

INTRODUCTION

Paraquat is a bipyridyl herbicide (IPCS, 1984), which is used widely in agriculture since 1962. It has been used in Chanthaburi province for several decades. Products of paraquat are commercially available both in liquid and granular form. Gramoxone is the most common trade name for paraquat (Watts, 2001). It is a non-selective contact herbicide and is used to prevent and eliminate moisture absorption weed.

The important of hazardous chemicals used in agriculture was documented in 2011 (January - March), which was illustrated that there were up to 36,434 tons of imported paraquat and expected to increase every year. The trend of agrochemical usages in Thailand was increased after organochlorine pesticides (OCPs), such as DDT, aldrin, dieldrin, and endrin, were banned during the years 1980-2004 (Keithmaleesatti et al., 2007). According to the report of land use in Chanthaburi province, farmers have turned to use paraquat, which resulted in the paraquat becoming the most favorite herbicides. The US EPA has classified paraquat as a plausible human carcinogen, where it is very toxic to aquatic organisms and may cause long-term adverse effects on human and ecological health, which leads to serious environmental problems. Paraquat has been used to eliminate weed in Chanthaburi province for many decades. Therefore, it is likely that it is widely distributed and accumulated in environment, in air, water, soil, plants, and animals. WHO (2009) has classified paraquat as the class II toxic substance (moderately toxic). It has been shown that the exposures of paraquat to farmers and agricultural workers can affect the development of nerve system or brain, skin, and the reproduction with possible birth defects (PAN, 1996).

Chanthaburi province is located in eastern Thailand where the land use in this province is mainly for agriculture. The majority of the land is used as orchards for the production of wide varieties of fruits. It has been reported that 70.46 % are fruit orchard (Provincial Agriculture Extension Office in Chanthaburi, 2009). The Chanthaburi River is one of the water sources for agricultural use in Eastern

Thailand. It runs through the agricultural areas in Chanthaburi provinces, with around 120 km long from the origin of the river (Jayakody, 2007; Leadprathom, 2009). The usage of paraquat as herbicides may cause a hazardous effect to living organisms in farmlands and also contaminate soil, water, and environment. It may exist as residues in soil or washed off into the river by rainwater runoff and accumulate in the sediment of the river water during the rainy season.

An assessment of potential environmental risks can be estimated numerically using the HQ approach (US EPA, 2006). The HQ is a ratio, which can be used to estimate whether the risk of harmful effect is likely or not due to the contamination of herbicides in the area.

The Water Quality Index (WQI) is an assessment of general water quality calculated from the various measured parameters of water quality. The values of WQI can be used to indicate the level of water quality of the water body.

MATERIALS AND METHODS

Sample preparation

The soil and water samples were randomly collected in the selected study area in both dry season (March 2011) and wet season (May 2011). The sampling was conducted in early wet season and also during the period of fruit-harvestings, where large amounts of pesticides were applied in orchards. Freshwater was also observed at stations 1 - 4, while brackish water was found at stations 5 and 6. Water samples were collected using Kemmerer sampler at mid-depth of the mid-stream for the determination of water quality and the detection of paraquat. Water samples used for an analysis of fecal coliform bacteria (FCB) were collected at the depth of 30 cm of the mid-stream of river water.

Surface soil samples were collected at the depth of 0 - 15 cm along the river bank. Three grab samples of composite soils were randomly collected for each sample to make a total of 1 kg, and transported to the laboratory for analyses. Soil samples were air-dried under shade, crushed, and sieved to remove the particles greater than 2 mm.

It has been shown that more than 90% of herbicide contaminants are those of particles smaller than 2

mm present in soil surfaces (Dennis and Zupko, 1995).

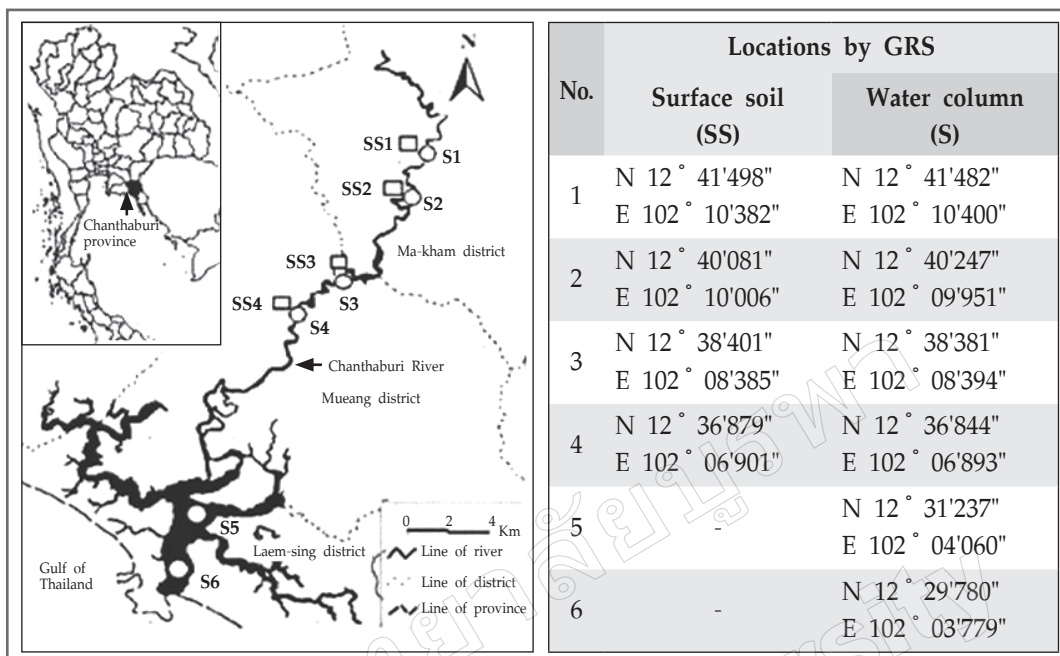


Figure1. Showing sampling locations for surface soil (SS □) and water column (S ○) in the Chanthaburi River and vicinity areas(modified from the Region of Environmental Office 13, 2010).

The quality control of analytical process in laboratory

Paraquat measurement was calibrated against three replicates of standard concentrations of paraquat dichloride obtained from Dr. Ehrenstorfer GmbH, Germany (<http://www.analytical-standards.com>) and used as reference materials for an analysis of paraquat residues

Analyses of the samples

Physical and chemical characteristics of surface soils were analyzed for following parameters, i.e., pH, organic matter (Walkey and Black, 1984), texture (Sheldrick and Wang, 1993), and cation exchange capacity-CEC (Chapman, 1965). The determinations of Paraquat concentrations in those collected surface soils and water samples were carried out using the method of spectrophotometer (Tatong, 2010).

The physical and chemical characteristics were analyzed both at the field stations and in the laboratory (APHA, 1998). The determination of water quality index (WQI) was estimated for eight parameters, i.e., dissolve oxygen (DO), biological oxygen demand (BOD), fecal coliform bacteria

(FCB), pH, total phosphate, nitrate-nitrogen (NO_3^- -N), turbidity, and total solids (TS) values. The WQI was calculated using equation obtained from the National Sanitation Foundation, as follows:

$$\text{WQI} = \sum_{i=1}^n w_i q_i \quad (1)$$

n = number of parameter

w_i = unit weight of parameter

q_i = the quality of parameter (PCD, 2010)

Potential environmental risks

The potential threat of adverse effects on living organisms and environment (HQ) may cause by several factors, i.e., effluents, emissions, wastes, and resource depletion, which resulting from community's activities. The HQ can be obtained by calculation using the following equation:

$$\text{HQ} = \frac{\text{EEC}}{\text{Screening benchmark}}$$

EEC = estimated maximum concentration of environmental contaminant in the soil or water at the selected sites.

Screening benchmark = maximum allowable concentrations of paraquat; if the concentration is lower than the concentration at this level, the contaminant is not likely to cause any harmful effects.

If HQ < 0.1 no hazard exists.
 If HQ 0.1- 1.0 hazard is low.
 If HQ 1.1 – 10 hazard is moderate.
 If HQ >10 hazard is high.
 (US EPA, 2006).

All data were processed and adjusted to obtain the 95% of confidence interval ($P < 0.05$) using SPSS statistical program for window (version 18.0).

RESULTS

Physical and chemical characteristics of samples

It was found that physical and chemical characteristics of surface soils samples collected from the selected study areas were considered to be a good quality for agriculture. They were consisted of loam and silt loam, with clay content lower than 26% and organic matter (OM) more than 2%.

Results are summarized in Table 1. The concentrations of paraquat detected in surface soils in dry and wet seasons were in the ranges of 3.33 to 8.28 and 1.30 to 9.15 mg/kg dw, respectively, as shown in Figure 2. The highest concentration of paraquat was found at station 1 in both seasons. However, there was no significant difference between seasons. The determination of HQ of surface soils by using the screening benchmark based on the lethal ingestion dose of paraquat in human (HSDB, 1992) showed that there were no evidence of potential environmental risks in both seasons, where the HQ < 0.1 with low hazardous effect, and HQ was in the ranges of 0.1-1.0.

The concentrations of paraquat detected in water samples collected from the selected study sites in dry and wet seasons were in the ranges of 0.13 to 7.13 and 0.07 to 13.05 $\mu\text{g/l}$, respectively, as shown in Figure 2. The determination of HQ using the screening benchmark based on the water criteria and protection of freshwater aquatic life (established by Canadian Council of Ministers of the Environment) showed that the potential environmental risks of paraquat in water samples were low concentration as almost the same as those in surface soils.

Table 1. Physical and chemical characteristics of surface soil samples.

Seasons	Stations	Sand (%)	Silt (%)	Clay (%)	Texture	pH	OM* (%)	CEC* (cmol/kg)
Dry season	SS1	22.5	52.4	25.2	silt loam	5.47	4.68	13.72
	SS2	26.2	49.6	24.2	loam	5.50	3.82	12.24
	SS3	41.1	40.4	18.5	loam	5.00	2.72	8.41
	SS4	28.5	45.1	26.4	loam	4.60	3.7	12.38
Wet season	SS1	24.7	49.0	26.3	loam	4.93	3.38	12.30
	SS2	26.1	48.6	25.3	loam	5.27	3.32	11.75
	SS3	44.3	36.5	19.2	loam	4.63	2.66	8.67
	SS4	41.1	38.5	20.4	loam	5.30	4.45	9.35

* OM = organic matter CEC = cation exchange capacity

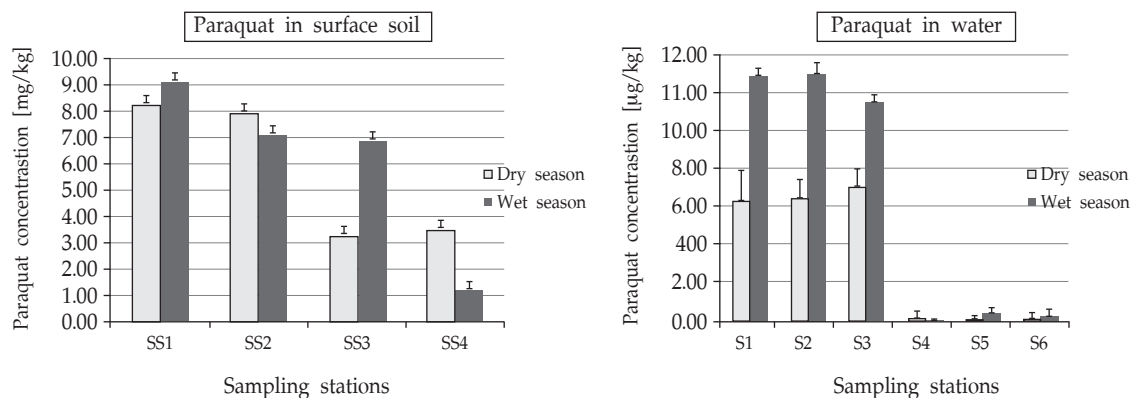


Figure 2. Paraquat concentrations detected in the river water collected at the selected sites of the Chanthaburi River and vicinity areas

It was found that there was no significant difference between paraquat concentrations detected in water samples collected in each season. Concerning water characteristics, as shown in Table 2 and WQI, water samples collected from the selected sites in

the Chanthaburi River were classified as good quality water as natural water, where the values were in the range of WQI = 71 -100. Results are summarized in Table 3.

Table 2. Physical and chemical characteristics of water samples collected from the selected sites in the Chanthaburi River.

Stations	Turbidity (NTU)	pH ^a	DO ^a (mg/l)	BOD ^a (mg/l)	Total Phosphate (mg/l)	NO ₃ ⁻ - N ^a (mg/l)	TS (mg/l)	FCB ^a (MPN/100ml)
Dry season								
S1	2.56	8.0	6.78	1	0.0108	0.17	36.00	40
S2	3.89	7.5	5.54	2	0.0038	0.19	28.00	70
S3	3.26	7.1	4.29	2	0.0073	0.07	32.00	40
S4	5.59	6.9	3.16	8	0.0231	0.07	21152.00	150
S5	4.57	7.5	5.69	7	0.0038	0.08	35397.33	300
S6	3.78	8.0	4.60	8	0.0021	0.10	37225.33	<30
Wet season								
S1	4.60	7.5	7.28	4	0.0401	0.39	188.00	2670
S2	4.56	7.5	6.39	4	0.0821	0.27	205.33	≥24000
S3	5.52	7.5	5.50	4	0.0576	0.24	222.67	1650
S4	9.65	7.2	6.33	4	0.0471	0.17	12078.67	930
S5	14.50	7.8	5.44	4	0.1468	0.73	34657.33	≥24000
S6	3.85	7.5	7.85	4	0.0725	0.13	25268.00	2100
Water quality standard	-	5-9	2-6	1-4	-	5	-	1,000-4,000
a = standard of water quality for surface water (PCD, 1992)								

TS = total solid; DO = dissolved oxygen; BOD = biological oxygen demand;
FCB = fecal coliform bacteria; NO₃⁻ - N = nitrate-nitrogen

Table 3. Water Quality Index (WQI) for river water samples collected from the selected sites of the Chanthaburi River

Class*	Water quality		Stations	Dry season		Wet season	
	Criteria	WQI		WQI	criteria	WQI	criteria
1	very good	-	S1	94	good	85	good
2	good	71-100	S2	90	good	74	good
3	fairly good	61-70	S3	87	good	84	good
4	bad	31-60	S4	69	fairly good	80	good
5	very bad	0-30	S5	78	good	63	fairly good
			S6	73	good	82	good

* Type of surface water (PCD, 1992)

Class1. Water resources, no waste water from all activities.

Class2. Water resources for consumption must sterile, aquatic animals conservation, aquaculture, swimming and water sports.

Class3. Water resources for consumption through the sterile process and improving water quality and agriculture.

Class4. Water resources for consumption through the sterile process and improving water quality and industrial.

Class5. Water resources used for transport.

DISCUSSION

Paraquat concentrations detected in water samples collected from the selected sites in the Chanthaburi River are considered to be at high levels. This may be due to the loose structure of soils existed in the study areas, allowing the rain water to wash off paraquat in soil and draining into river water. It was shown that the physical and chemical characteristics of soils collected from the study areas were loam with low content of clay. According to the properties of loam soil, the cation exchange capacity (CEC) is less than that of clay (Osotsapa et al., 1998). The adsorption of paraquat in this kind of soil is rather poor, particularly in wet season with high amount of water runoff. It also might be due to the large amount of paraquat which was applied prior to sample collections in early wet season before fruit harvesting. Paraquat in soil is quickly absorbed to the plant and can destroy green plant tissues. However, there are many types of soil microorganisms that can degrade the paraquat residual, such as *Corynebacterium fascians*, and *Clostridium pasteurianum* (Baldwin

et al., 1996). The soil capacity to adsorb paraquat may be limited if the clay content is low, resulting in the degradation occurs at a very slow process. The continuous applications of paraquat may cause toxic effects on crops (Isenring, 2006). Because the paraquat concentrations detected in soils and water samples did not exceed the level of the quality standard references, the hazardous effects on human health of local people might not be at risks. It has been documented that water criteria and protection of freshwater aquatic life established by Canadian Council of Ministers of the Environment should be at the concentration of 16 µg/l, and the lethal ingestion dose of paraquat in human is 35 mg/kg (HSBD, 1992). Even though the risks are very low and there are no environmental risks occur in this area, the application of paraquat should be done carefully and correctly for the safe ecosystem for the next generation.

Concerning the characteristics of water samples and WQI, the water body in the Chanthaburi River can be classified as good quality water as natural water. However, the values of some parameters

exceeded the values of the quality standard references (PCD, 1992), such as BOD at stations 4 and 6 during dry season, and FCB at stations 2 and 5 during wet season. The low quality of water samples collected at station 5 during wet season might be due to high activities of aquaculture as well as rain water runoff.

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