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Detection of Pesticide Residues in The Canal Irrigation System of The Upper Mekong Delta, Cambodia

Sombath Keo [a], Khy Eam Eang [a*], Chanvorleak Phat [b], Sereyvath Yoeun [b], Leakkhina Meak [b], Kong Chhuon [a], Sylvain Massuel [c]

[a] Faculty of Hydrology and Water Resources Engineering, Institute of Technology of Cambodia, Russian Federation Blvd., P.O. Box 86, Phnom Penh, Cambodia.

[b] Faculty of Chemical and Food Engineering, Institute of Technology of Cambodia, Russian Federation Blvd., P.O. Box 86, Phnom Penh, Cambodia.

[c] UMR G-EAU, IRD, Univ. Montpellier, Institute of Technology of Cambodia, Russian Federation Blvd., P.O. Box 86, Phnom Penh, Cambodia.

*E-mail: khyeam@itc.edu.kh

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Abstract

Pesticide refers to all chemical compounds which are mainly used in agriculture to control pests and weeds. In many developing countries, the increasing use of pesticides is due to agricultural activities for intensification purposes. The potential consequences for the environment, health and biodiversity are difficult to anticipate, as the presence of pesticides is difficult and rarely monitored. This is the case in the upper Mekong delta in Cambodia where many irrigation systems are being developed. The aim of the study is to provide a preliminary assessment of the situation by looking for the presence of pesticides in the water within a representative irrigation system. Water samples were collected in canals, river, irrigated rice field and groundwater in both dry and wet seasons. Solid-phase extraction (SPE) and gas chromatography-mass spectrometry (GC-MS) methods were used to purify and analyze the samples. Among 37 pesticides used by farmers and detectable, 6 were found in water. Paclobutrazol and propiconazole are moderately hazardous, hexaconazole is slightly hazardous, fluquinconazole presents acute toxicity and azoxystrobin is unlikely to present acute hazard. Hexaconazole and paclobutrazol are classified as highly persistent in water, while others are slightly to moderately persistent. Pesticides were found mostly in groundwater but they were found in the canals and rice field only in dry season. This means that pesticides may accumulate in the aquifer while the flooding has a flushing effect on pesticides. Further analyses should be extended to a bigger scale and be continued monitoring.

Keywords: Pesticide detection in water, Solid phase extraction (SPE), Gas chromatography-Mass spectrometry (GC-MS), Upper Mekong delta, Cambodia.

1. Introduction

Pesticide refers to all chemical compounds which are mainly used in agriculture to control pests and weeds (Kaur et al., 2019). Pesticides are natural, chemical, organic or inorganic, substances or mixtures intended to prevent, destroy, control or repel pests, and whose functional class commonly refers to their active ingredient and the type of pest they intend to control. Pesticide residues differ from pesticide since the residues result from the degradation of the active ingredient of the pesticide (Alavanja, 2009). Pesticides are able to move in various compartments of the environment through different ways such as drainage, drift, emission, leaching, or volatilization (WHO, 2008). This ability has serious implications for biodiversity and the food chain, posing high risks (Özkara et al., 2016). The use of pesticides has become essential in the modern agriculture around the world to improve the crop productivity and meet the quality standards of the agro-industry (Silva et al., 2019). Although pesticides play an important role in agriculture, massive use can bring negative impact on the environment, ecosystems and human health (Sharma et al., 2019). Agricultural activities are now considered as a major source of pesticides in the environment and have become the largest point and non-point source of pollution to surface water and groundwater (FAO & IWMI, 2017). This raises serious environmental and health concerns. The high rate of pesticide consumption and inappropriate methods such as spraying and direct application to water are considered the main cause of the environmental pollution (Deknock et al., 2019).

In Cambodia, pesticides were first used in the early 1960s. In 1980, only 7% of farmers used pesticides on their crops. From 1985–1994, this figure rose to 49%. According to a survey conducted in 2004 (Preap & Sareth, 2015), approximately 67% of farmers used chemicals on their crops at least once a year. Cambodia officially imported approximately 200 tons of pesticides in 2002, including insecticides, herbicides, fungicides, and rodenticides (Ministry of Environment Cambodia, 2004). In 2019, about 81,098 tons were imported from Thailand and Viet Nam. Some smaller amounts were also imported from the People's Republic of China and the European Union (ADB, 2021). At the same time, Cambodian farmers have experienced health problems caused by pesticide poisoning due to lack of practical knowledge of how to handle the products and the absence of technical advice (Matsukawa et al., 2016). Other health problems as well as ecosystem and biodiversity disruption can therefore be expected due to pesticide exposure. For example, the fishery is part of local livelihoods and may be threatened by pesticide poisoning. Floodplain such as the Bassac-Mekong River region is particularly vulnerable to these threats as it experiences expansion and intensification of agriculture in seasonally flooded areas. The circulation of water in these irrigated systems is not clearly defined, nor is the transport and distribution or storage of pesticides in water. The present paper thus proposes to draw up an initial assessment of the situation in the different hydrological compartments (river, canal, etc.) of a small representative irrigation system where mainly rice, vegetables and mango trees are grown. The study was conducted in both dry and wet seasons and water samples were analyzed for pesticides.

2. Methods

2.1. Study area

The study area was located in Koh Thum district, Kandal province, in the Cambodia upper Mekong delta (Figure 1). In this tropical region, the dry season extends from December to April, with total monthly rainfall less than 50 mm. During the wet season, the monthly total rainfall varies from 100 to 300 mm (Vandome, 2020). The canal irrigation system, namely the prek system, is a succession of earthen canals dug perpendicular to the river that divert the flood waters to the floodplain. Their erection dates back to the 20th century, during the French colonial period. The objective was to fertilize the floodplain and improve the crop yield. Multiple programs were recently funded to rehabilitate the prek system and promote agriculture intensification to reduce poverty (Pratx, 2017; Vandome, 2020). The study area focuses on two Preks, a rehabilitated (Prek Chann) and a non-rehabilitated (Prek Touch).

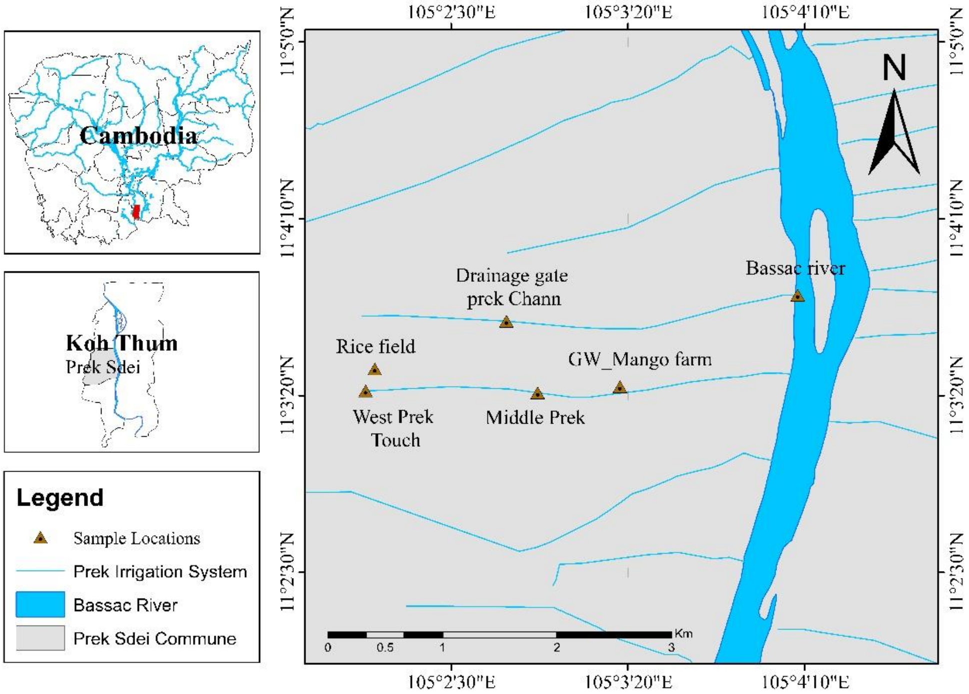


Figure 1. Sample locations and Prek systems in Koh Thum district

2.2. Determination of the pesticides in use locally

Having an interview of the pesticides used locally is important to help interpret the analyses, even though the sources of pesticides may come from upstream or from past uses. A non-exhaustive list of pesticide currently in use was obtained after interviewing the local farmers and retailers (Frick, 2020). The retailers interviewed served up to 9 villages and 300 customers in the Koh Thum area. The interviews were conducted with input from social scientists from the French National Research Institute for Sustainable Development (IRD) and the Royal University of Agriculture (RUA) in February 2020. In the region, retailers act as technical advisors and can provide detailed information on the products used, their targets and the times of use.

2.3. Reagents and standard solutions

Sodium phosphate buffer solution (pH=7.0, 1mol/L), dichloromethane (ACS BASIC), acetone, n-hexane (HPLC grade), sodium sulphate, nitrogen gas, PLS3 and activated carbon (AC) cartridges were used for sample preparation prior to gas chromatography and mass spectrometry (GC-MS) analysis. A 0.1 ml of Internal Standard (IS) was added into each sample solution before performing the GC-MS measurement. In addition, external standard solutions of pesticides were prepared with 6 different concentrations: 0.025 ppm, 0.05 ppm, 0.1 ppm, 0.125 ppm, 0.5 ppm and 1 ppm. They were obtained by dilution from the original standard solution at 10 ppm to determine, if present, the absolute concentration of a list of 27 pesticides.

2.4. Water sampling and sample preparation

The water samples were taken from all the hydrological compartments, namely the Bassac River, rehabilitated (Prek Chann) and non-rehabilitated (Prek Touch) canals, the aquifer and the irrigation water from a rice field. Samples were collected in March and in November 2020 (mid-dry season and late rainy season, respectively) (Figure 1). Water samples were collected in triplicate in pre-washed plastic bottles (1 L) at 6 sites and immediately stored in a cool box at 4°C before being transported to the SATREPS laboratory at the Institute of Technology of Cambodia, Phnom Penh, Cambodia.

The water samples were then filtrated through a 2-µm glass microfiber filter (Whatman GF/C^{TM}) using a vacuum pump to remove suspended solids and avoid blocking cartridges during extraction process (Darko et al., 2008).

The solid-phase extraction (SPE) was performed after the filtration. A volume of 1 mL of sodium phosphate buffer solution (pH=7.0, 1 mol/L) was added to the water samples to adjust pH, then homogenized and left to rest for 1h. The sorbent PLS3 attached with AC cartridge were activated by conditioning with 5 mL of dichloromethane, 5 mL of acetone and 10 mL of purified water. This ensures that the cartridge is moist and clean. Then the samples were passed through the cartridge by a vacuum pump at a flow rate of approximately 15 mL/min. All cartridges were then dried by evaporation with a nitrogen gas stream for 30 min. The dried cartridges were disassembled, and the PLS3 was washed with 2 mL of acetone and 5 mL of dichloromethane. The cartridge was finally eluted using 5 mL of acetone under suction by a vacuum pump. The mixed eluted solvent was collected in a glass tube and concentrated with nitrogen gas stream for approximately 1 h to obtain 1 mL of solution. Then, 10 mL of n-hexane was added to the concentrated solution and dehydrated by elution through a filter of sodium sulphate (Na_2SO_4). The solution obtained was concentrated again to a volume of 1 mL using nitrogen gas stream, and finally transferred into the vial. The vial was brought to analyze immediately with GC-MS or stored at -20ºC (Darko et al., 2008; Kafilzadeh, 2015; Liu et al., 2016; Jin et al., 2019).

2.5. Gas chromatography-mass spectrometry settings

Pesticides were analyzed using gas GC-MS device, model TQ8040 series (Shimadzu, Japan) with 451 pesticide molecules available in the mass spectrometer (MS)database for identification. The DB-5ms were used with a column 30 m long, 0.25 µm thick and 0.25 mm in diameter (30 m × 0.25 µm × 0.25 mm). Samples were injected with a volume of 1 µL into the GC-MS system under the following conditions: spitless injection mode, injector temperature of 230°C, ultra-pure helium as a carrier gas with constant flow mode of 1.46 mL/min. The column oven temperature was set for 2 minutes at 40°C and increased to 310°C for 5 minutes at a rate of 8°C/min. The ion source temperature was 200°C and the temperature of the interface was 300°C, while electron impact ionization was at 70 eV. The sample was analyzed by the scanned mode at mass range (m/z) from 45 to 600 (Table 1).

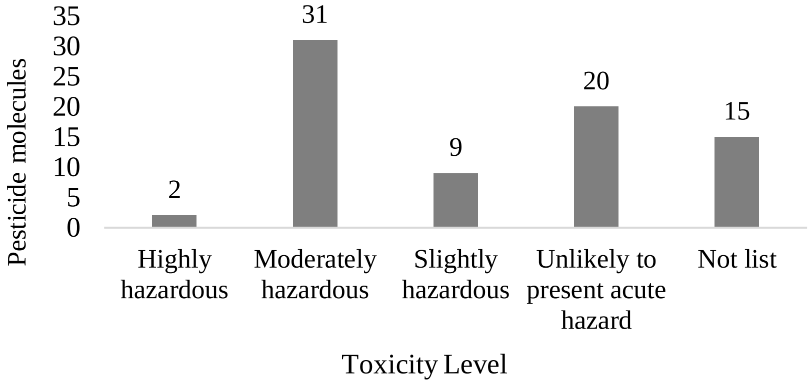
Table 1. GC-MS analytical conditions

GC-MS, model TQ8040 series (Shimadzu, Japan)			
GC	Condition	MS	Condition
Injection Temp.	250°C	Interface Temp.	300°C
Column Oven Temp.	40°C – 310°C (8°C /min)	Ion Source Temp.	200°C
Injection Mode	Spitless	Event Time	0.3 sec
Sampling Time	1 min	Mass Range	m/z 45–600
Carrier Gas Control	He (40 cm/sec)		
Injection Volume	1 µL		

3. Results

3.1 Pesticide usage in local

Results from interviews indicated a wide variety of products being in use. They were used to treat different types of pests, including insects, weeds, fungi, bacteria, mites, molluscs and rodents. The list mentioned, 77 different molecules were identified and potentially present in the water: 39% were insecticides, 30% were herbicides, 22% were fungicides and 9% were for other specific purposes. According to the WHO classification of pesticide toxicity (2019), most of them are classified moderately hazardous (31 molecules), but none of them are extremely hazardous (Figure 2). In details, the molecules identified were 28 different organochlorines contained in 63 products, 4 neonicotinoids contained in 16 products, 4 pyrethroids contained in 11 products, 1 organophosphorus (glyphosate) contained in 4 products (with high sales volumes according to retailers), 3 organophosphates contained in 11 products, 4 micro-organism derivative molecules contained in 16 products, 6 urea molecules contained in 10 products, 5 carbamate molecules contained in 5 products, 6 aryloxy phenoxy propionate molecules contained in 10 products, 1 strobilurin (also called azoxystrobin) contained in 5 products, and some other molecules with many nitrogen atoms and aromatic cycles. Among these 77 molecules, 37 were in the MS database, thus potentially detectable in the equipment.



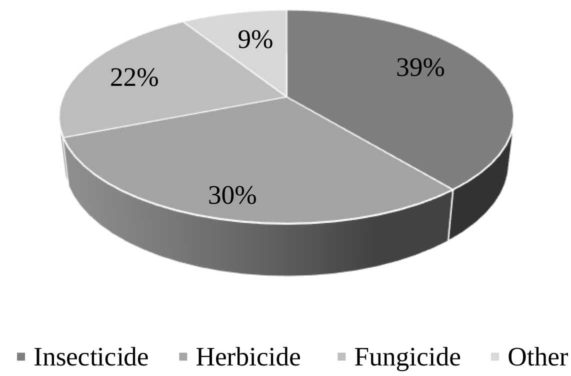


Figure 2. a) Classification of pesticide molecules in Koh Thum district based on WHO toxicity list b) Types of pesticides used in Koh Thum district

3.2 Pesticide analyses

The following 5 molecules were found in the mid-dry season samples: fluquinconazole, hexaconazole, pretilachlor, paclobutrazol, and propiconazole. None of them could be accurately measured as they were not included in the list of the 27 available standards. No pesticide was found in the Bassac River. Fluquinconazole was found in the drainage gate in Prek Chann and pretilachlor was found in the rice field water. Hexaconazole and pretilachlor were found in the middle of the non-rehabilitated Prek Touch. Hexaconazole, paclobutrazol, and propiconazole were found in groundwater. All molecules found were fungicides except pretilachlor that is herbicide. Regarding the WHO toxicity classification, hexaconazole is moderately hazardous, paclobutrazol, and propiconazole are slightly hazardous, and fluquinconazole is recognized as having an acute toxicity in the GHS classification (Globally Harmonized System of Classification and Labelling of Chemicals).

Table **Error! No text of specified style in document.**. Pesticide molecules detected in dry season in Koh Thum district

Pesticide compounds	Dry season					
	Bassac river	Drainage gate	Rice field	West Prek Touch	Middle Prek Touch	Mango farm
Fluquinconazole	-	+	-	-	-	-
Hexaconazole	-	-	-	-	+	+
Pretilachlor	-	-	+	-	+	-
Paclobutrazol	-	-	-	-	-	+
Propiconazole	-	-	-	-	-	+

-: not detected, +: detected

The following 4 pesticide molecules were detected in the water samples of the late wet season: hexaconazole, paclobutrazol, propiconazole and azoxystrobin. They were all found in groundwater and detected also in dry season, except azoxystrobin that is a fungicide and classified as unlikely to present acute hazard toxicity.

Table 3. Pesticide molecules detected in wet season in Koh Thum district

Pesticide compounds	Wet season					
	Bassac river	Drainage gate	Rice field	West Prek Touch	Middle Prek Touch	Mango farm
Hexaconazole	-	-	-	-	-	+
Paclobutrazol	-	-	-	-	-	+
Propiconazole	-	-	-	-	-	+
Azoxystrobin	-	-	-	-	-	+

-: not detected, +: detected

4. Discussion

A total of 6 different pesticides were detected in both dry and wet seasons. This figure seems low compared to other research in other countries. For instance, Duong (2022) has reported sixteen pesticide were identified in a total number of 15 samples in Giang province, Vietnam. However, few points were sampled and only water was analyzed. Some pesticides have better affinity with soil and biota. This could explain why only 6 pesticides were found among the 37 pesticides detectable by the equipment and used in the area. One pesticide (fluquinconazole) was detected but not listed as being currently used by farmers which probably means that further investigations are needed to complete the list of pesticides used or that fluquinconazole has been used in the past.

The spatial distribution of the detected pesticide provides interesting information. The Bassac River is unlikely a source of pesticide transport as there is no detection in both seasons. The dry season is a period with large cropping area. Farmers are pumping water from the preks and spray pesticides throughout the plant's growth cycle. The excess irrigation return flow is drained by the preks or is stored in ponds in the low-lying areas. This is when pesticides were detected in the preks and rice field. In the rainy season, much of the area is flooded and cannot be cultivated. The cultivated fields receive heavy rainfall and are drained by the prek system. The flow from the Bassac flushes the preks towards the south. This can explain why no pesticides were detected in the preks in wet season. However, pesticides were detected in both season in groundwater which means that there is a flow exchange with the surface water, probably a groundwater recharge through the ponds in the low-lying areas. The aquifers may accumulate and store some pesticides. These pesticides can be then pumped back by the local population for domestic use. This represents a significant health risk for the population in contact with this water or for aquatic life. The rehabilitated preks are deepened which may also increase the flow exchange with the groundwater and thus the pesticide transfer.

5. Conclusion

The detection of pesticides in the Cambodian upper Mekong delta during the dry and wet seasons was an important step to understand pesticide use and fate and potential health threat in the region. Despite the impossibility of carrying out quantitative analyses, the presence of 6 pesticides were detected in the different water samples, namely hexaconazole, pretilachlor, paclobutrazol, propiconazole, azoxystrobin and fluquinconazole. Only fluquinconazole was not listed as being currently used by farmers. No pesticides were detected in the Bassac River. In the dry season, pesticides were found in various part of the irrigation systems suggesting that this low flow period is favorable for the concentration of pesticides in surface waters. In the rainy season, the seasonal flooding has probably a flushing effect on canals and rice fields and no pesticides were detected. However, pesticides were present in groundwater in both seasons, meaning that pesticides can be transferred from the surface to the aquifer with the water flow exchange. A possible accumulation of pesticides in groundwater may represent a significant risk to local people who use groundwater as domestic water supply. It would be recommended to multiply the sample locations and to better understand the pesticide distribution in water. Pesticide with recognized toxicity should be selected and analyzed using standard solutions for better risk assessment.

6. Acknowledgments

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