Gas Chromatography
GPS	Global Positioning System
HBSL	Health-Based Screening Level
HPLC	High Performance Liquid Chromatography
IPM	Integrated Pest Management
LEP	Law on Environmental Protection
LOD	Limit of Detection
LOQ	Limit of Quantification
MARD	Ministry of Agriculture and Rural Development
MD	Mekong Delta
MDL	Method Detection Limit
MOH	Ministry of Health
MOIT	Ministry of Industry and Trade
MONRE	Ministry of Natural Resources and Environment
MRC	Mekong River Commission
MS	Mass Spectrometry
NPV	Nuclear polyhedrosis virus
PPD	Plant Protection Department
PRA	Participatory Rural Appraisals
SPE	Solid Phase Extraction

TOC	Total organic carbon
USGS	U.S. Geological Survey
WHO	World Health Organization
YES	Yeast estrogen screen
1M5R	One Must - Five Reductions
3R3G	Three Reductions - Three Gains



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*Chapter 1*  
**GENERAL INTRODUCTION**

**1.1 Background**

The Mekong Delta (MD), the biggest rice growing area in Vietnam, covers an area of approximately 3.9 million hectares accounting for about 12% of the country's total area. The tropical semi equatorial climate of the area is characterized with average temperature of approximately 27 °C, and the average humidity is between 83% and 87%. Average annual rainfall ranges from 1400 to 2400 mm with approximately 90% of the rainfall occurring during the rainy season. The average elevation of the Delta is 0.8 m above sea level. Peak flood occurs in the period between September and October. The dry season generally prolongs from November/December to April/May. The whole Delta is almost entirely irrigated by the Mekong River which is the tenth largest river in the world, with a dense stream system of natural creeks and small rivers. In addition, an artificial canal network for irrigation, drainage and water conveyance has been constructed throughout the region. The Mekong River flows into Vietnam via two branches, Tien River and Bassac River, with a total length of 460 km. Annually, the mean discharge of the Mekong River is approximately 475 km<sup>3</sup> (White, 2002).

Land used for rice farming and aquaculture covers about 2.4 and 0.7 million hectares respectively, corresponding to more than two-thirds of the total area of the Delta. It supplies more than 90% of rice for exporting, 60% of fishery and accounts for 27% of the total Gross Domestic Product of the whole country (Tuan and Be, 2008). Paddy is the main cultivated crop in this region. Rice (single and double) cropping is the dominant cropping system, taking up 70% of the agricultural land. Approximately 20% of land is planted with upland crops and perennial plants (MRC, 2007).

The population of the Delta is 17.2 million inhabitants and approximately 70% of the population is engaged in agriculture (GSO, 2009). An increase in population creates serious concerns because of the limitation of land, potential future food shortages, lack of clean water resources, etc.

The innovation policy (or *doi moi*) of 1986 reformed Vietnam's central economic system to a more market-oriented system. It significantly contributed to economic expansion activities by improving market sector efficiency. In particular, the policy of decollectivization in 1988 rapidly enhanced agricultural production by strengthening the farmers' land use rights and farm management autonomy. With this resolution, farmers were actually encouraged to invest in agriculture, especially in the rice sector (Pingali and Xuan, 1992). Originally relying on rice imports, Vietnam became an official rice exporter since 1989. The country exported 1.7 million tons of rice in 1989, 3.4 million tons in 2000, and 4.7 million tons in 2008 (Ha, 2009). Although rice cultivation plays a vital role for the national economic prosperity in terms of food procurement and security as well as surplus production for export, environmental problems need to be considered in terms of the sustainable development of the region. Together with pest management practices, a large amount of plant protection chemicals and nutrient compounds have been used in the MD (MRC, 2007). Inappropriate pesticide use results not only in actual yield loss but also in human health problems and damage to ecosystems such as destroying aquatic communities, extermination of useful predators and more generally air and water pollution (Margni *et al.*, 2002).

## 1.2 Problem Statements

Although pesticide use has grown rapidly and pesticide residues have potentially negative effects on human health and ecosystems, data of pesticide residue concentrations in surface water are generally not available in the MD. The fate and quantity of pesticide residues introduced into water bodies after application has not been extensively monitored. Pesticide residue monitoring in surface water is only concentrated on the main rivers or canals while such activities are lacking in irrigation canals where agricultural wastewater has a strong influence. Meanwhile surface water could be a source of water supply for drinking especially in remote rural areas, and consequently people could be drinking water that contains significant amounts of pesticide residues. Water quality monitoring and particularly pesticide analysis is in infancy stage in Vietnam. Limitation factors are expensive laboratory facilities and intensive analytical methods, the shortage of experts and monitoring activities that just started in the early 1990s (Danniso *et al.*, 1997). Huan (1999b) and Berg (2001) reported that there are many types of pesticides used by the farmers in the MD. Some of these compounds were banned or restricted by the Ministry of Agriculture and Rural Development (MARD). Toxicity of these compounds

for aquatic ecosystems and human health were demonstrated by a number of scientists (Dung and Dung, 2003; Meisner, 2005). Although pesticide residues may cause losses in the value of water resources, biodiversity in aquatic ecosystem (e.g. extinction of fish species) and negative effects to human health (e.g. acute or chronic effects) (Kamrin, 2000; Phuong and Gopalakrishnan, 2003), only few mitigation measures to reduce pesticide residues of the MD have been launched.

### **1.3 Hypotheses and Research Questions**

Given the discussion above, this study was implemented based on the following two hypotheses:

1. Pesticide pollution in surface water is currently a serious problem in the Mekong Delta (i.e. concentrations of residues are expected to be above international and national water quality norms).
2. Appropriate mitigation measures can be devised and implemented to reduce pollution through understanding farming systems and proper pesticide use.

In order to test the two above hypotheses, the following research questions were considered:

1. What types of pesticides are currently commonly used?
2. How do the farmers implement pesticide application and management measures?
3. What are the concentrations of commonly used pesticides in surface water in fields and canals?
4. What are the concentrations of commonly used pesticides in drinking water originating from surface water?
5. What mitigation measures could be proposed to reduce improper pesticide use and to reduce or prevent pesticide residues from entering surface waters as well as from drinking water in selected case study areas of the Delta?

### **1.4 Objectives of the Study**

The objectives of this dissertation are as follows.

- To find out what are the causes of pesticide contamination to surface water in fields and irrigation canals.

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- To determine and assess the concentrations of commonly used pesticide residues in surface water in fields and irrigation canals at two different sites.
  - To determine and assess the concentrations of commonly used pesticide residues in drinking water originating from surface water when treated via “traditional” treatment methods as well as exposure of human health to pesticides in drinking water.
  - To propose measures to properly use and manage pesticides, to mitigate the entry of pesticide residues into surface water as well as to remove pesticide residues from drinking water.

### **1.5 The Structure of the Dissertation**

Following the chapter on general introduction as well as statement of research problems, the dissertation continues with a chapter reviewing the literature on pesticide use and its influences to human health and the environment. This chapter also provides an overview of non-point (diffuse) and point sources of pesticides polluting surface waters. Subsequently, a brief summary of monitoring methods for pesticide residues in surface water, particular in the Mekong Delta is given. At the end of the chapter, the history of legislation relating to the management of plant protection chemicals in Vietnam is briefly presented.

Pesticide use and management at the household level researched through two case study areas of the Delta are reported in detail in chapter 3. In this chapter, investigation processes through household interview and group discussion methods are described. Practices on land use and farming patterns as well as respondent farmers' profiles are reported. Results on pesticide use practices (e.g. types of pesticides, application frequency, application time and dose) and management (e.g. purchase, storage and disposal) are reported and compared between the two study areas. Farmers' perception on pesticide residue impacts to human health and the environment is investigated. Concurrently, application of integrated pest management methods by the local farmers is reported. In the conclusion part, several measures aiming to limit improper pesticide use and management are proposed as considering the local practical conditions.

Chapter 4 reports on the intensive monitoring campaign for selected pesticide residues in surface water. This campaign was carried out from August 2008 to August 2009. Processes and methods regarding collection and analysis of water



samples are described. Results of selected pesticide concentrations detected in samples which were collected in fields and irrigation canals are reported. Occurrence as well as the mean/median concentration of detected pesticide residues in sampling events/ locations are compared in order to clearly show the influence of temporal factors (e.g. natural calendar seasons, cropping seasons and cultivation stages), spatial factors (e.g. up and downstream of canal, farming and non-farming areas), rainfall and flooding. A comparison of occurrence and concentration of detected compounds between two different farming patterns is also analyzed. Several mitigation measures are proposed in order to reduce pesticide residues entering water bodies from fields.

Surface water is used not only for irrigation and other daily domestic activities but also for drinking in areas where no access to a clean water supply system is available in the dry season. Hence, besides monitoring target pesticide residues in surface water in fields and irrigation canals, in chapter 5, selected pesticide residues in drinking water sourced from surface waters are also monitored. In this chapter, drinking water sources and the situation of drinking water supply in the Delta is presented. Water using practice for drinking and selected pesticide residues at each stages of water treatment process are investigated and monitored at selected households in a case study site in a suburban area of Can Tho City. Surface water treatment methods for household drinking water are described based on interview results. Processes and methods of drinking water collection and analysis are described in detail. Concentration of selected pesticide residues corresponding to each stage of water treatment processes are reported. The influence of boiling water on the fate of selected pesticides tested in the laboratory is also given. On the basis of selected pesticide residue concentrations measured in drinking water, exposure of human health to pesticides is analyzed and given in the assessment section. Measures on how to remove the detected pesticide residues from drinking water were assessed, and several solutions are proposed at the end of the chapter.

In the conclusion chapter, the current situation of pesticide use and management at the two case study areas is summarized. Similarly, selected pesticide residue concentrations in surface water and drinking water are mentioned again. With comparison to the guideline values of standards, the quality of surface water and

drinking water are assessed. Several recommendations on how to protect surface water quality from pesticide contamination are also emphasized in this chapter.

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*Chapter 2*  
**LITERATURE REVIEW**

### **2.1 Pesticide Use and Its Influences**

Pesticides are used in great quantities throughout the world in amounts of approximately two million tons per year. One-fifth the pesticides applied were used in developing countries, 45% in Europe, 24% in the USA and the remaining in other countries (Abhilash and Singh, 2009). In developing countries, the share of agrochemical use was highest for insecticides followed by fungicides, herbicides and then other pesticides. During the past two decades, organochlorine and organophosphate compounds were frequently used insecticides. Their use has been gradually reduced, and more recently pyrethroid and carbamate insecticides have been frequently employed to control insects. However, extremely and highly hazardous WHO category insecticides which were banned or restricted in developed countries were still used in developing countries. For example, among the various pesticides used in India, 40% of applied active ingredients belonged to the organochlorine class. Several highly hazardous organophosphate insecticides such as monocrotophos, metyl parathion were indiscriminately used in India (Abhilash and Singh, 2009). Improper pesticide use and management is mostly dependent on farmers' perception, knowledge and practices (Escalada and Heong, 2004). Rice farmers often make wrong decisions on the existence of pest problems and then on pesticide use. And, this therefore leads to yield losses, or in the worst case the farmers become victims of improper pesticide use. Pesticide misuse caused approximately three million poisonings, 220 thousand deaths and approximately 750 thousand cases of chronic illnesses every year worldwide (WHO, 2006).

In the Mekong Delta, pesticide use and management caused considerable concerns in the process of increased agricultural development. In parallel to the Green Revolution, the types of pesticides used and the number of applications have increased slightly in the 1970s and rapidly in the 1990s and 2000s (Ut, 2002; Huan, 2005). Pesticide use has been rapidly increasing in the MD when compared to other regions or countries in the world. For example, the Mekong River Commission recently reported that pesticides used by farmers in the MD were significantly higher than in the Red River Delta in the north of Vietnam. On average, pesticides were applied 5.3 times per crop season in the MD (MRC, 2007). Rice farmers still used

organophosphate and organochlorine insecticides, and the trend to use pyrethroids was rapidly increasing in the MD (Huan *et al.*, 1999b). Berg (2001) reported that 64 different active ingredients were used in rice cultivation in Can Tho and Tien Giang Provinces, and Van Mele *et al.* (2001) reported that highly hazardous pesticides were still used for orchards. Some types of pesticides have been used in the Delta although they were banned by the Ministry of Agriculture and Rural Development (MARD) due to their toxicity. These include methyl parathion and methamidophos (organophosphate compounds) which belong to WHO's category Ia and Ib (extremely and highly hazardous) respectively, and Endosulfan (organochlorine compound) belonging to category II (moderately hazardous) (Dung and Dung, 2003; Meisner, 2005). Their continued use after the ban is partly due to the relative low price of these pesticides compared to more modern and safer compounds but also due to their broad spectrum of pest toxicity. In addition, there were weaknesses in enforcement and control of the use of hazardous chemicals. In some cases there were few alternatives available to the farmer for substitution to control pest outbreaks.

Farmers spray insecticides in the early stages of the rice crop to prevent leaf feeding insect damage, especially leaffolder. They believe that this insect causes rice yield loss even in the vegetative stage of rice crop. Farmers' over reacting in terms of pesticide use toward this pest led to the outbreak of secondary pests such as the brown planthopper and therefore pesticide application yielded no economic but had a negative impact on health (Huan *et al.*, 1999b).

Pesticide usage in the MD mostly depends on local farmers' knowledge, behavior and economic conditions. Knowledge of pesticide application obtained by the local farmers is relatively diverse in sources. An investigation in some case study areas of the Delta showed that approximately 28% of the respondents received help from agricultural extension officials regarding pesticide use (Dung and Dung, 2003). These were often farmers who followed Integrated Pest Management (IPM) programs launched by the Plant Protection Department, and therefore acquired basic knowledge on pest management. The remaining farmers obtain knowledge from other means such as television, newspapers, pesticide retailers, radio. The research of Berg (2001) and Dung *et al.* (2003) pointed out that farmers practicing IPM used less pesticide amounts than non-IPM farmers. Application frequency and the amount of active ingredients used by the non-IPM farmers were 2 - 3 times higher than that used by

those practicing IPM on a crop basis. Generally, most farmers did not have good knowledge of pesticide use and consequently they applied pesticides inappropriately. Farmers often mixed 2 - 5 types of pesticides together for spraying, and they seldom followed the guidance of usage instructed on product labels. They seldom respected the recommended pre-harvest intervals, e.g. they harvested their crops a short time after pesticide application. In addition, farmers seldom used personal protection equipments when spraying pesticides and consequently they were directly exposed to pesticide contamination.

Pesticides are considered useful agents developed to control target pests. However, they can become poisons to non-target plants and animals, including human beings. Humans may be exposed to pesticides directly by breathing in the chemicals while spraying or indirectly by drinking contaminated water or consuming foods products such as vegetables and fishes containing pesticide residues. Humans exhibit many health symptoms when exposed to pesticides. For example, acute effects (headache, irritation, breathlessness, vomiting, etc.) are instantaneous impacts from pesticide exposure. In the Delta, pesticide residues were detected in farmer's blood (Dasgupta *et al.*, 2005b), and this phenomenon can cause harmful diseases such as cancer or other forms of tumors. Pesticide pollution causes negative effects to aquatic environments, preventing the growth or destroying the structures of aquatic ecosystems (Margni *et al.*, 2002). Indirectly, it also affects organisms which reach these polluted water sources such as migratory fish and aquatic birds (Khan and Law, 2005). These negative effects not only exist in the regions of application but also in downstream areas. Pesticide contamination can cause a loss in the value of water resources particularly in surface water in the rural area of the Delta (Phuong and Gopalakrishnan, 2003), where surface water is an important source for irrigation, personal hygiene, washing and especially drinking and cooking water in the dry season.

## **2.2 Pesticide Pollution Sources and Residue Monitoring in Surface Water**

Pesticides can be introduced into surface water, leach into soil, percolate down to groundwater or volatilize into the air. Water bodies may be polluted by pesticides in the following manner:

- Pouring leftover spray directly into surface water
- Spilling water used to wash sprayers
- Spraying pesticides along the edge of ditches, canals, etc.

- Runoff of pesticide-contaminated water and pesticide-contaminated soil particles
- Other hydrological pathways include polluted interlayer flow, drain flow and groundwater recharge
- Pesticides can be found in the rainwater

Surface water pollution by pesticides is derived from two sources: diffuse-sources (non-point sources) or point-sources (Carter, 2000). According to Reichenberger *et al.* (2007), diffuse-sources of pesticide inputs into water bodies result mainly from pesticide application to agricultural fields. In contrast, point-source inputs derive from localized situations and enter a water body at a specific or restricted number of locations. Thus, diffuse input pathways for pesticides into surface water are base flow, subsurface runoff and soil erosion from treated fields, spray drift at application and deposition after volatilization. Point sources are mainly farmyard runoff, sewage plants and accidental spills. There are also sources of pesticides from non-agricultural use, e.g. from application to roads or urban sealed surfaces for weed control, vector control and seed dressing to afford protection of stored grains against pests (Nhan *et al.*, 2001). In order to have a general view, the most important sources of pesticide input into surface water are briefly described below.

#### *Surface runoff and erosion*

Surface runoff is generated when infiltration capacity and surface storage capacity of soils are exceeded by incoming precipitation. Soil erosion by water consists of two processes: i) the detachment of soil particles from the soil surface, and ii) the subsequent transport down slope (Reichenberger *et al.*, 2007). Pesticides in runoff and erosion events leave the field either dissolved in runoff water or adsorbed to eroded soil particles. Pesticide losses through surface runoff deriving from agricultural fields are typically less than 0.05% unless extreme 1 - 2 week rainfalls happen during application time of pesticides (Carter, 2000). According to Leonard's research in 1990, cited in Reichenberger *et al.* (2007), pesticide lost by surface runoff is normally more serious than by erosion because soil particles eroded from agricultural fields is often less when compared to runoff volume. However, the proportion of pesticide residues lost in solution also depends on the pesticide physicochemical properties. For instance, weakly sorbing pesticides are less lost into surface runoff than compounds with intermediate sorption because the formers are quickly leached away from the soil surface by infiltration.

### *Spray drift*

Spray drift occurs when wind blows the pesticide solution at application time, and it can cause surface water pollution when spraying is conducted close to water bodies (Carter, 2000). Amounts of pesticide lost from spray drift depend on weather conditions, application methods, technical equipments and type of target crops. Spray drift refers to air-borne movement of a pesticide to non-target areas during a liquid application. It was observed that drift by spraying on crops leads to higher drift than on bare soil. However, spray drift losses are also dependent on chemical properties (Reichenberger *et al.*, 2006). Some field monitoring showed that a ground application of a pesticide on arable crops resulted in drift loss ranging from 0.5 to 3.5% of the normal application rate at a distance of one meter from the application area (Carter, 2000).

### *Leaching*

Leaching is the vertical downward displacement of the solutes to underlying groundwater or lateral transport to surface water. Pesticide residues can enter groundwater and surface water through this process. Losses of a substance by leaching are dependent on its characteristic and the environment. According to Renaud *et al.* (2004), leaching behaviour of different soil/solute combinations is influenced by five main factors. They include soil hydraulic properties, interaction between soil properties and sorption capacity of the solutes, degradation of the solutes in soil, variation of sorption kinetics between compounds associated with pesticide diffusion into soil aggregates and protection of the compounds by combination of intra-aggregate diffusion and the presence of preferential flow pathways. The highest loss typically takes place for weakly sorbed or persistent substances, high precipitation, low temperatures and soil with larger macropore flow and low soil organic matter content (Reichenberger *et al.*, 2007). Losses of an applied active ingredient by leaching may be up to 5%, but are typically less than 1% (Carter, 2000).

### *Drainage*

Drainage is responsible for removing excess water from slowly permeable soil, with a shallow groundwater in the field or draining water from fields for cultivation purposes.

Artificial drainage can significantly transport dissolved pesticide residues into water bodies from fields after pesticide application. This process can also carry pesticide bounded sediment due to runoff in particular when significant rainfall and subsequent drainage occur shortly after pesticide application. Consistent research has found that preferential flow phenomena are key contributors to the rapid pesticide transfer into drainage systems (Reichenberger *et al.*, 2007). Pesticide inputs into surface water due to drainage are affected by many factors such as pesticide properties, soil, drainage system, weather conditions and application time. Losses of pesticides due to drainage might be represented by up to 1% of the normal application rate, but typically are less than 1% (Carter, 2000).

### *Precipitation*

Precipitation after evaporation and atmospheric transport is also a nonpoint-source of pesticide pollution. Pesticide residues carried by precipitation can be deposited on surface water or other facial contacting materials. This process typically occurs to chemicals which are volatile under certain conditions. Most losses of chemicals by volatilization after application do not exceed 20%, with the exception of very volatile substances which can reach up to 90% (Carter, 2000). However, impacts of pesticide precipitation are negligible and insignificant compared to that from their direct agricultural application. The residues of a number of pesticides in rainwater were monitored in previous surveys; approximately 70% of the 99 researched pesticides were detected in rainwater, although the limit of detection for many of these substance residues were below any guideline values of environmental quality standards in Europe (Dubus, 2000).

### *Point sources*

Point sources of pesticide contamination can include farm areas where pesticides are improperly handled, or where the sprayers were washed or from pesticide storage facilities. In the Mekong Delta, relevant point sources of pesticides include sprayer overfilling and washing after pesticide application and improper disposal of containers (author's field observation). Monitoring research in European countries found that contribution at point sources to total pesticide load in surface water can range from 40 - 90% (Jaeken and Debaer, 2005). Industrial pesticide production activities also can cause pesticide residue discharge into surface water (Carter, 2000). These types of point sources can cause a significant pesticide residue contamination to surface water.



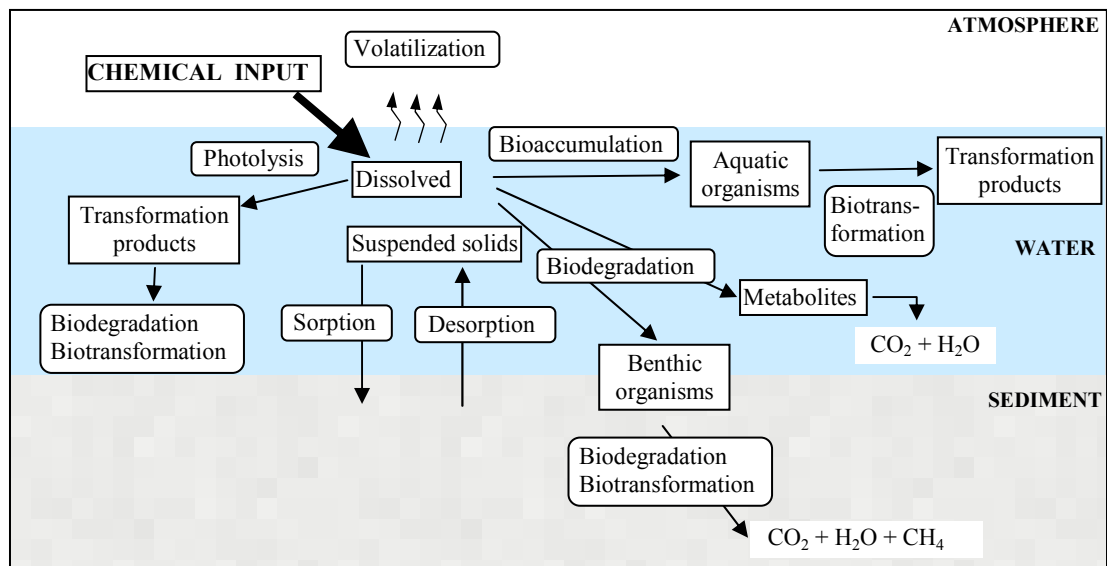
The concentration of pesticides in surface water at field or catchment scales has been monitored and assessed in European, American as well as Asian countries (Ebbert and Embrey, 2002; Müller *et al.*, 2002; Azevedo *et al.*, 2004; Nakano *et al.*, 2004). Samples of monitoring are collected via grab samples at regular time intervals during monitoring period. This sampling method has been extensively applied in monitoring surface water quality. The method sometimes results in non-representative sampling and gives miss-interpretation of water quality status, especially in small catchments with high hourly variations in concentrations of pesticides by runoff processes. This weakness is well documented and can be overcome by continuous monitoring through automatic sampling. However, the use of this sophisticated method is limited by financial and sometimes logistical aspects. Instead of continuous sampling the combined use of monitoring data and pesticide fate predicting models have been reported frequently (Holvoet *et al.*, 2007). Furthermore, biological methods have been developed to monitor the pesticide concentration in surface water. For example, biomarkers, biosensors, biological early warning systems, enzyme-linked immunosorbent assay (ELISA) and yeast estrogen screen (YES) are the most used biological monitoring techniques (Holvoet *et al.*, 2007).

Comprehensive studies on environmental pollution by pesticide residues in surface water have been lacking for the whole of Vietnam. Several recent studies on agrochemicals and persistent organic pollutants showed that DDT is a typical pollutant in aquatic environments. Organochlorine insecticides comprising DDT and its metabolites and lindane were monitored in soil and sediment in representative agricultural areas in the north of Vietnam. DDT was detected and its concentration ranged from 5.0 to 28 ng/g dry weight (Viet *et al.*, 2000). This compound was often found at locations close to villages or towns suggesting use of DDT for mosquito control. In the Mekong Delta, DDT was detected in sediments with concentrations ranging from 0.01 to 110 ng/g dry weight (Minh *et al.*, 2007). Several other persistent agrochemicals were also measured in surface water, sediment and biota in aquatic environment of the Delta. Among more than 70 monitored compounds, a number of pesticide residues were detected in water samples for diazinon, fenitrothion and endosulfan. Concurrently, many persistent compounds such as DDT, hexachlorocyclohexane (HCH) and endosulfan were found in sediment and biota (Carvalho *et al.*, 2008). A diagnostic study on water quality with regard to pesticide residues was carried out by the Mekong River Commission at three stations: Tan Chau (Mainstream), Chau Doc (Bassac River) and My An (Plain of Reeds) from 2003

to 2004. Concentrations of monitored pesticide compounds including organochlorine, organophosphate and triazine were all lower than the limit of detection in their study (MRCS, 2007). Data of recently used pesticide residues for assessing environmental quality are not available and there has not yet been a comprehensive study on the matter.

### 2.3 Pesticide Fate in Water

In the aquatic environment illustrated as Figure 2.1, pesticide compounds are subject to many processes (e.g. physical, chemical and microbiological) which depend on their physicochemical properties and the biotic or abiotic factors of the ambient environment (Petit and Cabtidenc, 1995; Renaud *et al.*, 2008). All these components determine the behavior and the fate of pesticides in water.



**Figure 2.1: Fate processes of pesticides in water (Petit and Cabtidenc, 1995)**

After entering water bodies the fate of pesticides is partly determined by their sorption behavior. Sorption is a physicochemical dynamic process of the pesticide - sediment - water interaction in which pesticides binds to sediment particles (Petit and Cabtidenc, 1995). This process depends on pesticide properties (solubility, polarity and octanol-water partition coefficient) and the characteristics of the solid phase (i.e. particle size distribution, clay content, organic matter content, cation exchange capacity). Sorption capacity also affects directly or indirectly the degradation of pesticides. The rate of sorption is often evaluated by two sorption coefficients: the sorption partition coefficient ( $k_d$ ) used for low pesticide concentrations and the adsorption coefficient

( $K_{oc}$ ) defined as the  $k_d$  which take into account the organic carbon content of the sediment. The higher  $K_{oc}$  is, the greater the role of sorption in the removal of a pesticide from water.

Bioaccumulation is another process by which chemicals like pesticides can affect living organisms. Bioaccumulation happens as a pesticide is taken up and stored faster than it is metabolized or excreted. Bioconcentration is a specific bioaccumulation process by which the concentration of pesticides in organisms becomes higher than its concentration in aquatic environment around those organisms. Bioconcentration after uptake through the gills or the skin for fish or other aquatic animals is the most important bioaccumulation process. Biomagnification refers to a process which results in the bioaccumulation of a pesticide in an organism in higher levels than are found in its own food. Biomagnification occurs when a pesticide becomes more and more concentrated at higher levels in the food chain (Kamrin, 2000).

In fields, when pesticides are applied by farmers, dissipation of pesticides begins immediately. In the beginning of the dissipation process, compounds dissipate at a rate that is a composite of the rates of individual processes such as volatilization, hydrolysis and biodegradation (Seiber, 2002). The process of accumulation like bioconcentration of pesticide residues from water by aquatic organisms and biomagnification in food chain of ecosystem, are also both dissipation processes.

#### **2.4 Legislative Context Relating to Pesticide Products Directive, Surface Water and Drinking Water Regulations in Vietnam**

Pesticide management in agricultural activities in the whole of Vietnam is regulated by the Plant Protection Department (PPD). This organization, established in 1961, is a State management section that is officially administrated from the Ministry for Agriculture and Rural Development (MARD) (the past Ministry of Agriculture and Food Technology). In order to regulate pesticide management, many regulations on plant protection products and their handling are enacted and employed in the entire of country as summarized briefly in the following.

One of the earliest macro-policies regarding pesticide management is Decree No.32 of 1984. The Decree merely mentioned the responsibility of relevant state

departments such as MARD, the Ministry of Health (MOH), and the Ministry of Industry and Trade (MOIT) regarding pesticide import, production, distribution and use. All pesticides and other agricultural inputs as well as outputs were centrally managed by the MARD (Hoi *et al.*, 2008).

Since 1986, a list of pesticide compounds was issued comprising the compounds legally used in Vietnam, and the list is updated by the MARD annually. In 1991, a legal list of 77 active ingredients was permitted for import, production, distribution and use in Vietnam, and this list is an important key for state pesticide management at the local level (Vien and Hoi, 2009). According to the list, pesticides were categorized into three groups: permitted pesticides, pesticides permitted with restricted use and banned pesticides.

The first comprehensive legal document for plant protection and quarantine including pesticide management was promulgated by the National Assembly in 1993, Decree No.92. The Decree aimed to improve state management on enhancing the effectiveness of resource management, introducing to a better production and protecting public health and the environment. In term of agricultural chemicals, this Decree regulated all activities relating to import, export, production, formulation, distribution and use are monitored and inspected by a plant protection system from central to district level. The Plant Protection Department of the MARD keeps a role as the key administrative authority in pesticide policy. The MARD determined and announced a list of pesticides permitted, restricted and banned for use as well as promulgated a testing process of the list periodically. Transport and use of pesticides which are not belonging to the regulated list are strictly prohibited. The same circumstance is for producing and selling fake, expired pesticides, pesticides of unknown origin, without trade mark or inappropriate pesticides regarding the quality to register the trade names or patents. In order to promote plant protection activities, the Decree encouraged all organizations or individuals which obtained a complete requirement according to the regulation on plant protection and quarantine by granting a license. They are allowed in pesticide production, import, export and distribution activities. Furthermore, the Decree mentioned to regulations regarding the security of human health, animals and the environments during the production, storage and transportation process of pesticides.

In 1995, the detailed regulations on plant protection as well as pesticides were published by MARD. In order to tighten registration, import, production, distribution and use of restricted pesticides, MARD stipulated that no new registration of these category pesticides was permitted (Hoi *et al.*, 2008). In addition, most of the Plant Protection Sub-Departments were no longer responsible for pesticide sales and distribution since 1995 (Dung and Dung, 2003). In order to encourage pest management and limited pesticide misuse, production both domestic and foreign agreed to invest in integrated pest prevention and control as well as to produce, formulate, distribute and sell plant protection chemicals in Vietnam. All these activities were managed by the Plant Protection Sub-Department at the provincial level. The MARD then recommended that companies which were established from either joint ventures or 100% foreign investment capitals were no longer issued a license for building pesticide producing factories.

When a new pesticide is imported or formulated in Vietnam, it has to obtain legal registration as stipulated by the MARD. A part of registration procedure involves a field trial stage which aims to determine pesticide efficacy as well as estimate the effects of pesticides on target plants, human health, animals and the environments. The field trial has to be conducted by two State Plant Protection Centers in the north and the south of Vietnam. However, the field trial is only applied for chemical pesticides. Biological pesticides do not follow this registration procedure, and they were prioritized in research, production, distribution and use through the regulations by MARD in 2002 (Hoi *et al.*, 2008). Consequently, a fast and uncontrolled development of biological pesticides happened so that field trial became a necessary step in its registration procedure recently.

Pesticides are required to be properly used according to guidance mentioned on instruction labels or taught by technical staff. However, there are not having rules in detail for enforcing or sanctioning violations on improper pesticide use or the use of banned or unknown-origin pesticides. Users are responsible for appropriate pesticide application activities regarding application time, dose and target crops.

Pesticide residues as a source of pollutant for water resources are a concern nationally. The Law on Water Resources was passed by the National Assembly in 1998. The law stipulates the utilization, protection, management, development of

water resources as well as the control and mitigation of any adverse influences caused by water. Toxic water, untreated wastewater or treated water not meeting allowance thresholds are forbidden to be discharged into recipient water bodies. The guidance of allowance thresholds relating to the quality of water resources is stipulated by legislations on environmental protection. Environmental protection activities are the responsibility for the Ministry of Natural Resources and Environment (MONRE). The first Law on Environmental Protection (LEP) was promulgated in 1993. For the first time, rights and obligations of individuals and organizations were clearly regulated with respect to environmental protection. This law was replaced by the LEP 2005, No. 53/2005/QH11, which was passed by the National Assembly in response to changes of national developing requirement. Compared to the LEP 1993, the LEP 2005 provides not only regulations on environmental protection activities, but also on policies, measures and resources for protecting the environment. In addition, legislations of the new law stipulate the rights and obligations to protect environment for the state agencies, organizations, individuals, overseas Vietnamese and foreign organizations and individuals carrying out activities in Vietnam. In order to protect surface water quality, the National technical regulation on surface water quality was enacted by the MONRE. The newest regulation, QCVN 08: 2008/BTNMT, stipulates the threshold values of surface water quality parameters categorized into four classes A1, A2, B1 and B2. These classes are in response to the quality levels of surface water which can be supplied for domestic consumption, aquatic animal conservation, irrigation and waterway navigation as well as other purposes, respectively. In this regulation, threshold values of pesticide residues in surface water are stipulated in accordance with the above four classes. They include eight organochlorine, two organophosphorus and three herbicide compounds (2,4D, 2,4,5T and paraquat). The responsibility for monitoring the presence of pesticide residues in the surface water environment is with the MONRE.

Regarding human health to pesticide exposure, the Ministry of Health (MOH) is responsible for monitoring pesticide residues in drinking water as well as agricultural products. The quality of drinking water and water used for food production is regulated based on the National technical regulation on drinking water quality, QCVN01:2009/BYT. This regulation is promulgated by the MOH on Jun 17, 2009. It includes the allowance threshold values for basic parameters regarding organic and inorganic substances in drinking water. Allowance threshold values of 32 pesticide compounds are available in this ordinance. Most of these pesticides are

organochlorine and organophosphorus compounds. All residues of these pesticides in drinking water are periodically tested at least every two years.

In summary, pesticide application in agricultural production is a necessary activity to protect and enhance the yield of crops. However, these agrochemicals can be hazardous to non-target plants, animals, human beings and the environment. Depending on the physicochemical properties of pesticides and ambient environmental conditions, pesticides could be introduced into environment. Pesticide residues are considered pollutants for water resources, and they can be monitored by many various methods. In Vietnam, the authoritative organizations enacted the regulations on pesticide use and management. Regulations on surface and drinking water quality with regard to pesticide residues have been also promulgated. However, data on pesticide residues in surface water as well as in other environmental components are almost not available. In the MD, literature reviews showed that pesticides are widely applied for agricultural production. Several highly hazardous pesticides are still being applied. In chapter 3, the current use and management of pesticides in agricultural production at two representative areas of the MD are reported.

Chapter 3

**PESTICIDE USE AND MANAGEMENT: A CASE  
STUDY IN THE MEKONG DELTA, VIETNAM**

**3.1 Introduction**

Together with enhanced agricultural productivity in Vietnam, the use of agrochemicals, in particular pesticides, has rapidly increased. According to the Plant Protection Department at the Ministry of Agricultural and Rural Development (MARD), the total amount of imported pesticides increased from 20,300 tons in 1991 to 33,637 tons in 2000 and then to 48,288 tons in 2004. In 1991, MARD established a list of 77 active ingredients which were imported, produced, distributed and used in Vietnam. Most of these were categorized as hazardous Ib and II pesticides according to the World Health Organization (WHO). The list is updated annually. The number of used active ingredients has doubled while the number of trade names has increased approximately 3.6 times from 1999 to 2008, (MARD, cited in Hoi et. al (2008)). According to surveys conducted by the Plant Protection Department at MARD in 1992, 1994, 1996 and 1997, pesticide application was a major method used in crop protection. More than 80% of farmers in Long An Province and 85% of farmers in the Mekong Delta (MD) used pesticides more frequently than other pest control methods (Mai *et al.*, 1994; Dung and Dung, 2003). Improper use of pesticides resulted in heavy pest infestations, e.g. via outbreaks of secondary pests. Prophylactic or direct pesticide spraying in early crop stages killed off leafhopper, but harmed natural enemies of pests (e.g. spiders). Application of pesticides to control target pests destroys biodiversity and natural pest control services, and this leads to the secondary pest outbreaks and makes the ecosystems vulnerable to pest invasions (Heong, 2008; Heong *et al.*, 2008b). A pesticide crisis developed due to the failure of pesticides in protecting crops causes significant losses of crop yields (Huan, 2005). The average pesticide application dose in the MD, at approximately 3.1 - 7.0 kg of active ingredients per hectare (kg a.i./ha) (Phuong and Gopalakrishnan, 2003), is considered low compared to developed countries such as Japan (14.30 kg a.i./ha) and South Korea (10.70 kg a.i./ha). However, this figure is much higher than other developing countries like the Philippines (1.56 kg a.i./ha) or Bangladesh (1.50 kg a.i./ha) (UNEP, 2005). Pesticide use has been changed with decrease of organochlorine and organophosphorus application and increase of use for pyrethroids, carbamates and less harmful compounds (Huan *et al.*, 1999a). Several



pesticides were recently banned or restricted for use in Vietnam as shown in Table 3.1.

Farmers typically do not wear protective gears which are necessary for pesticide application with knapsack sprayers. Acute poisoning of skin, respiratory, digestive and nervous system can result if exposed to pesticides (Dung and Dung, 2003). Moreover, pesticide contamination threatens the environment, particularly water resources and aquatic life (Cagauan, 1995; Phuong and Gopalakrishnan, 2003; Khan and Law, 2005). Phuong's research (2003) showed that the value of rural water resources significantly declined due to pesticide contamination in the MD.

In order to reduce pesticide use and effectively manage rice pests, Vietnam national Integrated Pest Management (IPM) program was launched in 1992. IPM has been an effective program in pest control with many positive impacts as well as success in many countries (Way and van Emden, 2000). In the MD, its initial success was revealed through the "Three Reductions - Three Gains" model. The concept of "Three Reductions" is reduction of three input factors, seeds, inorganic fertilizers and pesticides, in the rice growing process. The "Three Gains" refers to yield, rice quality and profit, which are the three high output factors in rice harvesting. Although pesticide use could indeed be reduced, significant gross margins were realized when this method was applied (Huan *et al.*, 2004).

**Table 3.1: Active ingredients (a.i.) banned or restricted for use in the lists of pesticides regulated in Vietnam, 1992 – 2005**

Year	Number restricted a.i.	Number banned a.i.
1992	14	20
1994	15	22 and 5 compounds banned for use on rice *
1996	21	22 and 3 compounds banned for import**
1998	19	23
2000	27	26
2005	17	29***

Source: Plant Protection Department (Huan, 2005)

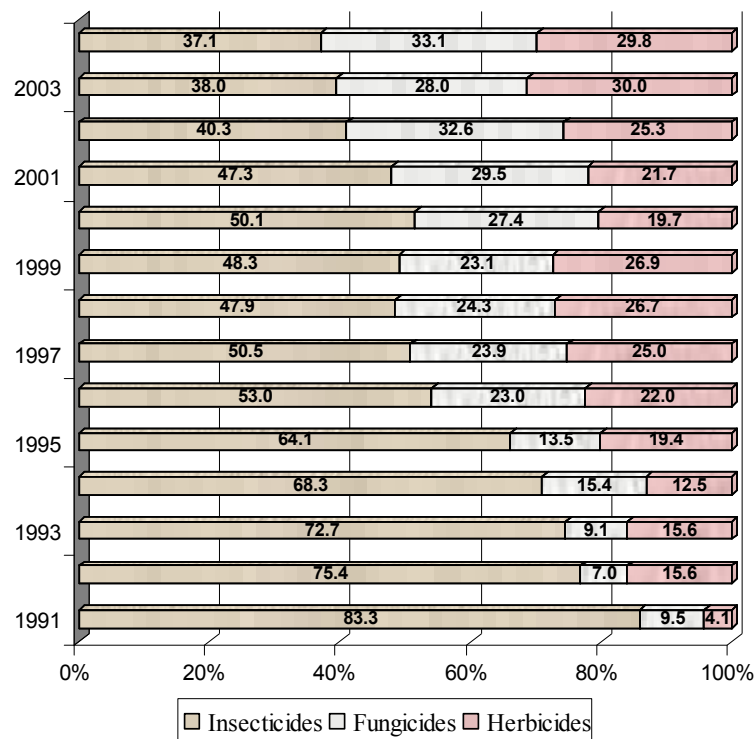
(\*): Five pesticides were banned for use on rice: carbofuran, monocrotophos, methamidophos, endosulfan and phosphamidon,

(\*\*): Three pesticides were banned for import: methamidophos, monocrotophos and carbofuran

(\*\*\*): Endosulfan was officially banned since 22 Oct, 2005

The benefit - cost ratio of IPM applying farmers was higher than those who did not apply IPM method (Berg, 2001; Dung and Dung, 2003). Additionally, media campaign models and farmer field school (FFS) played important complementary roles in significantly changing farmers' beliefs and practices on pesticide use (Heong *et al.*, 1995; Huan *et al.*, 1999b). Moreover, the share of harmful insecticides, of all agrochemical in pesticide imports was reduced from 83.3% in 1991 to 37.1% in 2004 as shown in Figure 3.1(Huan, 2005).

Despite the success of IPM practices, pesticide use in the MD still remains a considerable concern. Farmers use pesticides inappropriately, particular in regard to their overuse, and the number of improper users has increased in the recent years (Huan, 2005). A previous study showed that most farmers considered pesticide application as the most reliable pest management instrument (Heong and Escalada, 1997). IPM programs have not been yet fully introduced in the entire of country, especially in remote farming communities (Huan, 2005).



**Figure 3.1: Share of insecticides, fungicides and herbicides in imported pesticides in Vietnam (1991-2004). Source: Plant Protection Department (Huan, 2005)**

In order to obtain a practical overview of current pesticide use and management by local farmers, this study was implemented at two research districts of the MD,

focusing on the following objectives 1) to capture farming practices (land use and crop rotation), 2) to compile a list of pesticide compounds used by local farmers and 3) to assess common current pesticide use and management practices as well as disposal of wastes originating pesticides.

## **3.2 Materials and Methods**

### **3.2.1 Survey Methods**

#### **Exploratory Field Research**

Exploratory field research on farmers' pesticide use and management practices was conducted in the northwestern and central region of the MD. The addressed districts, Tam Nong and Cai Rang, of exploratory field research were proposed on the basis of the study objectives and the characteristics of these districts. Two exploratory research field trips took place in the Tam Nong and Cai Rang Districts on 6<sup>th</sup> and 9<sup>th</sup> of April 2008, respectively. In these districts, several areas were primarily surveyed to obtain a general overview of farming pattern. After completion of exploratory field research, only one study site per district was selected.

#### **Questionnaire and Household Interviews**

A household questionnaire was compiled aiming to record information on pesticide use and management practices and other farming activities as well. The questionnaire was structured into two parts: local farmers' profile and information on pesticide use and management. The former section included general information such as age of respondents, residential time, farming experience and family size. The later section focused on farmers' basic knowledge, attitude, concerns and practices on pesticide use and management. A questionnaire draft was developed in English and was pre-tested in several random household interviews. The questionnaire was then modified, as shown in Annex 1, and translated into Vietnamese for official interviews.

The interviews were implemented by the author and his assistants who were trained in advanced on how to conduct interviews. Normally, the interview process began with a general introduction, and the purpose of the interview was then explained to

the interviewee. The respondents were randomly selected households of which owners did not own fields at the two selected study sites, but lived within the two selected districts. Collected information was recorded, coded and analyzed with Excel.

A draft questionnaire was pre-tested with 11 farmers in Cai Rang District in April 2008. The questionnaire was then adjusted, adding several new questions which focused on pesticide application practices. In June 2008, the revised questionnaire was used during the interview process with 35 households in Cai Rang District. Interviews were conducted twice in Tam Nong District in July 2008 and October 2009 with 40 farmer households in total being interviewed. The respondents were randomly selected beyond the farmers who owned the fields at the two study sites.

In addition to the questionnaire used for household interviews, field owners located at the two study sites were interviewed and given a form to fill in information relating to their pesticide use. This form includes the time of pesticide application, the names of used pesticide and dose. These farmers were frequently reminded to fill in the form, and it was collected at the end of each cropping season. Moreover, several pesticide application events were recorded in the form providing information for possible peak concentrations of pesticide residues in water during monitoring campaigns.

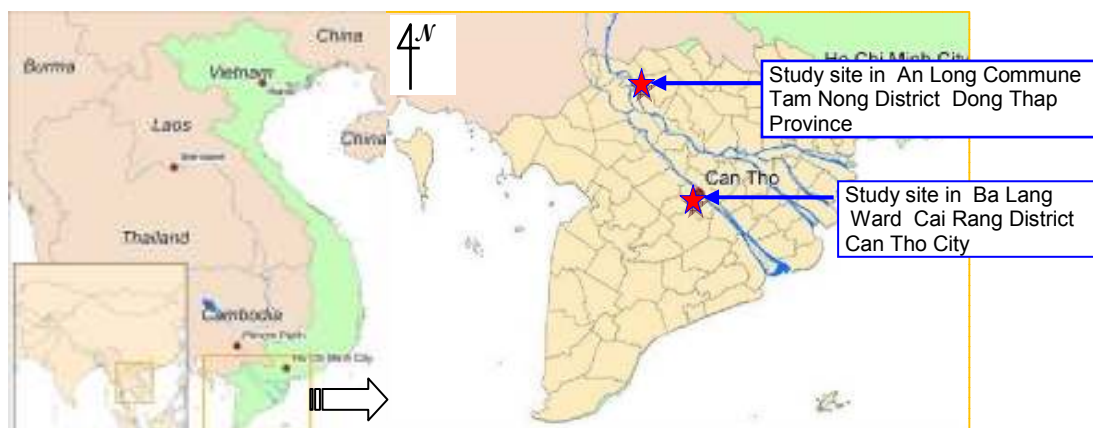
### **Group Interview**

Participatory rural appraisals (PRA), the second interview method, were only conducted with farmers who owned fields at the two study sites. These were used to obtain information on land use status, crop rotation and water management. Pesticide use practices were also further understood through this method. Group interviews consisting of approximately seven farmers per group were facilitated by the author. The meeting was started with general introductions of the members, cultivation and commercial issues concerning rice, vegetables and pesticides. Farmers were then asked to speak about their land use, crop rotation and water management practices. The interview results were documented on a paper sheet in the field and then analyzed with Excel.

Two PRAs were organized with participation of 13 farmers at Ba Lang, who farmed 15 fields at the study site. The first meeting was conducted with seven farmers in September 2008, and the second one consisted of six farmers in December 2008. At An Long, one meeting with eight farmers was organized in December 2008. These farmers owned 10 rice fields and one of these farmers worked in two other fields owned by a relative. One land owning farmer did not attend the meeting but was personally interviewed afterward. Through the PRAs, the following was completed: study site sketch maps were drawn; boundaries of each field were marked, cropping calendar was recorded at each field for the winter - spring, spring - summer and summer - autumn crop of 2008 and 2009, water management practices were recorded, pesticide use data (type, application time, dose) was collected.

### 3.2.2 Study Areas

Based on research objectives, two districts of the MD were selected as study areas. Tam Nong District of Dong Thap Province is located in the northwestern part of the Delta and upstream of the Mekong River, in Vietnam. Cai Rang District of Can Tho City is located in the central part of the MD. Both districts are characterized with tropical semi equatorial climate of the Mekong Delta. The general characteristics of the two districts are summarized in Table 3.2. For each district, a study site was defined to further explore pesticide use, crop rotation, land use and water management practices as illustrated in Figure 3.2. Moreover, a pesticide residue monitoring campaign was set up at these two study sites.



**Figure 3.2: Locations of the two representative research sites in the Mekong Delta, Vietnam (Source: Map from DLR, 2008, adapted.)**

### Tam Nong District

Tam Nong District is typically characterized with intensive paddy rice cultivated twice per year which is this district's most important crop. The winter - spring crop is cultivated from November/December until March/April, and the summer - autumn crop is cultivated from March/April to July/August. On average, the annual crop yield is 5.5 tons/ha. The average yield of the winter - spring crop is always higher than that of the summer - autumn crop. Some kind of pests or diseases often occurred in rice cultivation such as brown planthopper, leaffolder, rice grassy stunt or rice blast.

**Table 3.2: Summary of general characteristics of two districts, in 2008**

	Cai Rang	Tam Nong
Total area of district (ha)	6,900	47,430
Population size (people)	80,781	101,621
Agricultural area (ha)	4,722	31,845
Area of rice cultivation (ha)	2,392	30,185
Productivity of paddy rice (ton/ha)	4.2	6.2
Area of fruit trees (ha)	1770	88

*(Source: Statistical year books, 2008)*



*a) In the flooding time*



*b) In the dry season*

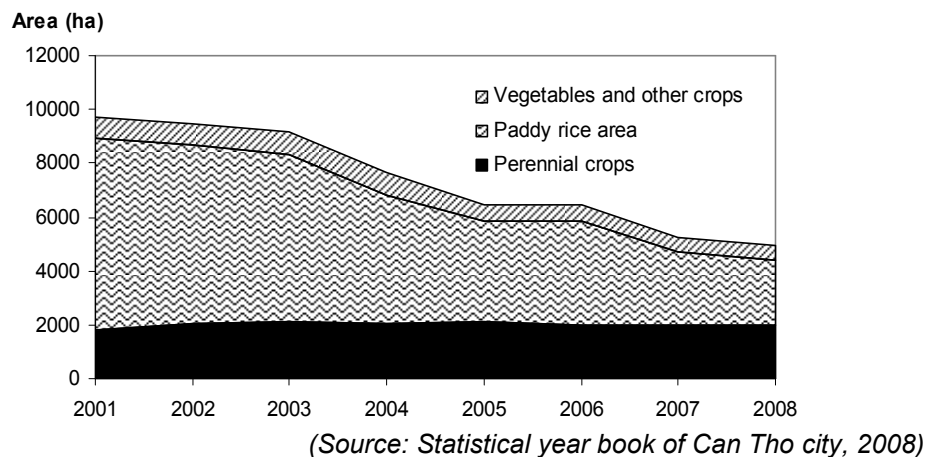
**Figure 3.3: The An Long study site at various periods in 2008**

Rice fields are irrigated via a canal system originating from the Mekong River. Annually, all fields are inundated during flood season. In the rainy season, flooding occurs from July until December as illustrated in Figure 3.3. Flooding is caused by the association of heavy local rainfall and large discharge originating from the upstream of the Mekong River. Water level inside fields can reach one meter or even more in depth at the flooding peak. In the district, one study area namely An

Long was selected comprising a total area of approximately 8.5 hectares. It covered thirteen small parcels with an average production area of 0.6 hectares ranging from 0.1 to 1.4 hectares as shown in Figure 3.6.

### Cai Rang District

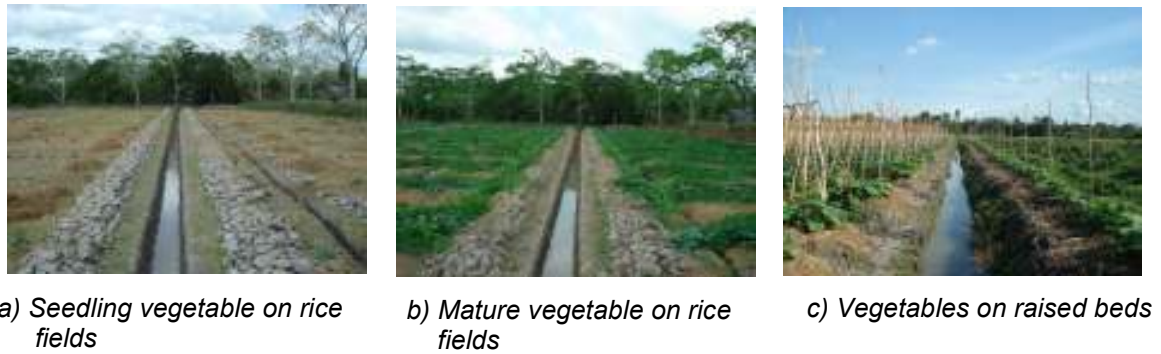
Cai Rang District is a suburban area of Can Tho City and characterized with a mixed cultivation of paddy rice, vegetables and fruit trees. Although its agricultural production is seen as potential activity, its land use area has decreased rapidly. Agricultural land has been used for other purposes such as public infrastructures and homesteads (Chi *et al.*, 2003; Thy *et al.*, 2008). As revealed in Figure 3.4, the area used for rice cultivation has decreased by approximately 66% from 7110 ha in 2001 to 2392 ha in 2008. Rice can be grown in three cropping seasons per year: the winter - spring, spring - summer and summer - autumn crop. Annually, average rice yield was 4.3 tons/ha, and the average yield of the winter - spring crop was always higher compared to the two remaining cropping seasons. Vegetables are often rotated with rice in the same fields or grown separately on raised beds. Rice, vegetable fields and orchards are mixed together creating a diverse agricultural area as illustrated in Figure 3.5.



**Figure 3.4: Changes of agricultural land use in Cai Rang District**

Pests or common diseases such as leaffolder, brown planthopper, rice blast on rice, armyworms, diamondback moths on vegetables often occurred in this area. Irrigation water is supplied through a dense canal and natural river network of the Hau River and its tributary, the Can Tho River. This area is also affected by flooding during the rainy season, but flooding periods are shorter and flooding peak lower than in Tam

Nong District. The highest peak of flooding often occurs in October, and only rice fields are inundated during this period. In this district, the Ba Lang study site was selected, which covered an area of approximately 5 hectares including fields owned by 13 farmers.



**Figure 3.5: Various farming patterns at the Ba Lang study site**

### 3.3 Results and Discussions

#### 3.3.1 Farmer Profiles

**Table 3.3: Farmer profiles surveyed at Tam Nong and Cai Rang**

	Tam Nong (%)	Cai Rang (%)
Field size (ha)		
< 0.5	5.0	82.9
0.5 - 1	27.5	17.1
1.1 - 2	35.0	0
2.1 - 3	17.5	0
3.1 - 4	7.5	0
> 4	7.5	0
Farming experience (years)		
< 10	2.8	11.4
10 - 20	25.0	22.9
21 - 30	22.2	20.0
31 - 40	30.6	25.7
> 40	19.4	20.0

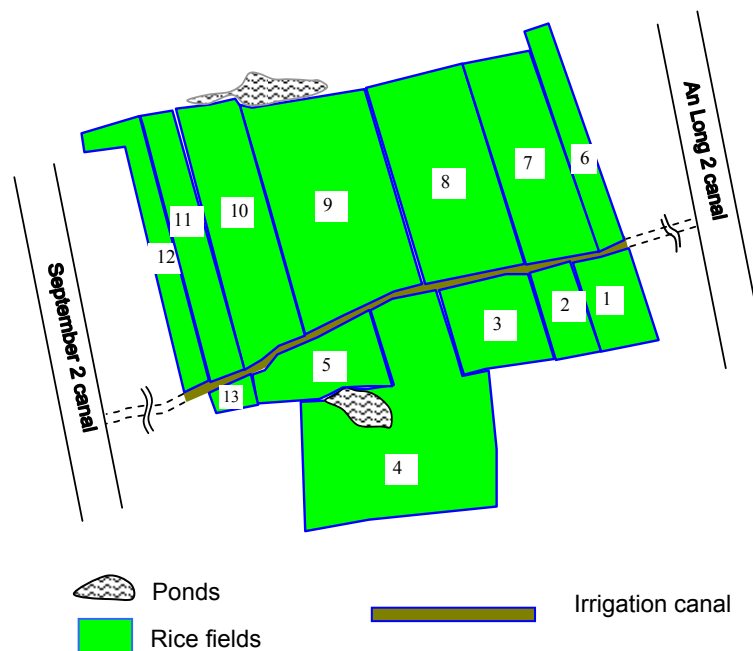
A summary of the respondent farmers' profiles is shown in Table 3.3. The respondent farmers at Tam Nong only cultivated paddy rice in the fields. More than 80% of these farmers owned rice fields with production area larger than 0.5 hectares. The majority of the Cai Rang respondent farmers (83%) owned a production area less than 0.5 hectares. Most of these farmers not only frequently grew paddy rice but also implemented crop rotation. In addition to rice fields, the Cai Rang farmers owned diverse gardens that included many varieties of fruit trees. The majority of



farmers at these two districts had at least 10 years of farming experience. At Tam Nong and Cai Rang, 78 and 69 % of respondent farmers reported 10 to 40 years of farming experience, respectively.

### 3.3.2 Land Use Status

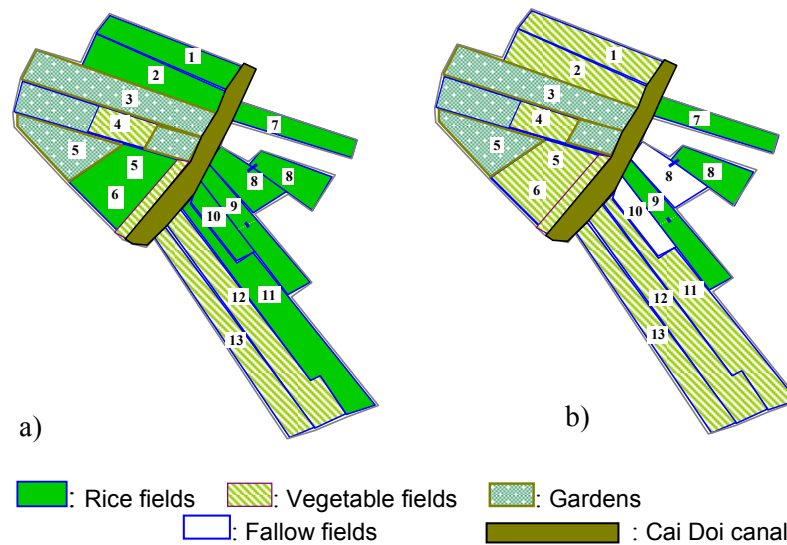
Land use at the An Long study site is illustrated in Figure 3.6. The boundaries separating fields as well as fields and irrigation canal are small bunds. These bunds are often destroyed by the flood water and rebuilt after each flood season. Paddy rice is grown in all of the fields during the two cropping seasons, and these fields are fallow during flooding periods. In the winter - spring crop, soil often experienced puddling before rice sowing when water levels in the fields reach approximately 10 - 20 cm in depth. In the summer - autumn crop, soil was often prepared again by tilling to change soil structure and destroy weeds, pests and diseases.



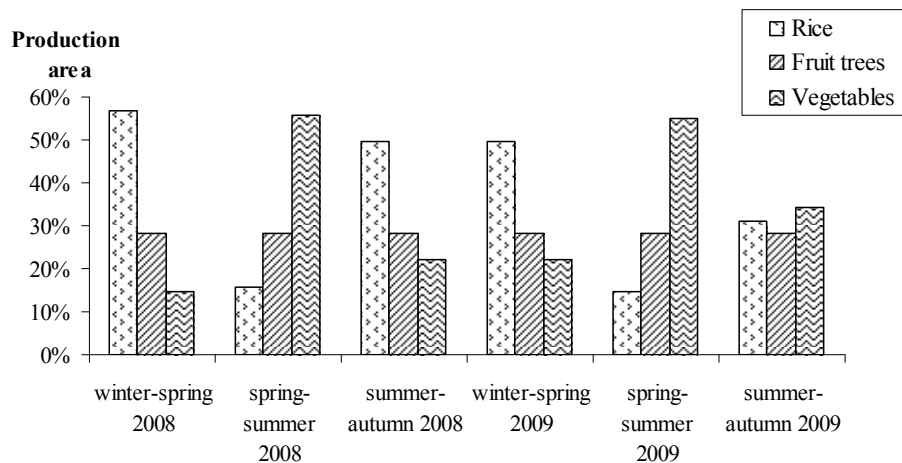
**Figure 3.6: Sketch of land use at the An Long study site**

At the Ba Lang study site, the fields were separated from each others by small bunds. In the rice fields, small ditches were dug to create ridges of 0.5 to 1 meter in width. Vegetables were grown in these ridges and rotated with rice. In the gardens, ditches were dug to construct raised beds at various widths (3 meters or bigger), and fruit trees were planted on these raised beds. Alternatively, ridges were created on the raised beds where vegetables were grown. Agricultural production at this study site

was more diverse than that at the An Long site, and land use changed from season to season as illustrated in Figure 3.7.



**Figure 3.7: Sketch of land use at the Ba Lang study site in a) the winter - spring 2008 - 2009 crop; and b) the spring - summer 2009 crop**



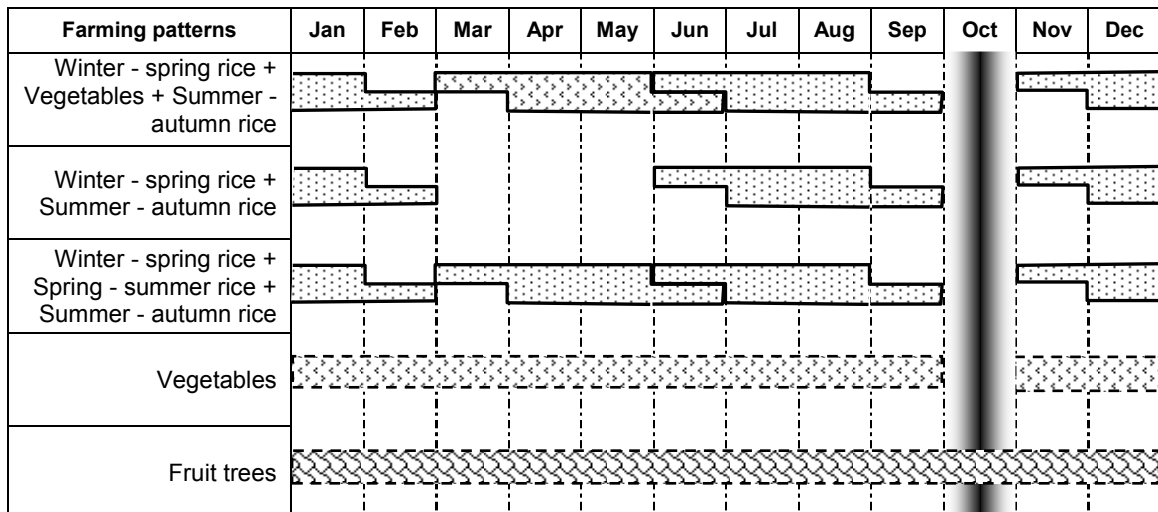
**Figure 3.8: Land use change at the Ba Lang study site**

Paddy rice was dominant during the winter - spring and summer - autumn crop. Its production area covered more than 50% of land use in the winter - spring crop, and the fruit tree growing area did not change as showed in Figure 3.8. Some fields were fallow during the spring - summer crop, and most rice fields experienced inundation of approximately 0.5 meter during the peak of the flooding season (October).

### 3.3.3 Farming Patterns

At An Long, paddy rice was the main crop and cultivated two seasons per year: winter - spring and summer - autumn. The winter - spring crop was started towards the end of the flood season (November/December). After the rice was harvested in February/March, rice straw was usually spread over the rice stubble and burnt to kill weeds, pests, and disease in the fields (Chiem, 1994; Tanaka, 1995). The soil was then often tilled for the summer - autumn crop from March/April. Germinated rice seeds were then sown and harvested before the flooding period (July/August). Most local farmers applied a variety of rice such as Jasmine 85, OM 1490 and OM 2718.

At the Ba Lang study site, farming pattern was more diverse than that at the An Long study site. According to the interview results, five farming types were found here as shown in Figure 3.9.



**Explanation:**

-  : Paddy rices
-  : Fruit trees
-  : Vegetables
-  : Flooding time

**Figure 3.9: Farming patterns at the Ba Lang study site**

- The first farming type consisted of two rice crops, winter - spring and summer - autumn, which were rotated with one vegetable crop between them. For the winter - spring crop, rice was sown in November/December and harvested in January/February. After the winter - spring rice was harvested, rice straw was usually spread over the rice stubble and burnt. Farmers dug small ditches which were connected to large drainage ditches, located in the middle or along

the bunds of the fields. A space between the two ditches, a ridge, was constructed. Vegetables were cultivated on the ridges during the spring - summer crop from February/March to June/July. The ridges were destroyed, and the ditches were filled with soil once the vegetables were harvested. Fields were then planed, and the soil was prepared for the summer - autumn rice crop. In the summer - autumn crop, rice was sown in June/July and was then harvested in August/September.

- Similar to the first farming type, the second pattern consisted of two rice crops including the winter - spring and the summer - autumn crop, and had a similar crop schedule. After the winter - spring rice was harvested in January/February, the fields were left fallow until the beginning of June. The summer - autumn rice crop then began in June/July.
- The third pattern consisted of a triple rice crop per year named the winter - spring, spring - summer and summer - autumn crop. They usually lasted from November/December to January/February, February/March to June/July and June/July to August/September, respectively.
- The fourth type was made up of upland crops which included vegetables. Ditches were dug parallel to construct raised beds which drained into the ditches. Vegetables were cultivated rotationally on the ridges of the raised beds the entire of year except during the peak flooding period of October.
- The fifth farming type was composed of perennial fruit trees in the gardens. A variety of fruit trees were planted on raised beds, located between the two ditches.

Some rice varieties cultivated at the site were IR50404, OM576 and OM 4900. Vegetables were the rotational crop, and they were often dominated in the spring - summer crop. A few types of vegetables were cultivated such as cucumbers (*Cucumis stativus*, *Cucurbitaceae*), winter melons (*Benincasa hispida*, *Cucurbitaceae*) and green mustard cabbage (*Brassica juncea*, *Brassicaceae*). Additionally, a variety of fruit trees were planted in the garden such as makoks (*Spondias dulcis*, *Anacardiaceae*), pomelos (*Citrus maxima*, *Rutaceae*) and bitter oranges (*Citrus aurantium*, *Rutaceae*).

It can be seen that farming pattern is large different between two study sites. The An Long site characterized with two intensive rice crops while a mixed farming with various crops is the representative of the Ba Lang site. This difference could be due to that they are influenced by different ecological and pedological conditions. The An Long site locates in upstream of the Mekong River and is inundated during flooding season annually. In addition, acid sulfate soil is a dominant component of land area suitable to rice cultivation. In contrast, the Ba Lang site locates in downstream of the Mekong River and is raised by alluvia soil suitable to various plants. Moreover, the Ba Lang site is in the proximity of urban centre.

### 3.3.4 Water Management

Irrigation water for the fields of the An Long site was supplied from the September 2 canal (Figure 3.6). Water pumped from this canal reached the fields through the irrigation canal and the shallow ditches in each field. The fields were connected to the irrigation canal by plastic tubes or small earthen gates. Water was often pumped into the irrigation canal every week from ten to fifteen days after sowing (DAS). Water entered the fields on demand by opening the tubes or gates. Water level in fields was usually kept at approximately 10 -15 cm during this stage. Two weeks before the rice harvest, water was drained from the fields through the irrigation canal. Furthermore, flood water had to be often drained off in the beginning of the winter - spring crop for rice sowing.

At Ba Lang, the crop irrigation scheme depended on water demand. Water was introduced into the fields, without pumping through the plastic tubes or open gates during the high tide in the Cai Doi irrigation canal. There were often six irrigation periods during the rice life cycle calculated from the day after sowing (DAS).

- 7 DAS: water intake followed by draining on 8 DAS
- 10 DAS: water intake followed by draining on 15 DAS
- 15 DAS: water intake for fertilizer application followed by draining on 25 DAS
- 25 DAS: water intake for fertilizer application followed by draining on 45 DAS
- 45 DAS: water intake for fertilizer application and water kept in fields until the end of the ripening stage

- 75 DAS: water discharged from the rice fields and gate closed until harvesting time.

Vegetables were usually irrigated twice per day during the early cultivation stage and once per day during the mature stage. For example, winter melons were usually cultivated in rotation with rice crops. Winter melons have a total cropping cycle of approximately 90 days. Their irrigation frequency was often twice per day during the first month after sowing, and once per day at the rest of the cycle. Water was often kept at a level approximately 20cm under the ridges' surface. Fruit trees were usually irrigated from small irrigation ponds of the gardens. Water levels were often kept at 40 to 60 cm under the ground surface of the raised beds.

### 3.3.5 Pesticide Application Practices

#### Types of Used Pesticides

According to the survey results, more than 100 pesticide trade names corresponding to more than 50 different active ingredients from more than 20 chemical groups were used at both districts (Annex 2). As shown in Table 3.4, the most commonly used pesticides were conazole fungicides (hexaconazole, propiconazole and difenoconazole) (11.8%) followed by pyrethroid insecticides (alpha-cypermethrin and cypermethrin), biopesticides (abamectin and validamycin), carbamates (fenobucarb) and chitin synthesis inhibitor (buprofezin). They had a frequency of 9.8, 8.8, 6.9 and 5.9%, respectively. The organophosphate pesticides, profenofos and chlorpyrifos ethyl, were still frequently used as well. Herbicides from the groups chlorinate phenoxy (2,4D, fenoxaprop-p-ethyl) and amide pesticides (butachlor and pretilachlor) were also popularly used.

There was a change in the share of insecticides between the survey result and the inventory of the Plant Protection Department (PPD) at national level. The survey results found an increase of the share of insecticides (48%) while the imported ratio of insecticides in the order of descending from 1991 to 2004, shown in Figure 3.1. It could be due to the infestation of insects in recent years, especially the outbreak of brown plathopper from 2006.

**Table 3.4: Percentage of chemical groups used by the respondent farmers**

No.	Groups of chemicals	Application proportion (%)
1.	Conazoles	11.8
2.	Pyrethroids	9.8
3.	Biopesticides	8.8
4.	Carbamates	6.9
5.	Chlorinate phenoxy	6.9
6.	Organophosphates	5.9
7.	Chitin synthesis inhibitor	5.9
8.	Amide	3.9
9.	Molluscicide	3.9
10.	Nicotinoid	3.9
11.	Phosphorothiolate	3.9
12.	Pyrazole	2.9
13.	Sulfonylure	2.9
14.	Nereistoxin	2.0
15.	Organochlorines	1.0
16.	Bipyridylim	1.0
17.	Nitroguanidine	1.0
18.	Anilide	1.0
19.	Quinolinecarboxylic acid	1.0
20.	Others	15.7

Half of used pesticides belonged to the WHO categories of II and III (moderately and slightly hazardous, respectively). Organophosphate and organochlorine pesticides were still applied by the farmers, and all of their active ingredients fall into category II. Organophosphate pesticides were used more than organochlorine pesticides. One organochlorine compound, endosulfan, was found to be still used by one Tam Nong respondent one year before the interview although this insecticide has been prohibited for use in Vietnam since 2005. In addition, pyrethroid insecticides were used frequently followed by biopesticides and carbamates. Compared to the previous research on pesticide use patterns in the Mekong Delta (Huan *et al.*, 1999b; Berg, 2001), farmers had clearly changed their preferences with respect to kind of insecticides used. Organochlorines and organophosphates have decreased in use while pyrethroids, carbamates and biopesticides have increased in application. Pyrethroids and carbamates were the most commonly used pesticides to control pests. These two compounds are classified as toxic chemicals for vertebrates, particularly for fish (Cagauan, 1995; Cong *et al.*, 2008). Pests may develop a resistance for these compounds causing an outbreak of the secondary pests. This occurrence may be due to misuse of these compounds by farmers (He *et al.*, 2007; Heong *et al.*, 2008b). Approximately 30% of the used fungicides and 20% of

insecticides correspond to the WHO toxicity category IV (practically nontoxic) or were not listed (NL). The majority of the used herbicide compounds also fell into category IV or was NL with the exception of the 2,4D compound which belongs to category II.

### **Pesticide Application Frequency**

Pesticide application was considered a major activity to control pests in these two districts. The survey results showed that 85% of farmers in Tam Nong and 86% of farmers in Cai Rang (Point 16 of Annex 3) only used pesticides as their main tool in pest control. These farmers generally used pesticides due to their relatively quick results after spraying. There was no change in priority of pesticide use in controlling pests compared to the previous studies. Rice farmers considered pesticide application as the dominant tactic to rely on regarding pest management (Heong and Escalada, 1997).

There were differences in pesticide use for rice farmers in the two districts. On average, the respondents' pesticide use frequency per rice cropping season was 8 and 5.7 times in Tam Nong and Cai Rang, respectively. Normally, pesticide spraying frequency was higher in the summer - autumn crop than the winter - spring crop (Cantho\_PPD, 2007). Pesticide application patterns basically reflected pest occurrence. In the 2008-2009 winter - spring rice crop, average pesticide use application in Tam Nong was 8 times per crop. Pesticide compounds were composed of approximately 54% insecticides, 31% fungicides and 14% herbicides as shown in Table 3.5. Meanwhile, pesticide application in Cai Rang was 5.2 times per crop on average. These pesticide compounds consisted of 35% insecticides, 54% fungicides and 14% herbicides. This difference in pesticide compounds make up might be due to a brown planthopper outbreak in Tam Nong. Usually, the insecticides used against this insect consisted of cypermethrin, fenobucarb, pymetrozine and buprofezin. In the 2009 summer - autumn rice crop, pesticide use frequency in Tam Nong was 7 times on average. During this period, fungicides were proportionally the dominant compounds, accounting for 65% of used pesticides. Additionally pesticide application frequency in Cai Rang was less than in Tam Nong. Average pesticide application frequency was 5 times, with 23% of its compound make up consisting of fungicides. The Tam Nong farmers applied a lot of fungicides in order to control sheath blight disease. The fungicides were frequently applied such



as isoprothiolane, validamycin and hexaconazole, similar to the types of fungicides used by Cai Rang farmers.

The percentages of insecticides often applied in these two districts included: cypermethrin (40.0%), abamectin (14.1%), pymetrozine (14.1%), fenobucarb (7.0%), buprofezin (6.0%) and others (18.8%). Among these insecticides, cypermethrin was the most frequently used compound (46.7%) in Tam Nong. Abamectin (32.9%) and cypermethrin (31.6%) were commonly used in Cai Rang. These insecticides were mainly used to control brown planthopper and leaffolder infestations (Point 15 of Annex 3).

**Table 3.5: Rice farmers' pesticide use in the two districts**

	The 2008-2009 winter - spring paddy rice crop		The 2009 summer -autumn paddy rice crop	
	Tam Nong	Cai Rang	Tam Nong	Cai Rang
Herbicides	14%	14%	6%	10%
Insecticides	54%	35%	31%	68%
Fungicides	31%	54%	65%	23%

Fungicides were regularly used in the two districts consisting of propiconazole (27.6%), difenoconazole (17.1%), validamycin (13.3%), isoprothiolane (9.5%), hexaconazole (7.1%) and others (25.4%). Propiconazole was the most commonly used fungicide, 22.3% and 38%, in Tam Nong and Cai Rang, respectively.

Pesticide use frequency in Cai Rang was less than Tam Nong during the survey. This difference is most likely due to two factors. The first factor was the possible relationship between pests and their natural enemies in the diverse farming system (Van Mele and Van Lenteren, 2000). The various types of farming patterns including rice crop, vegetable crop and fruit trees created a diverse agro-ecosystem and a great environment for biological balance in mixed cultivation areas. The types of organisms in the mixed cultivation were more diverse than that in mono-cultivation area. Populations of nature enemies and their foods (i.e. pests) may have been well represented in food chain of the mixed cultivation area. Therefore, a population balance of natural enemies and pests have possibly lead to fewer pests in the mixed cultivation. The second factor was the rice farmer's perception in the use of pesticides. Many rice farmers in Tam Nong overreacted to pest infestations, which

was similarly reported by Heong and Escalada (1997). Farmers applied pesticides when they saw pesticide application in neighboring fields. However, this was less practiced in Cai Rang due to the possible influence of mixed-cultivation. One type of pest or disease occurring in rice field was believed to have little or no effect on neighboring vegetable fields.

For vegetables in Cai Rang, farmers sprayed approximately 12 times per crop on average. This ranged from 3 to 17 times per crop depending on vegetable types. Pesticides such as abamectin, cypermethrin (insecticides) and validamycin (fungicides) were commonly used on vegetables. The pesticides were sprayed approximately once per week. The farmers sprayed pesticides as a precautionary measure even with no serious pest infestation in order to protect vegetables from pest damage and to keep the products in the best possible shape for the market. This result corresponded with previous research outcomes. Pesticides misuse seems to partly stem by pressure from vegetable consumers (Jipanin *et al.*, 2001). Vegetable growers satisfy consumers' demand for optically attractive (perceived as high quality) products by adopting these measures, keeping vegetables free of visible insect damage.

For fruit growers in Cai Rang, pesticide application ranged from 8 to 12 times per cropping season, averaging approximately 10 applications per season. Cypermethrin and fenoburcab (insecticides) were commonly applied to fruit trees. Farmers applied these compounds in order to control such insects as the citrus leafminer or mealybug. However, the majority of farmers (70% of the interviewed fruit growers) did not spray any pesticide on their fruit trees. The reason for this was their small scale production for personal household uses, or they had a mix of different fruit trees planted in the same orchard.

### **Pesticide Application Timing and Targets**

The majority of rice farmers (80% in Tam Nong and 77% in Cai Rang according to Point 6 of Annex 3) applied pesticides when they visibly discovered damage or recognized signs of damage on rice. After the first spraying, pesticides were then continuously applied at two day intervals, particularly in the 2008-2009 winter - spring crop during a brown planthopper infestation.

Nearly 17% of farmers, mainly the vegetable growers in Cai Rang, decided to spray pesticides based on the crop's schedule (Point 6 of Annex 3). In addition, consumer pressure was a factor in scheduling pesticide use as previously mentioned.

A minority of farmers (17% in Tam Nong and 6% in Cai Rang) sprayed pesticides when they saw pesticide application in neighboring fields. Rice farmers in Tam Nong, particularly, often overreacted to pest infestations when visible pest damage was detected. For example, farmers often decided to spray pesticides when they saw pesticide application in neighboring fields to prevent sheath blight. This was also done in an effort to prevent the transmission of the disease from adjacent fields. Similar behavior was documented regarding rice farmers in China (Li *et al.*, 1997). Farmers sprayed pesticides even though it was not necessary.

The brown planthopper was the main target pest for rice according to 98% and 100% of the respondents in Tam Nong and Cai Rang, respectively. In the 2008-2009 winter - spring crop, there was a significant breakout of the brown planthopper at the An Long site, and it was still being reported during other seasons while the study was on progress. Leaf damaging insects, especially leaffolder, were also considered as a particularly damaging insect according to interviewed farmers. More than 65% and 34% of farmers in Tam Nong and Cai Rang respectively reported that this insect was the second most important targeted pest, supporting farmers' belief of the harmful effects leaffolder has on rice. However, previous studies concluded that this insect causes negligible yield loss, although its damage can be highly visible in early crop stages (Heong *et al.*, 1994; Heong and Escalada, 1997). Sheath blight and rice blast, on the other hand, were two diseases that significantly affected crops as well.

### **Quantity of Used Pesticides**

In the two research districts, the total amount of pesticides used per crop recorded at all the fields of the two study sites, An Long and Ba Lang, were 3.619 and 1.852 kg a.i./ha on average, respectively. At both study sites, pesticide amount used in the summer - autumn crop was higher than the winter - spring crop. At the An Long study site, for example, the average pesticide amount used during the winter - spring crop was 1.853 kg a.i./ha while 5.384 kg a.i./ha was used during the summer - autumn

crop. Farmers' pesticide use in An Long was higher than that in Ba Lang, proving that the intensive rice farming requires more pesticide amount than the mixed cultivation. Compared to Dung's (2003) previous research, the average pesticide amount used in the Mekong Delta, with the value of 1.017 kg a.i./ha, was lower than the average amount used at the two study sites.

In terms of used pesticide amount, farmers in Tam Nong and Cai Rang, respectively, obtained their knowledge from the following sources: extension workers (3% and 0%, respectively), pesticide retailers (13% and 6%), pesticide instruction labels (20% and 17%), other farmers (55% and 63%) and other sources (e.g. mass media) (45% and 57%) (Point 5 of Annex 3). The farmers had little or no opportunity to obtain correct instructions in regard with the use of proper pesticide amounts from extension workers, although extension programs were deployed. Only a few farmers were advised by extension workers or by pesticide retailers on the proper pesticide amount to use. More than half of the respondents learned how to use pesticides from their neighboring farmers. When they saw that their neighbors apply a type of pesticide effectively, they inquired about the amount and also kept the labels of that pesticide container for the next application as necessary. The farmers who firstly applied a new type of pesticide obtained application knowledge from pesticide company's advertisements or through mass media. They then themselves taught how to use the new pesticide by directly applying it to their crops. The farmers obtained knowledge on pesticide use from the instructions on pesticide labels; however, these instructions were sometimes too vague for them to understand. This might led to use of incorrect amounts.

The proportion of farmers applying pesticide dose equal to the recommended dosage instructed on pesticide container labels was 55% and 66% in Tam Nong and in Cai Rang, respectively (Point 7 of Annex 3). The proportion of farmers applying pesticide dose equal to recommended dosage was high, but they easily increased pesticide dose if the first application was ineffective in protecting or improving crop yield. No farmers who used pesticide dose less than that recommended on the lables. The remaining respondents (45% in Tam Nong and 34% in Cai Rang) applied pesticide dose higher than recommended dosage on the label. According to these farmers, they had to use high dose in order to obtain the required effectiveness. Moreover, the farmers often mixed two or more types of pesticides in sprayers before

application. Respectively, 48% and 77% of respondents in Tam Nong and Cai Rang often mixed pesticides before spraying to get expected effectiveness (Point 8 of Annex 3). Respectively, 28% and 20% in Tam Nong and Cai Rang stated that they mixed pesticides because they did not believe in the products' quality. Other reasons for this practice included the following: (1) to save time and labor in spraying; (2) to prevent and repel many types of pests that could develop after pesticide application; and (3) to simply imitate other farmers when they recognize an effective application method.

### **Pesticide Purchase**

The majority of farmer respondents in Tam Nong (95%) and Cai Rang (83%) themselves decided on which types of pesticides to be purchased (Point 1 of Annex 3). Most farmers made this decision after personally viewing the pest infestation they had experienced. For the remaining farmers, purchase of pesticides was greatly dependent on their spouse's or other relatives' opinions. These farmers owned the fields but lacked pesticide use knowledge, or they were preoccupied with other tasks.

More than half of the interviewed farmers in Tam Nong (62%) and most of the farmers in Cai Rang (91%) bought pesticides at several retailers (Point 2 of Annex 3). There are two main reasons for this. Firstly, most farmers used several different pesticides not only for one cropping season but also for treating various pests or diseases (Point 3 of Annex 3). A variety of pesticides was used for different cropping stages in one crop. Meanwhile, the farmers expressed difficulty in finding all expected pesticides at one retailer. Secondly, there were several retailers at the same area given the liberalization of retailing pesticide. To compete, the retailers applied various strategies to attract their customers. Besides promotional programs such as gifts, the retailers also accepted late payment with interest. Also, due to an agreement on the late payment form with interest, a minority of farmers (38% and 9% in Tam Nong and in Cai Rang, respectively) usually bought pesticides at only one retailer. These farmers often did not have money enough to pay when they purchased pesticides.

### **Pesticide Spraying Practices**

Pesticide spraying was mainly conducted by the respondents (73% in Tam Nong and 74% in Cai Rang). The remaining farmers were assisted by their relatives or hired spraying operators (Point 4 of Annex 3). This depended on farmer's health, farming time and field size. Spraying was usually performed in the early mornings or late afternoons. These were most effective time in controlling pests and less negative influence on health of spray operator. Farmers are less exposed to pesticides in low temperatures at which pesticides' volatilization is less. On the other hand, weather condition also plays a significant role for occurrence of spray drift. Spray drift is the major factor in missing intended target, in reduced efficacy and in deposition in non-target areas. Before applying pesticides, most farmers (87% in Tam Nong and 91% in Cai Rang) changed water level in the fields (Point 14 of Annex 3). Water must be present in the rice fields before spraying. This prevents movement of insects downward during pesticide spraying. With this practice, the effect of spraying is improved because insects are more exposed to pesticides. However, through this practice, pesticides can readily enter the surface freshwater system. The spraying solution was prepared within the fields without protecting water or soil from possible spillage. Water used for mixing pesticides was often taken from irrigation ditches or ponds, and the mixing process was sometimes performed on canal banks.

### **Sprayer Maintenance and Safety**

Knapsack sprayers were used by most local farmers. These sprayers are made from either metal or plastic, and their maximum holding capacity varies from 8 to 24 liters. The heavy sprayers required considerable effort to operate, especially in hot weather conditions and waterlogged fields. Furthermore, most spray operators did not wear appropriate protection equipments (i.e. special protecting clothing, masks, gloves) which was often observed at the study sites. Given the hot conditions, the majority of farmers did not like to use the protection equipment as this made work more cumbersome and uncomfortable.

### **Pesticide Storage**

The survey showed unsafe practices regarding pesticide storage. With the exception of placing pesticides in locked cabinets all storage practices were considered unsafe. In the target households, there often were no designated areas for pesticide storage. Pesticides were casually kept in homes such as in easily accessed cupboards, left

hanging on walls or were housed with livestock. Pesticides were stored in these areas directly after application or use in the previous crop season. Furthermore, purchased pesticides were often stored together with old or left-over pesticides. Most farmers usually purchased pesticide products shortly before application.

### **Pesticide Wastes: Disposal Practices**

Most farmers in Tam Nong (95%) and Cai Rang (45%) directly discarded empty pesticide containers in fields after each application. Empty containers could be found in the fields such as along the small bunds between rice fields, in irrigation canals and in the orchards. These containers were often picked up by flood water and drifted far away during the flooding season. A minority of the respondents in Tam Nong (5%) and Cai Rang (28%) kept empty pesticide containers for selling (Point 11 of Annex 3). It is needed to note that this practice was only implemented when containers are sellable. These kinds of wastes were often piled at unsafe places in fields or around houses. Farmers also unsafely buried empty pesticide containers under the field ground. Toxic chemicals remaining in these containers can then easily reach groundwater.

Furthermore, the majority of farmers (88% in Tam Nong and 83% in Cai Rang) immediately rinsed sprayers at irrigation canals or ponds in the fields (Point 10 of Annex 3). Occasionally, this wastewater was then poured into rice fields or even in water bodies. Another rinsing practice was that farmers brought sprayers to main canals and rinsed them with water in the canals; however, only a minority of farmers (8% in Tam Nong and 14% in Cai Rang) reported doing this (Point 10 of Annex 3).

The disposal of left-over pesticide solutions after spraying was another problem. Approximately half of the respondents in Tam Nong (48%) and Cai Rang (65%) emptied the left-over pesticide solutions by spraying their crops again (Point 9 of Annex 3). This was generally conducted near field edges or at pest infestation hot spots. On the other hand, 43% of farmers in Tam Nong and 23% Cai Rang poured the left-over pesticide solutions directly into the fields (Point 9 of Annex 3). A minority of respondents (3% in Tam Nong and 6% in Cai Rang) reported emptying these solutions directly into canals (Point 9 of Annex 3). This practice leads to an immediate point source pollution of surface water, and exposures of humans, using the water for drinking or personal hygiene, and aquatic organisms.

### **Human Health and Environmental Impacts**

Farmers paid little attention to human health compared to other aspects in pesticide application. When asked about the most important aspect of pesticide application, 55% of Tam Nong farmers and 71% of Cai Rang farmers considered pesticide cost as their main concern (Point 12 of Annex 3). The prices of pesticides were often increased when pest infestation reached a critical stage. However, the farmers reluctantly accepted this commercial practice in the liberalized economy as long as the pesticides continued to be effective. Farmers disregarded their own health in order to protect crops. The survey showed that only 8% of farmers in Tam Nong and 6% in Cai Rang considered the effect that pesticide had on health as the most important aspect of pesticide application. Meanwhile, 53% of Tam Nong farmers and 37% of Cai Rang farmers expressed concern regarding the negative effects on health after pesticide use (Point 13 of Annex 3). The impacts to human health regarding pesticide application were not investigated in this research in detail. The acute and chronic symptoms due to pesticide exposure, which include eczema, pterygium (a vascular membrane that forms over the eye's cornea), coughing, vomit, diarrhea and headaches were widely investigated. Organochlorines, organophosphates, carbamates and 2,4D were considered chemical irritants to eyes, skin, lungs, and the nervous system (Pingali *et al.*, 1994; Dasgupta *et al.*, 2005a). An analysis regarding the economic impact between health, crop costs to pests, and the overall cost of using pesticide were also previously researched (Pingali *et al.*, 1994; Dung and Dung, 2003). When farmers took working days off due to health problems related to pesticide exposure, crop yield did not reach their maximum output even with additional pesticide use.

Environmental impact was considered the most important aspects of pesticide use by a rather large proportion of farmers in Tam Nong (30%) and in Cai Rang (23%) (Point 12 of Annex 3). According to farmers, these effects were visible in rice fields, and they particular noted the impact to aquatic organisms. Half of the farmers in Tam Nong and 63% of farmers in Cai Rang witnessed fish dying after pesticide application in fields. In Tam Nong and Cai Rang, 10% and 14% of farmers, respectively, confirmed that pesticides reduced fish growth in fields. A part of local farmers, 18% in Tam Nong and 3% in Cai Rang, saw other negative effects to organisms in fields after pesticide application. For instance, crabs climbed to field



bunds or non-target insects dropped down into the water in fields. The negative effects of pesticides to aquatic life, including fish, algae, zooplankton and non-target aquatic invertebrates, were already extensively monitored (Simpson and Roger, 1995; Cong *et al.*, 2008). Some pesticides were also considered as endocrine disruptors negatively affecting reproduction, growth and the development of wildlife species. This includes invertebrates, amphibians, reptiles, fish, birds and mammals (Khan and Law, 2005). Among the pesticides applied to rice fields, insecticides are the most potentially toxic agrochemicals to aquatic life, particularly those belonging to the organochlorine, organophosphate, carbamate and pyrethroid groups. In the rice-fish farming system, fish cultivation is negatively affected by pesticide use not only in the target fields but also in neighboring fields (Berg, 2001). Phuong (2003) estimated that pesticide pollution in the Mekong Delta caused the total value of rural water resource lost approximately US\$251 million per year.

### **Integrated Pest Management (IPM) Application**

Only a minority of farmers in Tam Nong (15%) and in Cai Rang (14%) applied IPM methods in their farming activities. According to the farmers, several methods were applied such as using resistant varieties (e.g. Jasmine, VD20), applying less rice seed per sowing area (20 kg/1000 m<sup>2</sup>) or using plastic mulch to cover ridges during vegetable cultivation. It is important to note that these farmers did not directly participate in IPM programs. They learned several IPM methods from agricultural extension advisory programs, from mass media or from other farmers. These farmers did confirm that they seldom applied IPM methods due to four reasons. Firstly, they were not officially trained in IPM approaches. They did not clearly understand their fields' ecological systems or the relationships between pests and their natural enemies. Secondly, farmers believed that it was too risky to apply IPM methods in their own fields while no one else was using these methods in surrounding fields. Thirdly, the extreme evolution of pests, the brown planthopper for example, and pressure from pesticide salespeople led to a dependence on agrochemicals. Fourthly, a low net profit was realized when implementing IPM, especially for farmers owning small fields. Given these reasons, IPM methods were not attractive enough to encourage the farmers to use them.

Although pesticide application is just one method involved in integrated pest management practices, this chemical control method is only recommended as the

final alternative to control pests. However, it was considered a regularly acceptable solution and improperly applied by most interviewed farmers. Meanwhile, IPM is known as an effective tool for farming activities and its advances in preventing and management contaminants in foods and the environment were reported (Way and van Emden, 2000; SP-IPM, 2009). The successful experiences of IMP program were proved at many places within the MD in changing farmers' perceptions and behaviors in pesticide use (Mai *et al.*, 1994; Escalada *et al.*, 1999; Huan *et al.*, 1999b; Huan *et al.*, 2004). For example, farmers did not spray pesticides to prevent the occurrence of leaffolder insects early in the rice crop as they believed the rice plants could better compensate in this particular stage without a yield loss. A media campaign also led to a reduction in insecticide spraying frequency. From 1992 to 1997, a decline from 3.4 to 1 application of insecticides per crop was recorded for most farmers in the Mekong Delta (Huan *et al.*, 1999b). Dung's (2003) economic analysis showed that the net benefits created by IPM farmers were higher than non-IPM farmers; IPM farmers had a benefit - cost ratio of 0.94 while non-IPM farmers had a benefit - cost ratio of 0.79. Furthermore, IPM farmers experienced a significant decrease in healthcare costs due to less pesticide exposure. Rice-fish farming combined with IPM practices has also proved to be a sustainable food production model. This model has helped farmers gain the highest possible net income, reduce resource use, avoid inappropriate use of agrochemicals, increase nutrient recycling and create a more balanced field ecosystem (Rothuis *et al.*, 1998; Berg, 2002). Citrus were planted with weed flora in order to maintain a population of pests' natural enemies such as predatory mites and parasitoids. This biological method controlled citrus leafminer and red mite pest population, and it also reduced toxic pesticide application on the citrus orchards (Van Mele and Van Lenteren, 2000).

### **3.4 Conclusions and Recommendations**

#### **3.4.1 Conclusions**

This study found typical differences between two researched areas in the Mekong Delta. In the area located upstream of the Delta, Tam Nong District, only two rice crops were cultivated per year and production areas were almost larger than 0.5 hectares in size. Meanwhile rice was often rotated with other crops in rice fields and farming pattern was characterized by mixed cultivation in Cai Rang District, research area located in a suburban of the Delta's centre. The majority of production areas

was less than 0.5 hectares in size. Most interviewed farmers in the two reaserch areas experienced at least 10 years for agricultural activities.

Pesticide application was the main activity used to control pests in agricultural production in the two investigated areas. The types of used pesticides were diverse in trade name, particularly active ingredients. This diversity provides farmers with more convenience in relation to protection of agricultural productions for pest infestation and improvement of crop yields; however, there is a potential risk when farmers improperly use these agrochemicals. It is important to note that many WHO class II pesticides were found such as profenofos and cypermethrin according to the surveys. The banned organochlorines compound, endosulfan, was confirmed to still be in use by several farmers.

Pesticide application frequency for rice in rice intensive farming area was higher than that in mixed cultivating area, with an average frequency of 8 and 5.7 applications per cropping season, respectively. Application frequency in the winter - spring crop was lower than the summer - autumn crop, depending on pest and disease occurrence. The usage ratio between pesticide types (i.e. insecticides and fungicides) also depended on the presence of pests or disease in each cropping season. On the other hand, pesticide application frequency for vegetables and fruit trees in Cai Rang was depending on cultivated plant types. However, pesticides were rarely applied for fruit trees in orchards at the study site of Cai Rang District due to mixed cultivation of the orchards and small farming area.

The amount of pesticide used in the intensive rice farming was almost double of that in rotational farming fields. Most farmers used much higher doses than those recommended on pesticide instruction labels. Comparing to Dung's study result (2003), the average pesticide dose found in the present study was higher than the average dose used in the Mekong Delta.

Pesticides were often applied to rice when farmers discovered pests or diseases in fields. However, a minority of farmers sprayed to prevent potential infestation when they saw pesticide appication in neighboring fields. The pests or disease most frequently found in rice fields were brown planthopper, leaffolder and rice blast.

The majority of farmers themselves purchased and sprayed pesticides in their fields. They rarely wore protective gears while spraying pesticides, putting their health at risk. In addition, pesticide products as well as its leftovers were generally stored inappropriately in houses and other areas close to homes.

The cleaning of knapsack sprayers, the pouring out of leftover pesticide solutions into the water in fields or canals and the disposal of empty containers in fields are all considered pesticide pollution sources for surface water. In addition, the practice of keeping water in fields for pesticide use creates a potential pesticide pollution source for surface water, particularly persistent and soluble pesticides. These practices may lead to aquatic organisms being exposed to pesticide residues in water. Notably, human health may also be affected by pesticide residues in surface water which is an important source for drinking water.

The survey results revealed that farmers considered pesticide cost as the most important issue regarding pesticide management even though they are generally aware of the negative effect to human health and surrounding environment. For example, when crops were attacked by pests, the farmers purchased pesticides at high prices in spite of not being able to make payment immediately.

The agricultural activities in these two researched areas chiefly relied on pesticides for pest control. Pesticide application was also considered as the main pest control activity among other IPM methods. Only a minority of farmers applied other IPM methods in their fields. The main reason for this limitation was that the IMP program was not officially implemented at these sites. Other IPM methods were used less frequently or not at all in farming activities.

#### **3.4.2 Proposed Mitigation Measures for Improper Pesticide Application**

The above findings related to pesticide use and management showed that local farmers typically applied moderately and even highly hazardous pesticides. Pesticides were improperly used regarding frequency, time and dosage of application. Lack of safety with respected to pesticide use and management was observed for a majority of the interviewed farmers. In addition, wastes originating from pesticide application were not appropriately managed and treated in fields as

well storage places. These shortcomings cause risks to human health and surrounding environment. Meanwhile, a majority of farmers neglected to protect themselves against pesticide exposure although a larger part of them recognized negative influences of pesticide contamination. How to reduce inappropriate application and management of pesticide products and its wastes is very necessary for sustainable agricultural development and the reduction of unintended impact. Several measures have been applied to reduce pesticide risks in the MD as well as other regions of the country. The Plant Protection Department is the authorized agency that designates pesticide application in Vietnam agriculture. This organization has a complete national network at district level on the whole of country. Since 1993, the Department has enacted many regulations on plant protection and pesticide use.

- The decree on plant protection and quarantine. In term of plant protection chemicals, some significant points for reducing pesticide risks include:
  - + The list of pesticides permitted, restricted and banned for use was defined and announced.
  - + Safety to the people and the environment during production, storage and transportation of plant protection chemicals must be ensured.
- Pesticide registration to ensure the technical efficiency, safety to human beings and the environment and other requirements of the regulation policy. The Pesticide Control Center was set up from 1994 to implement the State's function regarding the management of pesticide for quality, residues on agricultural and forestry products and testing of new pesticides.
- The Plant Protection Department has banned certain pesticides, including all category compounds I since 1995. The list of banned, restricted and permitted pesticides is revised annually.

The Ministry of Finance has imposed a tax on some pesticides since 1996. But given the levels involved, it is designed to raise revenue rather than affect behavior on pesticide use (McCann, 2005). Therefore, in order to reduce pesticide use a tax system should be improved and tax should be levied for all chemical pesticides imported and produced inside the country. In addition, a higher tax should be applied for toxic pesticides to eliminate their use, and revenue should be used to make an incentive in finding more environmental friendly pesticides.

IPM program's benefit is needed to be proved in order to encourage local farmers at the study sites as well as other remote areas before they can apply the program. This should be conducted through programs similar to previous ones held in several regions of the MD such as FFS, as well as through the mass media campaigns. These are necessary to have a multi stakeholder participation including plant protection section, extension services, scientists and local government. These programs are considered as efficient measures in changing farmers' attitudes, perceptions and behaviors on pest management practices (Escalada *et al.*, 1999; Huan *et al.*, 1999b; Escalada and Heong, 2007; Heong *et al.*, 2008c).

Pesticide should be judiciously selected and the most toxic compounds should not be used anymore (e.g. organochlorine, organophosphorus and carbamate pesticides). Moving to use new compounds which are less harmful, have a shorter half-life in environment and are effective to eliminate target pests should be the most important strategy in mitigating pesticide contamination. However, judicious pesticide use is affected by farmers' economic conditions, especially poor farmers. They are able to easily spray the harmful synthetic pesticides, illegally sold in the market, due to usually inexpensive prices and as they remain effective at killing pests. A strict pesticide legislation and enforcement to prevent the import, production, sale and use of dangerous pesticides is urgently required.

Pesticide use demand can be reduced through applying basic cultural controls in agricultural practices such as carrying out sanitation practices in the field, tillage operations, proper crop rotation, intercropping, resistant varieties use or respecting specific planting time schedules. These measures also lead to lower pest occurrence. Use of certified pest-free seeds is necessary to reduce pesticide use in early cropping season. Little or no chemical pesticide use periodically allows the natural enemies of pests and other benefit organisms remain in the field.

Biological controls should be applied to intervening agricultural ecosystem towards the benefit of natural enemies or useful organisms and the detriment of pests. The effectiveness of natural enemies already present in the field is enhanced by providing food or reducing insecticide use. A natural enemy, for example weaver ant *Oecophylla*, is introduced from one region to other regions where the species does not naturally occur. Pest species in the new regions are food sources of this ant, and

consequently the population of pest species is controlled and agricultural product quality is improved (Van Mele and Cuc, 2003). Ecological engineering can be applied to control pest population in rice fields, leading to reduction of insecticide use. Flower weeds are planted on the field bunds. These are food sources and even as refuges for natural enemies before they move into the field for preying. Therefore, biological diversity is enhanced and the population of insects is kept balance in the field (Huan, *et al.*, 2010). Enhancing application of bio-pesticides, *Bacillus thuringiensis* (Bt) or nuclear polyhedrosis virus (NPV), instead of chemical pesticides is also a great biological measure to reduce pesticide contamination (Hai *et al.*, 2008; SP-IPM, 2009). Bio-pesticides are pesticides of which active ingredient are pathogenic micro-organisms such as bacterium, virus, fungus, nematode or protozoa. Bio-pesticides are often used in a similar way to chemical pesticides, but their “live” ingredients are able to reproduce and to provide a continuing pest control effect. Another biological alternative, synthesis insect sex pheromone based strategy, can be applied in the MD (Vang *et al.*, 2008). Synthesis insect sex pheromones, a semiochemical or other formulations (attracticides), are biochemicals that include insects and other species. Chemicals produced from the mixture can stimulate particular behavior between individuals of the same species or interaction between different individuals. Insect sex pheromones are attractants usually produced by females to attract males, and sex pheromone trap are most useful semiochemical measure in IPM (SP-IPM, 2006). The main use of sex pheromone trap is to disrupt mating, thus reducing pest population. Pest species can be detected and monitored in the trap, and this helps farmers in deciding whether or not to spray their crops. Thus, sex pheromone traps can reduce pesticide abuse, ensure that the target pests are killed and benefit natural enemies. Another biological alternative, protected horticulture under nets, is also useful to keep crops out of the reach of insects. This makes pesticide use less necessary. However, protected horticulture structure is expensive, so is only applied to high value plants or for research purposes.

Chemical pesticide application is one of the last resorts if pest infestation exceeds critical threshold levels through regular field scouting. Pesticide use involves to farmer’s decision-making process which is affected by farmer’s perceptions, attitude and pesticide use practices. A pesticide application approach named “4 Rights,” was issued as a manual by the MARD through the Center for Agriculture Extension (changed into the National Centre for Agriculture Extension since 2010). A proper pesticide application includes four points: correct pesticide types, correct pesticide

dose and concentration, right on application time and appropriate application method. This approach should be further propagated the entire of the Delta. Surface water pollution from pesticide use can be reduced by enhancing farmer's decision-making process in proper operation and safety practices. Pesticide loading and mixing areas should be located as far away from points of entry to surface water as possible, and wastewater from these places should be collected and treated by a nearby located treatment system such as bio-beds and buffer zones. Pesticide should not be sprayed next to irrigation canals or knapsack's sprayer nozzle should be lowered nearer to crops. Leftover of pesticide mixes should be avoided or treated at the wastewater treatment system. It is necessary to take a small part of land area for wastewater treatment emanated from agricultural activity. Water in fields should not be kept too much during spraying events and should be kept in the field for as long a time as possible after pesticide application. Application equipments should be maintained in appropriate working conditions to avoid leakage problem. Knapsack sprayer and other equipment should be rinsed at the treatment system. Pesticide container disposal should be organized with safe mechanisms. Pesticide containers should be rinsed before disposal and water used for rinsing should be added to pesticide sprayer. Farmers are encouraged to be responsible for collecting and storing pesticide container properly after use. All above practices should be widely propagated through FFS or multi media as previously conducted in some regions of the Delta.

Continue to apply the "One Must, Five Reductions" (1M5R) program for all rice growing areas is a promised measure to reduce pesticide and fertilizer use as well. This program is developed on the success of "Three Reductions, Three Gains" (3R3G) model which has launched by MARD through the National Center for Agriculture Extension since 2003. Benefit of the program 3R3G was recorded with gross income on average of US\$ 35 and 58 per hectare in the summer - autumn and winter - spring rice crops, respectively (Huan, *et al.*, 2005). Together with three reductions: seed, pesticide and fertilizer rate, irrigation water and postharvest losses (5 Reductions) were proved to be lowed when the program 1M5R was applied in some provinces such as An Giang and Can Tho in the recent years. In addition, use of pest free certified seeds (1 Must) led to reduce pesticide use.



*Chapter 4*

## **MONITORING RESIDUE CONCENTRATIONS OF COMMONLY USED PESTICIDES IN SURFACE WATER**

### **4.1 Introduction**

The occurrence of pesticides in water systems is of global concern. Monitoring pesticide residue concentration in surface water is implemented in many countries in the world (Laabs *et al.*, 2002; Nakano *et al.*, 2004). Two main sources of pesticide contamination for surface water are from agronomic activities and public health measures such as vector control (Abhilash and Singh, 2009). In the Mekong Delta (MD), agricultural activities are considered a pollution source of pesticide residues in surface water. Although pesticides have significantly contributed in ensuring agricultural productivity of the region, contamination by these agrochemicals have created risks to human health and the environmental components (Margni *et al.*, 2002; Phuong and Gopalakrishnan, 2003). A medical blood test on rice farmers in the Delta showed that the incidence of poisoning from exposure to organophosphates and carbamates were quite high (Dasgupta *et al.*, 2005a). Pesticide contamination caused the loss of value of water resources (Phuong and Gopalakrishnan, 2003). Despite an official ban since 1995, persistent organic pollutants, such as hexachlorocyclohexane (HCHs), DDTs were still detected in the Delta as reported recently (Minh *et al.*, 2007). The concentrations of these compounds in sediments were higher than the allowed levels of Canadian Environmental Quality guideline, but of equal or lower magnitude when compared to other regions in Asia (Carvalho *et al.*, 2008). Limited pesticide monitoring of surface water at provincial level has been carried out in several provinces of the Delta such as Can Tho and Hau Giang. However, these have been focused on active ingredients including organochlorine and organophosphate substances regulated in the National technical regulation on surface water (QCVN 08:2008/BTNMT, 2008). Meanwhile, survey results showed that agrochemical application in agricultural work was very plentiful and diverse with active ingredients belonging to pyrethroid, organophosphate and carbamate compounds (e.g. presented in chapter 3). Aiming to fill the gap of information on pesticide concentration in surface water in particular currently used common pesticides, a monitoring campaign was conducted in this study at two study sites of the MD to (1) assess residue concentrations of commonly used pesticides in surface waters of agricultural fields and canals; (2) determine the influence of pesticides application, environment

conditions to the fate of pesticides in aquatic environment; and (3) compare pesticide residue concentrations caused by different farming conditions at the two study sites.

## 4.2 Study Sites

Research samples were collected at two study sites within the MD from August 2008 until August 2009. One site was located in the north-western part, and another study site was situated in the central part of the Delta. They were characterized by different farming conditions and were representative of two agricultural production patterns in this region. Their geographical locations are shown in Figure 3.2.

### 4.2.1 An Long

The An Long study site was selected as a representative area for intensive double rice production in the MD. It was located in a side of An Long 2 canal which is a secondary tributary of the Mekong River. The study site is belonging to the An Long Commune, Tam Nong District. Total area of the site was approximately 85.000 square meters. This is a relatively flat area, belonging to Dong Thap Muoi (the Plain of Reeds), with an average elevation of approximately 1.5 m a.s.l. In a calendar year of rice cultivation, winter - spring is the first cropping season lasting from November/December to March/April. The second cropping season, summer - autumn, is cultivated from March/April to June/July. The flooding season occurs after the second rice cropping season and usually lasts from August through November. This area is affected by flood with inundation depth of approximately one meter or higher.

Thirteen parcels were located along two sides of the irrigation/draining canal connected with An Long 2 canal as shown Figure 4.1. These fields were separated by small bunds. Most fields were drained off the water into the irrigation canal connected to the An Long 2 canal. The irrigation canal played the double role as both supplying and draining water for the fields of which gates were labelled AT1, AT2, AT3, AT4, AT5 and AT13, respectively. However, the remaining fields with gates AT6, AT7, AT8, AT9, AT10, AT11 and AT12, respectively, were indirectly irrigated through the fields and a pond which was located at their upstream side. For instance, the fields with gates AT11, AT12 (i.e. field 11, field 12) were irrigated by ponding water through field 10.

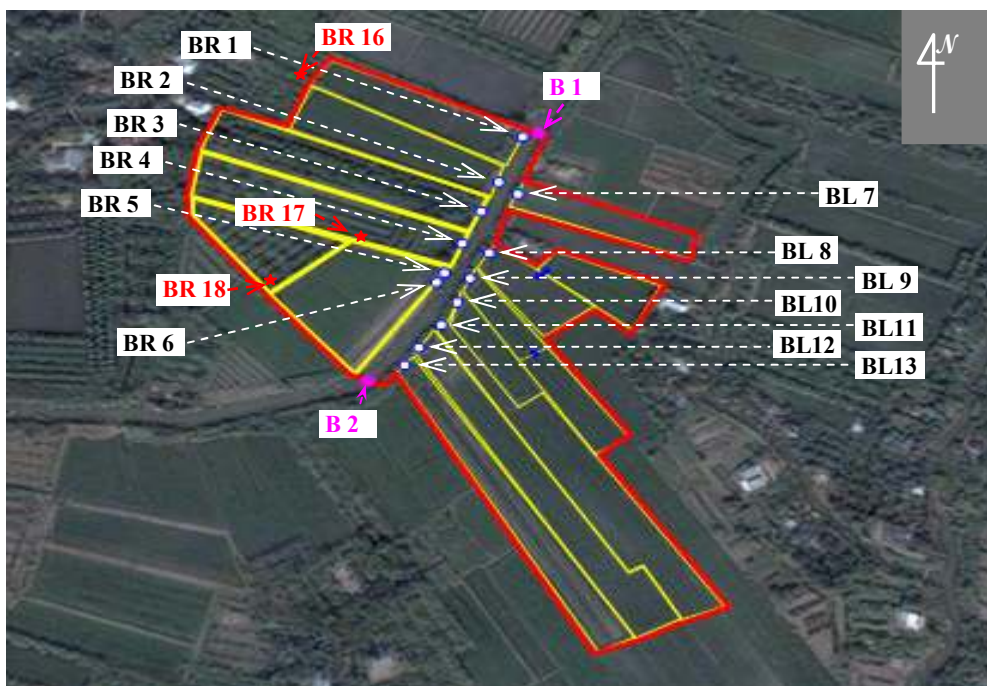


**Figure 4.1: Aerial photograph of rice fields and sampling points at the An Long site, modified from Google Earth**

On the other hand, field 5 was not directly connected to the irrigation canal, and its water was discharged to the pond located in field 4. Water in this pond and field 4 was discharged through gate AT4 to the irrigation canal. Since the 2009 summer - autumn crop, however, a new gate was built in field 5. The gate directly connected field 5 to the irrigation canal. Thus, 12 sampling points were located at the rice field gates in the 2009 winter - spring crop and two sampling points located up and down stream of the irrigation canal. Meanwhile, each sampling point was located at the 13 rice field gates in the 2009 summer - autumn crop. Name of sampling points were coded similarly to the name of field gates. Additionally, one sampling point ATO was situated in the An Long 2 canal towards downstream approximately 50 meters from the concrete gate connecting the irrigation canal and the An Long 2 canal. Furthermore, two sampling points were located at the pond of rice field 4 and 10, AL16 and AL17. In flooding season, the number of sampling points was less than that in cropping seasons. Samples were taken at sampling points located up- and down-stream of the An Long 2 canal, named AL3 and AL2 (i.e. ATO in cropping seasons), and one sample namely AL1 inside rice fields. Characteristics of sampling points were summarized in Table 4.3.

#### 4.2.2 Ba Lang

The Ba Lang study site was located in the south-western suburban area of Can Tho City, in the centre of the MD. It is a flat area with average elevation of 0.9 m a.s.l. The entire area was irrigated by the Cai Doi canal, a tributary of the Can Tho River. The study site was considered a mixed agricultural farming area. Along both sides of the Cai Doi canal, an area of approximately 50,000 square meters with mixed land use of paddy rice, vegetables and fruit trees was selected. There were thirteen fields in this area, and each parcel was separated from the others by small bunds. All parcels were irrigated and drained by the Cai Doi canal through plastic or concrete pipes. The double and triple rice crops, vegetables and fruit trees are agricultural products in the area. Crops were also changed in several fields from season to season. The land use sketch maps of the fields during sampling progress are illustrated in detail in chapter 3.



**Figure 4.2: Aerial photograph of rice fields and sampling points at the Ba Lang site, modified from Google Earth**

Thirteen sampling points were located at the gates which connect the fields with the Cai Doi canal. They were labelled BR1, BR2, BR3, BR4, BR5, BR6 and BL7, BL8, BL9, BL10, BL11, BL12, BL13 to the right and left sides of the Cai Doi canal, respectively. This was done in the direction from sampling point B1 to B2 located in the canal. B1 and B2 were two sampling points which were at down or upstream of the Cai Doi canal depending on direction of water flow and which provided boundary conditions. This is due to the fact that the Cai Doi canal was influenced by tidal effects

from the Can Tho River. The tide of the Can Tho River was semi-diurnal tide with two high and two low peaks within 24 hours. It was similar to the tidal scheme of the Mekong River. Additionally, this area was influenced by flood in the rainy season, especially in October. The association of local heavy rain and high tide cause adverse effects to agricultural work. Most of fields cultivated rice and vegetables were left fallow during this period. Furthermore, three additional sampling points (BR16, BR17 and BR18) were located at three ponds in the study site as shown in Figure 4.2. These ponds were dug in the orchards and raised bed fields, and the water was used to irrigate fruit trees, vegetables and even for paddy rice. The aquatic environment of these ponds was therefore assumed to be contaminated by pesticide residues from agricultural activities in the fields.

### **4.3 Materials and Methods**

#### **4.3.1 Selection of Studied Pesticides**

In order to decide which pesticides will be selected for the study, information on use frequency, physicochemical properties of pesticides and feasibility of analytical methods were considered in the selection. Firstly, a household interviewing campaign was implemented to understand how pesticides were used and managed by the local farmers. A questionnaire was designed in this process as reported in Annex 1. The interview campaigns were carried out at the two study sites. The participating households encompass the households of farmers who owned the fields inside and outside the study site. Secondly, the kinds of pesticides and their application for the crops were studied and recorded at the meetings which were organized as participatory rural appraisals with the farmers. Thirdly, information on pesticide use were continuously recorded and updated at spraying events at the study sites. This investigation was conducted at the same period with sampling events during the monitoring campaigns. The used pesticides were identified from the list of recorded compounds as reported in Annex 2.

A range of physicochemical properties of pesticides is considered in the selection of studied pesticides. They include solubility in water, hydrolysis half-life, octanol-water partition coefficient, soil sorption and soil degradation half-life. Additionally, pesticide toxicity to human health according to WHO classification was considered in the selection. Also, pesticide toxicity to aquatic organisms was taken into account in the selection through fish acute 96 hour LC<sub>50</sub> (or LC<sub>50, 96h</sub>) value. The concept of LC<sub>50, 96h</sub>

and other physicochemical properties of pesticides as well as their toxicity are briefly explained in Table 1, 2 and 3 of Annex 4.

**Table 4.1: List of studied pesticides with their physicochemical properties, WHO toxicity and fish acute poisoning**

Pesticides	Solu- bility in 20°C	Hydro- lysis half-life	Octanol- water partition coeff.	Soil sorp- tion	Soil deg. half-life	Toxicity (WHO) <sup>(*)</sup>	Fish Acute	Chemical property score
	S <sub>w</sub>	DT <sub>50, water</sub>	K <sub>ow</sub>	K <sub>oc</sub>	DT <sub>50, soil</sub>		LC <sub>50, 96h</sub>	
	(mg/L)	(avg, days)	(mL/g)	(mL/ g)	(avg, days)		(mg/L)	
<b>Insecticide</b>								
Buprofezin	0.46	Stable	4,8 (high)	10624	46.2	IV	0.33 (Moderate )	3
Cypermethrin	0.009	179	5,3 (high)	85572	69	II	0.0028 (High)	5
Endosulfan	0.32	20	3,13 (high)	11500	86	II	49 (Moderate)	4
Fenobucarb	420	-	2,78 (mod)	1068	-	II	1.70 (Moderate)	2
Fipronil	3.78	Stable	3,75 (high)	577	65	II	0.248 (Moderate)	5
Profenofos	28	Stable	1,7 (low)	2016	7	II	0.08 (High)	4
<b>Herbicide</b>								
Butachlor	20	-	-	700	12	IV	0.44 (Moderate )	2
Pretilachlor	50	Stable	4.08 (high)	-	30	IV	0.9 (Moderate )	4
Propanil	225	365	2,29 (low)	400	-	IV	2.3 (Moderate)	3
<b>Fungicide</b>								
Difenoconazole	15	Stable	4,2 (high)	3760	85	III	1.1 (Moderate)	3
Hexaconazole	18	30	3,9 (high)	1040	225	IV	3,4 (Moderate)	3
Isoprothiolane	54	Stable	3.3 (high)	1352	-	III	6.8 (Moderate)	3
Propiconazole	150	53.5	3,72 (high)	1086	214	II	1.3 (Moderate)	5
<b>Criteria</b>	<b>≥ 20</b>	<b>≥ 14</b>	<b>high</b>	<b>&lt;1000</b>	<b>≥ 14</b>	<b>&lt; II</b>	<b>high</b>	

(\*) : Based on WHO's classification with regard to toxicity for human health, II: moderately hazardous; III: slightly hazardous; IV: practically nontoxic or unlikely to present acute hazard in normal use. *Source:* Footprint pesticide database, 2009. Available at [www.herts.ac.uk/aeru/footprint/](http://www.herts.ac.uk/aeru/footprint/)

A criterion of physicochemical properties of pesticides was suggested to select studied compounds, based on the list of recorded pesticides (Annex 2). To be able to compare many compounds with different property and select studied pesticides for the monitoring a scoring system was applied. The system includes the following values: water solubility above or equal to 20 mg/L, hydrolysis half-life above or equal to 14 days, octanol-water partition coefficient above 3, soil sorption coefficient below 1000 mL/g, soil degradation half life above or equal to 14 day, belonged to WHO toxicity

class I or II, and high acute toxic to fish. Compounds received scores when their properties satisfy above values, and their chemical property scores were calculated as shown in Table 4.1. Although these values were set artificially, they allowed for the identification of a range of pesticides with different properties and potential interest in the monitoring. For example, profenofos is soluble and stable in the water, thus it can be assumed that it will be often detected in the surface water. It belongs to WHO toxicity class II and has a high potential to harm fish. However, the scoring system was only a decision support tool which was handled flexibly. For instance with fenobucarb, some of the values were missing leading to a low score, but this pesticide was still included due to its frequent use at the two study sites.

The feasibility of analytical methods was very important in selection of the studied compounds. This closely relates with the availability of analytical equipments as well as complexity of analytical methods used. Thus, only compounds were selected which could be included in a multi-residue analysis method based on solid phase extraction, separation with gas chromatography (GC) and detection with mass spectrometry (MS) as introduced in the following sections.

On the basis of integration of frequent use, chemical property score and the feasibility of analytical methods, fifteen studied pesticides were selected as showed in Table 4.1. They included buprofezin, butachlor, cypermethrin, difenozonazole,  $\alpha$ -endosulfan,  $\beta$ -endosulfan, endosulfan-sulfate, fenobucarb, fipronil, hexaconazole, isoprothiolane, pretilachlor, profenofos, propanil and propiconazole.

#### 4.3.2 Chemicals and Reagents

Fifteen pesticide standards, surrogate standard  $\delta$ -HCH ( $\delta$ -hexachlorocyclohexane) and internal standard (Fluorene-d10) with purity higher than 99% were obtained from Riedel-de-Haen. Stock solutions for each of these substances were prepared in acetone with concentration of 200  $\mu\text{g}/\text{mL}$  and were stored in a freezer ( $-20^{\circ}\text{C}$ ). Working solutions were diluted depending on research purposes. Information of solvents used to prepare stock and working solutions and rinse equipments are shown in Table 4.2. They were purchased from J.T. Baker. pH indicator paper and sodium chloride analytical reagent grade were purchased from Merck (Darmstadt, Germany). Glass fiber filters (Millipore AP 25 and AP 15) were produced by Millipore (Schwalbach, Germany). Glass wool for pre-filtration was purchased from Carl Roth (Karlsruhe, Germany). Strata C18-E (500 mg, 3 mL) silica-based reversed phase

cartridges for solid phase extraction were supplied from Phenomenex (Aschaffenburg, Germany).

**Table 4.2: Solvents used in laboratory analysis process**

Chemicals	Grade	
	HPLC	ACS
n-hexane	x	
Ethyl acetate	x	
Toluene	x	
Acetone	x	x
Methanol	x	x
Water	x	

Notes: ACS - American chemical society grade, and HPLC - High Performance Liquid Chromatography

#### 4.3.3 Monitoring Campaign

A monitoring strategy was established and implemented to collect water samples at sampling points in two study sites. Most samplings were conducted at selected sampling points in fields, ponds and canals as shown in Table 4.3. However, sampling frequency was different at the two study sites. In the mixed crop site, Ba Lang, sampling was conducted every three weeks approximately. This sampling frequency was selected based on cropping calendar of shortest life cycle crop and hydrolysis half lives of the studied pesticides. Harvest time of several types of vegetables (e.g. salad) is nearly one month after sowing day. The shortest hydrolysis half-life of studied active ingredients is 20 days. In the intensive rice cultivation site, An Long, sampling frequency was implemented for every six weeks approximately, depending on the workload related to sampling events at the Ba Lang site and cropping calendar as well. Samples taken in the fields at An Long and Ba Lang were collected from 12/2008 to 8/2009 and 8/2008 to 8/2009, respectively. There was no regular sampling event inside the fields of the An Long site from August to November 2008 because the fields were inundated. In addition, several samplings were carried out at the two study sites after pesticide application events to determine peak concentrations of pesticide residues at several sampling points. Samples were also taken in the flooding season to determine persistence of pesticide residues in flooding water. In detail, sampling events at An Long in the flooding season were only implemented at sampling points located in the canal and several representative points in the fields. Sampling events



were carried out in ponds of the two study sites from February 2009 (i.e. ponding water supplied for rice in the 2009 winter - spring crop at An Long). During monitoring process, the crop stage development (i.e. type, life cycle of crops, etc.) and pesticide application were recorded at each field. Additionally, one sampling point was located in Tram Chim national park (a protected wetland area) aiming to define background concentration of pesticide residues. This area was separated from surrounding areas by dyke system, and water was supplied from rainwater and surface water from outside area in the flooding season through sluice gates. There was no pesticide application in this natural wetland area.

#### **4.3.4 Sample Collection**

In one sampling event, 1 liter grab sample was taken at each sampling point at the two study areas. At the An Long site, the samples were taken at outlet points of thirteen rice fields. The manner in which these samples were taken depended on whether water was inside the rice fields, water was draining from the rice fields or whether no water was inside rice fields. For the first case, samples were taken in the ditch of the fields. For the second case, the samples were directly taken at the pipe mouth outside the fields. There was no sample collected for the third case. Two samples were collected both up- and down-stream of the irrigation canal from the study site. In addition, one sample was taken in the An Long 2 canal in the same sampling event. Two samples were collected at the two ponds when there was water inside. In the flooding season, all rice field parcels were flooded, only several representative samples were therefore collected in the fields. From the connecting gate with irrigation canal, one sample at the upstream and another at the downstream of the An Long 2 canal were collected at the same sampling event.

At the Ba Lang site, the samples were also collected at outlet of thirteen rice fields. The collection method of these samples was similar to that at the An Long site. One sample at the up- and another at the downstream of Cai Doi irrigation canal were also taken in each sampling event. Samples were also taken from three ponds in the study site.

**Table 4.3: Characteristics of the sampling points**

Sampling points	Code	Geological coordinate		Land use			Total area (ha)	Sampling period
		Latitude	Longitude	Rice	Veg.	Fruit		
<b>In Ba Lang</b>								
Field N°1	BR1	9°58'55.03"N	105°43'55.22"E	x	x		0.3	08/2008 - 08/2009
Field N°2	BR2	9°58'54.15"N	105°43'54.94"E	x	x		0.3	"
Field N°3	BR3	9°58'53.09"N	105°43'54.56"E			x	0.7	"
Field N°4	BR4	9°58'52.63"N	105°43'54.47"E		x	x	0.68	"
Field N°5	BR5	9°58'51.47"N	105°43'54.09"E	x	x		0.55	"
Field N°6	BR6	9°58'51.34"N	105°43'54.02"E	x	x		0.2	"
Field N°7	BL7	9°58'53.54"N	105°43'55.05"E	x			0.17	"
Field N°8	BL8	9°58'52.32"N	105°43'54.58"E	x			0.3	"
Field N°9	BL9	9°58'51.30"N	105°43'51.27"E	x	x		0.25	"
Field N°10	BL10	9°58'51.00"N	105°43'54.14"E	x			0.1	"
Field N°11	BL11	9°58'50.23"N	105°43'53.93"E	x	x		0.6	"
Field N°12	BL12	9°58'49.53"N	105°43'53.43"E		x		0.35	"
Field N°13	BL13	9°58'49.11"N	105°43'53.17"E		x		0.42	"
Cai Doi canal 1	B1	9°58'55.54"N	105°43'55.76"E					"
Cai Doi canal 2	B2	9°58'47.85"N	105°43'52.35"E					"
Pond outside field 1	BR16	9°58'56.49"N	105°43'50.41"E		x			02/2009 - 08/2009
Pond inside field 3	BR17	9°58'51.89"N	105°43'52.10"E		x			02/2009 - 08/2009
Pond inside field 5	BR18	9°58'50.72"N	105°43'50.38"E			x		02/2009 - 08/2009
<b>In An Long</b>								
Field N°1	AT1	10°43'7.71"N	105°24'40.26"E	x			0.32	12/2008 - 07/2009
Field N°2	AT2	10°43'6.99"N	105°24'38.85"E	x			0.25	12/2008 - 07/2009
Field N°3	AT3	10°43'6.26"N	105°24'36.82"E	x			0.4	12/2008 - 07/2009
Field N°4	AT4	10°43'5.39"N	105°24'35.19"E	x			1.2	12/2008 - 08/2009
Field N°5	AT5	10°43'4.31"N	105°24'33.96"E	x			0.27	04/2009 - 07/2009
Field N°6	AT6	10°43'8.21"N	105°24'40.22"E	x			0.32	12/2008 - 07/2009
Field N°7	AT7	10°43'8.02"N	105°24'39.91"E	x			0.7	12/2008 - 07/2009
Field N°8	AT8	10°43'6.66"N	105°24'37.12"E	x			1.15	12/2008 - 07/2009
Field N°9	AT9	10°43'6.44"N	105°24'36.32"E	x			1.4	12/2008 - 08/2009
Field N°10	AT10	10°43'4.05"N	105°24'33.17"E	x			1.0	12/2008 - 07/2009
Field N°11	AT11	10°43'3.28"N	105°24'32.58"E	x			0.5	12/2008 - 07/2009
Field N°12	AT12	10°43'3.02"N	105°24'32.20"E	x			0.5	12/2008 - 07/2009
Field N°13	AT13	10°43'3.23"N	105°24'32.76"E	x			0.05	12/2008 - 07/2009
Pond inside field 4	AT16	10°43'3.75"N	105°24'36.50"E					02/2009 - 07/2009
Pond outside field 10	AT17	10°43'9.66"N	105°24'30.91"E					02/2009 - 07/2009
Irrigation canal upstream	ATU	10°43'2.88"N	105°24'32.22"E					12/2008 - 08/2009
Irrigation canal downstream	ATD	10°43'8.32"N	105°24'41.08"E					12/2008 - 08/2009
An Long canal 2 downstream	ATO, AL2	10°43'10.03"N	105°24'44.45"E					08/2008 - 08/2009 Flooding seasons <sup>(*)</sup>
An Long canal 2 upstream	AL3	10°44'51.35"N	105°24'23.94"E					Flooding seasons <sup>(*)</sup>
Inside study site	AL1	10°43'6.69"N	105°24'35.97"E					Flooding seasons <sup>(*)</sup>
Tram Chim zone	TC	10°45'28.16"N	105°29'13.64"E					03/2009 - 08/2009

(\*) : from the end of July to the early December

In parallel to collection of water samples for analyzing studied compounds, physicochemical parameters (water temperature, pH, conductivity and dissolved oxygen) were also directly measured in-situ at the sampling points.

### **pH**

pH is an important parameter in assessing the quality of surface water contaminated by the chemical and biological pollutants. When the pH of water increases, the solubility of some chemicals is affected. pH of most natural water is between 6.0 and 8.5, although lower values can occur in waters with high of organic content, and higher values in eutrophic waters (Reeve, 2002). In unpolluted waters, pH is principally controlled by the balance between the carbon dioxide, carbonate and bicarbonate ions as well as other natural compounds such as humic and fulvic acids.

The natural acid-base balance of a water body can be affected by industrial effluents and atmospheric deposition of acid-forming substances. Changes in pH can indicate the presence of certain effluents, particularly when continuously measured and recorded, together with the conductivity of a water body.

### **Conductivity**

Conductivity is a measure of the ability of water to conduct an electric current. Conductivity is expressed as micro-siemens per centimeter ( $\mu\text{S cm}^{-1}$ ) and is related to the concentrations of total dissolved solids and major ions for a given water body. The conductivity of most freshwaters ranges from 10 to 1000  $\mu\text{S cm}^{-1}$ . Its value is high in polluted waters or those receiving large quantities of land run-off. In addition, conductivity is also a rough indicator of mineral content when other methods cannot easily be used. Conductivity can serve as an indicator of pollution zones, e.g. the extent of influence of run-off waters. Conductivity is highly dependent on temperature. It is usually measured in-situ with conductivity meter, and may be continuously measured and recorded.

### **Water Temperature**

Surface water temperature is affected by many factors such as altitude, time of day, seasons in year, weather conditions, water flow, plant cover, etc. On the other hand, water temperature influences the chemical, physical and biological processes

occurring in water bodies. The rate of the reactions in aquatic environment is accelerated when water temperature increases. Degradation of organic matters in aquatic environment is proportional to water temperature. When temperature increases, organic matter decays more rapidly. High water temperature causes a decrease of solubility of gases into water bodies, such as oxygen, carbon dioxide, nitrogen. Surface water temperature ranges from 0°C to 30°C or more in the tropic countries. Water temperature changes as it is taken out of water bodies. Therefore, this parameter must be measured right after the sample is collected.

### **Dissolved Oxygen (DO)**

Dissolved oxygen is a key substance in determining the extent and types of life in a body of water. Oxygen deficiency is fatal to many aquatic animals such as fish. The presence of oxygen can be equally fatal to many kinds of anaerobic bacteria. Although poorly soluble in water, oxygen is fundamental to nearly all chemical and biological processes within water bodies. Without free dissolved oxygen, streams become uninhabitable to aerobic organisms, including fish and most invertebrates. Dissolved oxygen is inversely proportional to temperature, and maximum amount of oxygen that can be dissolved in water at 0°C is 15 mg/L. The saturation value decreases rapidly with increasing water temperature.

Concentrations of dissolved oxygen in unpolluted waters are usually close to, but less than, 10mg/L. They also depend on the degradation processes of organic substances by micro-organisms. Waste discharge with high organic matter and nutrients can lead to the decrease of DO concentrations as a result of the increased microbial activity (respiration) occurring during the degradation of the organic matter. In severe cases of reduced oxygen concentrations, anaerobic conditions can occur (i.e. 0 mg/L of oxygen), particularly close to the sediment - water interface as a result of decaying of benthos.

#### **4.3.5 Sample Handling, Storage and Preservation**

Sample water was filled in 1 liter glass borosilicate bottles with Teflon sealed caps leaving air space. The bottles were previously washed with ethyl acetate, acetone, rinsed with distilled water and then burnt at 180 °C approximately. All collected sample bottles were immediately sealed and cooled with wet ice in cooling boxes.

They were then transported to the laboratory. The samples not immediately extracted were cooled in a dark refrigerator, adjusted to 4 °C, and the maximum recommended storage time is five days.

#### 4.3.6 Sample Extraction

Water samples were first passed through analytical grade glass wool and then two layers of fiber-glass filter with a pore size of 8 µm (Millipore AP 25) and 0.6 µm (Millipore AP 15) to remove suspended matter. Prior to extraction, 500 mL sample water was adjusted to pH 3.5 - 4, and 15 g of sodium chloride was then added. In the next step, the samples were solid-phase extracted with Strata C18-E cartridge. The cartridge was preconditioned by sequentially eluting 3 mL of n-hexane, 3 mL of ethyl acetate, 1 mL of methanol and 1 mL of HPLC water. The samples were then passed through the conditioned cartridge by a tubing adaptor with a vacuum flow rate of 2 - 4 mL/min. Afterwards the cartridge was cleaned with 2 mL of HPLC water to remove salt. In order to dry the C18 sorbent material, nitrogen gas was passed through it for 20 minutes. The solid phase extraction (SPE) cartridge was then packed in aluminium foil and stored at -20 °C until elution. Analytes were eluted from the cartridge by 6 mL of ethyl acetate and then 6 mL n-hexane. The evaporation process with working condition at 40 °C and -65 cm Hg was continued in order to concentrate the eluted solution. This was performed by a rotary evaporator after adding 300 µL of toluene into the eluted solution as keeper. The analytes concentrated in toluene were transferred to a vial, filled up to 1 mL and stored at -20 °C until analysis. After analysis vials were also stored at -20 °C or packed with dry ice for transportation.

#### 4.3.7 Analytical Methods and Quantification of Compounds

Pesticide residues were quantified by an Agilent Technologies 6890N gas chromatograph which was linked with an Agilent Technologies 5973 mass selective detector and equipped with an Agilent 7683 automatic sampler. The GC was fitted with an HP 5 fused silica capillary column: 30 m length x 0.25 mm ID x 0.5 µm film thickness. Helium was used as the carrier gas with a constant flow rate of 0.8 mL/min. The following temperature program was employed during analysis: 1) an 85 °C initial temperature within a duration of 2.5 minutes; 2) an increase at 15 °C/min to 220 °C; 3) another increase at 10 °C/min to 280 °C, held for 5 minutes; 4) then another ramp up 10 °C/min to 300°C, held for 5 minutes. The injector block temperature was held at

250 °C. The injection volume was 1 µL for all samples as well as for the standards. Pesticide compounds were determined according to the selected ion monitoring mode.

The analytical procedure was calibrated against a mixture of external calibration standards. This mixture included surrogate standard ( $\delta$ -HCH), internal standard (Fluoren-D10) with concentration as the same added in real samples and 15 standards of studied pesticides with concentration levels of 0.01, 0.05, 0.1, 0.5, 1.0 and 5.0 mg/L. Linear calibration functions of three, four, five or six points from the concentration levels of these mixtures were established with realizable square of correlation coefficient ( $R^2 > 0.99$ ). The mixture of external standards were together measured in each of measurement of real samples, and calibration functions were then established for quantification of studied compound concentration. The concentration of an analyte was calculated by multiplying extracted sample volume and its amount. The amount of analyte was determined based on the ratio of known internal standard amount and an amount ratio, which was calculated from relationship between two coefficients of calibration function of the analyte and the ratio of peak area between internal standard and the analyte.

#### 4.3.8 Method Validation and Quality Control

The analytical method was validated according to guidance of analytical detection limit developed by Laboratory Certification program of Wisconsin Department of Natural Resources, United States. Method validation is indicated by the method detection limit (MDL). This value is determined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix containing analyte (Ripp, 1996). The method detection limits are statistically determined values that are calculated via replicated experiments. The value of MDL is calculated as the following equation.

$$\text{MDL} = S \times t_{\text{value}}$$

Where S is sample standard deviation for the replications, and t\_value is the correct Student's value corresponding degrees of freedom, determined from the established available table.

Concerning the content of method detection limit, another terminology applied to define the limitation of an analytical method, called limit of detection (LOD). According

to Ripp (1996), LOD is stated as, “the lowest concentration level that can be determined to be statistically different from a blank (99% confidence)”. The LOD is approximately equal to the MDL for the purpose of analytical method assessment.

The MDL is verified by an average percent recovery for each analyte in sample which is determined after passing an extraction and analysis process as previously mentioned. The average percent recovery was calculated by the following equation:

$$\% \text{ Recovery} = (X_{\text{ave}}/\text{spike level}) \times 100\%$$

Where  $X_{\text{ave}}$  is the average concentration of an analyte in samples, and spike level is the real initial fortified concentration of that analyte.

Another concept concerning the validation of analytical method is the limit of quantification (LOQ). The LOQ is the level above which quantitative results are considered values in the research progress. This parameter is also recommended as a threshold value for controlling analytical quality in regulatory limits for pesticide residues in water by International Union of Pure and Applied Chemistry (Hamilton *et al.*, 2003). The limit of quantification (LOQ) of pesticide compounds was calculated for the method validation experiment according to the following equation:

$$\text{LOQ} = 10 \times S$$

Where, S is the sample standard deviation for an analyte’s concentration in one experiment.

In this study, LOD and LOQ were established with sample analysis of distilled water matrix spiked with studied pesticide compounds at three fortification levels: 0.004, 0.02 and 0.08 µg/L. For each spike level, an extraction was conducted with nine replications. Surrogate standard and sodium chlorine were added to the samples, pH was then also adjusted. The samples were extracted and analyzed with the procedure similar to real samples previously described. The results of method validation experiments including LOD, LOQ values and recovery in percentage were presented in Table 4.4.

Cypermethrin and group of conazole pesticides (difenoconazole, hexaconazole and propiconazole) were quantified at very high LOQ values compared to other studied compounds. In addition, average recovery of difenoconazole and hexaconazole were out of available range (70 - 120%). This may be a shortcoming in development of multi-residue analysis method for these compounds. It is needed to improve the

extraction method in the future. Measured concentrations of studied pesticide residues in multi-residue analysis processes below their LOQ values were marked as unquantifiable concentration values by this analysis method. However, the occurrence of these compounds was indicated as their concentration values were greater than their LOD values.

**Table 4.4: Summary on results of method validation parameters**

<b>Analyte</b>	<b>LOD</b> ( $\mu\text{g/L}$ )	<b>LOQ</b> ( $\mu\text{g/L}$ )	<b>Percent recovery</b> (Standard deviation, n=9)	<b>Spike level</b> ( $\mu\text{g/L}$ )
Buprofezin	0.009	0.030	111 (0.003)	0.02
Butachlor	0.001	0.003	79 (0.0003)	0.004
Cypermethrin	0.053	0.177	84 (0.018)	0.08
Difenoconazole	0.041	0.136	64 (0.014)	0.08
Endosulfan sulphate	0.001	0.003	72 (0.0003)	0.004
$\alpha$ -endosulfan	0.001	0.004	120 (0.0004)	0.004
$\beta$ -endosulfan	0.009	0.032	106 (0.003)	0.02
Fenobucarb	0.003	0.010	84 (0.001)	0.02
Fipronil	0.005	0.019	96 (0.002)	0.02
Hexaconazole	0.029	0.096	68 (0.01)	0.08
Isoprothiolane	0.004	0.014	112 (0.001)	0.02
Pretilachlor	0.002	0.005	93 (0.0005)	0.004
Profenofos	0.009	0.030	101 (0.003)	0.02
Propanil	0.004	0.012	82 (0.001)	0.02
Propiconazole	0.021	0.070	85 (0.007)	0.08

#### 4.3.9 Quality Assurance

During analytical processes of samples, blanks were analyzed together with each batch of samples. The concentrations of compounds detected in the blanks – if any – were subtracted from calculated sample concentrations for corresponding pesticide compounds, since they were referred to contamination from studied pesticides.

Real samples and blanks were spiked with a surrogate standard ( $\delta$ -HCH, 2.0  $\mu\text{g}$  in 100  $\mu\text{l}$  acetone). The recovery of the surrogate standard was used to monitor the extraction process. Surrogate recovery was evaluated by an internal standard (Fluoren-D10). This standard was added to concentrated extract before measurement with content of 1  $\mu\text{g}$  in 100  $\mu\text{L}$  toluene. The surrogate recovery was calculated based on the ratio of surrogate standard amount quantified from analysis progress and known surrogate standard amount used to spike into samples before extraction.



#### **4.3.10 Statistical Analysis Methods**

Recorded data were displayed in graphs which were plotted with the statistic software SigmaPlot. Statistical data comparisons were started with testing data distribution via Kolmogorov-Smirnov test. A P value of 0.05 for the test was selected as a threshold for concluding whether the data were normally distributed or not. If P value is greater than 0.05, the test indicated that data are normally distributed. Two statistical procedures were applied to compare differences of the recorded data set, consisting of “Compare Two Groups” and “Compare Many Groups” tests. The Compare Two Groups method is applied to test whether there is significant difference in mean or median values between two data groups. The Compare Many Groups method is used to test whether there are significant differences in mean or median values among three or more data groups. For the former comparison method, if the data set satisfies normal distribution conditions together with an equal variance, a t-test is applied. A P value of 0.05 was selected as threshold for concluding whether a significant difference between two data groups exists. If the computed P value is less than 0.05, a significant difference in mean values between the two data groups is confirmed. In case of non-normal distribution of the recorded data, a Mann Whitney Rank Sum test is applied for comparison. If computed P value of this test is less than 0.05, the two comparison groups are significantly different. For the Compare Many Groups method, if recorded data satisfies normal distribution with an equal variance, a One Way Anova test is applied. A P value of 0.05 was selected as a threshold indicating whether a significant difference in mean values among three data groups exists. If the computed P value is less than 0.05, differences of mean values among groups are statistically significant. If there is a non-normal distribution of the recorded data, a Kruskal-Wallis Anova on Ranks test is applied to compare median values of data groups. A P value was set as 0.05. If the P value computed from the test is less than 0.05, a statistically significant difference in median values among data groups is concluded (Toutenburg, 2002; Systat, 2008).

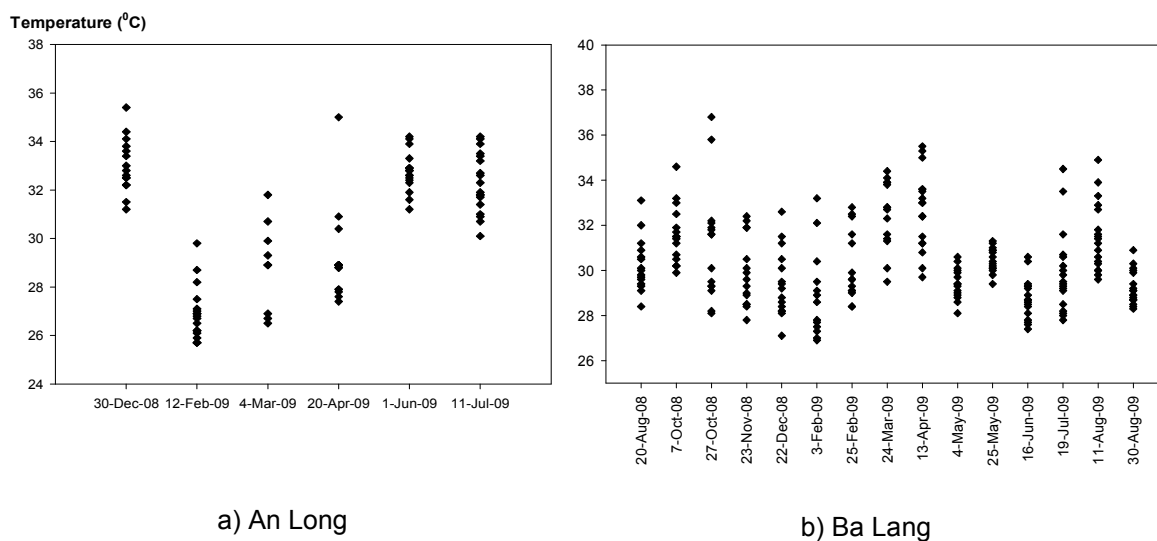
#### **4.4 Results and Discussion**

##### **4.4.1 Physicochemical Parameters and Their Influence on Pesticides**

###### **Water Temperature**

Water temperature measured at the sampling points as well as sampling events fluctuated during the monitoring period. Average temperatures were  $30.7 \pm 2.6$  and  $30.4 \pm 1.9$  °C at An Long and Ba Lang, respectively. Ranges of water temperature

were from 25.7 to 35.4 °C and from 26.9 to 36.8 °C at An Long and Ba Lang as showed in Figure 4.3.



**Figure 4.3: Water temperature of the samples collected at a) An Long and b) Ba Lang in sampling events**

In case of single sampling day, there were usually differences in water temperature among the sampling points. For instance on the sampling day in April 2009 at An Long, water temperature of An Long 2 canal and two points in irrigation canal was 35, 30.9 and 30.4 °C, respectively, while average temperature of other sampling points in rice fields was 28.5 °C. The variations of water temperature among sampling points in sampling events ranged from 3 to 5.3 °C at An Long and 2.5 to 8.7 °C at Ba Lang. The range of water temperature at the monoculture site was less than that at the mixture crop site. These variations may be affected by a few environmental factors such as weather conditions, water quantity in fields, cover of crops and flow of water. Crop covering strongly affected the water temperature in the fields. For examples, water temperature of the sampling in December 2008 (15 days after sowing (DAS) of rice) was higher than that of the sampling event in February 2009 (58 DAS) at the monoculture site. Whereas the period February and April is the hottest period in term of air temperature in the year. Water temperature in the ponds of the orchards was often lower and more stable than that of the rice fields. Water temperature of the irrigation canals was often more stable than that in the fields.

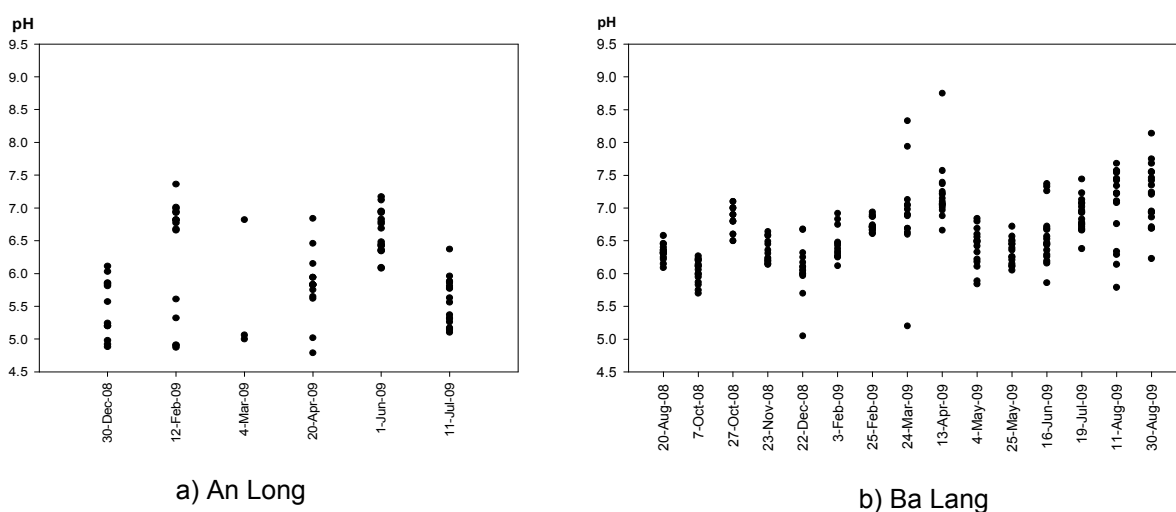
Temperature is an important parameter that governs hydrolytic degradation process of pesticides in aquatic environment. Observed temperature range might accelerate

hydrolytic degradation process of studied pesticides with exception of stable compounds. Hydrolysis half-lives of compounds were often reduced because all observed temperature values were high. Solubility of the compounds in water might also increase due to temperature enhancement. Getzin's research demonstrated that the half-life of chlorpyrifos declines from 20 to one day responding to water temperature changes from 5 to 45 °C (Gevao and Jones, 2002). It is referred that hydrolytic degradation rate of pesticides occurs in a large range of water temperature. When water temperature increases, pesticides molecules will obtain much more energy. They move quickly in water phase, and reaction with solutes is enhanced. Therefore, the rate of hydrolytic degradation process occurs rapidly. In addition, higher temperature make increase the volatilization rate of volatile pesticides. When temperature increases, vapor pressure will be enhanced. Therefore the volatilization rate of water and volatile compounds are increased. Temperature also affects the solubility of pesticides in water or other solvents. Normally, water solubility of pesticides increases when water temperature rise. However, the solubility of several compounds is inversely proportional to temperature (Freed *et al.*, 1977). For example, solubility of herbicide thiocarbamate decreases with an increase in water temperature. This is explained by the hydrogen bond formation between water and this chemical. Water temperature strong affects microbial degradation in aquatic environment. The higher water temperature is, the quicker microbial degradation (Linde, 1994). Furthermore, several pesticides will be more toxic to aquatic animals when water temperature increase. Cong's study (2008) on the effect of organophosphate insecticide diazinon in water in fields to muscle and brain of climbing perch (*Anabas testudineus*) showed that increasing of water temperature lead to more enzyme cholinesterase inhibition of brain and muscle samples.

## pH

Monitoring results revealed that pH of collected water ranged from slightly acid to neutral. As shown in Figure 4.4, average value of water pH at An Long was  $5.9 \pm 0.9$  with the minimum of 4.5 and the maximum of 7.8. At Ba Lang, average pH of water samples was  $6.7 \pm 0.5$ , ranging from the minimum of 5.5 to the maximum of 8.8. In general, water pH at An Long was lower than that at Ba Lang. This may be due to a greater presence of acid sulfate soil of An Long as opposed to Ba Lang. On the other hand, most sampling events at An Long were conducted near rainfall events. Therefore, water in fields and canals was influenced by rainwater. In addition, there was rather variety on water pH among the fields, particularly in the late stages of the

crop. This may be due to difference in farming patterns as well as biological characteristics of plants or fertilizer application regime. For example, difference in water pH of the samples collected in vegetable and rice fields were revealed at Ba Lang on 24 March 2009. For samples collected in the ponds of the orchard at Ba Lang, fluctuation range of pH was less than that of samples collected in the fields. Furthermore, water pH was also much affected by rainwater. For example, pH of water of samples collected on 7 October 2008 was generally lower than pH of samples collected in other sampling events at Ba Lang. It is because of a heavy rain on 6 October - one day before the sampling, and rainwater reduced the pH of water taken in fields and canal on 7 October. In general, observed water pH has little or no direct effect on the fate of studied pesticides in water in the fields and the canal because they ranged from slightly acid to neutral. The studied compounds such as cypermethrin, fenobucarb, profenofos and propanil are relatively stable under water pH conditions at the two study sites, as reported in Table 1 of Annex 4.



**Figure 4.4: Fluctuation of pH measured at sampling points at a) An Long and b) Ba Lang in sampling events**

Measurement of pH is an important test for defining physical and chemical properties of water environment. This parameter influences the fate of substances in water phase. In detail, pH affects ionization, volatilization process and toxicity to aquatic life for dissolved substances (Weiner, 2000). When water pH increases, water solubility of compounds is influenced, particularly with chemicals contained acidity groups. The polarity of these chemicals changes with different pH values due to their acid groups (Linde, 1994). Several hydrolysis processes rapidly occur in slightly basic or acidic environment. pH also affects weak acid or base compounds. For example, herbicide

2,4\_D occurs in nonionic form at  $\text{pH} < 6$  and in anionic form as  $\text{pH} > 6$ . In addition, acidity or alkalinity of a solution influences persistence and solubility of pesticides when they are introduced into that solution. For instance, solubility of herbicide triazine increases when water pH decreases (Freed *et al.*, 1977). In surface water with pH ranging from 5 to 9, the sorption of nonionic organic compounds is not influenced much by pH (Nowell *et al.*, 1999).

### **Dissolved Oxygen and Conductivity**

Two other physicochemical parameters, dissolved oxygen and electrical conductivity, were also measured during the monitoring phase. On average, dissolved oxygen was  $3.3 \pm 1.7$  and  $3.3 \pm 1.5$  mg/L at An Long and Ba Lang, respectively. In general, the average dissolved oxygen content was low in collected samples at the two study sites. The dissolved oxygen much fluctuated in the fields compared to that in the ponds and irrigation canals. This is possibly explained by the fact that dissolved oxygen content in water in the fields is much dependent upon biological characteristic of the plants, diffusion capacity of oxygen into water in the fields from the atmosphere and activities of aquatic organisms. In addition, the high water temperature in situ reduced dissolved oxygen content in water. Dissolved oxygen plays an important role for the fate of pesticide in the water environment. Dissolved oxygen is consumed by organisms to degrade (oxidize) organic compounds like pesticides in water. Therefore, it influences much metabolism of pesticides by higher organism like fish or other microbes. However, fish are only able to metabolize pesticides but they are not able to mineralize them. Microbial metabolism process is carried out by microbes such as bacteria, protozoa and fungi, and the final step of the process is changing pesticides into the basic components of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and mineral salts (Linde, 1994). Thus, when dissolved oxygen content in water is low the population of aerobic organisms is less abundant and so microbial metabolism processes is slow.

For electrical conductivity, the average value measured at An Long and Ba Lang was  $209.5 \pm 77$  and  $165.2 \pm 39$   $\mu\text{S}/\text{cm}$ , respectively. The variance of electrical conductivity was higher at An Long than at Ba Lang may be due to several particular events of soil preparation for rice sowing in April and flooding water in the fields in August at An Long. At the Ba Lang site, electrical conductivity was high in several sampling events due to heavy rain carrying dissolved ions together with runoff flow into the fields and

canals. Conductivity is used to know total inorganic salt content or the total amount of dissolved ions in water samples. It is affected by land runoff containing certain dissolved minerals. The occurrence of dissolved ions, especially six major ions including calcium, magnesium, sodium, sulfate, chloride and bicarbonate adversely affects the activities of some pesticides. This is especially true of salt-formulated herbicides such as glyphosate and 2,4\_D. If the amount of salts in water increases, the amount of adsorbed cationic chemicals generally decreases due to the competition for bonding sites on the soil (Linde, 1994). Occurrence of calcium and magnesium in water can reduce the effectiveness of glyphosate. However, if the electrical conductivity in water is less than 500  $\mu\text{S}/\text{cm}$ , it is unlikely that the pesticide effectiveness is affected (Litchfield, 2003).

In summary, water temperature and pH affect the persistence of pesticides introduced into aquatic environment. Degradation rate of pesticides are influenced by water temperature change depending on the type of chemicals. A laboratory experiment in dark incubator conditions showed that when water temperature rises, carbaryl and malathion were rapidly degraded, with half-lives of 2 - 3 weeks at 10  $^{\circ}\text{C}$ , and of 1 - 5 days at 25  $^{\circ}\text{C}$ . In contrast, other pesticides like atrazine and simazine were stable under temperature change. On the other hand, degradation rate of diazinon was quite variable for temperature change, with half-life of 9 days to no observed degradation (Starner *et al.*, 1999). Water pH affects not only the solubility of pesticides but also the fate of pesticides. When pH of water is greater than 7, it creates alkaline conditions causing chemical breakdown of some pesticides. Organophosphate and carbamate insecticides are more susceptible than organochlorine insecticides. For example, half-life of carbaryl at pH 7 is 27 days and at pH 8 is 2 - 3 days. Half-life of diazinon at pH 7 is 70 days and at pH 9 is 29 days. Degradation rate can be more rapidly in water pH range of 8 to 9. When pH of water increases one level, degradation rate can happen approximately 10 times quicker (Deer and Beard, 2001). Pesticide losses due to alkaline hydrolysis process governed by the degree of water alkalinity, the susceptibility of pesticides and the time of pesticide in contact with water.

#### **4.4.2 Studied Pesticides and Their Occurrence in Surface Water**

According to interview results with the local farmers previously mentioned in chapter 3, more than 100 types of different pesticide trade names corresponding to 50 various active ingredients which belong to more than 20 chemical groups, as shown in Annex

2, were recorded at the two study sites. Fifteen studied pesticides were measured in the collected water samples and their concentrations detected in the multi-residue analysis were summarized in Table 4.5.

**Table 4.5: Summary on residue monitoring results of the studied pesticides**

	Number of samples analyzed	Detection frequency (%)	Max. concentration ( $\mu\text{g/L}$ )	Median concentration ( $\mu\text{g/L}$ )
<b>At the An Long site</b>	109			
Buprofezin		61.5	11.21	0.18
Butachlor		27.5	1.20	0.05
Cypermethrin		10.1	4.89	1.26
Difenoconazole		42.2	2.59	0.45
$\alpha$ -Endosulfan		0.0	n.d	n.d
$\beta$ -Endosulfan		0.0	n.d	n.d
Endosulfan sulfate		17.4	0.07	0.01
Fenobucarb		90.8	5.00	0.11
Fipronil		57.3	5.68	0.05
Hexaconazole		94.5	3.00	0.16
Isoprothiolane		100	11.24	2.72
Profenofos		0.9	0.01	0.01
Pretilachlor		68.9	1.05	0.06
Propanil		2.8	0.02	0.02
Propiconazole		64.2	0.43	0.11
<b>At the Ba Lang site</b>	233			
Buprofezin		0.4	0.11	0.11
Butachlor		1.7	0.02	0.02
Cypermethrin		0.0	n.d	n.d
Difenoconazole		3.0	0.46	0.25
$\alpha$ -Endosulfan		0.0	n.d	n.d
$\beta$ -Endosulfan		0.0	n.d	n.d
Endosulfan sulfate		2.6	0.02	0.01
Fenobucarb		85.4	1.43	0.04
Fipronil		22.3	0.04	0.01
Hexaconazole		24.0	0.41	0.04
Isoprothiolane		96.3	12.86	0.15
Profenofos		4.3	0.35	0.02
Pretilachlor		31.4	0.21	0.02
Propanil		1.3	0.04	0.02
Propiconazole		18.0	0.78	0.11

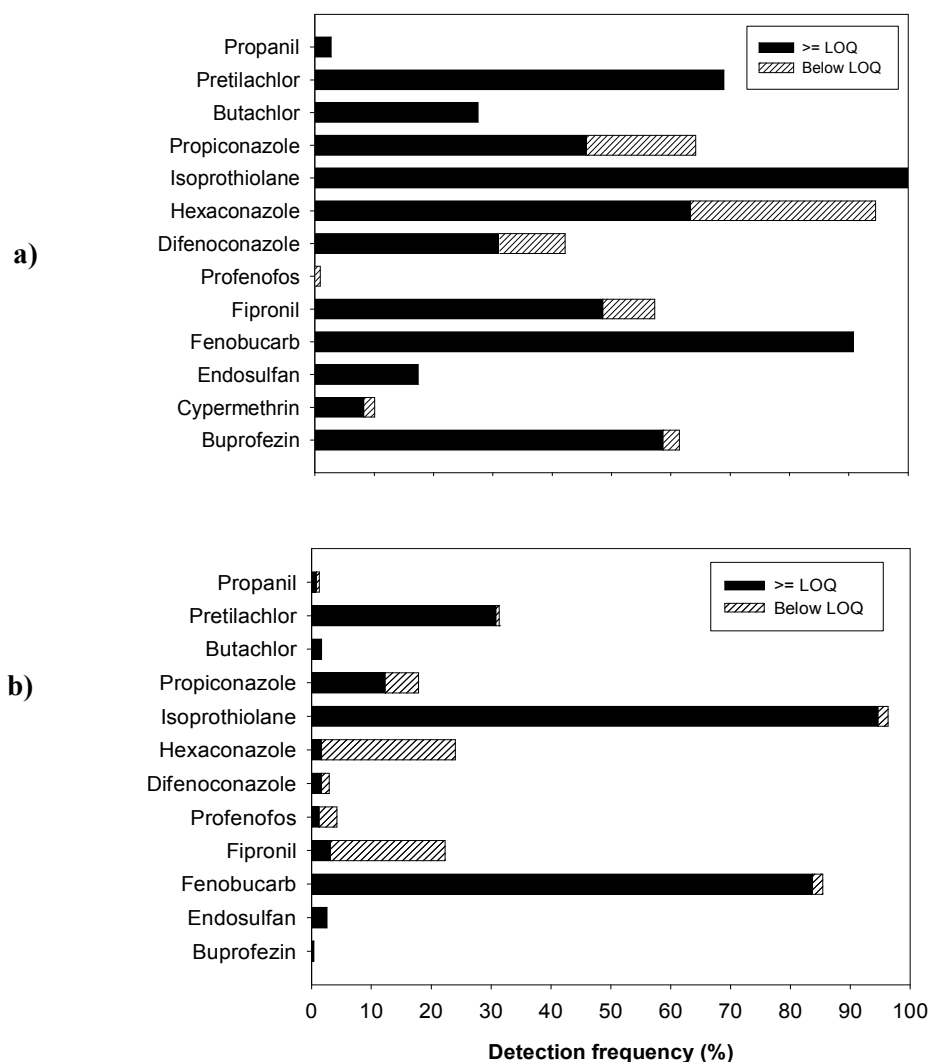
*n.d: no detection*

At the An Long study site, 13 studied compounds were detected during monitoring campaign except  $\alpha$ - and  $\beta$ -endosulfan. The maximum number of compounds detected in one sample is ten (2 out of 109 samples) of the 15 monitored pesticides.

Up to 90% of the samples had co-occurrence of three chemicals. As shown in Figure 4.5 a), profenofos was detected in 0.9% of the samples but all its concentrations were lower than the limit of quantification (LOQ). Propanil, pretilachlor, butachlor, isoprothiolane, fenobucarb and endosulfan were detected with corresponding frequencies of 2.8, 68.9, 27.5, 100.0, 90.8 and 17.4% respectively, and these values represented their quantification frequencies. Amongst detected compounds, isoprothiolane was quantified in all monitored samples, followed by fenobucarb. Three fungicide compounds: hexaconazole, propiconazole and difenoconazole were detected with frequencies of 94.5, 64.2 and 42.2%, respectively. However, their quantification frequencies were in succession of 63.3, 45.9 and 31.2%, respectively. Three other insecticides namely buprofezin, fipronil and cypermethrin were detected with frequencies of 61.5, 57.3 and 10.1%, and their quantification frequencies were 58.7, 48.5 and 8.3%, respectively.

At the Ba Lang site, the number of compounds as well as their detection frequencies was lower than that at An Long, shown in Figure 4.5 b). Twelve studied pesticides were detected during monitoring campaigns, excluding cypermethrin,  $\alpha$ - and  $\beta$ -endosulfan. The maximum number of compounds detected in one sample was eight (n=1 out of 233 samples). Half of collected samples had a co-occurrence of three compounds. Isoprothilane was detected with the highest frequency (96.3%), followed by fenobucarb (85.4%). Their detection frequencies were higher compared to quantification frequencies with values of 94.7 and 83.7% for isoprothiolane and fenobucarb respectively. Endosulfan, butachlor, and buprofezin were detected with low frequencies, and their detection frequencies were also the quantification frequencies with the values of 2.6, 1.7 and 0.4%, respectively. Hexaconazole and fipronil were detected with relative high frequencies (24 and 22.3%), but their quantification frequencies were much lower (1.7 and 3.2%). Pretilachlor was the herbicide compound which was detected with the frequency of 31.4%, and its quantification frequency was 30.9%. Propiconazole, profenofos, difenoconazole and propanil were detected with frequencies of 17.9, 4.3, 3.0 and 1.3%, respectively. Their presence was quantified with frequencies of 12.3, 1.3, 1.7 and 0.9%, respectively.





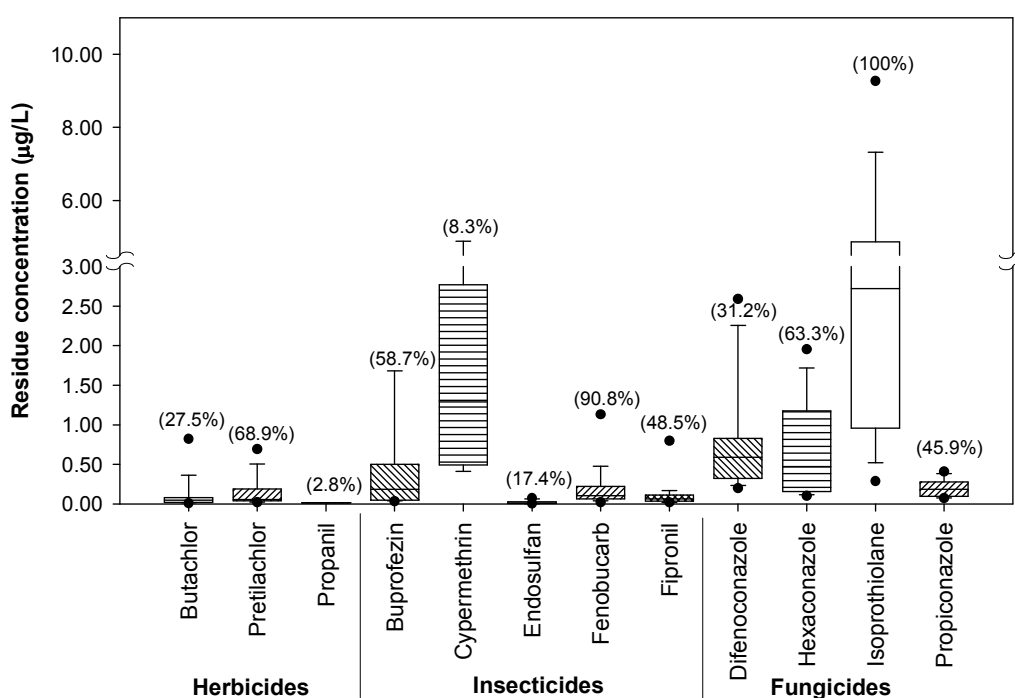
**Figure 4.5: Detection frequency of the studied pesticides below, above and equal to limit of quantification (LOQ) at a) An Long and b) Ba Lang**

The number of chemicals as well as their detection frequency at An Long was more than that at Ba Lang. According to the interview results in chapter 3, insecticide cypermethrin was mostly used at the two study sites, but its detection was lower compared to other insecticides or even not detected at Ba Lang. This may be explained by the fact that this compound has high  $k_{oc}$  (85,572 mg/L) and its water solubility is very low ( $S_w = 0.009$  mg/L, at 20°C). According to Bläsing (2010) residue concentration of cypermethrin in the soil of fields reached the highest value among studied compounds, with the maximum value of 41  $\mu\text{g}/\text{kg}$  in two sampling events of March 2008 and July 2009. Although the application frequency of isoprothiolane was

less than propiconazole, which is most frequently used among fungicides in the two study sites, the former's detection frequency was highest (100% in An Long and 96.3% in Ba Lang). It is possibly due to the fact that its usage amount was higher than other compounds, and it is a stable chemical in the water environment.

#### 4.4.3 Residue Concentrations of Quantified Compounds

There was a large variability in the concentration of the monitored pesticide residues. At An Long, twelve compounds were quantified and their residue concentrations are shown in Figure 4.6. Isoprothiolane was quantified with the highest concentration, ranging from 0.02 to 11.24  $\mu\text{g/L}$ , and its average concentration was 3.34  $\mu\text{g/L}$ . According to the interview results, the application frequency of two other fungicides (difenoconazole and propiconazole) was more than isoprothiolane, but their concentrations were less than this compound, with average concentration of 0.82 and 0.20  $\mu\text{g/L}$ , respectively. The other fungicide, hexaconazole, was quantified with average concentration of 0.72  $\mu\text{g/L}$ .



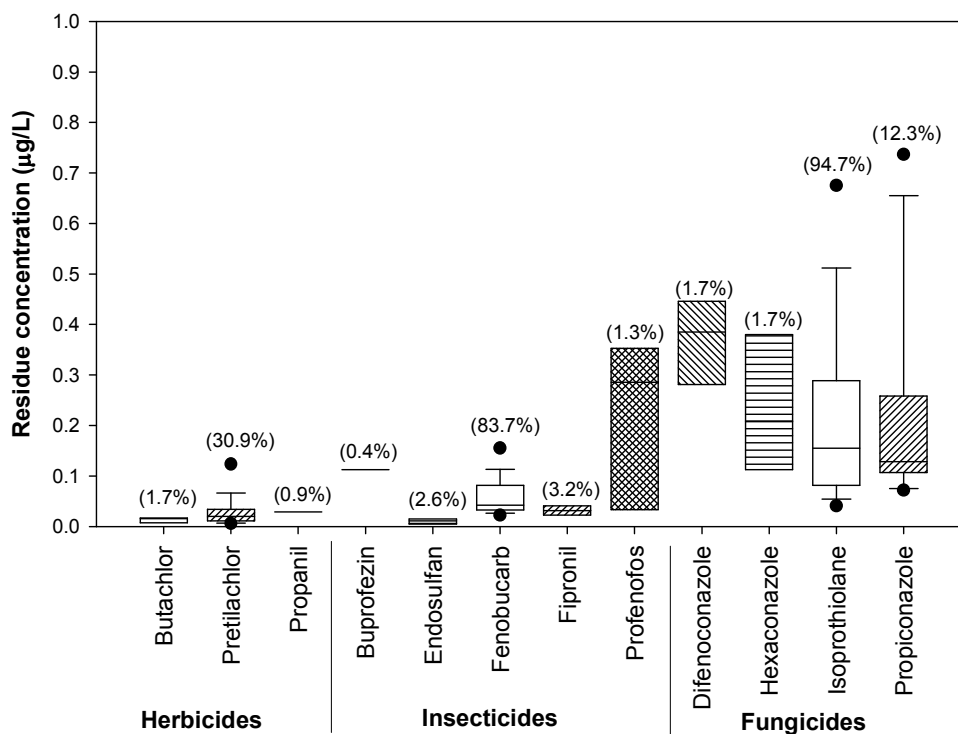
**Figure 4.6: Concentrations of pesticide residues at An Long. The numbers (in brackets above the box plots) show the quantification frequency. The box-plots show five values (10<sup>th</sup>, 25<sup>th</sup>, median, 75<sup>th</sup>, 90<sup>th</sup>), and two dots present for the 5<sup>th</sup> and 95<sup>th</sup> percentile**

Of five detected insecticides, although endosulfan was already strictly prohibited for agricultural use since 2005, it could be detected and average concentration of 0.02  $\mu\text{g/L}$ . Fenobucarb was the most frequently detected compound with average concentration of 0.25  $\mu\text{g/L}$ . Next insecticide was buprofezin with average concentration of 1.02  $\mu\text{g/L}$ . Fipronil had an average concentration of 0.22  $\mu\text{g/L}$ . Cypermethrin was the least detected compound although it was the most frequently used insecticide; its residue was quantified with highest concentration (1.77  $\mu\text{g/L}$ ). Pretilachlor, a commonly used herbicide, was frequently detected with concentrations ranging from 0.01 to 1.05  $\mu\text{g/L}$  and with an average concentration of 0.17  $\mu\text{g/L}$ . Two other herbicides, butachlor and propanil, had average concentrations of 0.12 and 0.02  $\mu\text{g/L}$ , respectively.

At Ba Lang, twelve of the studied compounds were quantified excluding cypermethrin,  $\alpha$ - and  $\beta$ -endosulfan. The overall concentrations of detected compounds were much lower than those detected at An Long study site as presented in Figure 4.7. Isoprothiolane was also quantified with the highest frequency, and its concentration ranged from 0.02 to 12.86  $\mu\text{g/L}$  with an average concentration of 0.30  $\mu\text{g/L}$ . Propiconazole was detected at concentration ranging from 0.07 to 0.78  $\mu\text{g/L}$ . The two remaining fungicides, difenoconazole and hexaconazole, were respectively quantified with average concentrations of 0.37 and 0.23  $\mu\text{g/L}$ . Fenobucarb was quantified with the highest frequency among insecticide compounds with an average concentration of 0.07  $\mu\text{g/L}$ , and its concentration ranged between 0.02 and 1.43  $\mu\text{g/L}$ . Endosulfan was also quantified with an average concentration of 0.01  $\mu\text{g/L}$ . Profenofos was quantified at this study site with low frequency and an average concentration of 0.22  $\mu\text{g/L}$ . Then was buprofezin and fipronil with average concentrations of 0.11 and 0.03  $\mu\text{g/L}$ . Herbicide pretilachlor was also a typical chemical, and its residue was quantified with an average concentration 0.03  $\mu\text{g/L}$ . Two other herbicides, butachlor and propanil were quantified with average concentrations of 0.01 and 0.03  $\mu\text{g/L}$ , respectively.

In summary, the majority of average concentrations of detected compounds were several times higher at An Long than at Ba Lang. For example, the average concentrations of isoprothiolane and fenobucarb quantified at An Long were respectively 11 and 4 times higher than that at Ba Lang. This finding follows the same trend as observed in the status of pesticide use data collected at the two study sites.

In addition, cypermethrin was also applied with high frequency (31.6%) compared to other pesticides in Ba Lang. However, its residue was not detected during sampling campaign. This is due to low dose in use of this pesticide at Ba Lang than that at An Long and its physicochemical properties as well.



**Figure 4.7: Concentrations of pesticide residues at Ba Lang. The numbers (in brackets above the box plots) show the quantification frequency. The box-plots show five values (10<sup>th</sup>, 25<sup>th</sup>, median, 75<sup>th</sup>, 90<sup>th</sup>), and two dots present for the 5<sup>th</sup> and 95<sup>th</sup> percentile**

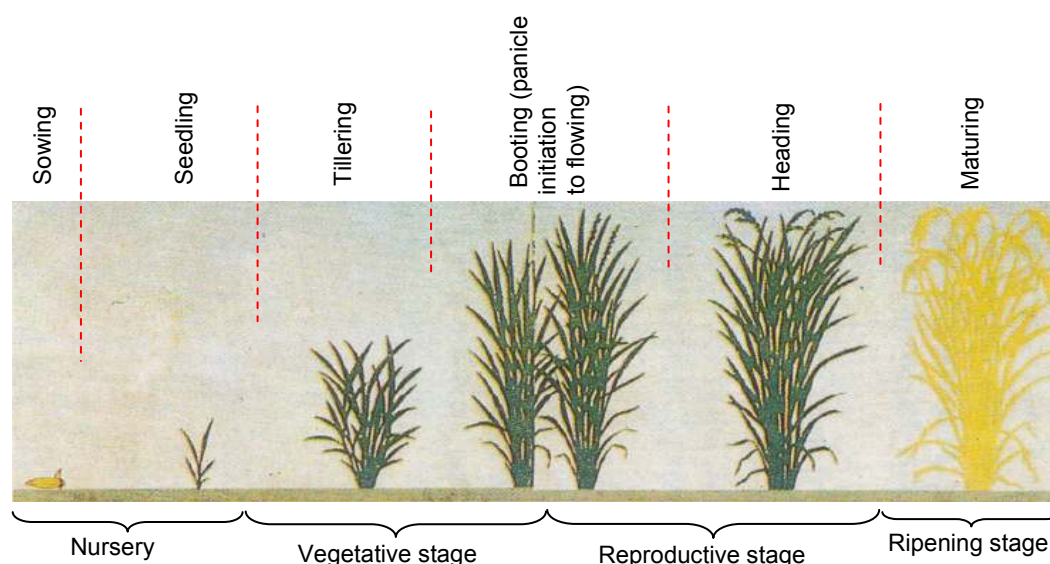
Most of the studied compounds are not covered in the national technical regulation of Vietnam for surface water quality, with the exception of endosulfan (QCVN 08:2008/BTNMT, 2008). The results of the monitoring showed that although it was seldom detected, average residue concentration of endosulfan slightly exceeded the threshold value B1 of Vietnam standard<sup>1</sup>. Additionally, in term of consideration as a source for drinking water, majority of the water samples collected at An Long (92%) already exceeded the EC drinking water guideline parameter for individual pesticide level (0.1 µg/L) (European Commission, 1998). This was 59% for the water samples

<sup>1</sup> The threshold value B1 is a grade of water quality at which water is appropriate to supply for irrigation and other similar purposes, or water supplying for river conveyance.

collected at Ba Lang. Considering the EC drinking water guideline parameter for multiple compounds (0.5 µg/L), 89 and 12% of the water samples exceeded that value at An Long and Ba Lang, respectively.

#### 4.4.4 Pesticide Residues at Each Crop Stage

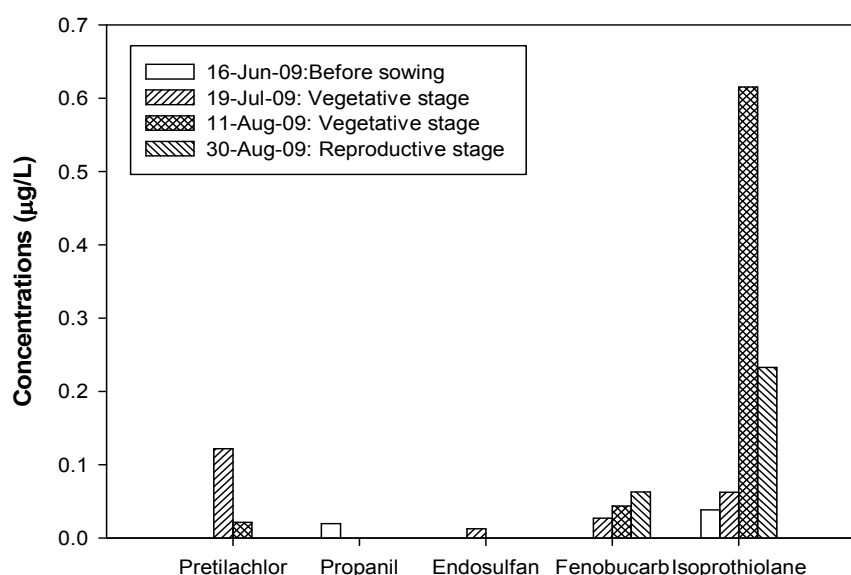
Herbicides and insecticides are usually used in the early nursery stage, and insecticides and fungicides are applied in the remaining (vegetative, reproductive and ripening) stages of paddy rice as illustrated in Figure 4.8. On the other hand, insecticides and fungicides are also applied to the fields of vegetables and fruit trees. This was revealed through information on pesticide application at the fields recorded during monitoring phase.



**Figure 4.8: The development stages of paddy rice**

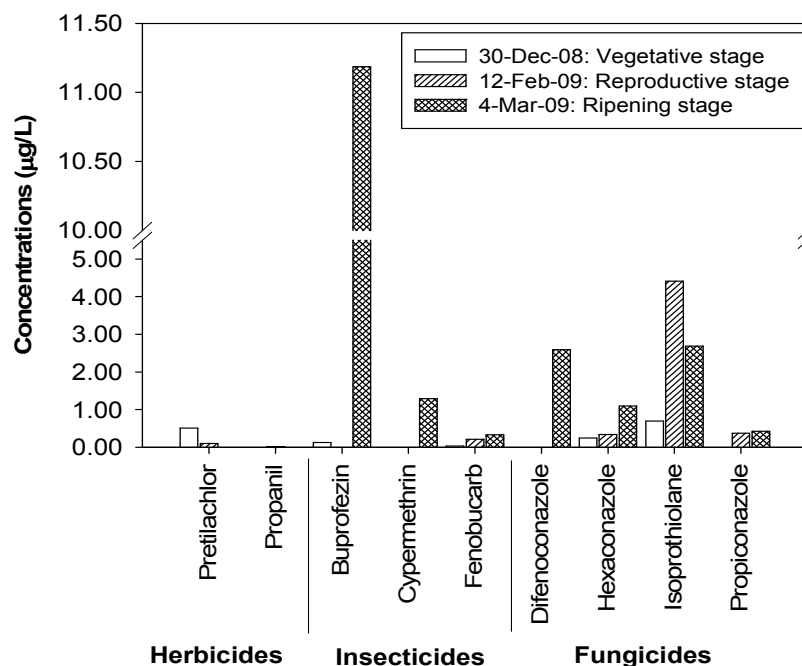
At Ba Lang, concentration residues of detected compounds in water in the rice fields, is illustrated in Figure 4.9, and shows that there was a relation between the types of used pesticides and the stages of paddy rice crop. Four sampling events were conducted between soil preparation time for sowing and 62 days after sowing of paddy rice in the field BL9 in the 2009 summer - autumn rice crop. The first sampling event (16-June) was conducted 13 days before rice was sown. Propanil and isoprothiolane were detected in this event. This may be due to the fact that these two chemicals were applied in other fields in the former spring - summer crop. They were introduced into water in the field through agricultural runoff. In the second sampling

event (19-July), when rice was 20 days of age, herbicide pretilachlor was detected with a concentration of 0.12  $\mu\text{g/L}$ . This compound had been sprayed two days after sowing with dose of 300 g a.i. per hectare. Fenobucarb and isoprothiolane were detected with concentrations of 0.03 and 0.06  $\mu\text{g/L}$  in the sample, although they had been not applied in the field. It is possible that water was polluted with residue of these compounds that were applied in the adjacent fields. Endosulfan was not use in the fields around this period, but its residue was detected with a concentration of 0.01  $\mu\text{g/L}$  in this sampling event. This compound may be introduced from soil due to soil preparation for sowing or impact of heavy rain. The third sampling event (11-August) continuously detected pretilachlor as it is stable in water. Fenobucarb was detected with concentration (0.04  $\mu\text{g/L}$ ) higher than that in the second sampling event, although there was no application reported of this chemical in the field. It may be the gate of this field was opened so that the residue of this compound was introduced in the field. The same reason is used to explain for higher concentration of isoprothiolane in this sampling event. In the fourth sampling (30-August), fenobucarb were detected with the concentration of 0.06  $\mu\text{g/L}$ . This compound was applied with dose of 240 g a.i. per hectare in the field 17 days before the sampling. Isoprothiolane was not applied on the field, but its residue was still detected. However, its concentration was lower than that the third sampling event. It is possibly this compound was gradually degrading. Moreover, the gate of this field was closed in this sampling time.



**Figure 4.9: Pesticide residue concentrations in water at the various stages of rice in the field BL 9 at Ba Lang**

At An Long, relation on concentrations of used pesticides and the stages of rice crop is representatively evidenced through the field AT10 during the 2008 - 2009 winter - spring rice crop. Three sampling events were carried out with the monitoring results shown in Figure 4.10. Herbicides occurred in the initial stage, and insecticides and fungicides mostly appeared at other stages towards the end of cropping season. This coincided with the results of pesticide application recorded in the field during cropping season.



**Figure 4.10: Pesticide residue concentrations in water at the various stages of crop in the rice field AT10 at An Long**

In the first sampling event (30-December), 19 days after sowing, herbicide pretilachlor was detected with a concentration of 0.51  $\mu\text{g/L}$ , although it was not applied in this field. This is explained by the fact that the gate of the field was opened, and the compound was introduced from adjacent fields. While herbicide butachlor was applied with dose of 360 g a.i. per hectare in this field, its residue was not detected. It is possibly because its half-life is rather short (0.5 to 5 days) in aquatic environment (Chen and Chen, 1979), and the extracted water volume is not large enough (370 mL) to detect its residue in the sample due to clogging in extraction process. Residues of other compounds, buprofezin, hexaconazole and isoprothiolane, were detected with the concentrations of 0.13, 0.25 and 0.70  $\mu\text{g/L}$ , although their application was not reported in the whole area since sowing day. They could have been applied in the former cropping season and they were introduced into water during soil preparation

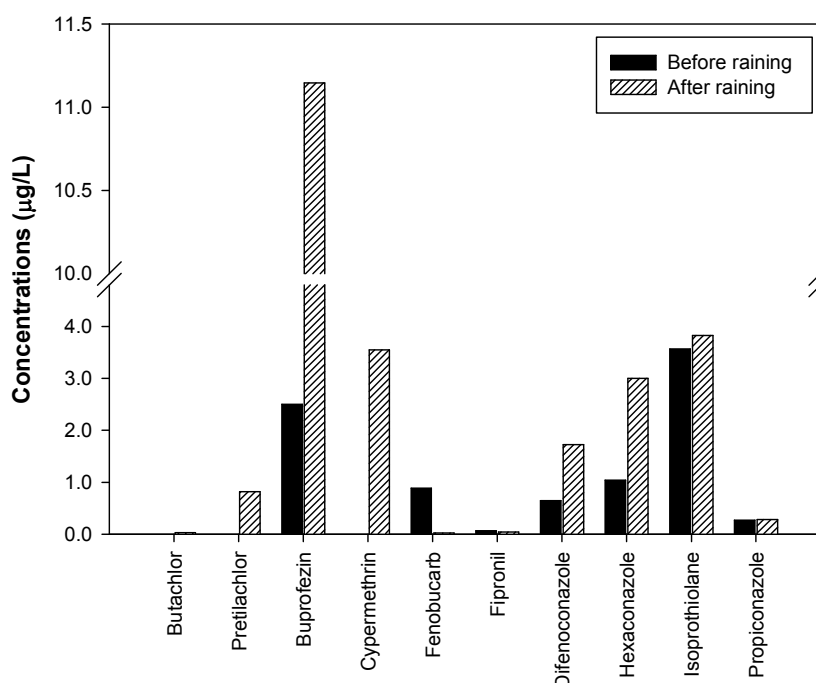
process. In the second sampling event (12-February), pretilachlor was again detected and the concentration ( $0.10 \mu\text{g/L}$ ) was lower than that in the first sampling event. This compound was gradually degrading after application in the early stage of the cropping season. Insecticide fenobucarb and fungicides (hexaconazole, isoprothiolane and propiconazole) were detected in higher the concentrations than those in the first sampling event, although their application was not reported in the field. All these compounds presented in the field may be due to dispersion from adjacent fields. The third sampling event (4-March) was conducted when paddy rice was 83 days of age (36 days before harvest). Most of studied insecticides and fungicides were detected in this sampling. Buprofezin was applied in the field 23 days before this sampling with dose of 307 g a.i. per hectare. Its residue was detected with very high concentration of  $11.19 \mu\text{g/L}$ . The occurrence of hydrophobic compound cypermethrin with high concentration ( $1.29 \mu\text{g/L}$ ) because it was introduced into water from soil and rice stems due to influence of rainfall happened in the night before sampling. Fungicide hexaconazole was detected with highest concentration ( $1.09 \mu\text{g/L}$ ) among three sampling events. It was applied in the field with dose of 62 g a.i. per hectare.

Above findings lead a conclusion that the occurrence of pesticide residues at one field at each stage of the crop could be emanated from different sources. First, the occurrence of residues closely related to pesticide application events in the field when there were no any other sources. Second, residues of several pesticides could be detected, but they were not applied in the field. These pesticides were applied in adjacent fields and were introduced into the field due to agricultural runoff or entering water from the opened gate. Third, residues of pesticides could be detected in the field by desorbing due to soil preparation or washing from crop due to heavy rainfall. Finally, detection of pesticide residues at a crop stage without their application could be able to depend on their physiochemical properties. A stable pesticide could be detected in a stage of crop although its application happened before that period. Such, residue of a pesticide detected in a stage of crop could not reflected application of that pesticide at that stage. Also, pesticide application investigated at a stage of crop in the field could not provide enough information on pesticide residues at that field. Pesticide residue occurred in a field at a stage of crop could be originated by multiple sources and much influenced by complex hydraulic system.



#### 4.4.5 Occurrence of Peak Concentration of Residues in Fields after Rain

The relation between residue concentration peak occurrence of monitored compounds and rainfall was investigated at field AT8 in the 2008-2009 winter - spring rice crop. One sampling was conducted before and another sampling after a significant rainfall event at the same place inside the field. Although rainfall was not measured, the rainwater depth in the field was approximately 12 cm after rain. The sampling event before rain was conducted two hours approximately after an application of cypermethrin. The second sampling was carried out after a one hour prolonging significant rainfall event. The concentrations of detected compounds are shown in Figure 4.11.



**Figure 4.11: Peaks of detected residue concentrations in the sample before and after a significant rainfall event in the field AT8**

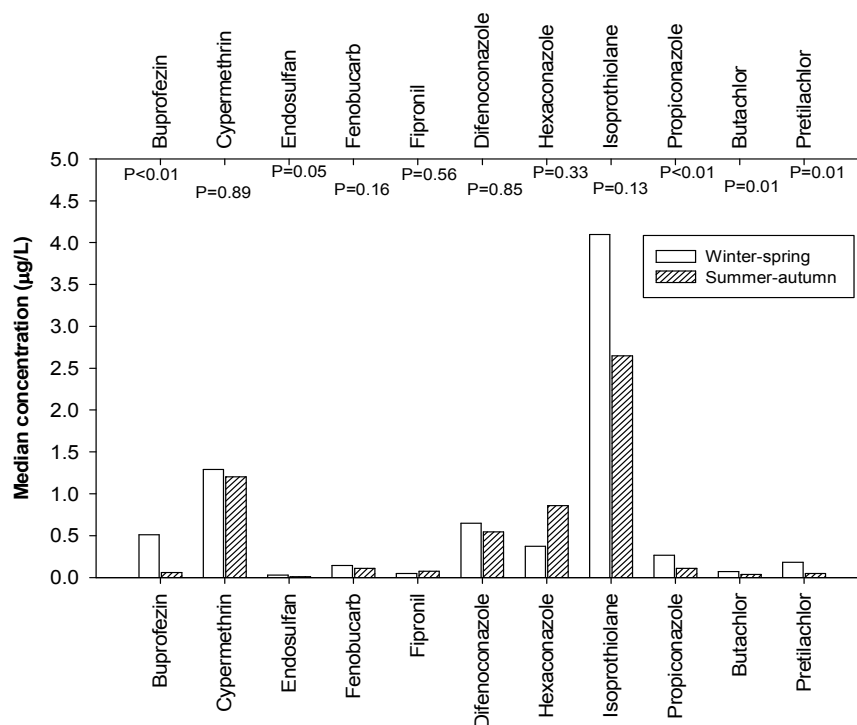
Most of the residue concentrations measured after rain were higher than those in the sample taken before rain. Pretilachlor and cypermethrin were detected with concentration of 0.82 and 3.55  $\mu\text{g/L}$ , respectively, although they were not detected in sampling before rain. In case of cypermethrin, its concentration was not detected in the sampling after two hours of application at a dose of 70 g a.i. per hectare. There was no use of pretilachlor at this application event. It was also no application of butachlor, buprofezin, fenobucarb, difenoconazole, hexaconazole, isoprothiolane and propiconazole in the field at this application. However, the concentration of the

compounds: buprofezin, difenoconazole, hexaconazole, isoprothiolane and propiconazole (11.15, 1.73, 3.00, 3.83 and 0.29  $\mu\text{g/L}$ ) in the sample taken after rain were higher than those (2.50, 0.65, 1.04, 3.57 and 0.27  $\mu\text{g/L}$ ) in the sample taken before rain, respectively. Normally, a compound is detected in water in fields with high peak just after application (Watanabe *et al.*, 2007b). In addition, a significant rainfall event just happened after application can carry a chemical amount on paddy rice into water (Ba and Triet, 2005; Watanabe *et al.*, 2007b). Compounds with a high octanol-water partition coefficient adsorbed to the surface of soil are desorbed during a certain period after application (Nakano *et al.*, 2004). Moreover, residue of several above compounds could be introduced into the field from adjacent fields due to agricultural runoff after heavy rain. Meanwhile, concentration peak of fenobucarb was lower in the sample taken after rain (0.02  $\mu\text{g/L}$ ) than in the sample taken before rain (0.89  $\mu\text{g/L}$ ). This is possibly due to water solubility of this chemical being high, and the compound was diluted by rainwater from the significant rainfall event.

#### 4.4.6 Concentrations of Pesticides During the Main Cropping Seasons

At An Long, pesticide residues quantified in the winter - spring and summer - autumn rice crops were compared based on their median concentrations as shown in Figure 4.12. Median concentrations of 11 out of 12 quantified pesticides in the two cropping seasons were compared, with the exception of propanil due to lack of data. There was a statistically significant difference between the two cropping seasons for the compounds: buprofezin, propiconazole, butachlor and pretilachlor. There was no significant difference on median concentrations of the remaining detected pesticides. The median concentration of buprofezin in the winter - spring (0.51  $\mu\text{g/L}$ ) was higher than that in the summer - autumn crop (0.06  $\mu\text{g/L}$ ). It was confirmed by the survey results that use frequency of this compound and number of fields applied with this chemical in the winter - spring rice crop was more than those in the summer - autumn rice crop. For two herbicides, butachlor and pretilachlor, their median concentrations in the winter - spring rice crop (0.18 and 0.07  $\mu\text{g/L}$ ) were higher than those in the summer - autumn rice crop (0.05 and 0.04  $\mu\text{g/L}$ ), respectively, due to partly their hydrolysis half-lives. Butachlor is fast degraded, and pretilachlor is relatively stable for hydrolysis. All sampling events in the winter - spring crop were carried out in the periods at least 15 days after application of these two chemicals. Meanwhile, the first sampling event in the summer - autumn crop was conducted at several fields one day before application event of two these chemicals. The second sampling event was

conducted 39 days after application event. Residues of these two chemicals were low detected in water in the fields. For fungicide propiconazole, its median concentration detected in the winter - spring rice crop (0.27  $\mu\text{g/L}$ ) was higher than that in the summer - autumn rice crop (0.11  $\mu\text{g/L}$ ). This chemical is soluble in water (150 mg/L). This fungicide was applied approximately the same rate in both cropping seasons. Water in the fields in the winter - spring rice crop was less affected by rainfall than in the summer - autumn rice crop.



**Figure 4.12: Comparison of median concentrations of the compounds quantified in the winter - spring and summer - autumn rice crop at An Long. P-values indicate Mann Whitney Rank Sum test results. The differences of median values are compared at significance level of 5%**

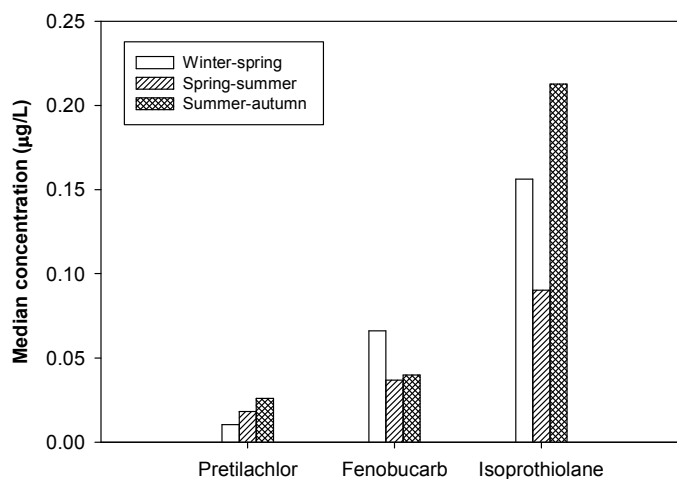
Although there was no statistically significant difference in the median concentrations of the remaining compounds, most median concentrations of these detected compounds in the winter - spring rice crop were generally higher than those in the summer - autumn rice crop. This is different in tendency compared with the average total amount of compounds used between two cropping seasons. According to the interview results, the average total amount of pesticides in the winter - spring rice crop was less than that in the summer - autumn rice crop. This may be due to the fact that all samples collected in the summer - autumn crop were diluted by rainwater because two out of three sampling events were carried out after rainfall events. Notably,

rainwater can wash pesticides from rice plant or can cause desorption of pesticides into the water, and hence residue concentration of pesticides increases if rainfall event take places just after application of pesticides as discussed previously. However, rainwater plays the role of residue concentration dilution in the water, and therefore concentration of pesticide residues in the water is decreased if there no pesticide application in fields before rain and/or a lot of rain in a period of time. Furthermore, the results of monitoring pesticide residues in soil, studied by Bläsing (2010), showed that most pesticide residues detected in soil were quantified in the water samples of this study. The survey results of Bläsing (2010) also revealed that the median concentrations of most detected compounds in soil samples taken in the summer - autumn crop were higher than that in the winter - spring crop. Her finding was in same tendency with the interview results of pesticide amount used in the two cropping seasons in this study.

At Ba Lang, the median concentrations of three compounds (pretilachlor, fenobucarb and isoprothiolane) were compared in three the 2008-2009 cropping seasons: winter - spring, spring - summer and summer - autumn, as shown in Figure 4.13. Other detected compounds are not mentioned in this analysis due to lack of data. The paired multiple comparisons between two cropping seasons for each compound are showed in Table 4.6. Overall, there was a gradual increase of the concentration of pretilachlor in this area during sampling time. In paired comparison, there was a statistically significant difference in the median concentration of this herbicide between the summer - autumn versus winter - spring crops while there was no significantly different between the winter - spring versus spring - summer crop and the spring - summer versus summer - autumn crop. This is due to the fact that this herbicide was only applied for paddy rice fields, especially cultivated in the winter – spring crop in this study site. This herbicide was mostly detected in soil samples taken in rice fields (Bläsing, 2010). In addition, it is a stable compound for hydrolysis.

For insecticide fenobucarb, there was statistically significant difference in its median concentration between the winter - spring with spring - summer and summer - autumn crop. The median concentration of this insecticide measured in the winter - spring crop (0.07 µg/L) was significantly higher than that in the spring - summer (0.04 µg/L) and summer - autumn crop (0.04 µg/L). This insecticide is very soluble in water (420 mg/L), and therefore it was possibly diluted by rainwater in the spring - summer and

summer - autumn crop. In addition, it was often applied for rice which was dominant in the winter - spring crop.



**Figure 4.13: Comparison of median concentrations of the compounds detected in three the cropping seasons: winter - spring, spring - summer and summer - autumn of 2008 and 2009 at Ba Lang**

**Table 4.6: Paired multiple comparisons of median concentrations of detected pesticides**

Pesticide compounds	Paired multiple comparisons <sup>(*)</sup>	P <sup>(**)</sup> <0.05
Pretilachlor	Winter - spring vs. spring - summer	No
	Spring - summer vs. summer - autumn	No
	Summer - autumn vs. winter - spring	Yes
Fenobucarb	Winter - spring vs. spring - summer	Yes
	Spring - summer vs. summer - autumn	No
	Summer - autumn vs. winter - spring	Yes
Isoprothiolane	Winter - spring vs. spring - summer	No
	Spring - summer vs. summer - autumn	Yes
	Summer - autumn vs. winter - spring	No

(\*): Paired comparison of Kruskal-Wallis Anova on Ranks

(\*\*): P-value used to conclude a statistically significant difference

Isoprothiolane was most frequently detected compared to other pesticide residues in the site during sampling campaign. The median concentration of isoprothiolane in the spring - summer crop (0.09  $\mu\text{g/L}$ ) was significantly lower than that in the summer - autumn crop (0.21  $\mu\text{g/L}$ ). The fact that this fungicide was stable for hydrolysis and it was often applied for rice in this study site. Meanwhile, vegetable was often cultivated in the spring - summer crop, and rice was dominant at the two remaining crops. Bläsing (2010) also demonstrated that this compound was detected with high median concentration values in soil samples taken from the rice fields. Therefore, it is correct when the concentration of this fungicide was highest in the summer - autumn crop.

#### **4.4.7 Influence of Flooding on Pesticide Residues**

The occurrence of flood was more serious at the An Long site compared to Ba Lang. All of the An Long fields were inundated from August, and water level began falling from November. At Ba Lang, the flooding occurred almost two months later than the An Long site. It lasted about one month, and only some fields were inundated. Therefore, in term of monitoring the influence of flooding on pesticide residues, only An Long site is considered in the assessment. As summarized in Table 4.7, six out of 12 quantified pesticides were detected in the site after one month of flood occurrence at approximately 0.5 m depth in the fields. This period was also one month after the harvest of the 2009 summer - autumn rice crop. All median concentrations of detected compounds in the flooding season were lower than that in the cropping season. Most detected compounds had high solubility and stability in water. The result of one sampling event at the end 2008 flooding season showed that only three compounds isoprothiolane, fenobucarb and pretilachlor were detected in the water samples. The residue concentrations were diluted by the flooding water, and the compounds could be carried away from the application site. In addition, the fate of pesticides is very much affected by flooded conditions. The half-life of pesticides is often shortened under flooded conditions (Roger and Bhuiyan, 1995). The transformation of pesticides via micro-organisms is dominant in the soil of flooded fields. For example, the degradation and transformation of fipronil is easier under flooded conditions than that under aerobic conditions (Tan *et al.*, 2008). It could be concluded that flooding conditions were reduced most of the concentrations of detected pesticides.

**Table 4.7: Residue concentration ( $\mu\text{g/L}$ ) of the monitored pesticides in flooding and cropping season at An Long**

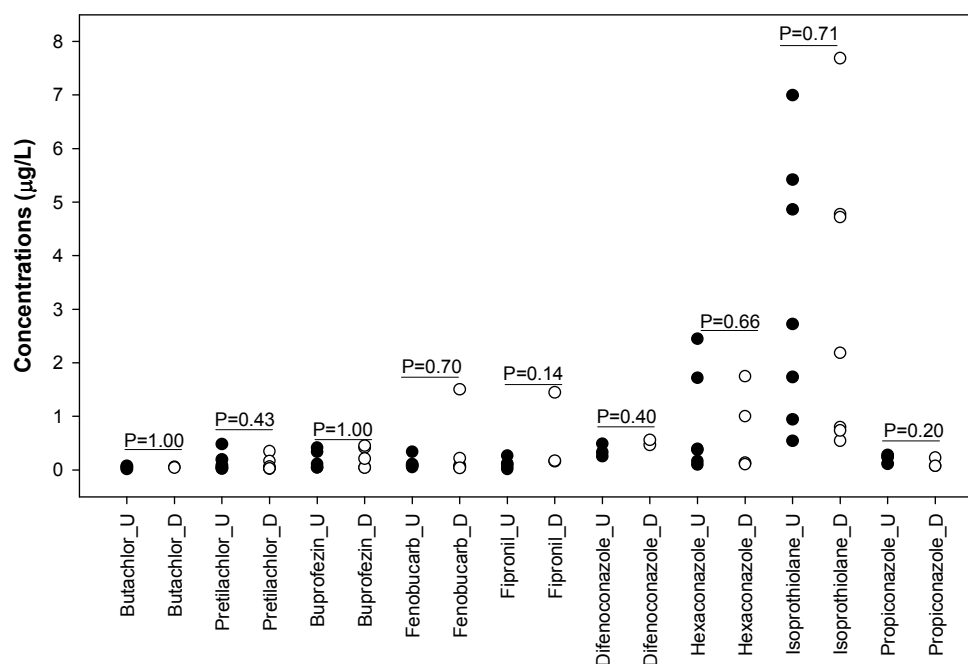
Compounds	Median		Standard deviation		Maximum	
	Flooding	Cropping	Flooding	Cropping	Flooding	Cropping
Propiconazole	0.08	0.20	0.003	0.11	0.08	0.43
Difenoconazole	n.d	0.56	-	0.69	-	2.59
Buprofezin	0.11	0.20	0.02	2.50	0.14	11.21
Fipronil	n.d	0.07	-	0.86	-	5.68
Isoprothiolane	1.73	2.91	0.82	2.67	1.95	11.24
Fenobucarb	0.08	0.12	0.02	0.60	0.09	5.00
Propanil	n.d	0.02	-	0.002	-	0.02
Butachlor	n.d	0.05	-	0.23	-	1.10
Endosulfan	n.d	0.01	-	0.02	-	0.07
Cypermethrin	n.d	1.27	-	1.47	-	4.89
Pretilachlor	0.05	0.06	0.05	0.19	0.14	0.74
Hexaconazole	0.43	0.56	0.23	0.62	0.65	2.45

n.d: not detected

#### 4.4.8 Pesticide Concentrations in Water at Up- and Downstream Points of the Irrigation Canals

The concentration of pesticide residues in the irrigation canal at An Long was assessed on the basis of the existence of pesticides at the up- and downstream points. Ten out of fifteen compounds were quantified in the samples taken at the upstream point with the exception of cypermethrin, profenofos, propanil,  $\alpha$ - and  $\beta$ -endosulfan. In survey results of Bläsing (2010), five compounds (fipronil, profenofos, endosulfan,  $\alpha$ -endosulfan and  $\beta$ -endosulfan) were not detectable in the soil 'samples. Cypermethrin and propanil were detected but they were not quantifiable. At the downstream point, ten compounds were also quantified except the remaining compounds like upstream point in the present study. In Bläsing's survey (2010), six compounds (fipronil, profenofos, propanil, endosulfan,  $\alpha$ -endosulfan and  $\beta$ -endosulfan) were not detectable, and cypermethrin was also not quantifiable in the soil samples. Cypermethrin was applied very commonly in the site, but its residue was not detected in water in the irrigation canal. Alternatively, this insecticide was detected under the limit of quantification in the soil samples. This is because the compound is strongly adsorbed in soil after going into aquatic environment. On the other hand, its residue concentration occurred in the sediment of the irrigation canal to be less than in the soil of the fields.

Only nine pairs of the compounds' median concentrations were compared between the up- and downstream points at the An Long site, except endosulfan due to lack of data, as shown in Figure 4.14. There was no statistically significant difference between the median concentrations of quantified compounds in the up- and downstream points. However, the median concentrations of some pesticides (e.g. difenoconazole, buprofezin and fipronil) were high, and the median concentrations of remaining detected pesticides were low in the downstream point. This may be explained that pesticide application was similar among the farmers at the stages of rice crop. The gates of the rice fields were often opened during cropping season. Among the quantified compounds, concentrations of isoprothiolane fluctuated in the widest range due to its stability in water and common use.

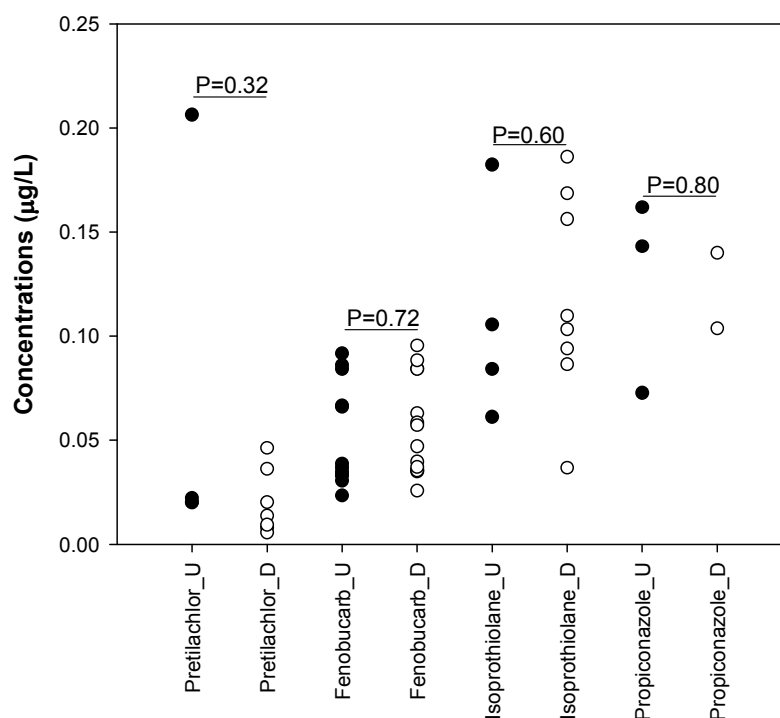


**Figure 4.14: Comparisons of the median concentrations of the compounds quantified in the up (U) and downstream (D) points at An Long. P-values indicate Mann Whitney Rank Sum test results. The differences of median values are compared at significance level of 5%.**

At Ba Lang, eight out of 15 studied compounds, excluding buprofezin, cypermethrin, profenofos, propanil, endosulfan,  $\alpha$ -endosulfan and  $\beta$ -endosulfan, were detected at up- and downstream points during monitoring phase. However, the concentration of three compounds (difenoconazole, fipronil and hexaconazole) was lower than the limit of quantification. The number of compounds detected in water was more than that in



soil samples. According to Bläsing's survey (2010), four compounds (buprofezin, fenobucarb, fipronil and isoprothiolane) were quantified in soil sample at downstream point in one rainy season sampling, and four compounds (cypermethrin, difenoconazole, fenobucarb and isoprothiolane) were quantified at both up- and downstream points in one dry season sampling. Cypermethrin was quantified with very high concentration in soil samples, but it was not detected in the water samples. It is due to its physicochemical properties. It is strongly adsorbed in soil as entering to aquatic environment. In general, the number of studied compounds detected in samples of the irrigation canal was less than of the fields. It is likely due to dilution by water in canals after or absorbed onto soil in fields before introducing into irrigation canal as found out by Nakano *et al.* (2004).



**Figure 4.15: Comparisons of the median concentrations of the compounds quantified in the up- (U) and downstream (D) points at Ba Lang. P-values indicate Mann Whitney Rank Sum test results. The differences of median values are compared at significance level of 5%.**

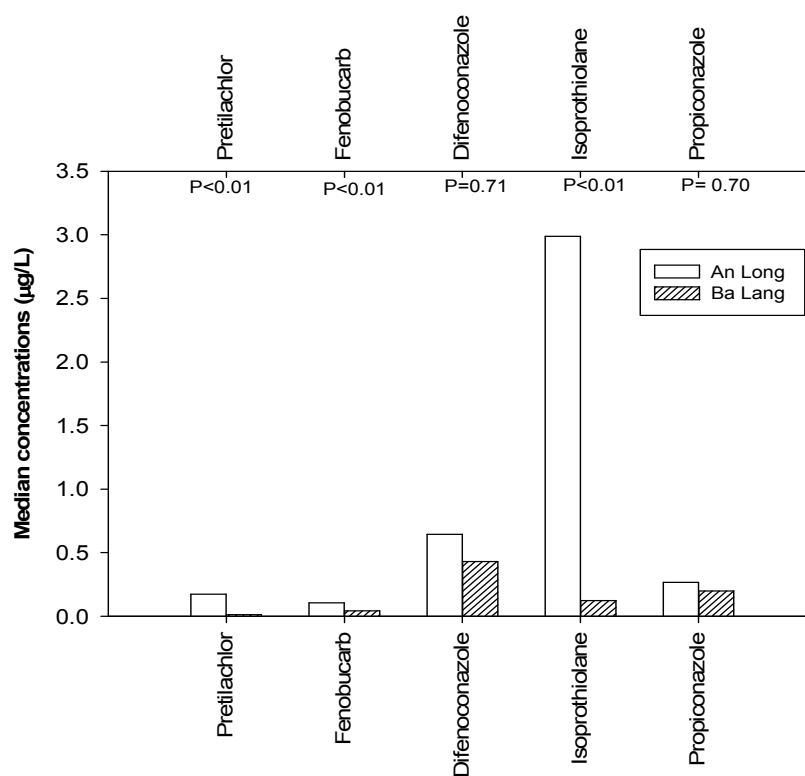
The median concentrations of quantified compounds were compared between the up- and downstream points in the irrigation canal as shown in Figure 4.15. Only four out of eight quantified compounds were compared due to lack of data, including fenobucarb, isoprothiolane, pretilachlor and propiconazole. There was no a significant difference in median concentrations of compared compounds between the up- and downstream points. Exceptionally, a high concentration value of pretilachlor (0.21 µg/L) was

measured at the downstream point on 19 July 2009. Application of this chemical in several fields was 20 days before the sampling event. This compound entered into the irrigation canal, and its dispersion would be limited via standing water in the canal at the downstream point due to dam construction towards further downstream since May 2009 and the dense development of water hyacinth plant (*Eichornia crassipes*) around this point. In general, there was no significant difference in median concentrations of quantified compounds between the up- and downstream points due to land use and hydrological situation of the study site. This site was characterized by mixed land use. Type of plants and pesticide application were different among the fields. The irrigation canal was affected by the tidal regime with two times of high and low tide per day. It means that the direction of water flow and water levels also change in a day. Therefore, due to turbulence the dilution of pesticides happened easily in the canal, and pesticides were transferred from the up- to downstream points and vice-versa.

#### 4.4.9 Pesticide Residues of the Two Study Sites in the Dry Season

In addition to the comparison of cropping seasons, a comparison of pesticide residues between two study sites in dry season was undertaken. The dry season covered the entire winter - spring crop at An Long and the winter - spring and half of the spring - summer crop at Ba Lang. The number of compounds quantified at Ba Lang (eight compounds) was lower than at An Long (12 compounds) although most the studied chemicals applied at An Long were also used at Ba Lang. Only the median concentrations of five compounds were compared in the study due to lack of data. They comprised pretilachlor, fenobucarb, difenoconazole, isoprothiolane and propiconazole with their median concentrations as shown at Figure 4.16. All median concentrations of the quantified compounds in the samples taken at An Long were higher than that at Ba Lang. There was a statistically significant difference between the two sites for the compounds: pretilachlor, fenobucarb and isoprothiolane. The median concentrations of these three compounds quantified in samples at An Long were 0.17, 0.11 and 2.99  $\mu\text{g/L}$  and were higher than those at Ba Lang with the values of 0.01, 0.04 and 0.12  $\mu\text{g/L}$ , respectively. These comparison results are in line with the comparison of their median concentrations in the soil samples measured by Bläsing (2010). The median concentrations of pretilachlor and isoprothiolane in soil samples taken at An Long were higher than that at Ba Lang. The difference may be explained as pretilachlor and isoprothiolane were applied much more for the rice

intensive farming area than the mixed cultivation area. However, there was no significant difference on the median concentration of fenobucarb in the soil samples.

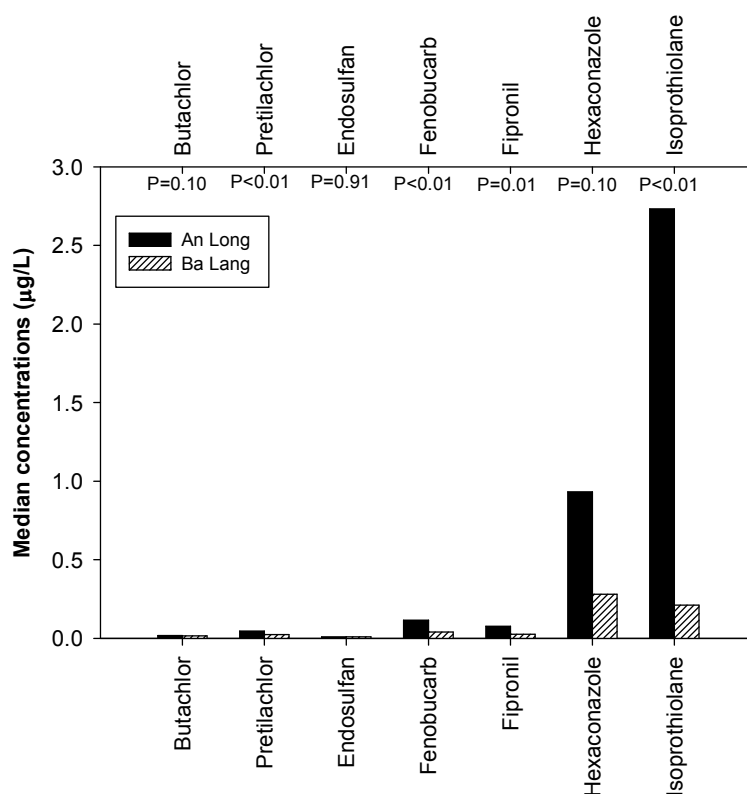


**Figure 4.16: Comparison of median concentrations of the compounds quantified at An Long and Ba Lang in the dry season. P-values indicate Mann Whitney Rank Sum test results. The differences of median values are compared at significance level of 5%**

#### 4.4.10 Pesticide Residues of the Two Study Sites in the Rainy Season

Number of compounds quantified in the water samples at the two sites in the rainy season was more than in the dry season. The time of the rainy season at An Long included the summer - autumn crop, but this season covered half of the spring - summer and the entire of the summer - autumn crop at Ba Lang. Eleven studied compounds were quantified at An Long with the exception of profenofos,  $\alpha$ -endosulfan,  $\beta$ -endosulfan and propanil. The numbers of quantified compounds at Ba Lang were nine pesticides excluding buprofezin, cypermethrin, difenoconazole, propiconazole,  $\alpha$ -endosulfan and  $\beta$ -endosulfan. A comparison of seven studied compounds with respect to median concentrations is shown in Figure 4.17. The comparison results showed that most median concentrations of the studied pesticides quantified at An Long were higher than at Ba Lang. However, statistically significant differences were considered for pretilachlor, fenobucarb, fipronil and isoprothiolane

only. Their median concentrations of the samples taken at An Long were quantified with values of 0.05, 0.12, 0.08 and 2.73  $\mu\text{g/L}$ , respectively. Meanwhile, their median concentrations at Ba Lang were measured with values of 0.02, 0.04, 0.03 and 0.21  $\mu\text{g/L}$ , respectively. It can be seen that the median concentrations of pretilachlor, fenobucarb, fipronil and isoprothiolane at An Long exceeded that at Ba Lang. According to Bläsing's survey (2010), the median concentration of these chemicals in soil samples at the two study sites were also similar tendency as this comparison, excluding fipronil due to lack of data. These differences were compatible with the results of pesticide use investigation at the two study sites. Pesticide use at An Long was approximately three times higher compared to Ba Lang in the 2009 summer - autumn crop.



**Figure 4.17: Comparison of median concentrations of the compounds quantified at An Long and Ba Lang in the rainy season. P-values indicate Mann Whitney Rank Sum test results. The differences of median values are compared at significance level of 5%.**

In summary, the number of quantified compounds and their median concentrations at An Long were more and higher than those at Ba Lang. Isoprothiolane and fenobucarb occurred most frequently in the samples during both dry and rainy seasons. Isoprothiolane showed the highest median concentration compared to other chemicals

in both seasons. The reason is because isoprothiolane was applied very much for paddy rice in the two sites. This fungicide dissolves well in water, and its residue is stable in aquatic environment. Fenobucarb is more soluble in water than isoprothiolane, but the former is less persistent in water than the later. Pretilachlor was also quantified at the two sites in both seasons. However, its median concentration was always lower at Ba Lang than at An Long. It can be concluded that the concentrations of the studied compounds were higher at An Long than at Ba Lang. In addition, the number of pesticides detected at An Long was more than that at Ba Lang. This was not only true to the water samples but also to the soil samples taken in both seasons. The interview results of pesticide use also showed that pesticide application at An Long was more frequent and intensive than that at Ba Lang. It demonstrated that pesticide use as well as their occurrence in water in the rice intensive farming site was higher than that in the mixed cultivation site with rice, vegetable and fruit trees.

#### **4.4.11 Pesticide Residues in Non-Farming Area**

The occurrence of the studied pesticides was also monitored at Tram Chim National Park wetland area, which is an area without farming activity and is controlled water level regimes by a system of dike, sluice gates and canals. Three out of 15 studied compounds were quantified as shown in Table 4.8. They consisted of fenobucarb, isoprothiolane and pretilachlor with the average concentrations of 0.05, 0.16 and 0.04  $\mu\text{g/L}$ , respectively.

It can be recognized that some studied compounds still occurred in the area although there was no pesticide application inside this wetland area for more than one last decade. The main reason for this occurrence is the transfer of the studied pesticides in the water environment. The surrounding of the wetland area was fields of rice intensive cultivation, grown in the two seasons a year and inundated in the flood season. Annually, the wetland area was supplied from rainwater and entry of surface water in flooding season through the sluice gates. These gates were closed in the middle of November and gradually opened until the beginning of June by the flash boards of gates (Ni *et al.*, 2006). Surface water contaminated by the studied compounds from surrounding farming activities could be a main pesticide pollution source for water in the wetland area.

**Table 4.8: Summary on the concentration of studied pesticide residues in water taken at the Tram Chim wetland area**

Pesticides	Concentration ( $\mu\text{g/L}$ )			
	Mean	Std. Dev	Maximum	Minimum
Buprofezin	n.d.	n.d.	n.d.	n.d.
Butachlor	n.d.	n.d.	n.d.	n.d.
Cypermethrin	n.d.	n.d.	n.d.	n.d.
Difenoconazole	n.d.	n.d.	n.d.	n.d.
Endosulfan sulphate	n.d.	n.d.	n.d.	n.d.
Fenobucarb	0.05	0.03	0.07	0.02
Fipronil	n.d.	n.d.	n.d.	n.d.
Hexaconazole	n.d.	n.d.	n.d.	n.d.
Isoprothiolane	0.16	0.05	0.22	0.11
Pretilachlor	0.04	-	0.04	0.04
Profenofos	n.d.	n.d.	n.d.	n.d.
Propanil	n.d.	n.d.	n.d.	n.d.
Propiconazole	n.d.	n.d.	n.d.	n.d.
$\alpha$ - Endosulfan	n.d.	n.d.	n.d.	n.d.
$\beta$ - Endosulfan	n.d.	n.d.	n.d.	n.d.

*n.d: no detection*

Physicochemical properties were the key factors that affect persistence of detected compounds in water collected in the wetland area. The literature research revealed that water in wetland areas was polluted by persistent pesticides and pesticides commonly used in surrounding agricultural areas. Sediment contained more persistent organochlorine pesticides and in greater concentration than surface water (Salvado *et al.*, 2006). It can be recognized that three compounds quantified in the wetland area were three most frequent detected pesticides at An Long during monitoring campaign. They are high soluble compounds in water, and pretilachlor and isoprothiolane are two stable compounds for hydrolysis.

## 4.5 Conclusions and Recommendations

### 4.5.1 Conclusions

Water contaminated by pesticide residues from agricultural activities in the Mekong Delta was demonstrated through the monitoring results of 15 commonly used active ingredients in the fields and irrigation canals at the two study sites. One area was representative for rice intensive farming (An Long). It was located in a region affected

by annual flooding. The other area represented mixed cropping cultivation (Ba Lang). It was located in the central part of the Delta.

The presence of the studied compounds in water affected by ambient environmental factors, their physicochemical properties and the amount of applied active ingredients was investigated and quantified in the study. Two environmental physicochemical parameters, water temperature and pH, are known as the factors that influence water solubility, volatilization and hydrolysis degradation of pesticides. They were monitored and their variation was assessed in this study. The measured high water temperature could affect the fate of the detected compounds while the slight to neutral pH of water was less influenced these compounds, especially several detected compounds which are stable under slight to neutral pH conditions.

During the monitoring period from August 2008 to August 2009, the numbers of water samples collected at An Long and Ba Lang were 109 and 233 samples, respectively. At An Long, 13 active ingredients were detected, and 12 out of them were quantified in water in the fields and the irrigation canal. The average concentrations of the quantified compounds ranged from 0.02 to 3.34  $\mu\text{g/L}$ . At Ba Lang, 12 active ingredients were detected and quantified. The average concentrations of the compounds ranged from 0.01 to 0.37  $\mu\text{g/L}$ . Co-occurrence of three compounds was in 90 and 50% of the samples taken at An Long and Ba Lang, respectively. The majority (92%) and more than half (59%) of the water samples collected at An Long and Ba Lang, respectively exceeded the EC drinking water guideline parameter for individual pesticide level (0.1  $\mu\text{g/L}$ ). 89% and 12% of the samples collected at An Long and Ba Lang exceeded the total pesticide level (0.5  $\mu\text{g/L}$ ), respectively. Meanwhile, surface water is the main source of drinking water for most local people who live outside of clean water supply networks. Therefore, it should be a priority to establish and keep active the monitoring network of pesticide residues in surface water in canals and rivers of the Delta. Endosulfan, a persistent organochlorine pesticide, was detected in 17.4 and 2.6% of the samples taken at An Long and Ba Lang, respectively, although the use of this compound was prohibited in 2005. Thus, the presence of persistent organochlorine pesticides in surface water should be also noticed in monitoring work.

There was a relationship between the occurrence of the detected pesticides in the water and rainfall. The residue concentrations of some compounds in the field, on

which rainfall occurred after pesticide application, were detected with peaks higher than that before rain. Several compounds were even detected in the sample taken after rainfall although these pesticides had not been used in the application event just conducted before rain. However, heavy rainfall also plays a very important role in diluting studied compounds. The concentration of most compounds was detected with low peak in the rainy season.

Flooding water was a key factor in dilution of the studied compound concentrations. The monitoring results at An Long in the beginning of the 2009 flooding season demonstrated that the studied pesticide concentrations in water were lower than that in the cropping season. On the other hand, flooding water might carry the studied active ingredients away from application site to non pesticide application areas, for example the protected natural wetland area.

The monitoring results also showed that the studied active ingredient concentrations detected in the water samples collected at the rice intensive farming area were higher than the mixed cultivation area. Additionally, the number of the studied compounds was detected more in the rice intensive farming area than the mixed cultivation area. This was also similar to the soil samples surveyed in another study at the same two sites. Monitoring work should be conducted at the areas characterized with other farming systems such as three rice crop intensive farming or fruit tree intensive cultivation areas in the Delta.

The survey results also showed that the concentrations as well as the numbers of studied compounds were greater in the agricultural area than the area less affected by agricultural activities. The studied compounds were found in the wetland area demonstrated that their occurrence in water was due to transfer from agricultural activity areas. Besides commonly used pesticide compounds, persistent pesticides should be monitored in soil and water in the wetland areas.

#### **4.5.2 Mitigation Measures for Pesticide Residues in Surface Water**

In order to mitigate pesticide entries into surface water, besides the measures (i.e. cultural controls, biological control and appropriate pesticide use) proposed in the previous chapter regarding pesticide use and management, the following mitigation



techniques should be applied corresponding to the various types of farming conditions in the Delta.

Loss of applied pesticides due to rainfall can reach 20 - 30% of application amount (Watanabe *et al.*, 2007a), and this leads to an enhance of pesticide residue concentration in water in fields and irrigation canals. As seen in the monitoring results demonstrated the relationship between the occurrence of the detected pesticides and rainfall in the present study, the concentrations of detected compounds after rain were higher than that before rain. The concentration of pesticide residues in water in the fields was enhanced after a significant rainfall event immediately occurred after pesticide spraying. Therefore, pesticide application should be postponed when significant rainfall events are forecasted. This can potentially prevent pesticides, or residues thereof entering surface water bodies. Farmers should keep the track of raining events reported on the daily weather forecast program at the public media (i.e. television, radio) when they intend to apply pesticides.

Drainage water management is a technique for mitigating pesticide residue inputs into surface water. Water is drained from the fields to remove excess water or in the case of crop cultivation as well as to avoid the pollution of the irrigation water in the fields. As investigated in water management part of chapter 3, water in rice fields were often drained five times per crop at Ba Lang. Water should not be drained immediately after pesticide application in order to reduce pesticide residue transport into aquatic environment (Nakano, 2003). Water holding practice was considered as an important measure for controlling pesticide discharge from the field. Depending on the kind of herbicides, keeping water in the fields after herbicide application reduces herbicide mass input to receiving waters significantly. A longer the retention period of at least 10 days after herbicide application is suggested as a good agricultural practice for controlling herbicide runoff from paddy rice fields (Watanabe, 2007). Regarding the studied pesticides, however, six compounds are stable for hydrolysis and the remaining compounds have at least 20 days of half-life in water. Limitation on draining water from fields after application of these compounds is the best measure to mitigate their residues entering into receiving water. Farmers should be recommended to take enough water responding to crop water demand in order to avoid drainage during cultivation time.

Pesticide losses in drainage water should be minimized by effectively managing irrigation water so that there is less runoff leaving the field. An efficient irrigation depends on many factors such as crop water demand, evapotranspiration, root zone depth and soil moisture. Farmers need to be informed or supported from extension workers and scientific staff regarding pest management practices in irrigation. Soil surface and the types of vegetation are main points to choose a correct irrigation method (Hanson and Trout, 2001). In the Mekong Delta, surface irrigation method is mostly applied for the fields. The efficiency of this irrigation method can be poor if the soil surface is uneven. Water losses from runoff and deep seepage can be substantial.

Mulching should be used in cultivation to provide soil cover and protection against soil erosion, reducing pesticide residue in agricultural runoff. Irrigation water demand of the crops is reduced due to limitation of evaporation in soil. Mulching also limits weed development, and consequently reduces the need for herbicide application. Recently, plastic mulches have been rather popularly used for cultivating the type of various vegetables such as watermelon, cucumbers, beans, etc. in the Mekong Delta. However, one potential negative impact of plastic mulch use is that it remains in soil after harvesting crop.

Buffer zones or filter strips are structures to reduce the transport of pollutants in surface or subsurface runoff. It is established from planted or indigenous bands of vegetation that are situated between pollution sources (e.g. agricultural areas) and receiving water (e.g. irrigation/drainage canals). Pollutants are dominantly removed by buffer zones including sediment and sediment bounded pollutants through infiltration and deposition mechanisms. The effectiveness of pollutant removal process evidently depends not only on the physical structure of buffer zones and on type of pollutants, but also on the distance between the buffer zone location and the pollution source (Norris, 1993). The buffer strips can serve as an effective contributor in reducing pesticide residue input surface water (Syversen and Bechmann, 2004; Dabrowski *et al.*, 2005). This measure may be suitable to characteristics of fields in the Mekong Delta. However, it is rather difficult to employ in the Delta due to small size of the fields as well as farmers' perception as reduced land size. It is only possible when there is intervention or subsidies from local government site in order to sacrifice a part of production area for construction of buffer zones.

Field borders are other edge-of-field buffers located nearby the edge of field like filter strip. However, this kind of buffer is a band or strip of vegetation established around fields. It can reduce pesticide residues in agricultural runoff when the runoff flows over the strip. Additionally, field borders can reduce pollution by spray drift because the spraying operation is physically separated from water bodies.

Conservation tillage is considered as a potential method in mitigating runoff loss of pesticide by reducing agricultural surface runoff and erosion volume. Conservation tillage can increase soil macro-porosity and so can contribute to a reduction in surface runoff (Shipitalo *et al.*, 2000). Conservation tillage increases infiltration rate and keeps the presence of crop residue on the soil surface, and consequently can improve structure of soil and natural biodiversity. Therefore it can minimize soil erosion and degradation, and reduce pesticide application for controlling pests (Holland, 2004). However, conservation tillage systems have different effectiveness in mitigating pesticide residue. For example, three conservation tillage methods (no-till, chisel-ploughing and ridge till) reduced herbicide runoff losses on average by 70, 69 and 42%, respectively, compared to conventional tillage (Reichenberger *et al.*, 2007). In the Mekong Delta, conventional tillage has been being applied as a typical ploughing technique for paddy rice farming. The majority of farmers use hand tractors to prepare soil for rice cultivation. Conservation tillage should be considered about its feasibility in the Delta due to its positive potentiality.

Constructed wetlands have been commonly used to treat municipal, industrial and agricultural wastewaters in Europe and North America during the last five decades (Vymazal, 2010). Constructed wetland system is an artificial shallow strip filled with several type of materials sorted such as gravel, sand or soil combined with various types of vegetation. Wastewater enters at the one end of the wetland, and then flows over the surface or under the subsurface. The physical, chemical or other biological processes such as infiltration, sorption and degradation take place in the system, and consequently wastewater finally discharges at the other site of the wetland with a better water quality. Constructed wetlands are proposed as a best management practices to mitigate agricultural runoff before introducing to aquatic system receiving water (Moore *et al.*, 2007, 2009). Pesticide runoff can be remediated by a conjunction of both biotic and abiotic functions in constructed wetland system. The Mekong Delta is recognized as a largest tropical natural wetland of Vietnam (Tuan *et al.*, 2009).

Therefore, constructed wetlands are effective to reduce pesticide inputs into surface water because of the availability of construction materials and the advantage tropical weather conditions for pesticide degradation. However, constructed wetlands consume land, and thus this mitigation measure is rather difficult to be applied in agricultural areas in the Delta unless the local government intervenes in order to sacrifice a part of agricultural land area for wetland construction.

Regular monitoring campaign should be organized to assess pesticide residue concentration in surface water. This campaign should be employed at least at provincial level. Compounds in the monitoring should not only include organochlorine and organophosphorus groups but also commonly and recently used pesticides belonging WHO category I and II.

The technical regulations for surface water quality in Vietnam should be regularly updated and taken into account for pesticide residues. These pesticides are highly and moderately hazardous compounds to human beings and living organisms according to WHO classification.

*Chapter 5*

**PESTICIDE RESIDUES IN DRINKING WATER:  
A CASE STUDY IN A SUBURBAN AREA OF  
CAN THO CITY**

**5.1 General Introduction**

**5.1.1 An Overview of Drinking Water Resources**

Freshwater is considered a critical factor influencing human life and the existence of other organisms. Besides quantity, the quality of water resources is a very important consideration, particularly regarding use for drinking. In the Mekong Delta (MD), water quality is of concern to people settling in rural and suburban areas. There are three main water sources for rural people without access to regular clean water supply scheme. They may use surface water, rainwater or groundwater to serve their domestic needs.

Surface water is one of the dominant water sources in the region. It is mainly supplied via the Mekong River system with a dense network of rivers and canals. The quantity of water, however, significantly fluctuates depending on seasonality in a year. Its mean annual discharge is approximately 475 km<sup>3</sup> per year. In the rainy season, the average flow rate measured is approximately 23,000 m<sup>3</sup>/s (White, 2002). This discharge creates an inundation covering an area approximately 1.2 to 1.9 million hectares and lasting for three to five months. Surface water can easily be collected during this period. In contrast, this is not easily accomplished during the dry season. The average discharge in the dry season is less than 2,500 m<sup>3</sup>/s or sometimes 1,700 m<sup>3</sup>/s (Tuan and Wyseure, 2007).

Surface water is usually used for daily domestic purposes such as bathing, washing, and irrigation. This behavior is dominant in rural areas, especially for households located along canals and rivers. In the dry season, when the clean water reserves become exhausted, surface water is used for drinking. Surface water is transferred to containers manually or by electric pumps. Due to a lack of appropriate sanitation and increasing agricultural activities in rural areas, surface water is significantly affected by contaminants such as organic wastes, agrochemical residues, nutrients, bacteria and other pathogens. Depending on water quality and the financial situation of

households, surface water is treated by various methods before drinking. Water is stored in the various types of containers like ceramic or concrete jars, concrete tanks after taken from rivers or canals. It is let settling freely or with flocculators (e. g aluminium sulfate, poly aluminium chloride). Water then can be disinfected by chlorine to destroy pathogeneous organisms. Afterward, water can be boiled or not boiled before drinking.

Rainwater is one of favorite drinking water source (Tuan, 2003) and it is also used for other purposes in rural areas, especially areas lacking surface or ground water. Annually, average rainfall ranges from 1,400 to 2,400 mm with more than 90% occurring between May and October. Rainwater is considered clean water and is directly used for drinking without treatment or boiling to destroy germs or insects. Recently, there have been concerns that industrial and agricultural contaminants maybe found in rainwater (Hau *et al.*, 2010). The research shows that rainwater is acidized in several areas and pH value is less than 5.6. People often do not collect this water in the early rainy season. Rainwater is collected from roof tops through plastic or metal gutters. Most people store this water in ceramic jars, barrels or tanks for gradual consumption. It is difficult for the poor people to store rainwater for use throughout the year due to lack of storage jars/containers. The poor rural households can collect rainwater by using dug ponds lined with plastic sheets and covered by thatches (Thang, 2002). Rainwater is also stored in large concrete tanks that can continuously supply drinking water the entire year. Moreover, in some regions affected by salinity intrusion or acidic sulfate soils, reservoirs were constructed to store rainwater.

Groundwater resources vary greatly from place to palce in the Delta. The underground is generally structured into four layers: Holocene, Pleistocene, Pliocene, and Miocene. Approximately 52% of the total groundwater is stored in the Pleistocene layer, which situates to a depth of 70 to 200 m. Most groundwater has been exploited in this layer. Groundwater at depth between 200 – 450 m is extracted by groundwater exploitation companies (Danh, 2008). Due to surface water contamination, groundwater plays a significant role in supplying water to people. As a source for drinking water, the needs for groundwater have increased in the delta since the mid-1990s. Groundwater in the Holocene layer is characterized with unpleasant odor and contamination by biological substances. The Pleistocene layer

is characterized with the occurrence of ferrous ion ( $\text{Fe}^{2+}$ ) and nitrate. Groundwater is simply treated by aeration method and through filtration step. It is usually boiled before being used for drinking. The public water suppliers treat groundwater through treatment systems and provide to households by pipe distribution systems. The average arsenic concentration in groundwater of these two layers in upstream regions of the Delta exceeded WHO guideline and Vietnamese allowance standard (Berg *et al.*, 2007). Groundwater in the Pleistocene layer has been also intruded with salt water in the Ca Mau peninsula, Long Xuyen Quadrangle and other regions located between the Hau and Tien Rivers from Can Tho City through East Sea. Therefore, groundwater of this layer can not be used after extraction by private wells.

In addition to the above three water sources, piped water is derived from surface or underground water which are employed by public or private companies and supplied to the community by distribution pipe networks. This water is only available in the community centers or the concentrated residential clusters. Recently, bottled water has become a common type of drinking water. Together with urban residents, only a small number of suburban people can afford this water. Bottled water is mostly derived from ground/surface water and is treated by various methods. However, there have been public concerns regarding bottled water quality, and hence there is a need to do official tests on this type of water by the Department of Health at provincial level.

### 5.1.2 Drinking Water Supply in the Delta

At the end 2008, approximately 75% of population had access to clean water in the rural areas of the whole country (MARD, 2009). The goal of Vietnamese Government is that all rural population will have access to clean water by 2020, and the average amount of clean water per capita is at least 60 liters a day. In general, the quality of water and the process of water supply have not met the recommended requirements. Only approximately 50% of inhabitants in the rural of the MD had access to clean water of which quality meets the standard for clean water (Standard No. 09: 2005/QĐ-BYT) promulgated by the Ministry of Health (MOH). Selected water supply sources have been known to be influenced by salty or acidic water, domestic wastewaters, heavy metals and arsenic (Buschmann *et al.*, 2008). Limited access to clean water is common in the remote and coastal areas of the Delta. In several areas, the average amount of clean water per capita is less than 20 liters a day.

Sustainable development of clean water supply projects in rural areas is limited due to a lack of financial budget for management, maintaining and developing processes. The monitoring and assessment of supplied water quality is not carried out on a regular basis and does not meet regulatory requirements, especially pertaining to small scale water supply units. People's perception regarding the use of clean water, hygiene and sanitation in rural areas is also a notable obstacle for clean water supply.

Clean water supply has been improved in the Delta since 1999, but many of the above mentioned problems still persist. Most water supply plants are constructed in cities, towns, and the center of residential zones. The water supplied to these plants is mostly from surface and groundwater sources. However, surface water is rapidly becoming more polluted from domestic, industrial and agricultural by-products. Furthermore, a majority of farmers still use surface water for drinking in the rural areas. On the other hand, the quantity and quality of groundwater is predicted to decline rapidly in the near future. According to the report of Wagner *et al.* (unpublished), the exploitation of groundwater resulted in groundwater level in the Pleistocene aquifer decreased up to 25 cm per year. Overexploitation seriously took place in the deeper layers (the Pliocene layers) led to distinct decreasing trend of more than 40 cm per year during the last 10 years. In the whole delta area, now, there are presently 400,000 household tube wells and hundreds of groundwater supply stations. The Pliocene layers have been the favorite target for new groundwater exploitation projects since 2003. If regulatory measures are not implemented soon on controlling over-exploitation, groundwater in several areas would be excessively drawdown by 2014 (Vietnamnews, 2010).

In short, water supply in the MD has been influenced by both quantity and quality of water. The situation of water supply will be analyzed in detail at a suburban area of the city located in the Delta centre. A drinking water source of local people will be investigated about its use, and its quality in respect to the residues of pesticides, which were mentioned in the previous chapters, will be monitored and assessed.



## 5.2 Pesticide Residues in Drinking Water Source at the Suburban Areas of Can Tho City

### 5.2.1 Situation of Water Supply

In the suburban areas of Can Tho City (CTC), water resources for drinking also include the sources mentioned above. Rainwater is considered to be a safe source of water. The rainy season lasts from May to November with an average annual rainfall of 1,597 mm. Approximately 92 – 97% of rainfall in this region occurs during this period. The collection capacity of this water depends on roof construction and the number of available containers storing the water. A recent household survey conducted in the suburban areas of CTC revealed that 67% of the population used rainwater as one of water source for drinking water (Herbst *et al.*, 2008).



a) Rain- and ground water collection



b) Surface water collection

**Figure 5.1: Collection forms of water for domestic demand**

Surface and groundwater sources are abundant in suburban areas of the city. Surface water is provided through a dense network of rivers and canals in the city totaling 2,500 km in length with a density of 1.8 km/km<sup>2</sup> (CanthoDONRE, 2009). This is a plentiful source for water supply during the rainy season. However, both quantity and quality of water decrease during in the dry season. The quality of surface water has been influenced by the discharge of domestic and industrial wastewater and agrochemical pollution. According to recent survey results as presented in Table 5.1 surface water in main canals of the city has been polluted by organic matter and pathogens (CanthoDONRE, 2009). According to monitoring results of the Can Tho Environmental Monitoring Center, organophosphate pesticides were detected in surface water at several canals and rivers in the City.

The groundwater of CTC is mostly exploited from the Pleistocene and Pliocene aquifers. The water quality in these layers is the best compared to that in other

layers. Groundwater is pumped to treatment tanks to remove unpleasant odors and pollutants, and clean water is then transferred to storage containers. Total groundwater reserve of the city is estimated to be 5.5 million m<sup>3</sup> (Danh, 2008). There were more than 32,000 small scale tube wells, over 400 groundwater supply stations with medium capacity of up to 20 m<sup>3</sup>/h and 20 large scale wells which are used to supply water for drinking and industrial purposes. Due to over-exploitation, however, the groundwater level appears to be rapidly decreasing. In some areas of CTC the ground water level was declined 0.7 m/year approximately (Nuber and Stolpe, 2008).

**Table 5.1: Average physicochemical parameter values of surface water quality**

	Unit	Vietnamese standard (QCVN 08:2008/ BTNMT)	2004	2005	2006	2007	2008
pH		<b>6-8.5</b>	7.20	7.09	7.15	7.18	6.99
COD	mg/L	<b>10</b>	14.90	14.70	14.00	17.20	15.20
SS	mg/L	<b>20</b>	86.10	75.10	70.10	62.10	40.30
Fe <sub>tc</sub>	mg/L	<b>0.5</b>	0.80	1.10	1.00	0.60	0.50
NO <sub>2</sub> - N	mg/L	<b>0.01</b>	0.029	0.034	0.030	0.024	0.027
NH <sub>4</sub> <sup>+</sup> - N	mg/L	<b>0.1</b>	0.33	0.54	0.63	0.68	0.74
Coliform	(1000MPN/100ml)	<b>2.5</b>	58	63	134	448	62

(Source: Can ThoDONRE, 2009)

According to the report of the Center for Rural Water Supply and Sanitation (CERWASS) of CTC, approximately 96,000 inhabitants (59.1%) settling suburban areas of the city has had access to clean water by the middle of 2009. Water is provided by stations with the following pumping capacities: 4-6, 6-10, 20 and 40 m<sup>3</sup>/h. The clean water supply has met with difficulties such as lack of financial budget, local people's behaviors in personal hygiene and sanitation. Moreover, water sources in rural areas are being seriously influenced by pollutants that are derived from farming and aquaculture activities.

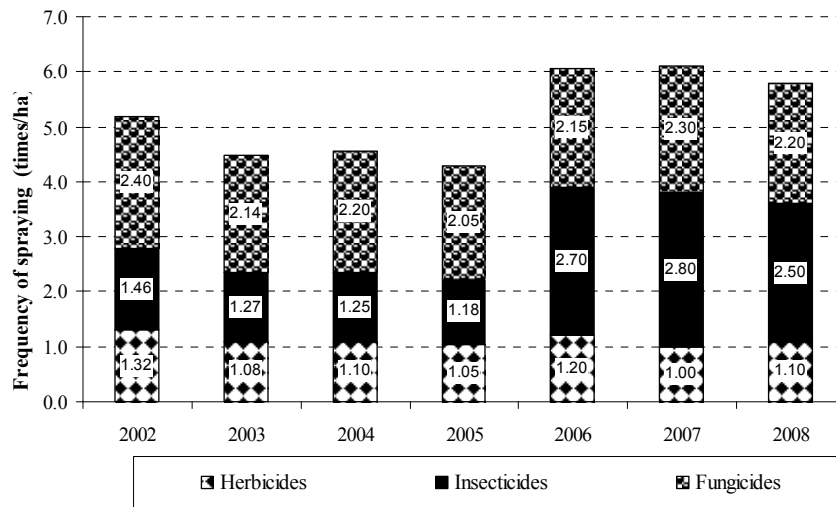
**Table 5.2: Average physicochemical parameter values of groundwater quality**

	Unit	Vietnamese standard (QCVN 09:2008/ BTNMT)	2004	2005	2006	2007	2008
pH		5.5 - 8.5	6.96	7.19	6.80	-	-
Hardness	mg/L	500	256.50	283.50	280.50	355	84
Cl <sup>-</sup>	mg/L	250	122.50	180.50	55.50	133	24
Fe <sub>tc</sub>	mg/L	5	1.54	2.02	2.20	2.59	1.4
NO <sub>3</sub> <sup>-</sup> - N	mg/L	15	0.40	0.20	0.25	0.3	0.5
SO <sub>4</sub> <sup>2-</sup>	mg/L	400	126.50	156.00	156.50	140	140
COD	mg/L	4	n.d	1.80	3.00	-	-
Coliform	MPN/ 100mL	3	17	25	160	1047	796

(Source: CanTho DONRE, 2009)

### 5.2.2 Monitoring Pesticide Residues in Drinking Water

As mentioned previously, surface water is used as a drinking water source in the suburban and rural areas of CTC. However, this source has been polluted by agrochemicals through run-off or leaching originating mainly from agricultural areas. According to the Can Tho Department of Agricultural and Rural Development (DARD) report, 110,290 tones of agrochemicals were used in the city in 2001. Pesticide use rapidly increased from 2002 to 2007 due to complicated and intensified reoccurrence of various types of pests on rice and vegetables. As shown about the share of pesticide use frequency in Figure 5.2, frequency use of insecticides was doubled in the period of 2005 - 2006 due to the outbreak of brown planthoper on rice. Recent monitoring results provided by the Can Tho Department of Natural Resources and Environment (DONRE) show that the residue of several monitored pesticides were not only detected in the rivers of rural areas but also in the rivers or canals of the city center, as reported in Annex 5. However, only two pesticide groups were monitored, including organochlorine and organophosphorus compounds.



**Figure 5.2: Frequency of pesticide spraying in Can Tho, 2002 – 2008**  
(CanThoPPD, 2008)

Pesticide residues have been monitored in drinking water as well as its sources in many countries, such as United State (Hladik *et al.*, 2008; Duirk *et al.*, 2010), European countries (Ormad *et al.*, 2008; Schriks *et al.*, 2010), India (Kumar *et al.*, 1995), Thailand (Kruawal *et al.*, 2005) and Kuwait (Al-Mudhaf *et al.*, 2009). In Vietnam, the monitoring of pesticide residues is still lacking, especially in drinking water as well as its sources. It was only conducted in some regions and mostly focused on organochlorine compounds (Hung and Thiemann, 2002; Wrigley, 2007). Collected data about the residue of recently used common pesticides in drinking water is almost not available in the MD. This chapter reports on investigations on (i) the practice of surface water use for drinking and (ii) pesticide residue concentrations in drinking water and its source, surface water, in a suburban of CTC. In detail, the chapter focuses on the follows.

- Study the practice of surface water use for drinking,
- Understand traditional surface water treatment methods,
- Monitor the existence of studied pesticide compounds in surface water which is often taken for domestic water demands at the household level,
- Assess the effectiveness of removing studied pesticide residues from surface water by using aluminium sulfate and boiling practices before drinking,
- Experiment on the persistence of studied pesticides in water medium regarding the boiling practices

- Determine local people's exposure to studied pesticides in drinking water at the household level, emanating from surface water.

### 5.2.3 Materials and Methods

#### Study Site Description

The surveys were carried out at Ba Lang, a suburban ward of Can Tho City. This study site is the same with one monitoring site where took place monitoring campaign of pesticide residues in the centre of the MD, reported in chapter 4. However, it was expanded to the households located in the downstream area of the irrigation canal Cai Doi. These households located along canals and rivers of which water source influenced agricultural activities from the previous study site through the tidal regime. Local people were assumed that they use surface water in the canals and rivers for drinking.

The study site is three kilometers away from the city center. The total number of inhabitants was 6,634 with a population density 1,195 people per km<sup>2</sup> in 2006. Although it is a ward of the city, agricultural production is the main economic activity for the majority of local people. Vegetables, rice and fruit trees are common agricultural products from this area; however, this has been changed. For example, this ward was considerably affected by urbanization with rice production areas shrinking from 483 hectares in 2004 to 307 hectares in 2006. Local people did not have access to clean water from distribution system of the city. A minority of local people had access to clean water from a small scale water supply station constructed by the CERWASS with capacity 5 m<sup>3</sup>/h. The remainder of residents themselves obtained clean water for domestic activities such as washing, cooking and bathing. Most households are located along the canals or rivers which are tributaries of the Can Tho River, originating from the Hau River. Influenced by the East Sea, the Hau River system is characterized with a semi-diurnal tidal pattern. There are twice high and low tides per day. Additionally, there are twice spring and neap tides each month.

### **Household Surveys**

Two household surveys were carried out in 2009. Initially, a survey approach was employed at the household level to collect information regarding household demographics and drinking water issues such as water collection, treatment, usage and consumption. At the research site, household interviews were randomly conducted. Interview respondents were most people who were involved in the process of obtaining drinking water and/or responsible for drinking water supply for their families. After an introduction and explanation of the research objectives, the respondents answered or commented the questions and issues were presented to them. A structured questionnaire was designed in English and then translated into Vietnamese for the practical interview process as reported in Annex 6. A household interview took approximately 30 minutes. In addition, the respondents showed where water was collected and stored for drinking at their houses. Interview data were recorded, coded and analyzed with Excel.

A second survey with the same households was carried out to collect additional information in order to address which households would be suitable for the drinking water sampling campaign. In order to meet the research objectives, studied households were families in which surface water is used as a source of drinking water. These households were located along rivers or canals and their locations were identified through Global Positioning System (GPS). The number of studied households was chosen according to the study objectives. Studied households were given an explanation of the water sampling plan. They were then invited to participate in the water sampling process after being guided through the planned sampling. Noticeably, the sampling method was planned according to respondents' traditional water management practices. A brief check list describing water sampling in Vietnamese language was given to the respondents. They were guided how on to check the list during the water sampling process and the completed check list was recorded at the end of each sampling time.

### **Water Sampling**

Water sampling was implemented at the studied households based on the survey results. Sampling was carried out three times in 2009. Three categories of grab samples were taken at each sampling point (each household) per event. The first

sample group was taken below the water surface in container after water was just obtained from the water bodies (i.e. rivers or canals) to the container. The containers of the studied households are made mainly from ceramic. The second sample group was stored in the same container after being treated with a flocculator, aluminium sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ ), shortly named aluminium sulfate afterwards. The third sample group was boiled after they had been taken from the same container and at the same time as the second sample. The boiled samples were then left to cool before being transferred to sampling bottles.

The entire water collection and treatment process was recreated as done by respondents. First, containers were cleaned before water was transferred into them. In the next step, water was stirred for one minute approximately, and aluminium sulfate was also added in the containers. After sediment and other suspended substances settled down bottom of the containers, water could be taken and boiled for drinking. Otherwise, water was transferred to other containers for long term use.

In order to monitor pesticide residue concentrations in drinking water and its surface water source, three sampling events were conducted at the selected households. Because of the author's prediction that pesticide residue concentrations could be low due to dilution after entering canals or rivers and rainfall in the rainy season, the volume and the number of samples and sampling events were organized as the following report. In addition, the time interval of taking samples in one sampling event were designed corresponding to waiting time for using drinking water after treatment.

Water samples were collected at nine sampling points in the first and second sampling events. In each sampling event, three sampling points were located at a level of water bodies classified responding to influence of agricultural activities. Sampling points were located at three levels of water bodies. The objective of this allocation was to monitor the fate of selected pesticides in water bodies. The first samples were directly taken in the containers after water was obtained from the water bodies manually or through electric pumps. The second samples were taken 15 minutes and 24 hours after treatment with aluminium sulfate for first and second sampling events, respectively, to study the effectiveness of treatment at various treatment time. The third samples included water that was collected during the same

time and same place with the second samples; the third samples were immediately boiled and then left to cool. Each sample consisted of one liter Teflon capped borosilicate bottle.

In the third sampling event, samples were only taken at three sampling points, representing three levels of water body affected by agricultural production. In addition, the second and the third samples in this sampling event were taken seven days after water was treated with aluminium sulfate. Furthermore, two liters of water were collected in each of these two types of samples and they were also contained in Teflon capped borosilicate bottles. Information related on water sampling is summarized in Table 5.3.

**Table 5.3: Summary on sample volumes and sampling time**

Sampling events	Types of sample					
	First samples (River water)		Second samples (After treated by aluminium sulfate in container)		Third samples (Aluminium-treated water after boiled)	
	Volume (L)	Sampling time <sup>(*)</sup>	Volume (L)	Sampling time <sup>(**)</sup>	Volume (L)	Sampling time <sup>(***)</sup>
I	1	Immediately after river water was filled up	1	15 minutes	1	
II	1	containers	1	24 hours	1	See notes below
III	1		2	7 days	2	

**Notes:**

(\*): Time of sampling when samples were collected in container after river water was filled up ceramic containers

(\*\*): Time of sampling when samples were collected after water stored in the same ceramic container with first samples was treated with aluminium sulfate

(\*\*\*): Time of sampling when samples were collected after water was boiled and left to cool since water were taken from ceramic container at the same time with the second samples. Real boiling and cooling time were calculated responding to each detail case.

Water collection, treatment and boiling processes were carried out by respondents, and these activities were regularly observed by the researcher. Important information of the process was recorded in the delivered check list. Sample bottles were



transported to the laboratory in ice cooled boxes and then stored in refrigerators at 4 °C until analysis.

### **Pesticide Analysis and Quality Control**

The existence of residues in water regarding the studied pesticide compounds (fifteen compounds and metabolites including: buprofezin, butachlor, cypermethrin, difenoconazole, endosulfan,  $\alpha$ -endosulfan,  $\beta$ -endosulfan, fenobucarb, fipronil, hexaconazole, isoprothiolane, pretilachlor, profenofos, propanil and propiconazole) was determined through an analysis process similar to the one was previously described in chapter 4.

### **Boiling Experiments**

Boiling the various types of obtainable water before use is widely applied by local residents to disinfect drinking water. In order to test the effectiveness of the boiling practice on the removal of studied pesticide compounds in water mediums, a laboratory boiling experiment was implemented. Nine samples of distilled water were prepared in 500 mL Teflon capped white borosilicate bottles. Among these samples, three were set up as blanks for quality control. Three samples were not boiled for a control and the remaining three were test samples which were boiled and left to cool to determine the existence of the studied pesticide compounds. The control and test samples were spiked with a mixture of fifteen studied pesticide compounds with an amount of 0.1  $\mu\text{g}$  a.i. The three spiked samples and one blank sample were boiled in stainless steel containers via electric heater. It took approximately 13 minutes to reach boiling, 100 °C; and the samples were left to boil for 15 minutes as to comparable with household's practices. The boiled samples were then left to cool, and the remaining volumes were determined. All samples were treated and analyzed with the same method developed for analyzing real samples.

### **Statistical Analyses**

Recorded data was statistically analyzed, and graphs were plotted via statistical software, SigmaPlot program version 11. Statistical analyses were conducted to test the differences in pesticide concentrations in water samples taken before and after

treatment with aluminium sulfate, before and after the boiling process and also between river water and boiled aluminium-treated water (finished drinking water). In other words, statistical analyses were used to test the effectiveness of traditional treatment methods and the boiling experiment in laboratory for studied pesticide persistence in water. Statistical procedures were conducted first by checking normal distribution of data set with the Kolmogorov-Smirnov test. In this study, the P value (0.05) of the Kolmogorov-Smirnov is selected to conclude whether the test passed or failed. If P value computed by the test is greater than 0.05, the test passes, and the data set has normal distribution. In contrast, a failed test indicates a data set with a non-normal distribution. For normally distributed data, the Paired t-test was then selected for analyzing differences. The P value (0.05) of the Paired t-test is the threshold in concluding the presence of a significant difference between two paired data sets when P value is smaller than 0.05. If the data sets are not normally distributed, the Wilcoxon Signed Rank test is selected. A significant difference is concluded if the computed P value of the Signed Rank test is smaller than 0.05 (Toutenburg, 2002; Systat, 2008).

## 5.2.4 Results and Discussion

### 5.2.4.1 Collection and Storage of Surface Water

At the study site, a survey was randomly conducted in May 2009. The identified household characteristics are summarized in Table 5.4. Overall, the survey included 21 households, which comprised 89 people (i.e. in average 4.2 occupants per household). Surface water was used for drinking in 19 out of 21 interviewed households. The interviewees were residents who were either mainly responsible for or were well versed in the process providing drinking water in their households. Their average age was 48.4 (ranging from 29 to 77).

**Table 5.4: Demographics of interviewed households**

	<b>n</b>	<b>Mean</b>	<b>Range</b>
Number of households	21		
Total population	89		
Family size		4.2	2 - 9
Age of respondent		48.4	29 - 77

Similar to most rural households in the Delta, these households were located close to rivers or canals of which water was used for daily activities such as cooking, washing and bathing. With regard to drinking water, 90.5% of households collected surface water for their drinking demand, especially during the dry season. Additionally, rainwater was collected by 81.0% of households and was considered the second important drinking water source. Only a minority of the household (4.8% and 19.0%) used groundwater and other sources as drinking water, shown in Table 5.5. In order to collect surface water for drinking from rivers/canals, various tools were used depending on the economic condition of families. The survey results showed that 73.7% of respondents usually obtained river/canal water with handling tools such as buckets or other vessels. Alternatively, electric pumps were used in collecting river water for 31.6% of households. After collecting river water, the water was then usually stored in ceramic jars. In addition, water was pumped into concrete containers at several households where it was then treated before drinking. The frequencies of surface water collection for drinking varied depending on water consumption and containing capacity of households. Surveyed households were classified into three groups based on their water collection frequency. For group one, river water was collected every less than two days. This group accounted for 10.5% of interviewed households and was comprised mainly of families in small size or families having a small number of ceramic jars. For group two, water was normally collected every two to seven days. This group accounted for 36.9% of those surveyed. The remaining group (52.6 %) consisted in households who collected river water after every more than seven days. This group had either large concrete containers or extra jars for storing drinking water.

**Table 5.5: Statistical summary on sources and collection of drinking water**

	n	%
<b>Sources of drinking water</b>		
Surface water	19	90.5
Rainwater	17	81.0
Groundwater	1	4.8
Other sources (bottled water, tap water)	4	19.0
<b>Tools of collecting surface water for drinking</b>		
Buckets, vessels etc.	14	73.7
Electric pumps	6	31.6
<b>Water collection frequency for drinking</b>		
Less than 2 days	2	10.5
2 - 7 days	7	36.9
More than 7 days	10	52.6

Most households collected water in the high tide periods, and this was usually done as the water level of river reached to its highest level. In addition, they often took water in the early morning. Respondents explained that water taken during these periods is normally best in quality (i.e. containing the least sediment and other substances). The finding also showed that most containers were washed before taking water in. This was often done by hand, and the settled sediment was removed from the containers.

#### **5.2.4.2 Surface Water Treatment Practices**

Households applied “traditional” methods in treating river water for drinking. In fact, 100% of respondents answered that they used aluminium sulfate as a flocculator to enhance the settlement of sediment in river water. This method was immediately conducted after containers were filled up with river water. After adding aluminium the water was stirred to support flocculation.

In 21.1% of the households, water treated with aluminium sulfate was then transferred to other containers for storage (Table 5.6). The remaining households kept the aluminium-treated water in their original containers and used this water not only for drinking but also for cooking and washing for example. There were various procedures regarding waiting time for using water after treatment with aluminium. The respondents were classified into three groups: those waiting less than two hours, those waiting between 2 - 24 hours and those waiting more than 24 hours. The proportions of surveyed households regarding these groups were 26.3%, 52.6% and 21.1%, respectively. It appeared that waiting time depended on water demand as well as storage capacity at the households. It was also noted that water was only treated with aluminium sulfate before use which was different compared to other several areas in the Delta. For example, water treatment with aluminium is followed by adding chlorinated solvents to disinfect. This chemical acts as a disinfectant destroying microbiological contaminants in drinking water (Wrigley, 2007).

In order to destroy potential pathogenic bacteria (i.e. faecal coliforms, E. coli, streptococci), most households (89.5%) boiled aluminium-treated water before drinking. Treated water was transferred to boiling vessels (e.g. aluminium kettles, stainless steel pots) from storage containers by plastic or metal mugs/cups. Boiling

practices were carried out on open fire using wood or liquefied petroleum gas. Boiling time usually varied depending on the volume of water. After water reached boiling, it was left a few minutes to boil and then removed from the heater. The survey investigated whether the boiled water was kept hot or left freely to cool before drinking. Only a minority of the respondents (17.6%) transferred boiled water to thermo-flasks to make hot beverages such as tea or coffee. 35.3% of the respondents transferred boiled water to other vessels which were left to cool for later consumption. Approximately half of the respondents (47.1%) applied both of these methods to preserve drinking water. Although the boiling water practice is considered an effective activity for destroying microbiological contaminants, boiled water was susceptible to recontamination (Clasen *et al.*, 2008b). Once boiled water begins to be cool, it is very susceptible to recontamination due to open storage means without cap or from no disinfectant utensils. The boiling water practice does not fully remove the risk of waterborne pathogens, especially for thermo-tolerant coliforms (Clasen *et al.*, 2008a).

**Table 5.6: Statistical summary on treatment and storage of water for drinking**

	n	%
<b>Treatment of drinking water</b>		
Aluminium sulfate	19	100.0
Transfer of water to storage containers	4	21.1
Waiting time after treatment with aluminium		
Less than 2 hours	5	26.3
2 - 24 hours	10	52.6
More than 24 hours	4	21.1
Boiling	17	89.5
<b>Preservation of boiled water</b>		
Keeping water hot	3	17.6
Cooling water	6	35.3
Both preservation methods	8	47.1

#### 5.2.4.3 Pesticide Residues in Drinking Water Source

Samples were taken in three sampling times in 2009. The first and second events were conducted towards the beginning of the rainy season, May and June, respectively. The third sampling event was carried out in August, the middle of the rainy season. For each sampling event, water samples were collected in turn at the

stages of traditional water treatment cycle as illustrated in Figure 5.3. Information related to sampling events is summarized in Table 5.7.

For the first sampling event, each water sample (first sample) in one liter bottles was taken immediately after water was transferred from the rivers/canals to container at the nine sampling points (nine households). After approximately 18 minutes of treatment with aluminium sulfate, each sample (second sample) was then taken in the same container with the first samples. Concurrent to second samples, water was also transferred to stainless steel kettles for boiling. It took approximately 30 minutes to reach boiling on open fire. This water was transferred to sample bottle (third sample) after being left to cool for approximately 1 hour.

Regarding the second sampling event, each water sample (first sample) was also collected in one liter bottles after water was transferred from the water body to the container. The second nine samples were then collected in the same containers with the first samples after 23 hours of treatment with aluminium sulfate. Next, each sample (third sample) in one liter bottle was also collected after water was transferred to the kettle at the same time of collecting the second sample, boiled and then left to cool.

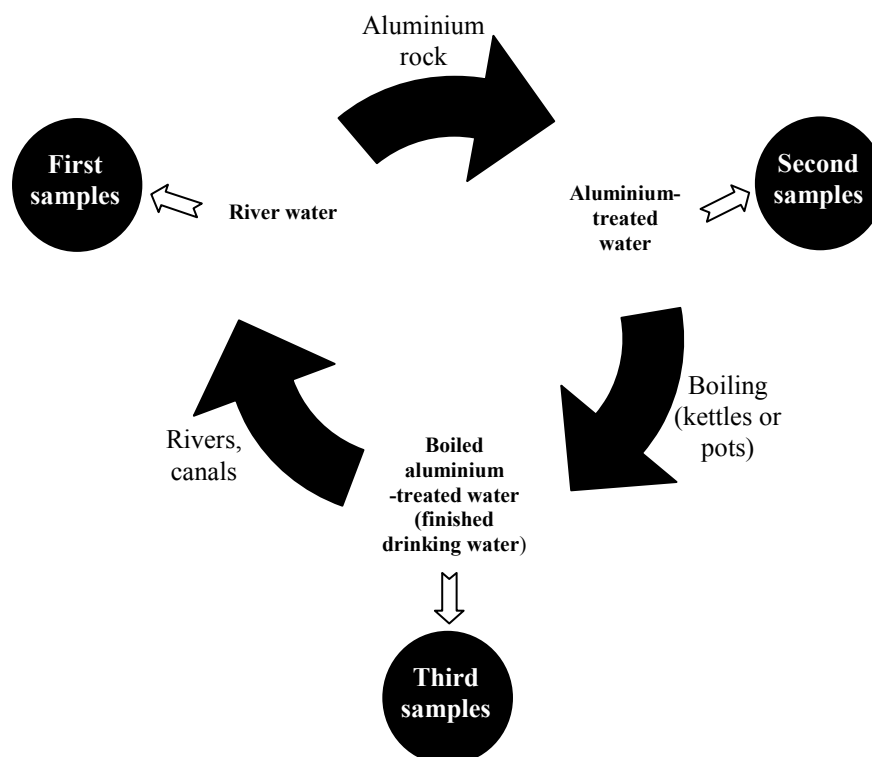


Figure 5.3: The cycle of traditional water treatment method

**Table 5.7: Information related to the real sampling events**

Sampling events	First samples (river water)	Second samples (Aluminium treated water)	Third samples (Boiled aluminium-treated water)			
	<i>Number of samples</i>	<i>Number of samples</i>	<i>Aluminium treating time</i>	<i>Number of samples</i>	<i>Average boiling time (min)</i>	<i>Average cooling time (min)</i>
I	9	9	18 minutes	9	30	56
II	9	9	23 hours	9	30	75
III	3	3	7 days	3	42	190

Regarding the third sampling event, the first three samples in one liter bottles were collected after water was transferred from the water bodies to the containers. The second three samples were taken after water was treated with aluminium sulfate for seven days. Parallel to the second samples, water was also transferred from the containers to the stainless steel pots. Afterwards, water was boiled on open fire for 42 minutes and left to cool for approximately 190 minutes. Then, the third three samples were collected. The second and third samples of this sampling event were in two liter bottles. The reason of volume increase was because water of these samples was stored longer than other samples after treated with aluminium, and consequently pesticide residues were expected to be less than the first and second sampling events. In addition, pesticide residues could be easy to quantify as analyzed with such extraction volume if they present in drinking water. The number of sampling points in this sampling event was less than in the two previous sampling events.

### Occurrence of Studied Pesticide Residues

The occurrence of studied pesticide residues was monitored in 62 samples during the study time. These samples were classified into three categories: river water (20 samples), aluminium-treated water (21 samples) and boiled aluminium-treated water (finished drinking water) (21 samples). The purpose of classification was to determine whether the occurrence of the studied pesticides was affected by water treatment methods. Table 5.8 reveals that 10 out of 15 compounds were detected in the analyzed samples. The maximum number of studied compounds detected in a single sample was six ( $n = 1$ , finished drinking water sample). Isoprothiolane and

fenobucarb were detected with the highest frequency of 100.0% and 100.0%, 90.2% and 95.2%, and 100.0% and 81.0% in river, aluminium-treated and finished drinking water, respectively.

**Table 5.8: Detection frequency of studied pesticides in river water, aluminium treated water and boiled aluminium-treated water**

Pesticide compounds	Number of detected samples (detection frequency, %)		
	River water	Aluminium-treated water	Boiled aluminium-treated water
Isoprothiolane	20 (100.0)	19 (90.5)	21 (100.0)
Fenobucarb	20 (100.0)	20 (95.2)	17 (81.0)
Pretilachlor	9 (45.0)	13 (61.9)	10 (47.6)
Fipronil	6 (30.0)	7 (33.3)	10 (47.6)
Hexaconazole	3 (15.0)	6 (28.6)	6 (28.6)
Butachlor	2 (10.0)	2 (9.5)	2 (9.5)
Propanil	2 (10.0)	0 (0.0)	0 (0.0)
Buprofezin	1 (5.0)	1 (4.8)	1 (4.8)
Difenoconazole	0 (0.0)	0 (0.0)	1 (4.8)
Profenofos	0 (0.0)	0 (0.0)	1 (4.8)
Cypermethrin	0 (0.0)	0 (0.0)	0 (0.0)
Endosulfan	0 (0.0)	0 (0.0)	0 (0.0)
Propiconazole	0 (0.0)	0 (0.0)	0 (0.0)
$\alpha$ Endosulfan	0 (0.0)	0 (0.0)	0 (0.0)
$\beta$ Endosulfan	0 (0.0)	0 (0.0)	0 (0.0)

**Note:** - Number of analyzed river water was 20 samples  
 - Number of analyzed aluminium-treated water was 21 samples  
 - Number of analyzed drinking water (boiled aluminium-treated water) was 21 samples

For river water, eight studied compounds were detected. The detection frequency of analyzed compounds, in descending order, were isoprothiolane (100.0%), fenobucarb (100.0%), pretilachlor (45.0%), fipronil (30.0%), hexaconazole (15.0%), butachlor (10.0%), propanil (10.0%) and buprofezin (5.0%), respectively. This detection percentage is in line with the results of pesticide monitoring in surface water recorded in chapter 4. Regarding aluminium-treated water, only seven of eight compounds detected in river water were present. It appeared that herbicide propanil was able to be excluded from river water by the flocculating process. For finished drinking water samples, nine compounds were detected with two new compounds (difenoconazole and profenofos) while herbicide propanil was still not detectable. The trend of detection frequency of the analyzed compounds was similar to river water. However, the detection frequency in finished drinking water samples was increased compared to river water samples. The occurrence of difenoconazole and



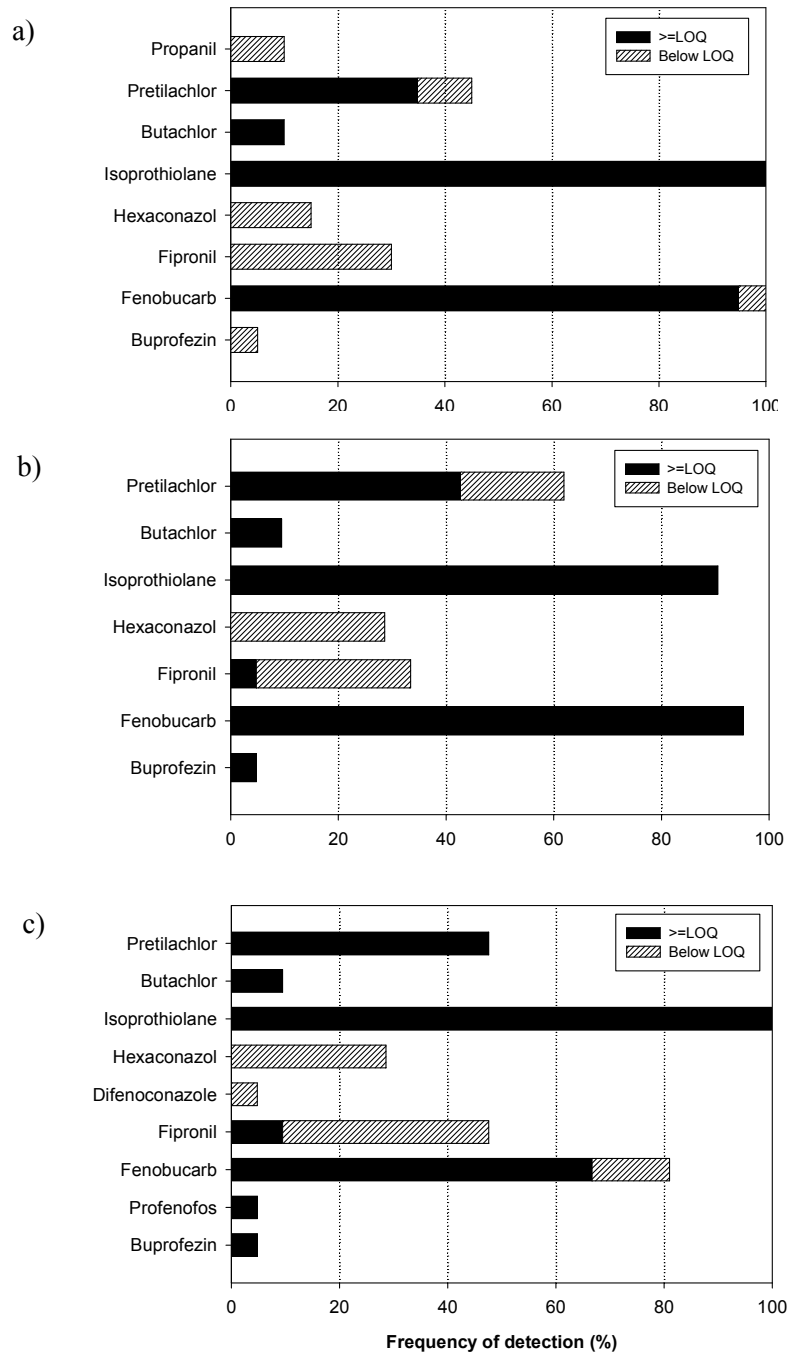
profenofos was only detected in finished drinking water. This is likely due to influence of extracted volume of samples and the physicochemical properties of the compounds. Extracted volume of finishing drinking water samples were often more than that of river and aluminium treated water samples due to clogging in the extraction processes for the latter. Therefore, concentration of some pesticide residues could be only quantified at the samples of which water volume was greater. Moreover, the concentration of several pesticides could have been increased due to influence of boiling, and consequently their residues in water samples may be detected after boiling.

### **Occurrence Frequency of Studied Pesticides with Concentrations $\geq$ LOQ**

An analysis of 62 samples revealed the differences between detection and quantification frequency of studied compounds in river, aluminium-treated and finished drinking water samples. Figure 5.4 a) shows that isoprothiolane and fenobucarb were quantified with a frequency of 100.0 and 95.0%, respectively. Pretilachlor was quantified with a relative high frequency of 35.0%. Although fipronil, hexaconazole, propanil and buprofezin were respectively detected with frequencies of 30.0, 15.0, 10.0 and 5.0%, they were lower than the limit of quantification (LOQ) (explained in chapter 4). The detection frequency of butachlor was 10.0%, and this was also its quantification frequency. For aluminium-treated water, seven out of 15 studied pesticides were detected. Hexaconazole fungicide was still not quantifiable in the analysis as showed in Figure 5.4 b). Although the detection frequency of fenobucarb and isoprothiolane were lower than what was found in river water, they were quantified with a frequency of 95.2 and 90.5%, respectively. Butachlor and buprofezin were quantified with a rather low frequency of 9.2 and 4.8%. Compared to river water, fipronil was quantified with a frequency of 4.8%. Additionally, the quantification frequency of pretilachlor was also higher than what was found in river water with a frequency of 42.9%.

Figure 5.4 c) depicts the occurrence of two new compounds, difenoconazole and profenofos, in finished drinking water. The results showed that nine out of the 15 studied pesticides were detected here. Nevertheless, difenoconazole and hexaconazole were not quantified in the analysis. On the other hand, isoprothiolane was quantified with a frequency of 100.0% in finished drinking water. Pretilachlor, butachlor, buprofezin and profenofos were all quantified with frequency of 47.6, 9.5,

4.8 and 4.8%, respectively. The quantification frequency of fenobucarb was lower compared to in aluminium-treated water, with a frequency of 66.7%. Fipronil in finished drinking water was detected with frequency higher compared to in aluminium-treated water, and its quantification also increased with frequency of 9.5%.



**Figure 5.4: Detection frequency of the studied pesticides in: a) river water, b) aluminium-treated water and c) finished drinking water**

There are differences in occurrence frequencies of studied pesticides and the number of compounds in the samples among three types of samples as above analysis. These differences are referred influence of four impact groups: the concentration of studied compounds in rivers/canals water, the physicochemical properties of studied pesticides, traditional water treatment methods and extracted volume of samples as passed through solid phase extraction cartridge columns. The influence of these factors is detailed in the following sections.

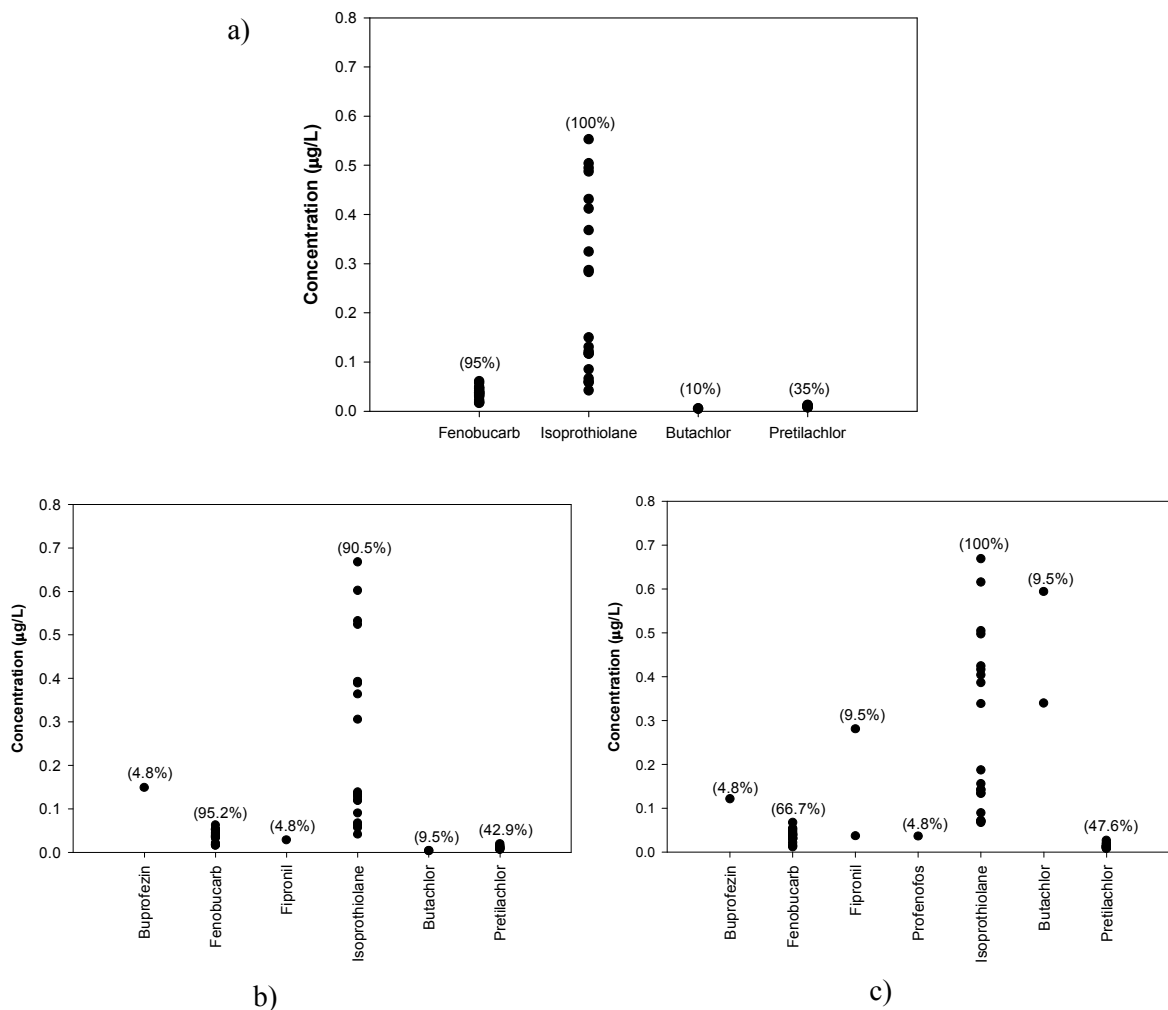
### **Concentrations of Quantified Pesticide Compounds in River, Aluminium-Treated and Finished Drinking Water**

The concentrations of studied pesticide residues in the river water samples are shown in Figure 5.5 a). Four out of 15 compounds were quantified including fenobucarb, isoprothiolane, butachlor and pretilachlor. Isoprothiolane was quantified in all samples, and its mean concentration was highest (0.26  $\mu\text{g/L}$ ). Fenobucarb was also quantified in the majority of samples (95%) with mean concentration of 0.04  $\mu\text{g/L}$ . Two herbicides compounds, pretilachlor and butachlor, were quantified in several samples with mean concentrations of 0.01  $\mu\text{g/L}$  for both.

Figure 5.5 b) depicted the concentrations of quantified pesticides in the aluminium-treated water samples. Isoprothiolane was detected with the highest mean concentration (0.26  $\mu\text{g/L}$ ) and quantification frequency (90.5%). Fenobucarb was the second compound detected in quantification frequency with the mean concentration of 0.04  $\mu\text{g/L}$ . Two herbicidal compounds, pretilachlor and butachlor, were still quantified with concentrations of 0.01  $\mu\text{g/L}$  for both. Two of other compounds, buprofezin and fipronil, were quantified with the mean concentrations of 0.15 and 0.03  $\mu\text{g/L}$ , respectively.

Seven pesticides were quantified in the finished drinking water samples as illustrated in Figure 5.5 c). Isoprothiolane occurred in all samples, and its mean concentration was 0.40  $\mu\text{g/L}$ . The mean concentration of fenobucarb was the same as in aluminium-treated water (0.04  $\mu\text{g/L}$ ), but its quantification frequency was reduced (66.7%). Pretilachlor and butachlor were quantified with the concentrations of 0.02 and 0.47  $\mu\text{g/L}$ , respectively. There was an increase in the mean concentration of

butachlor compared to its concentration level in aluminium-treated water. This herbicide was only detected in two samples of finished drinking water with high concentrations (0.59 and 0.34  $\mu\text{g/L}$ ) while there was no detection of this chemical in aluminium-treated water sample at two of these households. It could be due to contamination during boiling progress. Fipronil was also quantified with a higher concentration (0.16  $\mu\text{g/L}$ ) compared to aluminium-treated water. The mean concentration of buprofezin was 0.12  $\mu\text{g/L}$ . An insecticide compound, profenofos, was quantified with the mean concentration of 0.04  $\mu\text{g/L}$ .



**Figure 5.5: Concentrations of pesticide residues in a) river water, b) aluminium-treated water and c) finished drinking water samples. The numbers (in brackets above the dot plots) show the quantification frequencies.**

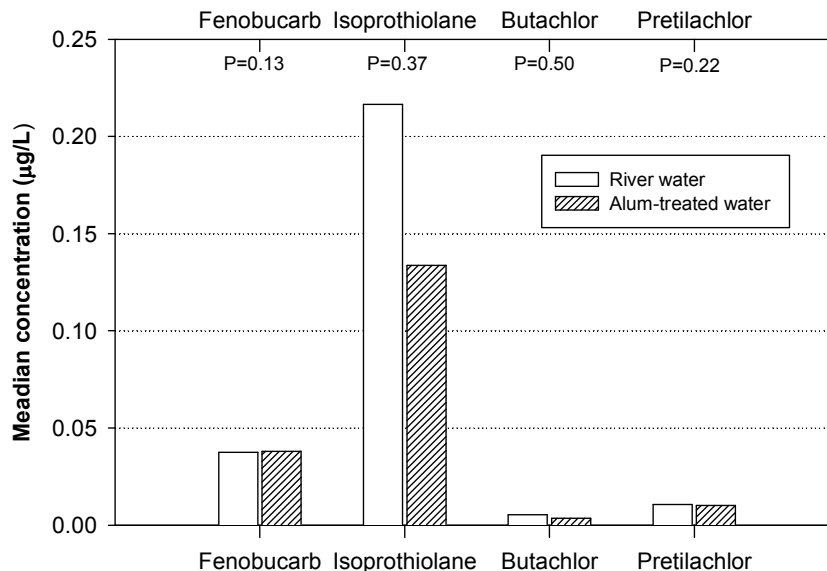
In water, the occurrence of pesticides as well as their concentration levels is dependent on physicochemical properties (solubility, hydrolysis  $DT_{50}$  and soil

absorption coefficient) and pesticide application frequency, use amount and time. In particular, treatment methods also affect the persistence of pesticides in the treated water samples. During the sampling period, both isoprothiolane and fenobucarb were detected in almost all samples. These two compounds are rather soluble in water, with solubilities of 54 and 420 mg/L, respectively (<http://sitem.herts.ac.uk/aeru/footprint/en/index.htm>). Isoprothiolane is also relatively stable in water, and the hydraulic  $DT_{50}$  of fenobucarb is 20 days (at condition of water temperature 20 °C, pH=7). Compared to other studied compounds, these two compounds were frequently applied to rice and fruit trees according to the pesticide use interviews. Pretilachlor was more frequently detected than butachlor. These two herbicides were mainly applied during the beginning of rice growing season (March and July of 2009) at the study area. Pretilachlor was used more commonly than butachlor by local people. Pretilachlor is soluble in water (50 mg/L) and relatively stable in water. Butachlor, on the other hand, is less soluble in water (20 mg/L) and its hydrolysis is quick (Chen and Chen, 1979). Buprofezin and fipronil were only quantified in aluminium-treated and finished drinking water, and they were present with low frequencies during the sampling time. This may be explained through their rather low solubility level (buprofezin: 0.46 mg/L and fipronil: 3.78 mg/L). However, they both are relatively stable in water. Moreover, this may be also influenced by extracted volume of samples. The extracted volume of river water samples were less than that of aluminium-treated and finished drinking water samples due to clogging of the cartridges. Once extracted volume is less, amount of a chemical in that volume is also less. If its concentration is low, the reduced extraction volume could be cause that the compound can not be quantified anymore. The occurrence and concentration of quantified pesticides affected the effectiveness of treatment methods were discussed in detail in the following.

### **Efficiency of Aluminium Sulfate for Removing Studied Pesticides from River Water**

The effect of aluminium sulfate was based on a paired comparison of pesticide concentrations between river water and aluminium-treated water (i.e. before and after water was treated with aluminium sulfate) at significance level of 5%. Figure 5.6 showed the median concentrations of four pesticides (fenobucarb, isoprothiolane, butachlor and pretilachlor), and P-value indicated whether difference of compounds in water before and after treated with aluminium sulfate. Buprofezin and fipronil were

not taken into the comparison due to insufficient data. It can be seen that there were no significant difference in the median concentration values of mentioned pesticides between river water and aluminium-treated water. The analysis results led to a conclusion that generally, aluminium sulfate was not significant at level 5% in removing the above mentioned pesticides from water.



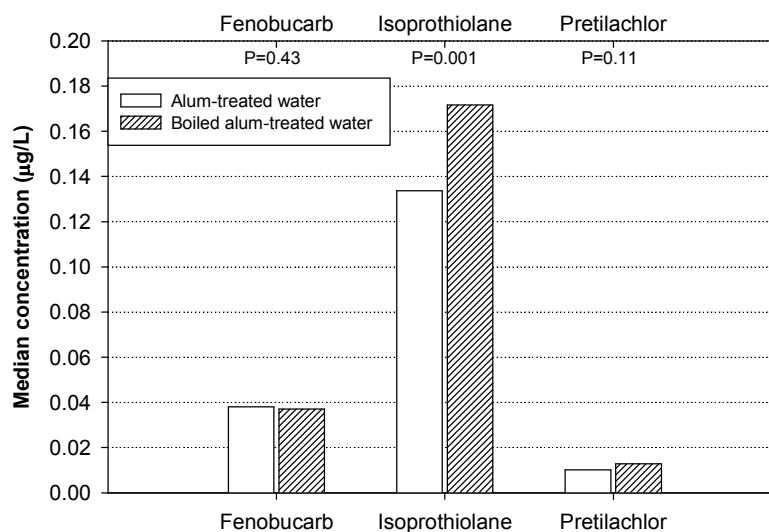
**Figure 5.6: Comparison of the median concentrations of pesticides in river and in aluminium-treated water. P-values indicate Wilcoxon Signed Rank test results. The difference of medians were compared at a significance level of 5%**

Aluminium sulfate is considered a typical coagulant which reduces the turbidity of water through removing suspended solids from water in water treatment system. This chemical is normally used in the beginning stage of water treatment process. Together with other chemicals (e.g. poly aluminium chloride, hypochlorite), aluminium sulfate is effective in reducing turbidity and destroying pathogen microbials (e.g. Escherichia Coli, Faecal coliform) (Sarkar *et al.*, 2006; Wrigley, 2007). It was found that no efficiency in using aluminium to exclude isoproturon (Sarkar *et al.*, 2006) and other organochlorine compounds (e.g. endosulfan-sulfate, hexachlorobenzene, heptachlor, aldrin) (Wrigley, 2007; Ormad *et al.*, 2008). The outcomes of this study are in line with the previous investigations for the quantified pesticides.

### **Efficiency of Boiling in Removing Studied Pesticides and Boiling Experiment**

The results of quantification previously showed that six studied compounds were detected in aluminium-treated water, and seven compounds were detected in boiled aluminium-treated water. Based on these results, it might be concluded there was no efficiency in boiling to reduce the detected pesticide residues. Hence, the efficiency of boiling was additionally investigated in a laboratory experiment. As showed in Figure 5.7, a paired comparison of three compounds fenobucarb, isoprothiolane and pretilachlor before and after boiling were conducted at a significance level of 5%. The remaining compounds were neglected due to lack of data. The results of comparison analysis indicated no significant difference on median concentrations of fenobucarb ( $P=0.43$ ) and pretilachlor ( $P=0.11$ ) in samples before and after boiling. In contrast, there was a significant difference of isoprothilane ( $P=0.001$ ) on median concentrations between aluminium-treated and boiled aluminium-treated water samples. The concentration of this pesticide residue after boiling was higher than that before boiling. The increase of residue concentration might be due to the relative high solubility (54 mg/L) and low volatility of isoprothiolane (its Henry's Law constant is  $1.00 \times 10^{-01} \text{ Pa} \cdot \text{m}^3/\text{mol}$ ). When samples were boiled, water in samples evaporated. Volume of water gradually reduced while isoprothiolane may be slowly or even not evaporated. Therefore, there was an increasing of isoprothiolane concentration after boiling. This could be the same to compounds which are less volatile than water. Their residues could be not quantified in samples before boiling if their concentrations are low. Nevertheless, they could be quantified after boiling due to that water in samples is lost, and therefore their concentration is increased.

When pesticides are present in water that would be boiled for domestic use, their fate might be mainly affected by volatilization and decomposes during boiling process. Therefore, a laboratory experiment on boiling water, which contained 15 studied pesticides, was conducted similar to local people's boiling practice to test the fate of pesticides.



**Figure 5.7: Comparison of the median concentrations of pesticides in aluminium-treated and boiled aluminium-treated water samples. P-values indicate Wilcoxon Signed Rank test results. The difference of medians were compared at a significance level of 5%**

Table 5.9 shows the results of the laboratory experiment. The recovery rate of the compounds in analytical process ranged from 83 - 114% with the exception of cypermethrin (33%). There were differences of the mean concentrations of these studied pesticides before and after boiling. Seven pesticides endosulfan, difenoconazole, propanil, fipronil, isoprothiolane, propiconazole and hexaconazole had an increase of concentrations after boiling. Six compounds had a reduction of concentrations after boiling. They include  $\alpha$ -endosulfan,  $\beta$ -endosulfan, profenofos, buprofezin, butachlor and pretilachlor. Insecticide fenobucarb likely not changed in its concentration before and after boiling process.

The environmental factors were neglected because all experiment samples were boiled under the same condition in the laboratory. Regarding the physicochemical properties, pesticides with the Henry's Law constant lower than  $10^{-2}$  Pa.m<sup>3</sup>/mol is found less volatile than water (Linde, 1994), and their concentrations in water often increase after boiling. The solubility also influence the volatility of pesticides in water. The higher pesticide solutes in water, the less its volatilization is. In addition, the weight of pesticide molecule and its concentration in water solution also rather affect to their volatilization. When molecular weight of a pesticide is large, its volatilization



is slow. And, the higher concentration of pesticide in water is, the faster it volatilizes because the more pesticide molecules present in water, so more pesticide reaches to surface and volatilizes (Linde, 1994). It could be reasoned for a compound less volatile than water that the lower its concentration is in water, it is less or even not volatile, and it therefore could be quantified in water sample after boiling.

**Table 5.9: Concentrations of pesticide compounds before and after boiling experiment and their recovery rate**

Compounds	Recovery rate (%)	Concentration (µg/L)			
		Before boiling		After boiling	
		Mean	Std. Dev	Mean	Std. Dev
Hexaconazole (*)	114.2	0.30	0.02	0.45	0.08
α_Endosulfan (**)	102.1	0.16	0.01	0.01	0.01
Propanil (*)	96.7	0.16	0.02	0.22	0.01
Pretilachlor (**)	95.4	0.17	0.02	0.16	0.01
Profenofos (**)	95.1	0.16	0.01	0.12	0.01
Buprofezin (**)	94.5	0.15	0.02	0.03	0.01
Butachlor (**)	92.7	0.16	0.01	0.05	0.01
β_Endosulfan (**)	92.5	0.15	0.01	0.07	0.01
Fenobucarb	91.9	0.15	0.02	0.15	0.01
Endosulfan (*)	89.3	0.16	0.01	0.17	0.002
Fipronil (*)	85.3	0.18	0.01	0.24	0.01
Isoprothiolane (*)	85.0	0.16	0.01	0.19	0.01
Difenoconazole (*)	82.8	0.17	0.03	0.21	0.06
Propiconazol (*)	82.6	0.17	0.01	0.22	0.01
Cypermethrin	32.6	0.05	0.01	n.d	n.d

**Notes:**

n.d : Not detected

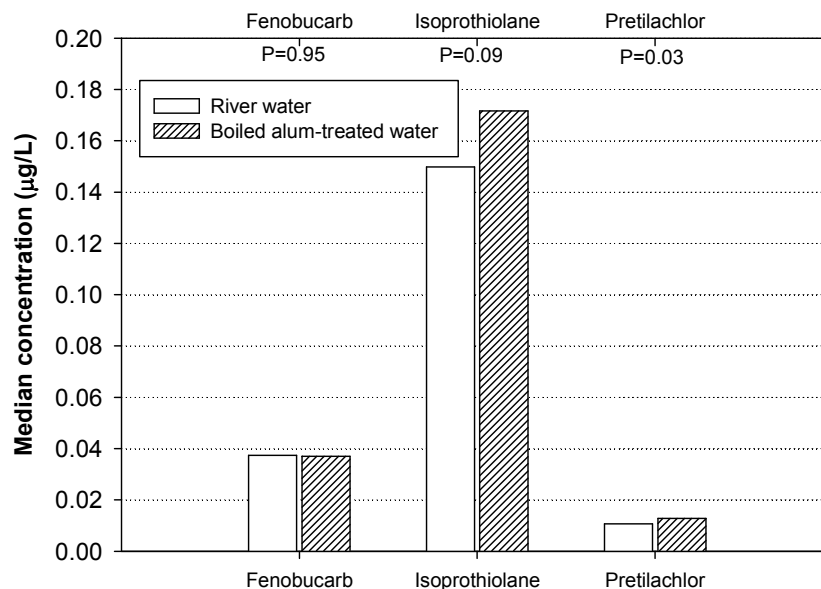
(\*) : Compound had a significant increase in concentration after boiling

(\*\*) : Compound had a significant reduction in concentration after boiling

The above properties were used to explain the difference of the mean concentration of pesticides before and after boiling. This is clearly underlying illustrated on the physicochemical properties of pesticides, shown in Table 2 of Annex 4. Furthermore, the literatures synthesized in Holland (1994) found that polar pesticides such as carbaryl was more soluble than the lower polarity ones. Compounds with low volatility or relative stability to hydrolysis (e.g. DDT, synthetic pyrethroids) might be low in loss of residues through boiling and their concentration were increased due to loss water, especially in cooking cereals or vegetables.

### The Effect of the Treatment Method in Removing Studied Pesticides from Drinking Water

The monitoring results showed that four studied compounds were quantified in river water source of drinking water, and seven compounds were quantified in boiled aluminium-treated water before drinking. In addition, it was noted that eight and nine compounds were detected in river and boiled aluminium-treated water, respectively. Without using statistical analysis procedure, it can be seen that traditional treatment method is not effective in removing the detected pesticides from drinking water. On the other hand, in term of concentration, a comparison of quantified residues between in river water and finished drinking water was conducted and displayed in Figure 5.8. The results showed that the difference was significant at 5% for pretilachlor ( $P=0.03$ ). The median concentration of this pesticide in drinking water was higher than in river water when water samples were passed traditional treatment method. There were not significant difference at 5% for fenobucarb ( $P=0.95$ ) and isoprothiolane ( $P=0.09$ ). The physicochemical properties of pesticides and environmental conditions as above mentioned are the factors that influence the efficiency of traditional treatment method in removing pesticide from drinking water.



**Figure 5.8: Comparison of the median concentrations of pesticides in river and boiled aluminium-treated water. P-values indicate Wilcoxon Signed Rank test results. The difference of medians were compared at a significance level of 5%.**

In summary, the traditional treatment method was not effective in removal of the studied pesticide compounds from drinking water. In contrast, this method created an enhancement of residue concentrations of several quantified pesticides. This finding showed that the traditional treatment method can not remove some pesticide residues from water for drinking purpose. This is opposite to several methods which were researched in the literatures previously. Pesticides could be removed from drinking water treatment processes such as oxidation, precipitation and adsorption techniques.

#### 5.2.4.4 Human Exposure Assessment to Pesticide Residues in Drinking Water

In this study, human health exposure to pesticide residues focused on exposure via digestive route (i.e. oral intake of drinking water originating from surface water). The assessment of exposure was carried out with determined exposure concentrations of pesticides at the sampling points (the households). The concentrations of quantified pesticide residues in water that local people used as drinking water were summarized in Table 5.10.

**Table 5.10: Descriptive statistics of exposure concentrations ( $\mu\text{g/L}$ )**

Pesticide compounds	Quantification frequency (%), n = 21	Min.	Mean	Median	Max.	WHO
						toxicity class
Isoprothiolane	100	0.07	0.27	0.17	0.67	III
Fenobucarb	66.7	0.01	0.04	0.04	0.07	II
Pretilachlor	47.6	0.01	0.01	0.01	0.03	IV
Butachlor	9.5	0.34	0.47	0.47	0.59	IV
Fipronil	9.5	0.04	0.16	0.16	0.28	II

The quantified frequency of the pesticides reflected the level of exposure to human health for these pesticides. The frequency of quantification ranged in descending order: isoprothiolane (100.0%), fenobucarb (66.7%), pretilachlor (47.6%), butachlor (9.5%), fipronil (9.5%), buprofezin (4.8%) and profenofos (4.8%). The mean concentration of pesticides were determined: 0.28  $\mu\text{g/L}$  for isoprothiolane, 0.04  $\mu\text{g/L}$  for fenobucarb, 0.01  $\mu\text{g/L}$  for pretilachlor, 0.47  $\mu\text{g/L}$  for butachlor, 0.16  $\mu\text{g/L}$  for fipronil, 0.12  $\mu\text{g/L}$  for buprofezin and 0.04  $\mu\text{g/L}$  for profenofos. None of these pesticides have guideline values in the National Technical Regulation of Vietnam for Drinking Water Quality (QCVN\_01, 2009). Several of these pesticides exceeded the

European Commission (EC) parametric guideline values for individual pesticides (0.1 µg/L) and the total of quantified residue concentration was also higher the EC guideline value for total pesticides (0.5 µg/L) (European Commission, 1998). In detail, the parametric guideline value for total pesticide concentrations was exceeded 24% of the samples. Regarding the parameter guideline value for single pesticide concentration, isoprothiolane, butachlor, fipronil and buprofezin were exceeded with a frequency of 76.2%, 9.5%, 4.8% and 4.8% of samples, respectively. Compared to United State national guideline, Health-Based Screening Level (HBSL), on drinking water quality established by U.S. Geological Survey (USGS), guideline values of the quantified pesticides does not set, with exception of profenofos (0.4 µg/L). Compared to Japanese guideline for drinking water, the detected pesticides are also not included in, except fenobucarb (20 µg/L) and isoprothiolane (40 µg/L). Japanese guideline values of each specific chemical in the quality standard for drinking water are calculated by assuming that a 50 kg person drinks 2 litres water per day (Hamilton *et al.*, 2003). Furthermore, World Health Organization (WHO) has also set guideline values for a number of pesticides in drinking water, but they do not include the pesticides in this study. In addition, according to WHO classification regarding the toxicity concept, fenobucarb and fipronil are moderately hazardous chemicals, and isoprothiolane is classified as a slightly hazardous chemical.

The exposure concentration (i.e. the chemical concentration at the point of contact) of pesticides was influenced by temporal and spatial effects. In regard to the temporal factor, the statistical analysis results of paired comparison showed that the median concentration of isoprothiolane was different at significance level of 5% ( $P=0.01$ ) between two sampling events: May and June. Meanwhile, the median concentration of fenobucarb was not significantly different ( $P=0.58$ ) between these two sampling periods. The difference might be due to time, amount and frequency of isoprothiolane use in agricultural activities at the study site. May was the end period of spring - summer rice crop, and June was the beginning period of summer - autumn rice crop. Fungicide isoprothiolane was often applied since the middle of rice growing stage. Isoprothiolane is also known to be stable to hydrolysis. Furthermore, concentration of contaminants in agricultural runoff in the beginning of rainy season is normally high (Schulz *et al.*, 2001).

Regarding spatial factor, the exposure concentrations of pesticide residues were compared in the samples taken in rivers and irrigation canals. The statistical results revealed that there was no significant difference in median concentration of isoprothiolane ( $P=0.12$ ) and pretilachlor ( $P=0.87$ ). However, there was a significant difference in the median concentration for fenobucarb ( $P=0.02$ ) between water in rivers and irrigation canals. The concentration difference between two levels of water bodies seemed due to solubility in water and pesticide application. Fenobucarb is good soluble in water (420 mg/L).

The exposure was also depending on the attitude of local people on the quality of river water used for domestic purpose. The interview results for the status of surface water quality showed that approximately 53% of respondents answered that surface water was polluted. More than 26% of respondent did not have answer about the quality of the water. The remaining stated that surface water was not polluted. Although local people knew that river water was polluted, they still had to use this source for domestic activities including for drinking with traditional treatments. On the other hand, several members of the households worked away from their home. For example, children studied in the school; adults farmed on the fields. If an assumption is given that exposure concentrations in drinking water away from home were equal to home exposure concentrations, all the people exposed to the pesticides in drinking water daily. In short, the above analysis showed that the local people were exposed to the quantified pesticides in drinking water. It may be referred that these people have been facing to risk from pesticide in their drinking water, sourced from surface water.

### **5.3 Conclusions and Recommendations**

#### **5.3.1 Conclusions**

Surface water is one of the main sources used as drinking water for residents living in rural and suburban areas of the Delta. The monitoring results revealed that the surface water of rivers and canals referenced in this research was polluted by several commonly used pesticides. Among the quantified compounds, isoprothiolane was detected in all samples (100%) with the highest mean concentration of 0.26  $\mu\text{g/L}$ . This was then followed by fenobucarb, pretilachlor and butachlor with detection frequencies of 95, 35 and 10% and mean concentrations of 0.04, 0.01 and 0.01  $\mu\text{g/L}$ , respectively.

Surface water was frequently treated with the traditional treatment methods, flocculation with aluminium and boiling. These methods have been effectively applied to eliminate turbidity and destroy waterborne pathogens in water for domestic demand. Nevertheless, these treatment methods could not remove the quantified pesticide residues from drinking water. Use of aluminium is effective in accelerating the settlement of sediment in water, but the quantified pesticide compounds could not be excluded from river water by this mechanism. Boiling practice could not remove several of the quantified pesticides. Unexpectedly, this practice could enhance the concentration of quantified pesticide residues due to the evaporation process. The most frequently quantified pesticide, isoprothiolane with the highest mean pesticide concentration (0.26 µg/L) in river water was lower than the concentration (0.28 µg/L) found in boiled water. The boiling practice was also tested with all of the studied compounds in a laboratory experiment. The results showed that phenomenon is similar to the pesticides quantified in the field samples. In addition, the experiment showed that boiling practice could reduce the concentration of few studied compounds such as buprofezin and profenofos. Storage time of aluminium treated water to pesticide residue concentration should be researched further in detail to assess efficiency of this practice.

Based on the monitoring results, it may be concluded that the participants in the study area were constantly exposed to pesticide residues. The exposure levels of several pesticides were critical compared to the European Union parametric guideline values. Presently, there are no guidelines regarding these compounds in the Vietnam national technical regulation on drinking water. Moreover, there may be serious health concerns when taking into account the WHO toxicity classification. However, it seems that the local communities are not aware of these dangers, and the water quality issue was rarely considered due to poor living conditions and lack of knowledge. It is necessary to implement research in detail on exposure to pesticide residues and the risks to human health and the environment in the Mekong Delta, especially in rural areas where surface water is the main source of drinking water.

### **5.3.2 Removal Measures for Pesticide Residues from Drinking Water**

The residues of studied pesticides were detected in surface water, which is one of the main sources of drinking water in rural area of the MD, particular in the dry

season. Consequently, the occurrence of these pesticide residues in non-treated drinking water is a certainty. Unfortunately, these pesticides are still present in drinking water that was treated by traditional treatment techniques which are applied by most local people. Field and laboratory experiments in this study showed that the current treatment techniques were ineffective in removing the quantified pesticides from drinking water, and it could enhance residue concentrations of several quantified pesticides due to evaporation mechanism. Other treatment methods including flocculation, sedimentation and filtration also were found to be impractical for removing the low concentration organic substances in drinking water (Chen *et al.*, 1996). In order to remove pesticide residues from drinking water it is essential to work with the people in rural area of the Delta.

Although the above mentioned traditional water treatment methods could not remove most detected pesticide residues from drinking water these methods should be advised for wide use because they can remove suspended materials and destroy pathogenic organisms from drinking water. Effective measures to mitigate pesticide residues in drinking water are appropriate pesticide use and management and application of mitigation measures to reduce pesticide residues in water from agricultural fields as proposed in the two previous chapters.

In order to mitigate exposure to pesticide residues from drinking water, local people should enhanced their knowledge and practice as to what is clean water use. The majority of rural farmers have little knowledge concerning clean water and the quality of the surrounding living environment. Farmers have to be aware of the presence of pesticide residues in surface water and other environmental problems. With assistance from local government, they can improve their own living environment.

Speeding up the Rural Clean Water Supply Program is a key measure in protection of rural populations from pesticide exposure through drinking water. This program has been employed by the National Centre for Rural Water Supply and Environment Sanitation since 1999. It is financed by the National budget and funded through international organizations such as World Bank (WB), Asian Development Bank (ADB), The United Nations Childrens' Fund (UNICEF), etc. However, the program has not yet reached its goal due to budget limitations. In addition, the cooperation of local people is an important point which decides the success of the program.

Therefore, a strategy of education and communication regarding clean water supply and use are very important for the program in the future. Once farmers enhance their knowledge of what is clean water use, the demand for clean water will increase. They would be willing to protect clean water supply systems and make financial contributions to construction of water supply facilities.

The Ministry of Agriculture and Rural Development and other relevant ministries as well as other social organizations have to provide farmers with necessary information about the water supply situation in the MD and create awareness of the link between water use and health. These organizations have responsibilities for establishing, supervising and managing policies and plans for rural water supply development.

Funds for construction of water supply systems in rural areas must be given strong attention. It could be supported from various sources such as government budget in the form of grants or loans, international donors, non-governmental organizations or even from farmer contributions. Funds for implementation of education and communication regarding to clean water use has to be put on the priority.

One of immediate measures to access clean water in rural area of the MD is to increase the number of jars or other container types used to collect rainwater. Rainwater should be a priority for use for both drinking and cooking. In order to employ the program of Rural Clean Water Supply, the development of appropriated and suitable water treatment systems is essential. The following methods were effective in removing some types of pesticide residues from drinking water. They should be tested in removing currently used common pesticides from drinking water in the Delta.

Preoxidation by chlorine could completely degrade some pesticides such as chlorpyrifos, dimethoate and molinate; however the technique was not effective in removal of other compounds. An average overall removal efficiency of 60% was achieved when treating a mixture of 44 different pesticide compounds in a sample by this technique. When ozone was used as an oxidant in the preoxidation process, the effectiveness of removing pesticide residues was up 70%. Preoxidation by ozone was incomplete in removing triazine compounds in the mixture. An intensive



treatment with ozone as an oxidant combined with coagulation-flocculation and activated carbon adsorption could remove up to 90% of the pesticide mixture (Ormad *et al.*, 2008). Ozone based advanced oxidation processes were proved effective in aqueous degradation of four major pesticide groups: carbamates, chlorophenoxy compounds, organochlorines and organophosphates (Weiner, 2000; Ikehata and El-Din, 2005).

The feasibility of a treatment method to remove pesticides from drinking water does not only depend on the effectiveness of treatment but also investment costs, particular in the cost of the main components of such a treatment system. Five low cost adsorbing materials, including wood charcoal, rubber granules, bottom ash, macro fungi *sajor caju* and *florida* were tested for effectiveness of removing 2,4-D and atrazine herbicides from drinking water. Wood charcoal showed the best effect in removing 2,4-D (92.7%) and atrazine (95.5%) followed by rubber granules (Alam *et al.*, 2000). In the Mekong Delta, wood charcoal is an abundant material and not expensive compared to rubber granules. However, wood charcoal may create disposal problems after it is exhausted from treatment system. When this herbicide adsorbing material is burnt at high temperature, it may lead to additional air pollution problems.

A residue mixture of pesticides could be removed from drinking water by using advanced oxidation techniques with photo catalyst (Chiron *et al.*, 2000; Herrmann and Guillard, 2000). According to Senthilnathan and Philip's report in 2009, three pesticides dichlorvos, methyl parathion and lindane or their mixture could be completely degraded and mineralized from drinking water by applying photodegradation with photo catalyst suspended or immobilized  $\text{TiO}_2$ . The degradation rate of these compounds was dependent on their initial concentration and degradation pattern. The impact on mixed pesticide samples was not similar to that of single compound.

Another intensive treatment process the coagulation - adsorption - nanofiltration approach can be used to remove pesticides from drinking water. Coagulation mainly reduces suspended, colloidal solids and microbial content in raw water due to formation of flocs at the time of coagulation. The adsorption process can remove several heavy metals and toxic organic compounds including pesticides. Activated

carbon is more effective in removing pesticides than other adsorbent substances such as bentonite or chitosan. The nanofiltration membrane was very effective in excluding pesticides and separating natural organic matters present in surface water. Nanofiltration was also efficient in reducing chemical oxygen demand (COD), total organic carbon (TOC) and hardness in water (Sarkar *et al.*, 2006). Hence, a combination of coagulation - adsorption - nanofiltration process is very effective in producing drinking water from surface water.

Pesticides and nitrates derived from agricultural effluent can be removed from water for drinking by combining biodenitrification and sand filter systems. The biological denitrification and pesticide adsorption takes place in continuous reactors equipped with plastic coil materials and powdered activated carbon. Nitrates in the effluent can be consumed by denitrification microorganisms living on supported plastic materials, and pesticides can be removed by plastic materials and powdered activated carbon. The effluent from the biodenitrification stage then enters the sand filter unit. Some pesticides could be removed with sand columns as they had a capacity to adhere to sand (Aslan, 2005). This treatment technique is effective not only in removing pesticides and nitrates but also turbidity as well as suspended solids from drinking water.

Pesticide residues from drinking water could be effectively reduced by the above intensive treatments. However, these intensive treatments are associated with high investment costs and sophisticated technologies. Energy demand and human capacity are also a hindrance for their application. Hence, the above intensive treatment methods can be only applied to centralized systems on a large scale in high density population zones. In rural areas of the Mekong Delta, people mostly live sparsely along rivers and canals or in residential clusters in the flooding areas. Decentralized water supply systems should then be a suitable model for clean water supply. Drinking water treatment stations on a small scale could be located inside or nearby residential clusters or communes. They would be low cost in construction, operation and in maintenance processes. In addition, the distribution piping system would be simple to construct and manage. A completed water treatment system is a key point to ensure a high quality water supply particularly with respect to pesticide residues. Given the above intensive treatment methods, a treatment method might be effective in removing pesticide residues and could be designed for drinking water

treatment in the rural and suburban areas of the MD. Such a system would include the following steps: primary settling - flocculation (aluminium sulfate) - settling - filtration (gravel/sand and activated carbon) - disinfections (chloride). This process could remove pesticide residues and other contaminants (sediment and pathogens) from water.

The technical standard for drinking water quality with regards to pesticide residues should be updated based on pesticide use as well as with reference of other established drinking water quality guidelines. Establishing this standard would be an effective tool in reducing and controlling pesticide residues in drinking water when it is used in regular monitoring campaigns.

*Chapter 6*  
**CONCLUSIONS**

The present study results revealed that agricultural production was significantly dependent on pesticides at the two study areas where intensive double rice cultivation and mixed agricultural farming was carried out in the Tam Nong District, Dong Thap Province and the Cai Rang District, Can Tho City of the Mekong Delta, respectively. The research conducted in the present study identified the types of pesticides presently being used in the Mekong Delta. Local farmers were shown to be using more than 100 types of pesticides containing up to 50 different active ingredients. Organochlorine and organophosphorus compounds were not predominant while insecticides consisting of pyrethroids, carbamates, nicotinoides and biopesticides and fungicides belonging to conazole group were frequently used.

All local farmers used knapsack sprayers for pesticide spraying and they seldom used personal protective clothing during pesticide application. Handling of pesticides before and at application (loading, mixing, washing and treating leftover pesticide solutions) was inappropriate and was carried out close to surface water bodies. There were no measures taken for preventing pesticide residue inputs into water bodies. Empty pesticide containers were in most cases improperly handled and discarded after use. In many cases pesticide containers were observed laying in the fields or near farmers' homes. The results of the present study also analyzed the problems associated with pesticide application and management by local farmers. The improper use and management practices used were found to be a serious cause for increased pesticide residue pollution in surface water in fields and irrigation canals of the Delta.

The present study demonstrated that the pesticide amount and spraying frequency in intensive rice cultivation were higher than that in mixed agriculture. Negative effects of improper pesticide application to human health and the environment were recognized by the majority of interviewed farmers. However, due to poor economic conditions and limited risk knowledge, farmers tended to favor pesticides as their key approach to pest management for enhancing crop yield. There was little consideration of environmental and health consequences. Environmentally friendly

farming measures, such as integrated pest management, have not been widely applied by the interviewed farmers and would add significantly to reducing pesticide contamination in surface water.

The intensive monitoring campaign for 15 commonly used pesticide active ingredients at the two study sites detected 13 pesticide residues in surface water in fields and canals. The number of samples with multiple occurrence of three pesticides was approximately 90% and 50% of collected samples at the intensive rice cultivation site at An Long (the Tam Nong District) and the mixed agricultural farming site at Ba Lang (the Cai Rang District), respectively. The two compounds most frequently detected at the two study sites were isoprothiolane and fenobucarb. Average concentrations of detected compounds ranged from 0.02 to 3.34  $\mu\text{g/L}$  at An Long and 0.01 to 0.37  $\mu\text{g/L}$  at Ba Lang. The study found that the average concentration of the compounds detected at the intensive rice cultivation site were mostly higher than that at the mixed agricultural farming site. The studied pesticides are not listed in the national technical regulation on surface water quality (QCVN: 08, 2008) with the exception of endosulfan pesticide. The average concentration of this compound exceeded the threshold value of surface water used for irrigation, with detected sample percentage of 2.6 and 17.4 % at Ba Lang and An Long, respectively. According to European Commission drinking water directive, the guideline parameter for a single compound (0.1  $\mu\text{g/L}$ ) was detected up to 92% and 59% of samples collected at An Long and Ba Lang. Approximately 89% and 12% of samples were detected with regards to guideline parameter for multiple compounds (0.5  $\mu\text{g/L}$ ) at An Long and Ba Lang, respectively. Given the present monitoring results, the first hypothesis of the study was correctly confirmed: that surface water in fields and irrigation canals of the MD is contaminated with residues of commonly used pesticides. Occurrence as well as concentration of pesticides is influenced by temporal factors (e.g. the stages of crop cultivation, calendar seasons and cropping seasons), spatial factors (e.g. up and downstream of canals, non - farming and farming areas), flooding and rainfall.

Surface water is one of the important water supplying sources for daily domestic activities as well as irrigation demand in the MD. In the areas without clean water supply system, local people use surface water for drinking. Surface water was usually treated by traditional methods consisting of flocculation, settling and boiling.

The present study found that when surface water was contaminated by several pesticide compounds, the traditional methods could not remove the pesticides from drinking water. Similar results were obtained in a laboratory experiment. Given these monitoring results, local people have been exposed to several pesticide residues in drinking water. The concentration of four out of seven compounds exceeded the guideline parameters for a single pesticide as stated by the European Commission drinking water quality directive. Furthermore, the detected compounds are not listed in the national technical regulation for drinking water quality by the Ministry of Health, in Vietnam. Additional, risk assessment research on the impact of for pesticide residues in surface water on human health and environment is essential.

Mitigation measures aimed at reducing pesticide contamination in water so as to increase human health and reduce environment pollution is urgently necessary. Appropriate mitigation measures in terms of proper pesticide use and management, limitation of pesticide residues in surface water from agricultural areas and removal of pesticide residues from drinking water were proposed in the research report. However, these measures will only be effective in improving health and living conditions of the farming community when local people's knowledge and farming practices as they relate to pest management are enhanced. In addition, significant government assistance and strong enforcement from central and local authorities is a critical pre-condition for success in limiting pesticide pollution and improving water quality. Co-operation of stakeholders is an important factor in order to first guide the farmers on how to use pesticides properly, second to increase yields and the quality of crops, and third to improve environmentally friendly agricultural production. If this is not done, the quality of surface water will be seriously decreased and agriculture development in the MD might become unsustainable in the future. It is also necessary to develop a comprehensive monitoring system associated with strict regulations and strong enforcement for causing pesticide pollution. The national technical regulations for water quality have to be regularly updated and effectively applied in monitoring and managing water environmental quality.

The program on Rural Clean Water Supply and Environmental Sanitation needs to be given a higher priority and the process streamline in order to make progress in the near future. People living in suburban and remote rural areas can access clean water by 2020 according to the plan of this national program. However, it is highly

possible that human health and the environment in a major part of the rural areas of the Delta would still be exposed to pesticide residues in drinking water if there are no mitigation measures to pesticide residues in place during the above planned period in these areas.

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## ANNEXES

### Annex 1: Pesticide Use in the Mekong Delta, Vietnam (Interview questionnaire)

Number: .....

Name of interviewee:.....

Date of interview: ....., Time started:....., Time finished:.....

Province:....., District:....., Commune:.....

#### I. General information of the interviewee

1. Gender  Male  Female
2. Age Year:.....
3. How long have you been staying in this commune?..... years.
4. How long have you been working in farming?..... years.
5. How many people live in your household presently?  
Number of family members:..... people

#### II. Information of agricultural activities

6. What is the size of your land for use?  
Production area: ..... (m<sup>2</sup>)  
Of which:
  - Paddy rice area:..... (m<sup>2</sup>)
  - Orchard area:..... (m<sup>2</sup>)
  - Other area:..... (m<sup>2</sup>)
7. Could you tell me about the crop(s) produced last year on this farm?

N <sub>0</sub> .	Type of crop	Crop season (exact time)	Cultivation area
			(m <sup>2</sup> )
1.			
2.			
3.			
...			

8. Which methods did you use to control and skill pests?
  - a.  IPM method
  - b.  Pesticide mainly

9. Pesticides were used in the last cropping season:

	Type of Crop	Name of pesticides	Stage of crops (Seedling, ... harvesting)	Time of use (Month or Season)	Amount /Dose (kg/ha)
Rice					
Veg.					
	....				

10. Who is the main person in deciding which types of pesticides are bought?

a.  The respondent

b.  Other family member. Please specify .....

11. Do you buy pesticides from one retailer?

a.  One

b.  Many retailers

12. Do you always buy the same brands of pesticides?

a.  Always the same

b.  Change regularly

c.  Change sometimes

13. Who is the main person in deciding when to apply the pesticides?

a.  The respondent

b.  The other family member. Please specify.....

14. Who is the main person in spraying pesticides?

a.  The respondent

b.  Other family members

c.  Hired applicators

15. Whom are you guided to use pesticides from?

a.  From pesticide shops/retailers

b.  From brand of pesticides

c.  From other famers

d.  From the extension workers

e.  Others (yourself from television, newspapers...)

16. Do you mix different types of pesticides before application?

a.  Yes

b.  No

16.1 If YES, do you mix the required quantity (recommended on the label) of each brand in the same water volume?

a.  Yes

b.  No

16.2 If YES, please specify the brand and mixture you use for the last cropping season.

Water volume of spraying container	Brand names	Dose of mix (gr or ml)/ container's volume
1. .... liter container		
....		

*Note: Volume of spraying container: 8 or 16 liter container*

16.3 Why do you mix the pesticides?

- a.  Unsure about the quality of pesticides
- b.  Uncertain about the effectiveness of pesticides
- c.  Imitating other applicators
- d.  Other reasons (please specify).....  
.....
- e.  No answer

17. What do you do for the leftover pesticides in the sprayer after application?

- a.  Pour into the fields/irrigation ponds
- b.  Pour into the canals
- c.  Store in the sprayer
- d.  Other, please specify.....

18. Where do you rinse sprayer after used?

- a.  In the fields/irrigation ponds
- b.  In the main canals
- c.  Others

19. Do you use any pesticide recommended for other crops, but you use them for rice?

- a.  Yes
- b.  No
- c.  No answer

If YES, please specify the following

Name of pesticides	Target crop specified on the label
1.	
2.	
3.	

20. What aspect is the most important in application of pesticides?





- a.  Yes                      b.  No                      c.  No answer

31. If YES, how many days after pesticide application?

Number of day: ..... days

**Annex 2: Category of pesticide compounds applied in two districts**

<b>No.</b>	<b>Groups of chemicals</b>	<b>Active ingredients</b>	<b>Trade names of pesticides</b>	<b>Chemical a.i. hazard category<sup>(1)</sup></b>	<b>Type of pesticides</b>
1.	Organophosphorus	Diazinon	Basudin 40 EC	II	Insecticide
		Dimethoate	Bitox 50 EC	II	Insecticide
		Profenofos	Selecron 500 EC	II	Insecticide
		Chlorpyrifos Ethyl	Dai Bang Do 700EC	II	Insecticide
		"	Mapy 48 EC	"	Insecticide
		"	Subside 505 EC	"	Insecticide
2.	Organochlorines	Endosulfan	Thiodan 35 ND	II	Insecticide
3.	Carbamates	Fenobucarb	Bassa 50 EC	II	Insecticide
		"	Bassan 50 EC	"	Insecticide
		"	Hopsan 75ND	"	Insecticide
		"	Anba 50 EC	"	Insecticide
		Carbofuran	Furadan 3 G	lb	Insecticide
		Carbaryl	Padan Nhat	II	Insecticide
	Propineb	Antracol 70 WP	IV	Fungicide	
4.	Pyrethroids	Alpha- cypermethrin	Cyper- alpha 5ND	II	Insecticide
		"	Fastac 5 EC	"	Insecticide
		"	Mospha 80 EC	"	Insecticide
		Cypermethrin	Cyrux 25EC	II	Insecticide
		"	Tungcydan 55 EC	"	Insecticide
		"	Serpal super 55EC	"	Insecticide
		"	Triceny 500 EC	"	Insecticide
		Deltamethrin	Decis 2.5 EC	II	Insecticide
		Lambda -cyhalothrin	Karate 2.5 EC	II	Insecticide
	Etofenprox	Trebon 20WP	IV	Insecticide	
5.	Conazoles	Difenoconazole	Tilt super 300EC	III	Fungicide
		Propiconazole	"	II	Fungicide
		Propiconazole	Filia 525EC	II	Fungicide
		Tricyclazole	Filia 525EC	II	Fungicide
		Hexaconazole	Anvil 5SC	IV	Fungicide
		"	Hexavil 8 SC	"	Fungicide
		"	Centervin 5SC	"	Fungicide
		"	Vivil 5 SC	"	Fungicide
		Propiconazole	Tilt 250 EC	II	Fungicide
		Tebuconazole	Nativo 750 WG	III	Fungicide
	"	Folicur 430 SC	"	Fungicide	
6.	Nicotinoids	Thiamethoxam	Actara 25WG	III	Insecticide
		Acetamiprid	Otoxex 200 SP	NL	Insecticide
		"	Mospha 80 EC	"	Insecticide
7.	Nitroguanidine	Dinotefuran	Oshin 20WP	NL	Insecticide
8.	Biopesticides	Abamectin	Abakill 3.6 EC	NL	Insecticide
		"	Abatimec 1.8 EC	"	Insecticide
		"	Abafax 1.8 EC	"	Insecticide
		"	Sieufatoc 50EC	"	Insecticide
		Validamycin	Validamycin A	IV	Fungicide
		"	Validacin 3 DD	"	Fungicide
		"	Validacin 5DD	"	Fungicide
		"	Tidacin 3SC	"	Fungicide
	Trifloxystrobin	Nativo 750 WG	III	Fungicide	
9.	Chlorinate phenoxy	2,4D	2,4D	II	Herbicide
		"	Anco 720DD	"	Herbicide
		"	Tiller S	"	Herbicide
		Fenoxaprop – P –	Whip – S 7.5 EW	NL	Herbicide

	Ethyl	Turbo 89 OD		Herbicide	
	”	Tiller 5EC		Herbicide	
	”	Tiller S		Herbicide	
	”				
10.	Amide	Butachlor	Meco 600 EC	IV	Herbicide
	”	”	Taco 600 EC	”	Herbicide
	”	”	Butanil 55 EC	”	Herbicide
	Pretilachlor	”	Sofit 300 EC	IV	Herbicide
11.	Sulfonylure	Ethoxysulfuron	Sunrice 15WDG	NL	Herbicide
	”	Pyrazosulfuron	Sirius 10 WP	IV	Herbicide
	”	Bensulfuron Methyl	Ankill 40 WP	IV	Herbicide
12.	Pyrazole	Fipronil	Regent 0.2 G; 5SC	II	Insecticide
	”	”	Chief 520WP	”	Insecticide
	”	”	Sespa gold 750WG	”	Insecticide
13.	Chitin synthesis inhibitor	Buprofezin	Aplaud 10 WP	IV	Insecticide
	”	”	Sam set 25 WP	”	Insecticide
	”	”	Hello 250 WP	”	Insecticide
	”	”	Apolo 40WP	”	Insecticide
	”	”	Penalty 40WP	”	Insecticide
	”	”	Difluent 10 WP	”	Insecticide
14.	Nereistoxin	Thiosultap- Sodium	Apashuang 95 WP	NL	Insecticide
	”	Bispyribac –Sodium	Nominee 10 SC	IV	Herbicide
15.	Quinolinecarboxylic acid	Quinclorac	Facet 25 EC	IV	Herbicide
16.	Phosphorothiolate	Isoprothiolane	Fuan 40 EC	III	Fungicide
	”	”	Fuji-one 40 EC	”	Fungicide
	”	Isoprothiolane + Tricyclazole	Bump gold 80WP	III	Fungicide
	”	”	”	II	Fungicide
17.	Molluscicides	Niclosamide	SP – Snailicide 700WP	NL	Molluscicide
	”	”	Snail 250 EC	”	”
	”	Metaldehyde	Nel Super 700 WP	II	Molluscicide
	”	”	Bolis 6B	”	Molluscicide
	”	”	”	”	Molluscicide
	”	”	”	”	Molluscicide
18.	Bipyridylim	Paraquat Ion	Cỏ cháy 20 SL	II	Herbicide
19.	Anilide	Propanil	Butanil 55 EC	III	Herbicide
20.	Others	Pyribenzoxim	Pyanchor 5EC	NL	Herbicide
	”	Pymetrozine	Chess 50 WG	III	Insecticide
	”	Fthalide + Kasugamycin	Kasai 16.2 SC	NL	Insecticide
	”	Azoxystrobin	Amistar top 325SC	NL	Fungicide
	”	Bismerthiazol	Sasa	IV	Fungicide
	”	”	Damaza Anti-xo 200WP	”	Fungicide
	”	”	Asusu 25WP	NL	Fungicide
	”	Indoxacarb	Asusu 25WP	”	Fungicide
	”	Chlorfluazuron	Ammate 150 SC	”	Insecticide
	”	Nitro benzen	Chief 520WP	NL	Fungicide
	”	Thiophanate – Methyl	Boom	IV	Fungicide
	”	Imidacloprid	Topsin M 70 WP	IV	Fungicide
	”	”	Sespa gold 750WG	NL	Insecticide
	”	”	Phenodan 10WP	IV	Insecticide
	”	”	Anvado 100 WP	II	Insecticide
	”	”	”	”	Insecticide
	”	MCPA (2-methyl-4-chlorophenoxyacetic	Tiller S	III	Herbicide

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acid) Carbendazim	Carbenvil 50 SC	IV	Fungicide
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<sup>(1)</sup>: Based on WHO's classification with regard to toxicity for human health, Ib: highly hazardous; II: moderately hazardous; III: slightly hazardous; IV: practically nontoxic or unlikely to present acute hazard in normal use; NL: Not listed (or un-classified). *Source*: Footprint pesticide database, 2009. Available at [www.herts.ac.uk/aeru/footprint/](http://www.herts.ac.uk/aeru/footprint/)

**Annex 3: Percentage of respondent farmers' answers concerning pesticide use and management in the two study sites**

	<b>Tam Nong</b>	<b>Cai Rang</b>
1. Who is the main person deciding which types of pesticides are bought?		
The respondent	95	83
Other family members	5	17
2. Do you buy pesticides from one retailer?		
One retailer	38	9
Many retailers	62	91
3. Do you always buy the same brands of pesticides?		
Always in same brand	0	0
Change sometimes	85	66
Change regularly	15	34
4*. Who are persons in spraying pesticides?		
The respondent	73	74
Other family members	13	20
Hired applicators	40	14
5*. Whom are you guided to use pesticides from?		
From pesticide shops/retailers	13	6
From brand of pesticides	20	17
From other farmers	55	63
From the extension workers	3	0
Others (yourself from television, newspapers...)	45	57
6. How do you decide to spray pesticides?		
Base on crop's symptom	80	77
Base on crop's schedule	3	17
Others (from other farmers...)	17	6
7. Do you mix the required quantity (recommended on the label) of each brand in the same water volume?		
Equal to recommended dose	55	66
Higher than recommended dose	45	34
Lower than recommended dose	0	0
8. Why do you mix the pesticides?		
Unsure about the quality of pesticides	28	20
Uncertain about the effectiveness of pesticides	48	77
Imitating other applicators	0	3
Other reasons	15	0

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No answer	9	0
9. What do you do for the leftover pesticide in the sprayer after application?		
Empty by spraying again	47	65
Pour into the field/ irrigation ponds	42	23
Pour into the canals	3	6
Others (store in the sprayer...)	8	6
10. Where do you rinse sprayer after use?		
In the fields/irrigation ponds	88	83
In the main canals	8	14
Others	4	3
11. How do you treat to empty pesticide containers after use?		
Apply simple treatment methods	0	23
Leave off in the fields/orchards	95	49
Keep around house for selling	5	28
12. What aspect is the most important in application of pesticides		
Costs of pesticides	55	71
Health effects	8	6
Environmental impacts	30	23
Other	7	0
13*. How are negative effects of pesticides after they are used?		
Kill fish	50	63
Decrease fish growth	10	14
Kill other organisms	18	3
Their health problems	53	37
No answer	0	0
14. Do you change the status of field before spraying?		
Yes	87	91
No	13	6
No answer	0	3
15*. Could you tell me which insects often damage crop?		
Leaffolder	65	34
Stem borders	3	0
Thrips	3	0
Brown planthopper	98	100
Other insects	0	11
16. Which methods did you use to control and kill pests?		
IPM method	15	14

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Pesticide only	85	86
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**Note:** (\*): Multi answers

#### Annex 4:

**Table 1: General description of the studied compounds**

Pesticides	Description
Buprofezin	Buprofezin is a chitin synthesis inhibitor for whitefly control. It is stable in acidic and alkaline media, and it is compatible with most other pesticides. Its commercial product is named Applaud, Penalty...
Cypermethrin	Cypermethrin is a pyrethroid insecticide applied to control a wide range of pests, especially Lepidoptera. This chemical is relatively stable in neutral and weak acidic media, very optimum stability at pH 4. It is compatible with many insecticides and fungicides, but incompatible with alkaline materials. Its trade names consist of Arrivo, Basathrin, Tungcydan, Triceny...
Endosulfan	Endosulfan is an organochlorine insecticide used to control sucking, chewing and boring insects on a wide range of crops. It is a mixture of two stereoisomers: $\alpha$ -endosulfan (Endosulfan I) and $\beta$ -endosulfan (Endosulfan II). It is slowly hydrolyzed in aqueous acids and alkalis. It is compatible with most pesticides, but incompatible with strongly alkaline materials. Its commercial names consist of Thiodan, Thionex...
Fenobucarb	Fenobucarb is a carbamate insecticide used to control a range of sucking insects including thrips, leafhopper and leaf rollers on rice and other crops. It is stable under normal storage conditions and hydrolyzed by acids and alkalis. Its commercial names consist of Bassa, Bassan, Hopsan...
Fipronil	Fipronil is a phenyl pyrazole insecticide used to control a wide range of pests including thrips, rootworms, weevils and termites on a variety of crops or non-crops. Its commercial products name Regent, Chief...

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Profenofos	Profenofos is an organophosphorus insecticide used on a wide variety of crops to control many pests, but mainly Lepidoptera and mites. It is relatively stable under neutral and slightly acidic conditions, and unstable under alkaline conditions. Its trade name includes Selecron, Curacron...
Butachlor	Butachlor is an amide herbicide used for pre-emergence control of grasses and some broad-leaved weeds, particularly rice crops. It is decomposed at 165 °C. It is compatible with other herbicides. Its trade name consists of Meco, Taco, Butanex...
Pretilachlor	Pretilachlor is also an amide herbicide used to control the main annual grasses, broad-leaved weeds and sedges in rice crops. It is relatively stable to hydrolysis. Its commercial products are named Sofit, Rifit.
Propanil	Propanil is an anilide herbicide used for broad-leaved or annual grass weeds control in rice and other crops. It is hydrolyzed in strongly acidic and alkaline media and stable at normal pH range. It is incompatible with a number of pesticides, particularly with carbamates and organophosphates. Its trade name consists of Butanil, Propanex...
Difenoconazole	Difenoconazole is a conazole fungicide with novel broad-range activity protecting the yield or crop quality by foliar application or seed treatment. It is stable up to 300°C. Its trade name includes Score, Tilt-supper.
Hexaconazole	Hexaconazole is also a conazole fungicide used to control both seed-borne and soil-borne diseases, particularly Ascomycetes. It is stable for over nine months at normal temperatures. Its commercial products are named as Anvil, Planete, Hexavil...
Isoprothiolane	Isoprothiolane is a fungicide with protective and curative action, adsorbed by the leaves or roots. It is used to control a range of diseases including rice blast, rice stem rot and other diseases. It is compatible with other pesticides. Trade names of this fungicide consist of Fuji-one, Fuan...

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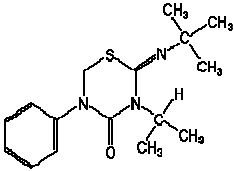
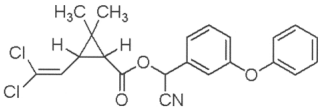
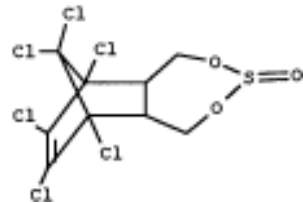
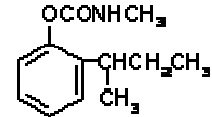
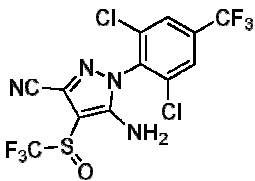
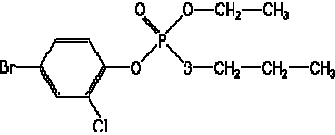
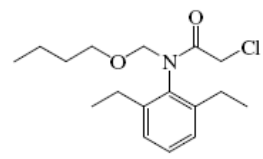
Propiconazole

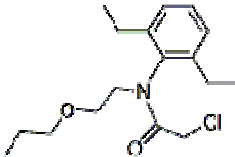
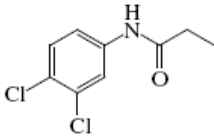
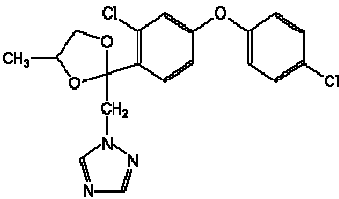
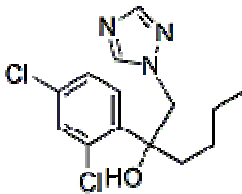
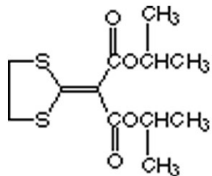
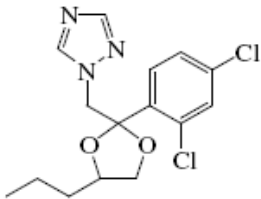
Propiconazole is also a conazole fungicide with a broad range of activity. It controls diseases on rice and other crops. It is stable up to 320 °C, and no significant hydrolysis. It is compatible with other fungicides. Its trade name consists of Filia, Tilt, Radar...

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**Sources:** Footprint pesticide database, 2009. Available at [www.herts.ac.uk/aeru/footprint/](http://www.herts.ac.uk/aeru/footprint/)

**Table 2: Several physicochemical properties of the target pesticides**

Pesticides	Chemical Formula	Molecular structure	Molecular mass	The Henry's Law constant (Pa. m <sup>3</sup> /mol) at 25 °C	Hydrolysis half-life DT <sub>50</sub> (days) at 20 °C and pH 7
<b>Insecticide</b>					
Buprofezin	C <sub>16</sub> H <sub>23</sub> N <sub>3</sub> OS		305.44	2.8 x 10 <sup>-02</sup>	Stable
Cypermethrin	C <sub>22</sub> H <sub>19</sub> Cl <sub>2</sub> NO <sub>3</sub>		416.30	2.00x10 <sup>-02</sup>	179
Endosulfan	C <sub>9</sub> H <sub>6</sub> Cl <sub>6</sub> O <sub>3</sub> S		406.93	1.48	20
Fenobucarb	C <sub>12</sub> H <sub>17</sub> NO <sub>2</sub>		207.27	-	-
Fipronil	C <sub>12</sub> H <sub>4</sub> Cl <sub>2</sub> F <sub>6</sub> N <sub>4</sub> OS		437.15	2.31x10 <sup>-04</sup>	Stable
Profenofos	C <sub>11</sub> H <sub>15</sub> BrClO <sub>3</sub> PS		373.63	1.65x10 <sup>-03</sup>	Stable
<b>Herbicide</b>					
Butachlor	C <sub>17</sub> H <sub>26</sub> ClNO <sub>2</sub>		311.90	3.74x10 <sup>-03</sup>	-

Pretilachlor	$C_{17}H_{26}ClNO_2$		311.85	$8.10 \times 10^{-04}$	Stable
Propanil	$C_9H_9Cl_2NO$		218.08	$4.4 \times 10^{-04}$	365
<b>Fungicide</b>					
Difenoconazole	$C_{19}H_{17}Cl_2N_3O_3$		406.26	$9.0 \times 10^{-07}$	Stable
Hexaconazole	$C_{14}H_{17}Cl_2N_3O$		314.21	$3.33 \times 10^{-04}$	30
Isoprothiolane	$C_{12}H_{18}O_4S_2$		290.40	$1.00 \times 10^{-01}$	Stable
Propiconazole	$C_{15}H_{17}Cl_2N_3O_2$		342.22	$9.20 \times 10^{-05}$	53.5

**Sources:** Footprint pesticide database, 2009. Available at [www.herts.ac.uk/aeru/footprint/](http://www.herts.ac.uk/aeru/footprint/)

**Table 3: Several parameters related to the physicochemical properties of studied compounds**

Parameters	Explanation	Thresholds	Classification
Solubility (mg/L)	The mass of a given chemical that can dissolve in a given water volume at 20 °C	< 50	Low
		50 - 500	Moderate
		> 500	High
Octanol - water partition coefficient (LogP)	The ratio of chemical concentration in octanol divided by its concentration in water. LogP is the logarithm of partition coefficient between octanol and water.	< 2.7	Low bioaccumulation
		2.7 - 3	Moderate
		> 3	High
Soil degradation half life (days)	The required time of a chemical concentration under field conditions to decline to 50% of the amount of application	< 30	Non persistent
		30 - 100	Moderately persistent
		100 - 365	Persistent
		> 365	Very persistent
Aqueous hydrolysis DT50 (days) at 20 °C and pH 7	The rate of a chemical decomposition induced by water at pH 7, expressed as DT50	< 30	Non persistent
		30 - 100	Moderately persistent
		100 - 365	Persistent
		> 365	Very persistent
Henry's law constant at 20 °C (dimensionless)	A measure of the concentration of a chemical in air over its concentration in water	> $2.5 \times 10^{-5}$	Volatile
		$2.5 \times 10^{-7}$ - $2.5 \times 10^{-5}$	Moderate volatility
		$2.5 \times 10^{-5}$	
		< $2.5 \times 10^{-7}$	Non volatile
Fish acute 96 hour LC50 (mg/L)	The lethal concentration of a pesticide required to kill half the member of	> 100	Low
		0.1 - 100	Moderate

	tested fish population after a 96 hour duration of test.	< 0.1	High
Aquatic invertebrates acute 48 hour EC50 (mg/L)	The concentration of a pesticide that can be expected cause a defined lethal effect in 50 percent of tested aquatic invertebrate population for 48 hour.	> 100 0.1 - 100 < 0.1	Low Moderate High

**Sources:** Footprint pesticide database, 2009. Available at [www.herts.ac.uk/aeru/footprint/](http://www.herts.ac.uk/aeru/footprint/)

### Annex 5:

#### Pesticide residues in surface water at sampling locations of Can Tho City in 2008

No.	Sampling locations	Organochlorine group (µg/L)	Organophosphate group (µg/L)
<b>Ninh Kieu District</b>			
1	Ben pha Xom Chai	n.d.	n.d.
2	Rach Tham Tuong	n.d.	n.d.
3	Cau Can Tho	n.d.	n.d.
<b>Binh Thuy District</b>			
4	Vam Sang Trang	n.d.	n.d.
5	Vam Tra Noc	n.d.	n.d.
6	Nha may nuoc 2	n.d.	n.d.
7	Tram Y te An Dong	n.d.	n.d.
8	Nga tu ong Huyen	n.d.	n.d.
<b>Cai Rang District</b>			
9	Cho Cai Rang	n.d.	n.d.
10	Vam Ba Lang	n.d.	n.d.
11	Vam Cai Con	n.d.	0.44
12	Vam Cai Nai	n.d.	n.d.
13	Vam Cai Cui	n.d.	0.12
14	Vam Cai Son	n.d.	n.d.
<b>O Mon District</b>			
15	Vam O Mon	n.d.	n.d.
16	Cho O Mon	n.d.	n.d.

17	Vam Rach Chanh	n.d.	0.21
18	Cho TT Bang Tang	n.d.	n.d.
<b>Co Do District</b>			
19	Cau Quay - TT Co Do	n.d.	n.d.
20	Cho Thoi Lai	n.d.	n.d.
<b>Thot Not District</b>			
21	Vam Thot Not	n.d.	n.d.
22	Cau Thot Not	n.d.	0.19
23	Nga Ba Ba Chieu	n.d.	n.d.
24	Cau Thom Rom	n.d.	n.d.
25	Vam Thom Rom	n.d.	n.d.
26	Vam Can Tho Be	n.d.	0.21
27	Cau Can THo Be	n.d.	n.d.
28	Cau Bac Duon	n.d.	n.d.
<b>Phong Dien District</b>			
29	Vam My Khanh	n.d.	n.d.
30	Cho Phong Dien	n.d.	n.d.
31	Nga ba Trang Tien	n.d.	n.d.
32	Nga ba S. Tra Nien	n.d.	n.d.
33	UBND xa Giai Xuan	n.d.	0.13
34	UBND xa Tan Thoi	n.d.	n.d.
35	Cau Lang	n.d.	n.d.
36	Nga ba Ong Hao	n.d.	n.d.
<b>Vinh Thanh District</b>			
37	Nga ba kenh so 10	n.d.	n.d.
38	Thi tran Thanh An	n.d.	n.d.

- n.d.: not detected

(Source: Can Tho DONRE, 2008)

**Annex 6:****Questionnaire on water use for drinking at the suburban of the Can Tho City****I. General information**

Number: .....

Interviewee's name:..... Gender:..... Age:.....

Date: ....., Time:.....

Address: .....

Coordinate of sampling location: .....

Residential time:.....years

Family size:.....people

**II. Information relating on water collection**

1. Which is the main type of water used for drinking water in your family?

- Surface water
- Rainwater
- Groundwater
- Other sources (tap water, bottled water)

2. Have you ever used surface water (from rivers, canals) for drinking?

- Yes
- No
- No answer

3. Why do you use surface water for drinking in your family?

.....  
.....

4. Which means do you often use in order to transfer water to jars?

.....  
.....

5. When do you often take water from rivers/canals into jars?

.....  
.....

6. Which tide do you offer to take water at (high tide, low tide, or as need)?

.....  
.....

7. How often do you take water into jars?

.....  
.....

8. How many liter of water does your family drink in a day?

.....  
.....

### III. Information related on water treatment

9. Do you treat surface water before drinking?

- Yes
- No
- No answer

10. If yes, could you talk about your water treatment ways?

Explanation:

.....  
.....

11. Which kind of chemical do you use to treat water after it is transferred from rivers/canals to jars?

.....  
.....

12. After treatment, do you transfer treated water in jars to other containers?

- Yes
- No
- No answer

13. After treatment, how long can you use water for drinking?

.....  
.....

14. Do you boil treated water before drinking?

- Yes
- No
- No answer

15. Could you tell me how you reserve boiling water?

- Keep hot water as hot beverages
- Keep cooling for drinking

16. Have you been ever heard that surface water is polluted?

- Yes
- No
- No answer



# CURRICULUM VITAE

## QUALIFICATIONS

<b>Years</b>	<b>Academic institutions</b>	<b>Major/ Specialty</b>	<b>Academic degree</b>
2007- Now	United Nations University & Bonn University, Germany	Pesticide use and monitoring their residues in surface water	PhD. Degree
2004-2006	The Catholic University of Leuven, Belgium	Water Resource Engineering	MSc. Eng.
1994-1999	Can Tho University, Vietnam	Hydraulic Engineering	B.Eng.

## PROFESSIONAL EXPERIENCE

<b>Years</b>	<b>Institution and address</b>	<b>Position and Responsibilities</b>
2007 - now	Department of Environmental Engineering, College of Environment and Natural Resources, Cantho University, Vietnam	Lecturer
1999 - 2007	Department of Environmental Engineering and Water Resources, College of Technology, Cantho University, Vietnam	Lecturer

## EXPERTISE AND RESEARCH INTERESTS

### Research interests

- Pesticide use and management in agricultural activities and monitoring their residues in surface water
- Monitoring and assessment on surface water quality and proposing the system of the score of indicator (benthic macro-invertebrates) for assessment water
- Monitoring and assessment on surface water quality through physicochemical parameters
- Participating on research on Water Resource Management in the Mekong Delta, Inco - Delta project

- Environmental Impact Assessment

### Research grants received

No	Project name	Funding institution	Project duration	Position/ role in the project
1	Water Related Information System for Sustainable Development in the Lower Mekong Delta-WISDOM	BMBF	2007-2010	PhD researcher
2	Undergraduate Curriculum Development for Environmental Engineering_VLIR E2	VLIR-IUC	1998-2007	Member and Master degree

### Publications and accomplishments

Pham Van Toan, Le Hoang Viet, Zita Sebesvari and Fabrice Renaud. 2011. Pesticide residues in drinking water: a case study in a suburban area of the Lower Mekong Delta. Can Tho University science journal, pp. 11.

Pham Van Toan, Zita Sebesvari, Vo Phuong Hong Loan and Fabrice Renaud. 2010. Monitoring and modeling the fate of commonly used pesticides in surface water of the Lower Mekong Delta. Proceeding of the EGU General Assembly 2010. Vienna, Austria. Vol. 12, EGU2010-743.

Toan Van Pham, Zita Sebesvari, Ingrid Rosendahl and Fabrice Renaud. 2009. Monitoring residue concentrations of recently used pesticides in surface water at two representative study sites of the lower Mekong delta Viet Nam. Proceeding of the International Session in the 18th Symposium on Environmental Chemistry. Tsukuba – Japan. 2E-11. June, 2009.

Pham Van Toan, Le Hoang Viet. 2008. Testing and establishing of bio-indicator scoring systems for assessment of fresh surface water quality in Can Tho, Vietnam. Can Tho University science journal. Pp. 931-941.