Pesticides in Kalisat River: water and sediment assessment

[1,2]Muhammad Musa, [1,2]Nanik R. Buwono, [1]Mutiara N. Iman, [1]Setya W. Ayuning, [1,2]Evellin D. Lusiana

[1] Faculty of Fisheries and Marine Sciences, Universitas Brawijaya, Malang, Indonesia; [2] AquaRES Research Group, Brawijaya University, Malang, Indonesia. Corresponding author: N. R. Buwono, buwonoretno@ub.ac.id

Abstract. Pesticides are chemicals that are intentionally introduced into the environment for the management of plant pests. The use of pesticides can deteriorate or eliminate river water quality through runoff. The Kalisat River flows over an agricultural area so pesticides and fertilizers can easily contaminate the waters. Therefore, a study was designed to determine the assessment of pesticide residues in the water and sediments of the Kalisat River. Pesticide residues found in water and sediments consist of 2 active ingredients, namely carbamate and cyfluthrin. The results showed that pesticide residues in water were below the maximum residual limit (MRL) set by the Ministry of Health Regulation of the Republic of Indonesia No. 416 of 1990. However, the residues in the sediments were above the MRL set by the EU pesticides database.

Key Words: pesticide residues, pollution, monitoring, water quality, chemicals.

Introduction. Pesticides are usually considered toxic materials to the surrounding environment and humans, even though they are used to control pests and diseases that take toll from the plant (Adriyani 2006). Pesticides can discharge into water bodies by direct application through spray drift, aerial spray, atmospheric fallout, soil erosion, runoff from agricultural areas, industrial discharge and domestic sewage. In water bodies, pesticides can affect water quality, sediment and ultimately threat non-target organisms that are connected to the food chain (Kaushik et al 2010). Almost all types of pesticides are poisonous of varying category and can be a source of pollution for aquatic resources and the environment.

The Kalisat River flows in Selorejo Village, Dau District, Malang Regency. A number of activities were developed in the Sungai Kalisat region, such as settlement, agriculture and tourism. However, the dominating activity is agriculture and plantation land. The most cultivated plant commodities consist of vegetables and fruits, such as oranges, carrots and tomatoes. The community relies on the application of pesticides for the management of pests and diseases. So it can be suspected that the use of pesticides by local farmers will contribute to the input of pesticide residues in the waters of the Kalisat River. In addition, the location is also used as a tourist place, Malang Bedengan Tourism, orange picking tours and campsites. Transforming land into agricultureand plantations can reduce the quality of river water flowing in the area (Lusiana et al 2017). The Kalisat River which is close to agricultural and plantation areas is the main source of pesticide residues to easily contaminate waters and reduce water quality.

The interaction between the environmental processes of living things and the physico-chemical properties of water can determine the influence, intensity, and extent of the spread of pesticide pollution (Connel & Miller 1995). Therefore a combination of pesticide residue analysis and measurement of water quality parameters were performed to provide more optimal results, in order to deliver a more accurate evaluation of the water quality status.

Material and Method

Description of the study sites. This research was conducted in the Kalisat River in Selorejo Village, Dau District, Malang Regency from January to February 2019 which was still in the rainy season. The Kalisat River flows through two villages, namely Selorejo and Petungsewu Village. According to Sarari (2014), the topography of Dau Subdistrict is a fairly high area, rich in water resources and the topography of the Selorejo Village is classified as a highland or hilly area. The sampling site consisted of five stations, each with two sampling points, determined using the purposive sampling method that is based on land use (Figure 1). The samples were taken once per month. The total number of water and sediment samples was 20. The research was based on replicated observation and used descriptive analysis in data processing.

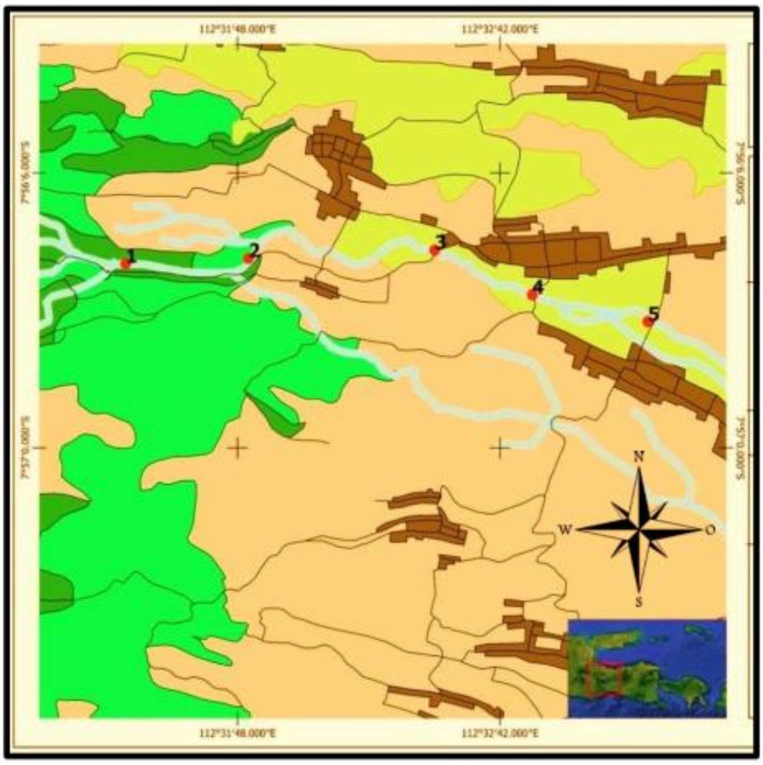

Figure 1. Sampling location in the Kalisat River.

Purposive sampling was carried out based on the criteria and considerations determined by Senam & Uwem (2014). Station 1 is an area that has not been contaminated with waste from people activities. Station 2 is located near the campsites. Station 3 is an area close to the plantation, station 4 is located between agricultural land and residential areas and station 5 is a residential area. The coordinate points for the five sampling stations can be seen in Table 1.

Table 1

The coordinate points of the sampling station

Sampling station	*Latitude*	*Longitude*
Station 1 (ST 1)	-7.939951°	112.523610°
Station 2 (ST 2)	-7.939654°	112.530621°
Station 3 (ST 3)	-7.939210°	112.541269°
Station 4 (ST 4)	-7.941650°	112.546847°
Station 5 (ST 5)	-7.943114°	112.553457°

Collection of water and sediment samples. The materials of this research were pesticide residues in water and sediment in the Kalisat River. Water sampling was carried out by using clean 200 mL water bottles. A sample was taken by dipping the bottle ±20 cm below the water surface with the position of the mouth of the bottle opposite to the direction of water flow. Water samples were inserted into the bottles horizontally and the volume of the water samples was the same from each sampling point (SNI 1991). Pesticide residues sampling was carried out in 5 stations by preparing clean bottles. The sediment samples were taken at depths of 0-5 cm. At least 200 mg of sediment load were introduced into a bottle using a shovel and then the bottle was labeled (SNI 2008).

Analysis of pesticide residues. The water samples and sediment samples were identified based on standard operation procedure at the Chemistry Laboratory of the University of Muhammadiyah Malang using High Performance Liquid Chromatography (HPLC Shimadzu). The measurement of carbamate pesticide residues was performed using a SPD 20 A UV-Vis Detector, column type Shim-pack VP ODS 5 μm 150x4.6 mm, maintaining 40°C column temperature consists of 2 mobile phases namely mobile phase A (0.1% H_3PO_4 in water) and mobile phase B (0.1% H_3PO_4 in acetonitrile) with a ratio (A:B=95%:5%), isocratic method flow rate of 1 mL/min, injection volume of 20 μL, detector wavelength 210 nm and allowed to stand for 10 minutes. The measurement of pyrethroid pesticide residues was performed using a SPD M20-A Photo Diode Array Detector; column type Shim-pack VP ODS 5 μm 150x4.6 mm; column temperature 25°C; hexane mobile phase: dichloromethane (80:20 v/v); isocratic method of mobile phase; flow velocity of 1.2 mL/min; injection volume of 20 μL, detector wavelength of 265 nm and allowed to stand for 10 minutes.

Data analysis. Water quality parameters such as temperature, pH, dissolved oxygen and stream velocity were also analyzed. The method used was the descriptive analysis of pesticide residues data in water samples, pesticide residues data in sediment samples and water quality data. Pesticide residue data were compared with the maximum pesticide residue limit using the Ministry of Health Regulation No. 416 of 1990 of the Republic of Indonesia and the maximum residue limits of the European Commission pesticides database (EU 2019). The data of water quality parameters are related to water quality standards following the Government Regulation of the Republic of Indonesia No. 82 of 2001 and from other reference standards.

Results. The Kalisat River flows along the plantation and agricultural areas at Selorejo Village, where the land is widely used for citrus plantations. Based on the results of the interviews with citrus local farmers, the pesticide is usually sprayed every morning and evening. The most widely used type of pesticide is carbamate. In a riverine ecosystem the river flow speed can influence the distribution of pesticides or other substances. Runoff that flows on the surface of the soil has the energy to erode the surface layer of the soil so that the pesticide residues and the soil will flow to a lower place. The results of our research on pesticide residues in the waters and sediments of the Kalisat River for the active ingredients type of carbamate group obtained the 3 highest active ingredients, namely propoxur, carbofuran and carbaril. The concentrations of pesticide residues in waters at different sampling points are presented in Figure 2 and Figure 3.

The highest concentration of pesticide residues was detected in the water samples collected at station 5 ranging between 0.027–0.0053 mg L^{-1}, while the lowest concentration pesticide residues were detected at station 1 ranging between 0.007-0.014 mg L^{-1} (Figure 2). Figure 3 shows the similarity of trends with Figure 2, where the concentration of pesticide residues was the highest at station 5 ranging between 0.531-0.823 mg L^{-1} and the concentration of pesticide residues was the lowest at station 1 ranging between 0.147–0.222 mg L^{-1}.

The results of the research on pesticide residues in the sediments of the Kalisat River are presented in Figure 4. The data showed that the residual content detected in the sediment samples was higher than in the water samples (Figure 4). The concentration of carbofuran was the highest among the pesticide residues of 0.778±0.367, followed by propoxur (0.668±0.315), carbaril (0.4±0.367) and the lowest was cyfluthrin (0.314±0.146).

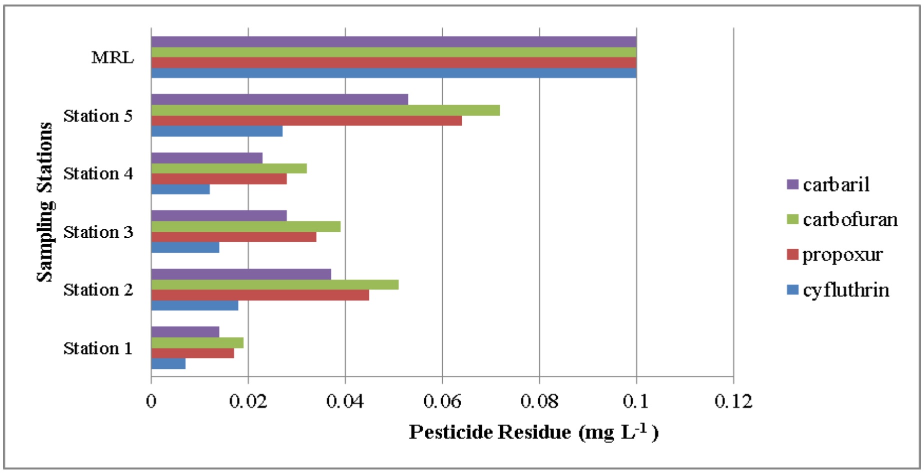

Figure 2. Composition and concentration of pesticide residues in water samples.

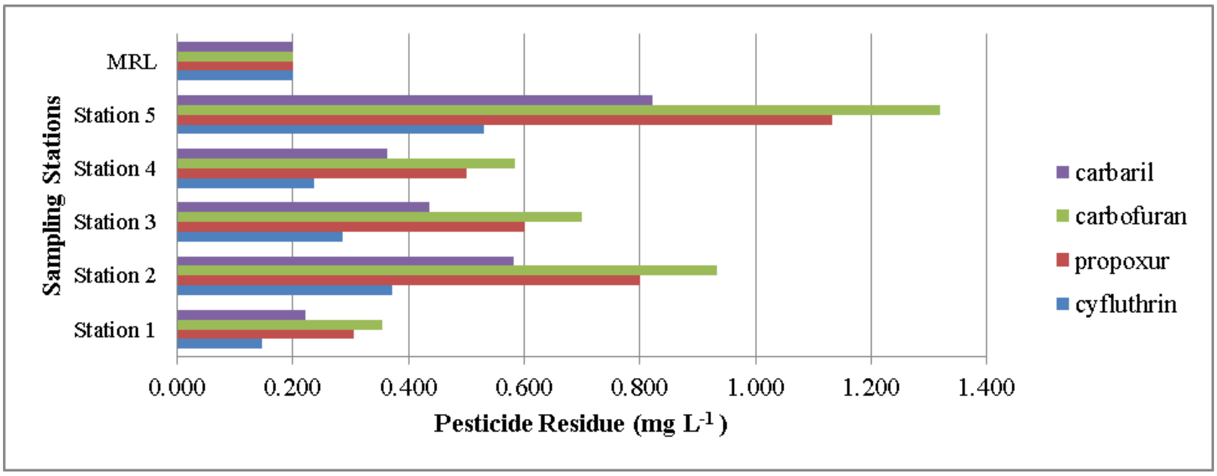

Figure 3. Composition and concentration of pesticide residues in sediment samples.

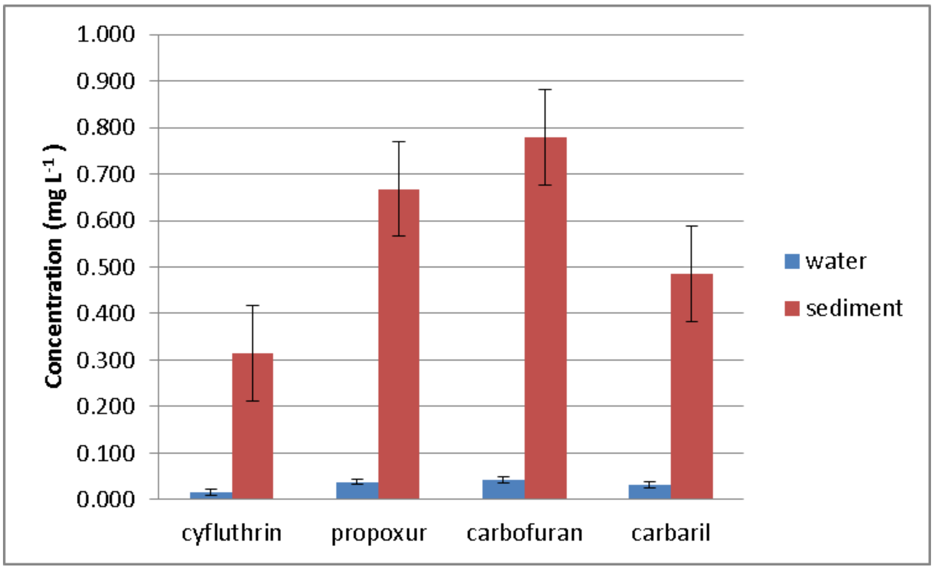

Figure 4. Comparison of pesticide residues concentration between water and sediment samples in the Kalisat River.

The data in Table 2 show that the concentration of pesticide residues detected in the water samples was below the maximum residue limit (MRL) regulated by the Ministry of Health Regulation No. 416 of 1990 of the Republic of Indonesia which is equal to 0.1 mg L^{-1}.

It can be stated that the waters in the Kalisat River were polluted by pesticides under the limits set by the Ministry of Health Regulation of the Republic of Indonesia. The highest pesticide residue at each station is of carbofuran type with a range of 0.019-0.072 mg L^{-1}, while the lowest pesticide residue at each station is cyfluthrin with a range of 0.007 to 0.027 mg L^{-1}.

However, the concentration of pesticide residues detected in sediment samples exceeded the maximum residue limit set by the EU Pesticide Database (2019), so it can be stated that sediment samples in the Kalisat River have been contaminated with pesticides.

Table 2

Comparison of concentration pesticide residues in water samples with MRL

Sampling station	*Maximum residual limit**	*Concentration of pesticide residues in water samples (mg L^{-1})*				*Category*
		Cyfluthrin	*Propoxur*	*Carbofuran*	*Carbaril*	
ST 1	0.1 mg L^{-1}	0.007	0.017	0.019	0.014	Unpolluted
ST 2		0.018	0.045	0.051	0.037	Unpolluted
ST 3		0.014	0.034	0.039	0.028	Unpolluted
ST 4		0.012	0.028	0.032	0.023	Unpolluted
ST 5		0.027	0.064	0.072	0.053	Unpolluted

* Ministry of Health Regulation No. 416 of 1990 of the Republic of Indonesia.

The highest pesticide residue at each station is from the type of carbofuran with a range of 0.355–1.319 mg/L, while the lowest pesticide residue at each station is cyfluthrin with a range of 0.0355-0.0793 mg/L (Table 3).

Table 3

Comparison of concentration pesticide residues in sediment samples with MRL

Sampling station	*Maximum residual limit**	*Concentration of pesticide residues in sediment samples (mg L^{-1})*				*Category*
		Cyfluthrin	*Propoxur*	*Carbofuran*	*Carbaril*	
ST 1	0.2 mg L^{-1}	0.147	0.305	0.355	0.222	Polluted
ST 2		0.371	0.801	0.933	0.582	Polluted
ST 3		0.286	0.601	0.701	0.437	Polluted
ST 4		0.238	0.501	0.583	0.364	Polluted
ST 5		0.531	1.132	1.319	0.823	Polluted

***** EU MRL 2019.

The water quality parameters of the Kalisat River are shown in Table 4. The data show that the water quality of the Kalisat River was relatively optimal and in accordance with the quality standards using the Government Regulation of the Republic of Indonesia No. 82 of 2001. The water quality parameters were in the range of: temperature between 19–22°C, pH between 6.1–6.5, dissolved oxygen 7.5–7.6 mg L^{-1}, and stream velocity 0.56–0.78 m/s.

Table 4

Physical and chemical parameters of water quality in the Kalisat River

Water quality	*ST 1*	*ST 2*	*ST 3*	*ST 4*	*ST 5*	*Standard**
Temperature (°C)	19	20	20	21	22	22-28
pH	6.5	6.4	6.2	6.1	6.3	6-9
DO (mg L^{-1})	7.7	7.7	7.7	7.5	7.6	>4
Stream velocity (m/s)	0.78	0.66	0.65	0.56	0.59	0.5 -1 (fast flow)

* Government Regulation of the Republic of Indonesia No. 82 of 2001.

Discussion. The highest pesticide residue found in the Kalisat River was carbofuran, which is a granular type of pesticide, the exterior part of the granules is covered with a thin layer of pesticide. These granules are usually sprinkled or buried around the roots so that they dissolve slowly in water and be taken up by the plant (Nofyan et al 2017). With these properties, the active ingredient (carbofuran) is not easily washed by the splash water so that the residue is more likely to be absorbed in the soil than in waters. The residual effects of carbofuran can be seen on a number of individuals, complications in the activity and replacement of organisms (Tannock & Wessel 2003).

The high levels of pesticides at each station are influenced by topography, steepness of the location, soil humidity, rainfall and types of pesticides used. The samples from station 1 showed the lowest content of pesticide residues (0.007 mg L^{-1}) probably because this station is located far from the agricultural area and is at higher altitude than the other stations, so it is likely to receive fewer pollutants. The aquatic environment receives a high load of pesticides because of the intensive agricultural activities (Kuster et al 2008). In addition, station 1 has steep river topography so the stream flow is faster. These conditions cause water replacements more quickly so that pesticide ingredients do not stay long enough to settle or get absorbed in the sediments of this station. Station 5 has the highest residual content (0.072 mg L^{-1}) because its location is in a lower area than the other stations, so it receives more pollutants (pesticides) that are carried away from the previous stations. In addition, the topography of the river at station 5 is relatively flat so that the water flow is rather slow and causes the pesticide to stay longer and eventually settle. The difference in pesticides levels per station can be influenced by current speed, rainfall, spraying dose, type of pesticide and pesticide spraying time.

In the sediment samples, the highest concentration of pesticide residues was detected at station 5 (1.319 mg L^{-1}), while the lowest concentration was detected at station 1 (0.147 mg L^{-1}). The presence of pesticide residues in the sediments is influenced by the characteristics of the pesticide and by the sediment type. Chemicals will fall to the ground when spraying pesticides, then during the erosion process, soil containing pesticide residues will be eroded by surface runoff air. High levels of pesticides are also influenced by location steepness, soil moisture, rainfall and the type of pesticides used (Manuaba 2009).

The presence of pesticide residues in water and sediment is also influenced by environmental factors such as soil pH, which is playing an important role in regulating the adsorption process and degradation of pesticides. Acidity can change pesticides that have a negative to positive or zero charge. Naturally the soil has negative charged particles, so pesticides with positive charges will be readily adsorbed by the soil (Permatasari 2007). Research has revealed that pesticides present in water are preferably absorbed into sediments or bioaccumulation in fish because of the low solubility of pesticides in water. This might be the reason for the lower detection of pesticide residues in the analyzed water samples in this study compared to the sediment samples (Caldas et al 1999). Pesticides can be found in two forms: unstable if dissolved in water and stable if accumulated in the soil. Pesticides that are often found, but at low concentrations, include compounds which tend to be adsorbed by the soil while the amount dragged by runoff can be constant but low. The compounds at high frequency and concentration are very stable and are not degraded in water (Masiá et al 2013; Pacual-Aguilar et al 2017).

Conclusions. Residues of active ingredients of pesticides found in water and sediments in the Kalisat River are cyfluthrin, propoxur, carbofuran and carbaril, the highest concentration being measured for the carbofuran residues. Pesticide residues contained in water are still in accordance with the MRL values below 0.1 mg/L, while sediment residues have exceeded the MRL 0.2 mg/L. From this study it can be concluded that the water quality in the Kalisat River is still relatively optimal.

References

Adriyani R., 2006 [Business environmental pollution control due to the use of pesticides in agriculture]. Jurnal Kesehatan Lingkungan 3(1):95-100. [In Indonesian].

Caldas E. D., Coelho R., Souza L. C., Silva S. C., 1999 Organochlorine pesticides in water, sediment, and fish of Paranoá Lake of Brasilia, Brazil. Bulletin of Environmental Contamination and Toxicology 62(2):199-206.

Connel D. W., Miller G. J., 1984 Chemistry and ecotoxicology of pollution. Environmental Science and Technology, A Wiley InterScience, New York, 444 p.

Kaushik A., Sharma H. R., Jain S., Dawra J., Kaushik C. P., 2010 Pesticide pollution of River Ghaggar in Haryana, India. Environmental Monitoring and Assessment 160(1-4):61-69.

Kuster M., Lopez de Alda M. J., Barata C., Raldúa D., Barcelo D., 2008 Analysis of 17 polar to semi-polar pesticides in the Ebro river delta during the main growing season of rice by automated on-line solid-phase extraction-liquid chromatography-tandem mass spectrometry. Talanta 75(2):390-401.

Lusiana N., Rahadi B., Anugroho F., 2017 [Identification of conformity of agricultural land use and river water pollution level in the upper Brantas watershed of Batu City]. Jurnal Teknologi Pertanian 18(2):129-142. [In Indonesian].

Manuaba I. B. P., 2009 [Contamination of carbamate pesticides in Lake Buyan Buleleng Bali]. Jurnal Kimia 3(1):47-54. [In Indonesian].

Masiá A., Ibáñez M., Blasco C., Sancho J. V., Picó Y., Hernández F., 2013 Combined use of liquid chromatography triple quadrupole mass spectrometry and liquid chromatography quadrupole time-of-flight mass spectrometry in systematic screening of pesticides and other contaminants in water samples. Analytica Chimica Acta 761:117–127.

Nofyan E., Lamin S., Patriot I. T., Kanedi M., 2017 Physiological effects of carbofuran on earthworm *Pheretima javanica* Gates. Advances in Life Sciences 7(2):21-25.

Pascual-Aguilar J. A., Andreu V., Campo J., Pico Y., Masia A., 2017 Pesticide occurrence in the waters of Júcar River, Spain from different farming landscapes. Science of the Total Environment 607-608:752-760.

Permatasari E., 2007 [Bioindicator of organophosphate insecticide pollution in agricultural soil]. Tugas Akhir, Program Studi Teknik Lingkungan, Fakultas Teknik Sipil dan Lingkungan. Institut Teknologi Bandung, pp. 55-70. [In Indonesian].

Sarari A., 2014 [Determination of subsurface aquifers using the resistivity geoelectric method Case Study Boarding School Tahfidzul Quran Dau-Malang District]. Jurnal Resistivitas 2. [In Indonesian].

Senam N., Uwem A., 2014 The survey communication research. International Journal of Education and Research 2(10):461-478.

Tannock J., Wessel C. L., 2003 Determination of carbofuran residues and metabolites in plant material. Pesticide Science 12:228-234.

*** EU (European Commission Pesticide Database), 2019 Pesticide residues and maximum residue levels. (http://ec.europa.eu/food/plant/pesticides/eu-pesticidesdatabase/public/event=pesticide.residue.CurrentMRL&language=EN).

*** SNI (Indonesian National Standard), 1991 SNI 06-2412-1991 [Field of public works regarding water quality]. Badan Standarisasi Nasional, Jakarta. [In Indonesian].

*** SNI (Indonesian National Standard), 2008 SNI 3414:2008 [Procedure for taking samples of sediment loads in the river by depth integrity based on debit distribution]. Badan Standarisasi Nasional, Jakarta. [In Indonesian].

Received: 01 September 2019. Accepted: 23 October 2019. Published online: 29 October 2019.
Authors:
Muhammad Musa, Brawijaya University, Faculty of Fisheries and Marine Science, Veteran Street, 65145 Malang, Indonesia, e-mail: musa_ub@yahoo.co.id
Nanik Retno Buwono, Brawijaya University, Faculty of Fisheries and Marine Science, Veteran Street, 65145 Malang, Indonesia, e-mail: buwonoretno@ub.ac.id
Mutiara Nurul Iman, Brawijaya University, Faculty of Fisheries and Marine Science, Veteran Street, 65145 Malang, Indonesia, e-mail: mutiaraanrl@gmail.com
Setya Widi Ayuning, Brawijaya University, Faculty of Fisheries and Marine Science, Veteran Street, 65145 Malang, Indonesia, e-mail: setyawidhi45@gmail.com
Evellin Dewi Lusiana, Brawijaya University, Faculty of Fisheries and Marine Science, Veteran Street, 65145 Malang, Indonesia, e-mail: evellinlusiana@ub.ac.id

How to cite this article:
Musa M., Buwono N. R., Iman M. N., Ayuning S. W., Lusiana E. D., 2019 Pesticides in Kalisat River: water and sediment assessment. AACL Bioflux 12(5):1806-1813.