Occurrence and behavior of pesticides in surface waters and aquatic organisms from Indonesia

Agus Sudaryanto[1], Dwindrata B. Aviantara[1], Asep Nugraha Adiwinata[2], Suherman[1], Rumi Tanoue[3], Tatsuya Kunisue[3]

1 Research Center for Environmental and Clean Technology, National Research and Innovation Agency, KST BJ. Habibie, Tangerang Selatan, Indonesia
2 Research Center for Horticulturet and Plantation, National Research and Innovation Agency, KST Sukarno-Hatta, Cibinong, Indonesia
3 2 Center for Marine Environmental Studies (CMES), Ehime University, Bunkyo-cho 2-5, Matsuyama 790-8577, Japan

Introduction

Contamination of the aquatic ecosystem by pesticides is the most common problem of water current situation which thus have been a matter of global concern (Riaz et al., 2021). Pesticides are defined as a broad spectrum of chemical and organic mixtures including insecticides, fungicides, plant growth regulators, etc. The primary source of pesticides in the ecosystem are agriculture and forestry (Riaz et al., 2021; Rozaki, 2020). For the majority of the Indonesian population, the agricultural sector plays an important role in their economic development and income (Rozaki, 2020). In this regards, pesticide remains an essential production input for the control of pests and diseases (Skevas at al., 2013), although the ability of farmers to identify and recognize pests and diseases is also a major barrier to controlling them (Abang et al., 2014). Synthetic pesticides are widely applied by farmers to control pests and diseases in Indonesia. The level of pesticide use in Indonesia has been increasing over the last few decades (Joko et al., 2020; Mariyono et al., 2018), and more than 4,000 pesticide brands are currently registered with the Ministry of Agriculture of Indonesia and permitted to be marketed in Indonesia (Darwis et al., 2020).

Despite the potential to increase agricultural production, pesticides are poisonous and dangerous materials (Polanco, 2012). For instance, usage of pesticides in several developing countries have shown that farmers' practices are often unsafe and can result in health problems (Sharma et al., 2019). Furthermore, due to improper use of pesticides is still prevalent in many areas, a number of negative impacts has been anticipated, such as poisoning freshwater, reducing biodiversity in freshwater, reducing numbers of natural predators, interfering with the pollination process, and threatening food production (Chagnon et al., 2015), as well as causing various health issues in humans and animals (Leong et al., 2020). Indeed, health issues due to synthetic pesticide exposure are frequently found in farmers who apply synthetic pesticides, including Indonesian farmers (Joko et al., 2020; Mariyono et al., 2018).

In the aquatic environment, the pesticide can adsorb or desorb on suspended solids and further settle down in the bottom sediments including bioaccumulation in biota through food chain (Riaz et al., 2021). Pesticides reach aquatic systems mainly through two processes, namely runoff, and leaching. These two main processes are directly connected with the hydrological cycle (Riaz et al., 2021). However, there is limited information regarding the occurrence of pesticides in aquatic environment of Indonesia. This condition highlight concern on how their contamination in aquatic environment and biota as well as their potential health risk to ecosystem and human.

This study aims to determine a wide range of pesticides in surface waters and aquatic organisms from selected locations of Indonesia in order: (a) to understand their occurrence, distribution and sources, (b) behavior of pesticides from their application in agricultural sector, and (b) to estimate their potential health risk to aquatic ecosystems and human. The result of the proposed study would be a first report on wide range of pesticides in the aquatic environment of Indonesia and serve as baseline data which will enrich the inventory of pesticides pollution.

Material and Methods

Sampling

A total of 36 grab water samples were collected during rice growing season on the period of 2024 from water bodies of distinct typology such as paddy field, stream, irrigation channels, rivers and lakes located at regions of West Java Province with high agricultural activity at

Citarum River Basin as well as other location in Bekasi River during 2023. The sampling locations consist of 5 regency's case study sites including Cianjur, Bandung, Krawang, Purwakarta and Bekasi. The study design particularly at paddy field included sites related to rice growing stage such as location at beginning of rice growing to location where the rice almost will be harvested following their status of pesticides application. Table 1 shows characteristics of water bodies used for sampling of the present study whereas. A part of water samples, certain biota samples were also collected in selective aquatic environment including in the waters directly in paddy field as well as irrigation channels and river waters. After collected the samples, the samples were temporally stored at -20^oC in BRIN and then bring to CMES, stored in es-BANK at -20^oC before chemical analysis.

Table 1. Sampling locations at water bodies of West Java Province.

No	ID	Site	Location	Date	Typology
1	PFK-01	Kerawang	-6.407901, 107.377674	28/08/2024	Paddy Field, newly grown rice
2	PFK-02	Kerawang	-6.407662, 107.377598	28/08/2024	Paddy Field, newly grown rice
3	PFK-03	Kerawang	-6.408281, 107.377854	28/08/2024	Paddy Field, newly grown rice
4	IPFK-01	Kerawang	-6.408432, 107.377569	28/08/2024	Tertiary Irrigation Channel
5	PFB-04	Bandung	-6.989025, 107.655863	28/08/2024	Paddy Field, the rice is growing
6	PFB-05	Bandung	-6.990133, 107.657731	28/08/2024	Paddy Field, the rice is growing
7	PFB-06	Bandung	-6.989206, 107.657796	28/08/2024	Paddy Field, the rice is growing
8	IPFB-02	Bandung	-6.989453, 107.657125	28/08/2024	tertiary Irrigation Channel
9	PFB-07	Bandung	-6.998834, 107.662329	28/08/2024	Paddy Field, the rice is growing
10	PFB-08	Bandung	-6.999352, 107.663187	28/08/2024	Paddy Field, the rice is growing
11	IPFP-03	Kerawang	-6.436879, 107.369780	28/08/2024	Primary Irrigation Channel
12	IPFK-04	Kerawang	-6.443668, 107.380968	28/08/2024	Primary Irrigation Channel
13	PFK-09	Kerawang	-6.427392, 107.382630	28/08/2024	Paddy Field, the rice grains begun to appear.
14	PFK-10	Kerawang	-6.426920, 107.383255	28/08/2024	Paddy Field, the rice grains begun to appear.
15	PFK-11	Kerawang	-6.427471, 107.383189	28/08/2024	Paddy Field, the rice grains begun to appear.
16	IPFK-05	Kerawang	-6.427418, 107.382875	28/08/2024	Tertiary Irrigation Channel
17	PFC-12	Cianjur	-6.809549, 107.268774	28/08/2024	Paddy Field, the rice is almost harvested
18	PFC-13	Cianjur	-6.809239, 107.268917	28/08/2024	Paddy Field, the rice is almost harvested
19	PFC-14	Cianjur	-6.809365, 107.268667	28/08/2024	Paddy Field, the rice is almost harvested
20	IPFC-06	Cianjur	-6.809381, 107.268538	28/08/2024	Tertiary Irrigation Channel
21	IPFC-07	Cianjur	-6.809406, 107.268323	28/08/2024	Secondary Irrigation Channel
22	PFK-15	Kerawang	-6.406940, 107.379410	29/08/2024	Paddy Field, the rice is almost harvested
23	PFK-16	Kerawang	-6.407248, 107.379431	29/08/2024	Paddy Field, the rice is almost harvested, spraying pesticides

24	PFK-17	Kerawang	-6.407012, 107.379817	29/08/2024	Paddy Field, the rice is almost harvested, spraying pesticides
25	IPFK-08	Kerawang	-6.407396, 107.379432	29/08/2024	Tertiary Irrigation Channel
26	BKSR-15	Bekasi	-6.132731, 107.057592	11/09/2023	Bekasi River
27	BKSR-16	Bekasi	-6.139772, 107.052987	11/09/2023	Bekasi River
28	BKSR-17	Bekasi	-6.153378, 107.044998	11/09/2023	Bekasi River
29	BKSR-18	Bekasi	-6.171585, 107.046738	11/09/2023	Bekasi River
30	BKSR-19	Bekasi	-6.185946, 107.042325	11/09/2023	Bekasi River
31	CLPF-02	Cirata	-6.713363, 107.333551	28-Aug-24	Cirata Lake
32	CLPF-03	Cirata	-6.694727, 107.345938	28-Aug-24	Cirata Lake
33	CLPF-04	Cirata	-6.718941, 107.257470	28-Aug-24	Cirata Lake
34	CLPF-05	Cirata	-6.747245, 107.275917	28-Aug-24	Cirata Lake
35	CLPF-06	Cirata	-6.764361, 107.272801	28-Aug-24	Cirata Lake
36	CLPF-07	Cirata	-6.769213, 107.288053	28-Aug-24	Cirata Lake

Sample Preparation

Concentrations of 367 pesticides in water samples were determined the following method. All water samples were filtered through glass-fiber filters (pore size: 0.7 μm; Whatman, Maidstone, UK) to remove suspended solids. An aliquot (30 mL) of the filtrate was spiked with internal standards (20 ng/mL, 75 μL). The sample solution was then loaded onto an Oasis HLB Plus Light cartridge (30 mg, Waters, Milford, MA, USA). Before sample loading, the Oasis HLB cartridge was preconditioned with acetone:methanol (1:1, v/v, 3 mL), followed by methanol (3 mL) and Milli-Q water (3 mL). After loading, the cartridge was washed twice with Milli-Q water (3 mL each) and then dried under vacuum. Pesticides retained in the Oasis HLB cartridge were eluted with acetone:methanol (1:1, v/v, 3 mL). The eluate was evaporated to 0.3 mL under a gentle stream of N_2, then diluted to 0.6 mL with Milli-Q water. The final sample solution was injected into a Prominence UFLC XR system (Shimadzu, Kyoto, Japan) coupled with a Sciex X500R QTOF System (Sciex, Tokyo, Japan), operating in electrospray ionization (ESI) positive mode with the SWATH acquisition (data-independent acquisition, DIA) method for the quantitation of 367 pesticides. Chromatographic separation was performed using an Ascentis Express C18 analytical column (2.7 μm, 100 × 2.1 mm; Supelco, Bellefonte, USA) at a flow rate of 0.25 mL/min. The mobile phase consisted of 10 mM acetic acid-ammonium acetate buffer (phase A) and 10 mM acetic acid-ammonium acetate buffer in methanol/acetonitrile (1:1, v/v) (phase B). The gradient started at 5% B, increased gradually to 95% B over 15 min, remained at 95% B for 5 min, returned to 5% B within 0.5 min, and was maintained for an additional 4.5 min. Quantitation was based on the peak area of TOF-MS chromatograms for the protonated ion $[M+H]^+$ (± 0.01 Da relative to the theoretical m/z) at the corresponding retention time (± 0.05 min, compared to native standards). Qualification was performed using the TOF-MS isotopic pattern and TOF-MS/MS fragmentation data. Target pesticide concentrations were determined using the isotope-dilution method. Calibration curves with at least seven points were constructed by plotting the peak area ratios of the native compounds to their respective internal standards against their concentration ratios. Internal standards were added at a fixed concentration to all calibration solutions. One procedural blank sample was analyzed per batch of 12 samples to monitor potential contamination during sample preparation. The limits of detection (LODs) and limits of quantification (LOQs) for pesticides were determined using the signal-to-noise method, where LOD and LOQ were defined as the concentrations corresponding to signal-to-noise ratios of 3 and 10, respectively.

Results

Pesticides were detected in water bodies of the present study. Of the 367 pesticides analyzed, 26 pesticides were detected at the study site including 12 classes of insecticides (Carbofuran, Chlorantraniliprole, Chlorpyrifos, Chlorpyrifos Oxon, Clothianidin, Clothianidin-desmethyl, Fenobucarb (BPMC), Imidacloprid, Isoprocarb (MIPC), Profenofos, Propoxur (PHC), Thiamethoxam), 9 fungicides (Azoxystrobin, Carbendazim, Difenoconazole, Dimethomorph Isomer 1, Dimethomorph Isomer 2, Isoprothiolane, Metalaxyl, Thiabendazole, Tricyclazole) and 5 herbicides (Ametryn, Atrazine, Diuron (DCMU), Pyrazosulfuron-ethyl, Terbutryn). Table 2 summarizes the pesticides detected from the 36 sampling points.

Table 2. Occurrence and concentration of pesticides (ng/L) in water of the present study.

Pesticides	Class	No of Samples	No of Detected	% Occurrence	Maximum	Median	Mean	Minimum
AM	HE	36	25	69	89,2	2,5	4,8	<MDL
AT	HE	36	21	58	13,7	5,4	4,8	<MDL
AZ	FU	36	35	97	8880	5,5	570,2	<MDL
CD	FU	36	28	78	55,5	7,9	13,8	<MDL
CF	IN	36	29	81	46,4	3,4	11,9	<MDL
CT	IN	36	19	53	2725	5	219	<MDL
CP	IN	36	4	11	8001	<MDL	279,4	<MDL
CO	IN	36	4	11	573,7	<MDL	22,6	<MDL
CA	IN	36	4	11	56,4	<MDL	4,7	<MDL
CM	IN	36	3	8	52,8	<MDL	3	<MDL
DC	FU	36	6	17	8600	<MDL	431	<MDL
DI1	FU	36	5	14	62,9	<MDL	7,4	<MDL
DI2	FU	36	7	19	196	<MDL	23,9	<MDL
DR	HE	36	31	86	53,6	6,3	12,1	<MDL
FE	IN	36	29	81	393,6	15,1	42,2	<MDL
IM	IN	36	15	42	9,8	<MDL	2,6	<MDL
IC	IN	36	6	17	13,2	<MDL	1,2	<MDL
IT	FU	36	5	14	2	<MDL	0,2	<MDL
ME	FU	36	25	69	7,2	<MDL	1,6	<MDL
PF	IN	36	1	3	51,3	<MDL	1,4	<MDL
PP	IN	36	2	6	11	<MDL	0,6	<MDL
PZ	HE	36	15	42	22,2	<MDL	6,1	<MDL
TE	HE	36	12	33	6,6	<MDL	1,3	<MDL
TB	FU	36	8	22	6,8	<MDL	1	<MDL
TM	IN	36	4	11	1781	<MDL	161,1	<MDL
TR	FU	36	23	64	3,5	1,4	1,2	<MDL
∑P	PS	36	36	100	30458	130	1830	25,4

Note: AM= Ametryn, AT= Atrazine, AZ= Azoxystrobin, CD= Carbendazim, CF= Carbofuran, CT= Chlorantraniliprole , CP= Chlorpyrifos, CO= Chlorpyrifos Oxon, CA= Clothianidin, CM= Clothianidin-desmethyl, DC= Difenoconazole, DI1= Dimethomorph Isomer 1, DI2= Dimethomorph Isomer 2, DR= Diuron, FE= Fenobucarb, IM= Imidacloprid, IC= Isoprocarb, IT= Isoprothiolane, ME= Metalaxyl, PF= Profenofos, PP= Propoxur, PZ= Pyrazosulfuron-ethyl, TE= Terbutryn, TB= Thiabendazole, TM= Thiamethoxam, TR= Tricyclazole, ∑P= Total Pesticides, HE= Herbicide, FU= Fungicide, IN= Insecticide, PS= Pesticides

Among the pesticides detected, the presence of Azoxystrobin was the highest found in all sampling points reaching 97%. Azoxystrobin is a systemic fungicide used to control various types of fungi in plants. In Indonesia, Azoxystrobin has been widely used on various types of plants. Then followed by Diuron (86%), Fenobucarb and Carbofuran (each 81%), Carbendazim (78%), Ametryn and Metalaxyl (69%), Tricyclazole (64%), Atrazine (58%) and Chlorantraniliprole (53%). Meanwhile, other pesticides were found in less than 50% of the sampling points, ranging from 3% (Profenofos) to 42% (Imidacloprid and Pyrazosulfuron-ethyl).

The total concentration of pesticides detected was in the range of 25-30458 ng/L with a median value of 130 ng/L and an average of 1830 ng/L. The maximum concentration of Azoxystrobin (8880 ng/L), Difenoconazole (8600 ng/L), Chlorpyrifos (8001 ng/L), Chlorantraniliprole (2725 ng/L), Thiamethoxam (1781 ng/L) is one to three orders of magnitude higher than other pesticides. The use of pesticides such as Azoxystrobin, Difenoconazole, Chlorpyrifos, Chlorantraniliprole, and Thiamethoxam is quite common in Indonesia, especially in agriculture. Indonesia is one of the largest pesticide users in the world, with total pesticide use reaching 283 kilotons in 2021 (Buol, 2023). Furthermore, the detection of high concentration of

Among typology of the locations (Table 3), relatively high concentrations of pesticides (Azoxystrobin, Chlorantraniliprole, Chlorpyrifos, Difenoconazole, etc.) were found in samples collected from Kerawang, West Java, in particular samples collected from paddy field with just received spraying pesticides during sampling campaign such in sampling point of PFK-15, PFK-16, PFK-17, and IPFK-08 (data not shown). Whereas other locations of similar typology location in paddy field were much lower. Other study area in irrigation channels, river as well as in Lake Cirata were also lower. It was surprised to find that Chlorpyrifos, an insecticide recently recommended for addition to the list of banned POPs, was detected at high concentrations with maximum of 8001 ng/L at Kerawang paddy field water.

Table 3. Total pesticides (ng/L) according to different typology locations.

Typology	Site	Characteristics	Median	Average	Minimum	Maximum
Paddy Field	Kerawang-1	Rice just growing, not yet sprayed (n=3)	168	170	25	214
	Kerawang-2	Rice seed appear, a week sprayed (n=3)	131	131	70	194
	Kerawang-3	Almost harvested, spraying (n=3)	11857	18050	11836	30458
	Bandung-1	Rice growing, sprayed (n=3)	124	93	25	129
	Bandung-2	Rice growing, sprayed (n=2)	28	28	27	28
	Cianjur	Almost harvested, sprayied (n=3)	339	334	309	354
Channel Irrigation	Kerawang-1	Primary irrigation channels (n=2)	-	479	-	-
	Kerawang-2	Secondary irrigation channels (n=1)	-	80	27	-
	Kerawang-3	Secondary irrigation channels (n=1)	-	6934	28	-
	Bandung-1	Secondary irrigation channels (n=1)	-	62	28	-
	Bandung-2	Secondary irrigation channels (n=1)	-	-	28	-
	Cianjur	Secondary irrigation channels (n=2)	406	406	396	416
River	Bekasi	Main River Bekasi (n=5)	149	144	117	162
Lake	Cirata	Main Cirata Lake (n=6)	33	43	28	75

Future Perspective

Pesticide use in Indonesia is expected to continue to increase in line with the growth of the agricultural sector. However, this will also increase the risk of environmental pollution and pesticide bioaccumulation in living organism. Further research will conduct an analysis of pesticide bioaccumulation in biota that has not been completed at this stage, including conducting an analysis of environmental and human health risks from potential pesticide exposure. To reduce the risk of environmental pollution and pesticide bioaccumulation, efforts need to be made to reduce pesticide use and increase awareness of the importance of safe and sustainable pesticide use. In the long term, it is hoped that pesticide use in Indonesia can be reduced and negative environmental impacts can be minimized.

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