Measurement of Organochlorines Residue (OCs) in water, sediment and soil from Jakarta and West Java

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Abstract. Organochlorine compounds (OCs) are widely used as pesticides in the past and several of them have been prohibited. Some of these organochlorine compounds have persistent properties that can last long in the environment so that they have been included in the list of groups of persistent organic pollutants (POPs). The bioconcentration and bioaccumulation properties of organochlorine compounds increase the negative impact on the health of living organism. The purpose of this study was to measure the organochlorine compounds in the environment, including samples from agricultural soil, sediment, and river water. Sampling was collected in November and December 2018. Sample of agricultural soils were taken in Bogor and Cianjur regencies while water and sediment samples were taken from the rivers in the Jakarta and Cianjur regencies. Total of 24 organochlorine compounds were then measured using Gas Chromatography Mass Spectrophotometer (GCMS). Recovery of water samples was 72% to 82%, for the soil was 79% to 103% and for sediment was below 40%. The OCs detected in the water was in the range of 0.010 µg/L – 0.4 µg/L and in the soil was in the range of 0.4 µg/Kg – 18.55 µg/Kg. Measurement of OCs in sediments from the estuary or downstream of the river in Jakarta was done, however the result was uncertain due to the difficulties in the sample preparation of oily sediments, and hence the results were not provided here. Therefore, it was necessary to develop a testing methodology, especially the proper refining process so that good recovery data could be obtained in the future. The small amounts of organochlorine that were detected in the environment indicated that these compounds are still existing up to now. The purpose of this study is to produce the proper methodology to examine the matrix effects from sticky and oily samples.

1. Introduction
Organochlorine compounds, chloro carbon, chlorinated hydrocarbons are groups of organic compounds that contain at least one chlorine atom that is covalently bound in the given molecule as such that bounds affects the chemical properties of the molecule [1, 2]. The variety of structures and chemical properties of organochlorines lead to the many naming and applications of compounds in this group [3]. Organochlorine is used in various applications, one of them is as an active compound widely available in pesticides, however, this active compound has a detrimental effect in nature, and some of them cause serious environmental problems [4, 5]. Most of the organochlorine compounds are groups of persistent organic pollutants (POPs) or long-lasting organic compounds in the environment [6, 7].

Several studies regarding the residual effect of organochlorines have been reported, and the results strongly indicated that this toxic, hazards material can threaten human health and the environment.[8-
Moreover, threats to humans include, disorders of the reproductive system (infertility), decreased immunity in infants and children, physical and mental disorders, triggers cancer, disorders of functioning organs such as liver, lungs, kidneys, thyroid, hormonal endocrine system, and reproductive organs [11-14].

In the framework of implementing the Stockholm convention in Indonesia [15], namely the reduction and eventual elimination of the use of 12 persistent organic pollutants (POPs), there is a need for organizing preliminary information regarding the level of pollution of these materials in Indonesia. Owing to the fact that POPs are the result of chemical synthesis, POPs can enter the environmental system at each stage of this chemical production cycle (life cycle) starting from the production of POPs, processing, transport and storage, formulation, use, and not to mention the disposal [11], [16].

The measurement of organochlorines compounds persisting in the environment is a critical issue, however effort to get rid off the matrix effect in sample preparation like oily and dirtiness still hamper the successful in analyzing organochlorines containing material [17]. Problems related to the sample preparation and laboratory work have to be solved [18]. This research was designed to examine the presence status of OCs in agricultural and horticultural soil in Cianjur, water and sediments river sediments in Jakarta. Moreover, this research was also designed to compare organochlorines reading conducted in 2018 with that of conducted in 2014 in the case of agricultural and horticultural soil in Cianjur [19]. In other words, evaluation of organochlorines concentration trend in the soil is considered to be important.

2. Material and Methods

2.1. Material

River water, river sediment, and agricultural soil samples were collected for the target analysis of OCs. Analysis of OCs compounds used glass materials and tools that are free from organic compounds contaminant. The chemicals used were hexane, acetone, diethyl ether (all three with grade for residual analysis) [20], NaCl, Na$_2$SO$_4$, concentrated H$_2$SO$_4$, Cu wire, and activated Florisil. While the equipment used was a 2 L, 500 mL, and 250 mL separator funnel, beaker glass, 300 mL heating flask, 30 cm long glass column (1 cm diameter), evaporator, and GCMS.

2.2. Methods

2.2.1. Sampling. Sampling of river water and river sediments were executed by using the grab method[21]. In the mean time, soil samples were collected compositly from upper 10 cm of the soil surface. Method for sampling are refer to SNI 8520:2018. Water and sediment samples from Jakarta were collected from the Ciliwung river in the Cilincing, Kali Sunter, Mangga Dua, North Manggarai, Grogol and Muara Angke areas on April 21$^{th}$-22$^{th}$, 2018, while water samples, sediment and soil samples from West Java were taken in Bogor and Cianjur areas on May 4$^{th}$-5$^{th}$, 2018. Location of sampling points is presented in Figure 1. Further detail informations of sampling locations are summarized in Table 1.
Figure 1. Satellite Image of Sampling Location (Google Earth)

Table 1. Location of sampling points

| Code | Location                                      | Coordinate                      |
|------|-----------------------------------------------|---------------------------------|
| A1   | Cibeureum river, in the sub-unit of the       | 06°48'14.1" S; 107° 5'21.8" E  |
|      | Cijedil PLTMH, Cianjur                       |                                 |
| A2   | Cilincing River, North Jakarta                | 06°06'36.6" S; 106°56'26.9" E  |
| A3   | Sunter River, North Jakarta                  | 06°06'55.4" S; 106°53'47.1" E  |
| A4   | Mangga Dua, Central Jakarta                  | 06°08'07.1" S; 106°49'53.7" E  |
| A5   | North Manggarai, Central Jakarta             | 06°12'40.4" S; 106°51'15.1"E    |
| A6   | Grogol River, West Jakarta                   | 06°08'17.8" S; 106°47'09.1"E    |
| A7   | Muara Angke, West Jakarta                   | 06°06'35.9" S; 106°46'27.7" E  |
| T1   | Soil from carrot and onion farm, Cianjur     | 06°46'01.4" S; 107°03'22.1" E  |
| T2   | Paddy field soil, near PLTA Cijedil          | 06°48'12.8" S; 107°05'00.9" E  |
| T3   | Farm soil, Sukatani village                  | 06°44'55.1" S; 107°01'51.5" E  |
| T4   | Farm soil, Agropolitan company               | 06°44'59.4" S; 107°00'30.7" E  |
| T5   | Farm soil, Sindang Jaya village              | 06°44'14.6" S; 107°01'30.9" E  |
| T6   | Paddy field, Bogor                           | 06°44'55.1" S; 107°01'51.5" E  |
| T7   | Farm soil, Ciomas                            | 06°34'19.1" S; 106°45'19.6" E  |
| T8   | Paddy field, Ciomas                          | 06°34'43.6" S; 106°44'56.1" E  |

2.2.2. Sample preparation. The analysis method refers to USEPA 8270D. The water sample was extracted with hexane while the soil and sediment samples were extracted with acetone first then followed by extracting it into the hexane phase [22]. All samples and blanks were added by surrogate p,p-DDE 13C12 before extraction was carried out. Surrogate is used to control analysis accuracy. The extracts were concentrated and purified before being injected into GCMS. Florisil, which had been activated for 3 days at 150°C, was used as a stationary phase for the refining process. Besides florisil, Na₂SO₄ anhydrous was also used. If the elution was still yellowish, then the refining was done again until the elution was colorless. After that, it was concentrated until the volume was ± 1 ml and then injected as much as ± 2 µl through the injector system. Before being injected, chrysene-d12 and phenantrene-d10 were added as internal standards. The instrument/tool used was the ISQ LT type GCMS scientific with a DB-5MS capillary column (30m x 0.25mm id x 0.30 µm thickness).
the method used is a standardized method that has been validated and accredited by a national accreditation agency.

3. Results and discussion
The results of the analysis in water samples indicated that several OCs compounds, such as HCH groups (alpha, beta, delta, and gamma), DDT and their derivatives, endrin, endosulfan I and endosulfan II were still detected in the river water. OCs were detected in the range concentration of <0.01 - 0.37 ng/ml. Gamma-HCH (Lindane) had the highest concentration (0.37 ng/ml) in river water collected from downstream of Muara Angke River, Jakarta, followed by endosulfan II (0.29 ng/ml) collected from a river located in north Manggarai Jakarta. DDT and its derivatives were detected fluctuated in several locations in the range of <0.01-0.035 ng/ml. Alpha-HCH and endosulfan II was detected in all sampling locations with the range concentration, respectively 0.016 – 0.14 ng/ml and 0.012-0.29 ng/ml.

As for sediments, the test results are not presented in this report simply because there were several problems encountered in sampling, preparation work so that further analytical verification still needed for reading improvement. In fact, the sediment samples were very smelly, dirty, sticky and oily and this condition cause difficulties in the clean-up process. The final extract which should be colorless and aqueous[23], had a yellowish color and was quite thick even though it had been through 2-3 times of the purification process. This caused the chromatogram peaks to be disproportionate and even the internal standard peaks were covered, possibly by the presence of fat which was still eluted in the final extract. The concentration of organochlorine compounds in water samples is presented in Figure 2.

![Figure 2. Concentration of organochlorine in river water](image)

OCs were found in almost all of the soil samples in the concentration range of 0.44 - 19 ng/g. The soil samples were originated from Cianjur and Bogor areas. It is extremely important to note that OCs parameters that were detected, included beta-HCH, lindane, heptachlor, heptachlor epoxide, Aldrin, endosulfan, dieldrin, endrin, DDT and its derivatives are still persisting in the soils. Even though those toxic materials present at low concentrations, however this product are actually already banned by the government [24, 25]. Compared to 2013 data, the concentration of DDT and its derivatives decreased almost in all the sampling location 3.6 ng/g – 62 ng/g [19]. The concentration of organochlorine compounds in soil samples is presented in Figure 3.
Figure 3. Concentration of organochlorine in soil

Regarding to this study, some POPs were still detected in the environment. That is to say that many stakeholders, including civil society in the country have to be aware of this situation, and think about controlling the distributions of banned material in the future.

4. Conclusion
Organochlorine compounds were detected almost in all water and soil samples. In addition, endosulfan and lindane are compounds that had been detected in the water and soil samples in the most cases, besides beta-HCH, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, DDT and its derivatives. The concentration of OCs that had been detected in the water were range from 0.016 to 0.37 ng/ml. OCs were found in almost all of the soil samples with concentration range from 0.44 to 19 ng/g. The sediment organochlorine test results were not shown in this report due to technical reason.

Organochlorine compounds that had been found in sampling locations in Jakarta (water and sediment) and West Java (water and soil) indicated that these compounds still exist. It is important to run the same research in other places in the future for better understanding about the status of organochlorines in the country. Furthermore, it is also necessary to find out the proper methodology to eliminate the interferences in analysis of complex matrix in sediment in order to get better results.

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References
[1] M M A, Abdulmalik H.
[2] Winterton N. 2000. Green Chemistry.2(5):173-225
[3] Ohorella A, Daud A. 2013.
[4] Jayaraj R, Megha P, Sreedev P. 2016. Interdisciplinary toxicology.9(3-4):90-100
[5] Mansouri A, Cregut M, Abbes C, Durand M-J, Landoulsi A, Thouand G. 2017. Applied biochemistry and biotechnology.181(1):309-39
[6] Suryono CA, Rochaddi B, Irwani I. BULETIN OSEANOGRAFI MARINA.5(2):101-6
[7] Suryono CA, Suwartimah K, Rochaddi B, Sarjito S. 2016. Jurnal Kelautan Tropis. 18(3):139-46
[8] Smith AG. Toxicology of ddt and some analogues. Hayes' handbook of pesticide toxicology: Elsevier; 2010. p. 1975-2032
[9] Cahyaningrum D, Denny HM, Adi MS. Jurnal Promosi Kesehatan Indonesia. 13(1):32-45
[10] Daoud JR, Hegazy HM, Ahmed AM. 2011. Journal of South Valley University for Environmental Researches. 145(589):1-14
[11] Aritonang FA, Saraswati LD, Udiyono A. 2015. Jurnal Kesehatan Masyarakat (e-Journal).3(1):127-34
[12] Sinulingga K. 2006.
[13] Wahyuni S, Ardiwinata A, Sudiana I, editors. Isolasi bakteri pendegradasi senyawa persisten organoklorin poluttans asal tanah inceptisol karawang. Prosiding Seminar Biologi; 2013
[14] Rignell-Hydrom A, Rylander L, Hagmar L. 2007. Human & experimental toxicology. 26(5):447-52
[15] Santoso WY. 2009. Mimbar Hukum-Fakultas Hukum Universitas Gadjah Mada. 21(1):53-66
[16] Stockholm convention, (2011)
[17] Zheng G, Han C, Liu Y, Wang J, Zhu M, Wang C, Shen Y. 2014. Journal of dairy science. 97(10):6016-26
[18] Saadati N, Abdullah MP, Zakaria Z, Sany SBT, Rezayi M, Hassonizadeh H. 2013. Chemistry Central Journal. 7(1):63
[19] Syofyan Y, Andiri Y. 2014. Jurnal Ecolab. 8(2):78-84
[20] Therdteppitak A, Yammeng K. 2003. ScienceAsia. 29(2)
[21] Pratono T, Razak H, Gunawan I. 2009. Jurnal Ilmu dan Teknologi Kelautan Tropis. 1(2)
[22] Agency USEP. Method 8270d semivolatile organic compounds by gas chromatography/mass spectrometry. United States 2014
[23] Schenck FJ, Howard-King V. 2000. Journal of Environmental Science & Health Part B. 35(1):1-12
[24] Rahmawati S, Margana G, Yoneda M, Oginawati K. 2013. Procedia Environmental Sciences. 17:3-10
[25] Yuantari CM, editor Dampak pestisida organoklorin terhadap kesehatan manusia dan lingkungan serta penanggulangannya. Prosiding Seminar Nasional; 2011