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Impact of Pesticide Use on Organophosphorus and Organochlorine Concentration in Water and Sediment of Rawa Pening Lake, Indonesia

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ABSTRACT
Rawa Pening, a Lake in Central Java, Indonesia, serves as a source of power, irrigation and flood control and is used for fishing. Due to highly intensity agriculture activities surround the lake, it might be contaminated by pesticides. The aims of this study were to survey the pesticide usage and to detect pesticide concentrations on water and sediment of Rawa Pening Lake. A questioner observation was used to inventory the types of pesticides used. Gas chromatography equipped with Flame Photometric Detector (FID) detector was used to analyze selected pesticide concentrations of water and sediment samples. The findings survey showed that profenofos organophosphate are most commonly being used in the Rawa Pening Lake, followed by Carbamate, Deltamethrin, Imidachloprid, Fentoat, Carbosulfan, Carbofuran and Lamda Sihalotrin. No organochlorine pesticide was used by the farmers. Both pesticide residue levels of selected organophosphates and organochlorines in water ranged from Below Detection Limit (BDL) to 0.054±0.039 mg L^{-1} and Below Detection Limit (BDL) to 0.016±0.008 mg L^{-1}, respectively. Whereas, the residue level of organophosphates detected in sediment samples ranged from Below Detection Limit (BDL) to 0.199±0.083 kg^{-1}, while organochlorine ranged Below Detection Limit (BDL) to 0.067±0.032 mg kg^{-1}. Profenofos was the highest detected pesticides and exceeded the prescribed standards. This study proved that the presence of organophosphorus contamination in the Rawa Pening Lake due to pesticide usage in Rawa Pening Lake areas. While, the banned organochlorine pesticide compounds were still detected in the lake because of possible usage of these chemicals illegally at the present or in the past.

Key words: Lake Rawa Pening, pesticide residues, organophosphorus, organochlorine

INTRODUCTION
The use of pesticides, herbicides and fungicides in Indonesia began when the government launched various intensification programmes, such as, 'BIMAS' (mass guidance), 'INSUS' (special intensification) and 'SUPRA INSUS' (super special intensification) in 1970s (Mariyono *et al.*, 2010). They have introduced an integrated rice cultivation system known as '*Panca Usaha Tani*' (Five Farming Effort) in which one of the content of this program was pesticide usage for the eradication of Crop Pest and Disease (Mariyono, 2009). Consequently, large-scale application of these toxic materials in agriculture areas might contribute to the presence of those compounds in

surface and ground water, lakes, estuary and ultimately in the coastal areas. Contamination can occur through drainage from surrounding terrain, precipitation from the atmosphere, accidental spills of pesticides in the watershed area or a cross-connection in a distribution system (Flint, 2012).

Rawa Pening Lake is situated in a low area surrounded mountains and rolling hills so that water flows from the upper reaches flow through the flow of the river to the estuaries at Rawa Pening. The area surrounding this lake is highly intensive agricultural activities where pesticides are largely used. Rice paddy and vegetables are cultivated in the border lake that either sprayed with large amounts of pesticides during growing season. This condition causes the occurrence of pollution in the Lake Rawa Pening catchment area that led to disruption of ecological balance. The pesticide pollution problem is persistent bioaccumulative toxic substances that do not degrade easily in the environment, slowly metabolized, often increasing in concentration within the food chain (Alava and Gobas, 2012). The pesticide residues may pose the problem of chronic toxicity to animals and humans surrounding lake through air, water and foods intake (Pazou *et al*., 2013).

Organophosphate is the type of pesticide that big enough utilized to replace chlorinated hydrocarbon pesticides after banned and restricted circulation based on the Stockholm Convention on May 22, 2001 (Yoder, 2003). This pesticide compounds contains H_3PO_4 (phosphoric acid), which are toxic but the active ingredients of pesticides organophosphate more easily degraded in nature, sooner lost activeness (Balali-Mood and Saber, 2012). While, organochlorine pesticides are very persistent, bioaccumulative and toxic and its residues remain possible still accumulated in the water and sediments of Lake Rawa Pening (Sucahyo *et al*., 2008).

Evidence from a variety studies of pesticide pollution within the last decade proved that pesticide residues are still being detected in the biotic, water and sediment of the lake (Darko *et al*., 2008; Musa *et al*., 2011; Erkmen *et al*., 2013; Otieno *et al*., 2014; Pazou *et al*., 2014). Few studies of pesticide residues has been carried out in Indonesia, such as organochlorine residue in pepper plantation (Wiratno *et al*., 2007), coral tissues (Sabdono *et al*., 2007a, b), human milk (Burke *et al*., 2003), foodstuff from traditional market (Shoiful *et al*., 2013) and household wells (Sabdono *et al*., 2008). To date, no study or survey of pesticide residues has been carried out in Rawa Pening Lake, a natural Lake in the Central Java that has experienced a negative long term detrimental effects due to an high agriculture intensity, sedimentation, pollution and even tourist related damage. Recently, the pollution of lake waters have attention by the government and Lake Rawa Pening is one among 15 lakes which need to be protected from water pollution (MoE., 2013). Therefore, the study of organophosphorus and organochlorine contents in water and sediments of Lake Rawa Pening is urgently needed. The purposes of this study were to survey the pesticide usage and to detect pesticide concentrations on water and sediment of Rawa Pening Lake.

MATERIAL AND METHODS

Pesticide usage survey: A simple structured questionnaire observation was designed in Java language used to do survey of pesticide usage in Rawa Pening farmer. Data was collected through a farm survey by face-to-face interviews with farmers/farm workers during farming activities. Interview was done directly on 22 respondents that selected randomly from 9 rice farm areas around Lake Rawa Pening.

Water and sediment sample collection: Sampling of water and sediments were collected from 3 selected sites of Rawa Pening Lake on July, 2013 (Fig. 1). The sampling was stressed on the river mouth of Panjang river (7°16'25.32" S ,110°25'46.33" E), Tuntang river (7°17'8.65" S,

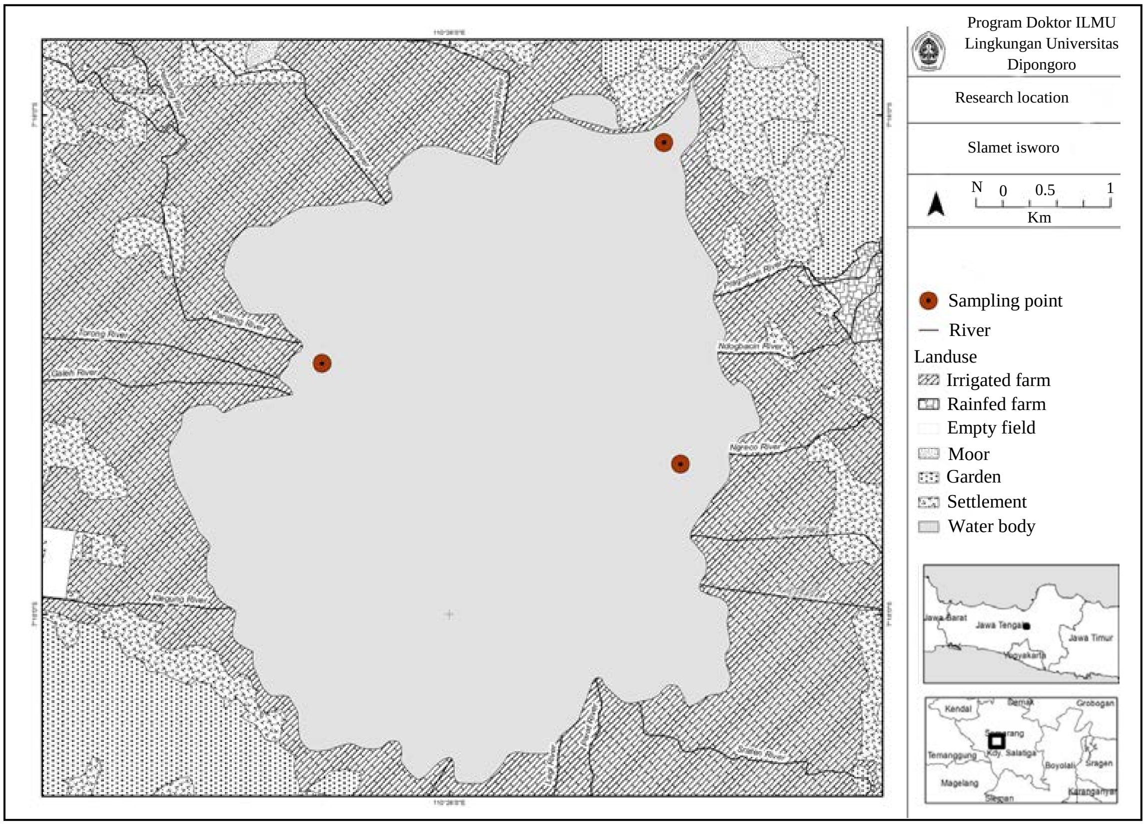

Fig. 1: Sampling site location of Lake Rawa Pening

110°24'58.95" E) and Galeh river (7°16'45.43" S, 110°25'8.65" E) due to the nearest locations that surrounded by high intensity agricultural areas. Samples were collected from 3 different points of each location. Water samples were collected from about 0.5 m depth below the water surface, filtered with Whatman's paper and maintained in 1000 mL polyethylene plastic bottles by adding 5 mL of concentrated H_2SO_4. Bottles were properly labeled and tightly sealed. While, sediments were sampled from the lake's bottom by using grab sampler and packed in black polythene bag. All the samples were kept in ice-box, brought to the laboratory and stored at -4°C before performing organophosphorus and organochlorine analyses. The psycho-hydrochemical properties such as pH, salinity and temperature were measured at the time of samples collection but were not presented in this study.

Sample extraction and clean up: Identification of pesticide in quantity made based on standard operating procedures for water sampling methods and analysis (USEPA., 2001). One hundred milliliter of water sample was transferred into a 500 mL separatory funnel, added 5 mg NaCl powder and pH measured. A 50 mL n-heksana was added to the sample and shaken for 10 min. The sample was allowed to settle for 30 min to enhance separation of two phases. The upper organic layer was collected in 300 mL Erlenmeyer flasks, while the lower aqueous layer was transferred into a 500 mL separatory funnel. The extractions were repeated two times using 50 mL n-hexane. The upper organic phase was cleaned by adding 100 mL purified water and shaken for 3 min. The sample was allowed to settle to enhance separation of two phases and then discarded the lower aqueous layer. The extractions were repeated two times using 100 mL purified water. The extracts were added with 5 mg anhydrous sodium sulphate and concentrated to about 1 mL using a vacuum rotary evaporator operating at 25 rpm and temperature of 35°C.

The sediment samples were dried up on room temperature in the lab, grinded by mortar-pestle and sieved with 2 mm sieve pore. Twenty gram sediment samples were placed in 250 mL Erlenmeyer flask, added with 40 mL acetone and shaked for 30 min. After separation was achieved, the extracts were decanted. The sediments were reextracted for twice. The extracts were concentrated to about 30 mL using a vacuum rotary evaporator operating at 25 rpm and temperature of 35°C. The extracts were added with 100 mL 10% NaCl and 50 mL n-hexane, shaken for 20 min. The sample was allowed to settle to enhance separation of two phases and decanted the lower aqueous layer into 250 mL separated funnel. The following procedure was similar to the water sample procedure above mentioned except the final results of concentrated extracts were 5 mL.

Each of the crude extracts was then dissolved in 10 mL hexane and were cleaned by passing through chromatographic column that filled by florisil and anhydrous sodium sulphate. The clean extracts were concentrated on a rotary evaporator to approximately 2 mL.

Chromatographic analyses: After extractions, the samples were then analyzed by gas chromatograph FPD (Flame Photometer Detector) model SHIMADZU GC-FID 2014 at the Environmental Agriculture Research Institute, Pati, Central Java. The GC was equipped with AFC (Advanced Flow Controller), APC (Advanced Pressure Controller), Autosampler unit and column length-25.0 m, 0.32 mm (ID) and 0.50 μm film. Column temperature was programmed at 280°C (1 min), changed at 70°C min^{-1} to 200°C (0 min) and 50°C min^{-1} to 350°C. Injector temperature was maintained at 260°C for the detector, whereas flow pressure of 100 kPa of Helium gas Ultra High Pure (UHP) was applied as carrier gas. Sample size of 2 μL was injected on GC.

RESULTS AND DISCUSSION

Pesticide usage in Rawa Pening Lake: Organophosphate pesticide, such as carbamates, phenoxy, triazine, bipyridilium and pyrethroids, is the most widely used pesticides in Indonesia (Sabdono *et al*., 2007a). The most commonly used pesticide is probably based on farmers' knowledge on pesticide application in relation to effectiveness of pesticides, pests, farm size and price and weather condition (Ngowi *et al*., 2007). The farmers in Rawa Pening Lake grow vegetables and paddy rice use many types of pesticides to control pests and diseases that attack these crops. Based on the use of questionnaires and interviews that were conducted in field, the types of pesticides used by the farmers in the study areas were Profenofos, followed by Carbamate, Deltamethrin, Imidachloprid, Fentoat, Carbosulfan, Carbofuran and Lamda-Sihalotrin (Fig. 2). The large amounts organophosphate pesticides used in agriculture activity surrounding Rawa Pening Lake may impact on the ecological aquatic system in the short term before they degraded to non-toxic compounds. Akan *et al*. (2013) stated that the organophosphates is suspected to have serious toxicological impacts on wildlife and human being. No organochlorine pesticide was found to be used by the farmer. It is not surprisingly due to the banned usage of organochlorine pesticide. However, even these pesticides are already banned but are still used illegally due to reasonably priced that find freely on sale in the local market.

Organophosphorus and organochlorine residues: organophosphorus and organochlorine concentrations of all the samples from sampling sites of Rawa Pening Lake was summarized in

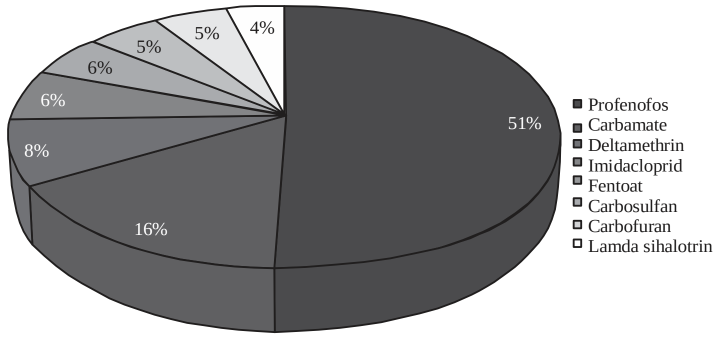

Fig. 2: Pesticide most commonly used in Rawa Pening Lake during the study period

Table 1: Mean and standard deviation concentration of organophosphorus pesticide residues in water and sediment samples from Rawa Pening Lake Indonesia

Pesticide names	Water (mL L^{-1})	Sediment (mg kg^{-1})
Chloropyrifos	BLD	BLD
Profenofos	0.054±0.039	0.199±0.083
Diazinon	0.005±0.001	0.012±0.006
Fenitrotion	BLD	0.066±0.032
Malation	0.047±0.009	0.083±0.033
Metidation	BLD	BLD
Parathion	BLD	BLD

BLD: Below detection limit

Table 2: Mean and standard deviation concentration of organochlorine pesticide residues in water and sediment samples from Rawa Pening Lake Indonesia

Pesticide names	Water (mL L^{-1})	Sediment (mL kg^{-1})
γ⁻BHC	BLD	0.009±0.001
Heptachlor	0.004±0.0	0.005±0.001
Aldrin	BLD	0.067±0.032
Endosulfan	0.011±0.007	0.009±0.001
Dieldrin	BLD	0.053
DDT	BLD	BLD
Endrin	0.016±0.008	0.016±0.008

BLD: Below detection limit

Table 1 and 2. The results have shown that organophosphorus and organochlorine residues are present at high concentrations in water and sediments samples from Lake Rawa Pening. Both pesticide residue levels of organophosphates and organochlorine in water ranged from Below Detection Limit (BDL) to 0.0815 -0,0257 mg L^{-1}, respectively. Whereas, the residue level of organophosphates detected in sediment samples ranged from Below Detection Limit (BDL) to 0.2839 mg kg^{-1} and organochlorine pesticides ranged Below Detection Limit (BDL) to 0.1038 mkg^{-1}. No result comparisons were done in this study due to no previous study regarding to pesticide residues in the Rawa Pening Lake. However, in Lake Tondano, Sulawesi, Kumurur (2002) reported that the organochlorine pesticide residues ranged from 3.77-15.68 mg kg^{-1}. Whereas, Manuaba (2007) stated that organochlorine residue in Lake Buyan, Bali was 0.0015 mg kg^{-1}. There were several previous studies from other countries regarding to organophosphate and organochlorine pesticide residues in the lake were reported, such as Lake Biwa (Sudo *et al*., 2002), Lake Taihu, China (Wang *et al*., 2007), Lake Bosomtwi, Ghana (Darko *et al*., 2008), Lake Manyas, Turkey (Erkmen *et al*., 2013), Lake Naivasha, Kenya (Otieno *et al*., 2014) and Lake Nokoué and Cotonou Lagoon in the Republic of Bénin (Pazou *et al*., 2014). Comparing among these lakes, the concentrations of pesticide residues in water and sediment samples of Lake Rawa Pening was the highest one.

Profenofos pesticide residues in water and sediments were the highest among other organophosphorus compounds. The survey showed that a number of organophosphates including profenofos and carbamate were being used in the paddy and vegetable fields of Rawa Pening Lake. The pesticide usages would imply to influence the concentration of pesticides in the lake. The highest profenofos pesticide concentrations detected in the water and sediment of river mouth sites were in harmony with the result of profenofos pesticide usage. When the pesticides applied on the paddy field and discharged into water run off to the river within a relative short time on the mouth river, they move toward to the lake without enough time and connection with river beds necessary for absorption and degradation.

The present study has shown that the organochlorine pesticide compounds are still detected in the lake even though based on the survey have not been used anymore by the farmers. This may suggest due to their ability to persist in the environment and accumulate in sediments. Sparovek *et al*. (2011) stated that organochlorine compounds showed a capacity for accumulation in sediments and soil organisms. Another suggestion is that some farmers are probably still applying them illegally, therefore there is the need to control more strictly for this compounds usage.

CONCLUSION

The finding of the preliminary data from this study showed that the organophosphorus and organochlorine residues in water and sediments were below the minimum standard levels and may not pose environmental and human risks to farmers, except for profenofos that exceeded the prescribed standard (0.1 mg kg^{-1}). It is important to continue monitoring pesticide residues by expanding the number of sampled area in different seasons in order to understand the processes of contaminant occurrence and distribution.

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