IDENTIFICATION OF POP$_S$ ORGANIC COMPOUNDS IN SEDIMENT IN THE CISANGKUY WATERSHED USING GC-MS ANALYSIS METHOD

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Abstract

The Cisangkuy Watershed is a tributary of the Upper Citarum River located in the Bandung Basin, West Java. Based one previous research, one organic pollution in the Cisangkuy Watershed is the presence of POPs (Persistent Organic Pollutants) compounds. POPs are organic compounds that can last a very long time in the environment (persistent) and have toxic properties for organisms. This study aims to identify and analyse the organic content of POPs and sediments in the Cisangkuy Watershed, as well as to analyse the source of pollutants and categorise them based on the Stockholm Convention on Persistent Organic Pollutants. Identification of POPs compounds using gas chromatography-mass spectrometry (GC-MS) technique. Sediment sampling was conducted by grab sampling that involved 20 sampling points from upstream to downstream of the Cisangkuy Watershed (CS-1 to CS-20). Samples were collected from 9 sub-districts. The research location shows that the land activities at the sampling point include asphalt hot mix, pharmaceutical, textile, and manufacturing industries. The results showed the presence of 1,2-Benzenedicarboxylic acid, mono (2-ethylhexyl) ester, 4,8,12-Tetradecatrienenitrile, 5,9,13-trimethyl-, and 2-Hexyl-1-octanol compounds at sampling points from upstream to downstream. These compounds were derived from chemical industry effluents, fossil fuel combustion, and agricultural activities. The compounds are classified as 'industrial waste' and 'industrial waste with antibiotic properties' by the Stockholm Convention on Organic Waste Management.

Keywords: *Cisangkuy Watershed, GC-MS, POPs, sediment*

Introduction

Persistent Organic Pollutants (POPs) are organic pollutants that persist in the environment as they degrade through chemical, biological, and photolysis processes. These compounds are poorly soluble in water but tend to dissolve in fats, so they become increasingly concentrated and widespread in the environment. In addition, these compounds are semivolatile, allowing them to exist in the vapour phase or be trapped in dust particles, enabling POPs to capture long-distance air transport before being deposited in the body (Syofyan & Andiri, 2014). A significant environmental problem besides POP compounds in the Cisangkuy watershed is pollution caused by heavy metals and others organic POP compounds. These organic compounds can persist for a long time in the environment and have toxic properties for organisms. They can also be bioaccumulated and bioconcentrated through the food chain, resulting in increased concentrations in organisms at higher trophic levels, which can seriously impact human health (Rokhwani, 2010).

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The high turbidity value in the Cisangkuy Watershed is more caused by the high fecal coliform parameters that were dominant during 2011-2016 from domestic and livestock waste discharges, as well as several parameters that exceeded the quality standards in certain years such as nitrite, free ammonia, cadmium, COD, and detergents. The high COD content is caused by the large amount of organic matter contained in the Cisangkuy watershed. The amount of land also greatly affect the amount of pollution load from the agricultural sector. The larger the land, the greater the pollution load generated. (Sampe et al., 2018)

In catfish samples taken from several locations along the upper Cisangkuy Watershed, organochlorine pesticide residues such as heptachlor, enndosulfan and DDT were found. (Harsanti et al., 2021)

Agricultural intensification in the upper Cisangkuy Watershed has increased the use of pesticides. The are 31 types of pesticides use by farmers in the upper Cisangkuy Watershed and the pesticide residue content in the water of the upper Cisangkuy Watershed has reached a risky level for river biota. (Utami et al., 2020)

Heavy metal content also found in the Cisangkuy Watershed, such as the concentration of Cd metal found in water samples of the upstream Cisangkuy watershed with Dayeuhkolot, Cisirung and Nanjung segments. (Affum et al., 2020). Sources of heavy metals in agricultural land other than irrigation water can also come from industrial activities and agricultural cultivation carried out by farmers by applying chemical fertilizers and pesticides during the planting period. The accumulation of heavy metals in agricultural soil corelates with the distance from an industry (Rahi et al., 2022)

The use of Cisangkuy watershed as a source of irrigation and the application of agrochemicals in agricultural cultivation in the Upper Cisangkuy watershed, this study aims to provide information on the level of heavy metal contamination on agricultural land in Bandung Regency (Upper Cisangkuy watershed) by analyzing contamination factors, ecological risk factors, pollution load index and heavy metal accumulation levels originating from anthropogenic sources. (Handayani et al., 2022)

Heavy metals (Cd, Cr, Cu, Hg, Ni, and Zn) are hazardous pollutants found in the Cisangkuy River. Industries that potentially produce heavy metal waste are the textile industry, metal processing, wood processing, printing, leather tanning, fertilizer factories, electroplating, and others. (Febrita & Roosmini, 2022)

This study aims to identify the content of POPs organic compounds in Cisangkuy Watershed sediments using GC-MS analysis. The results are expected to provide in-depth information about the types and categories of POPs found in the Cisangkuy Watershed and insight into the sources and impacts of such pollution on the environment and human health.

Research Methodology

Sampling was conducted at the Cisangkuy Watershed in Bandung Regency in October 2023. CS-1 to CS-20 are sediment sampling points (Figure 1).

Sample Analysis

Sediment sample analysis was conducted at the Geological Resources Research Centre Laboratory, National Research and Innovation Agency (BRIN). Compound preparation and analysis Persisten organic pollutants (POPs) in sediment samples were carried out based on Standard Operation Procedure (SOP, 2013) Organic Chemistry Laboratory of the Oceanographic Research Center of LIPI.

Sediment samples were collected from the Cisangkuy Watershed, Bandung Regency, and put into labelled plastic bags. The samples were then put into a cooling box containing ice gel to preserve them during sampling.

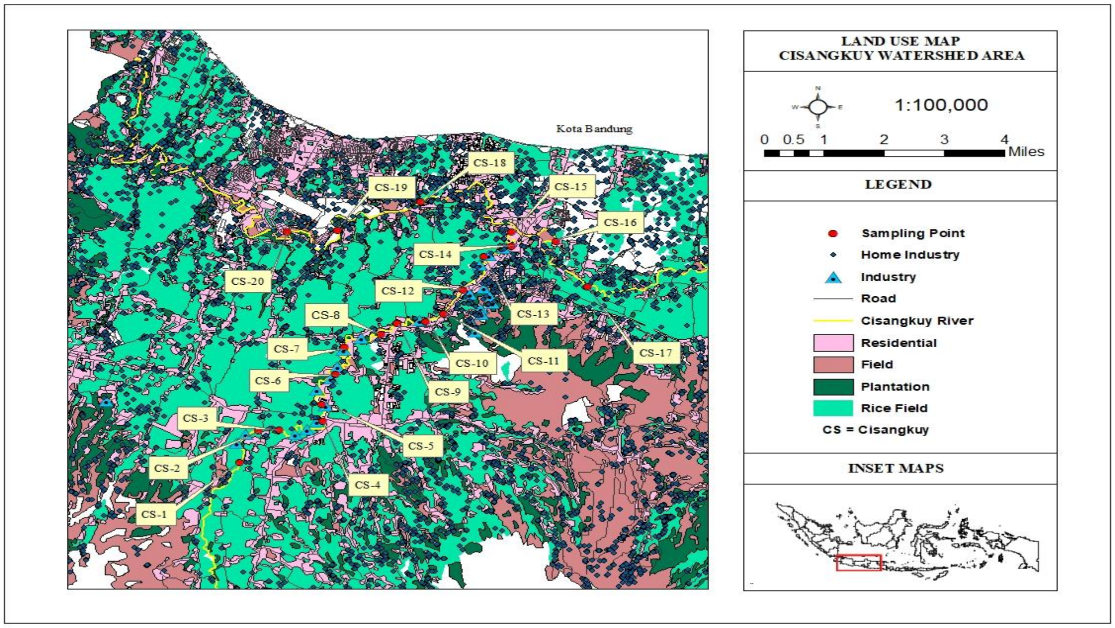

Figure 1 Land Use Cisangkuy Watershed

The tested samples were dried at room temperature or 25°C until dry. The dry sediment samples were then crushed using a mortar and pestle, after which they were sieved with a shaker with a sieve measuring 100 mesh (0.147 mm) to obtain homogeneous sediment grains. (SOP, 2013)

The filtered sediment sample was extracted in as much as 8 grams and then put into a centrifugal bottle with 25 ml of n-hexane and dichloromethane solution. The sediment was then separated from the solution using ultrasonic Branson 3510 for 30 minutes. This ultrasonic treatment is essential as it aids in the separation of the sediment and solution. The sample was filtered to separate the sediment and organic solution. The organic sample was put into a new centrifugal bottle, put into the extraction flask and shaken for 3-4 minutes. Every 10 seconds, open the lid of the extraction flask to release the gas. The extraction flask that has been shaken is allowed to stand there until the organic compounds and water separate; then, the organic compounds are put in a centrifugal bottle. (SOP, 2015)

The Gas Chromatography-Mass Spectrometry (GC-MS) method is a particularly effective analytical technique for detecting POPs in sediments. When heated, gas chromatography separates volatile compounds under high vacuum and low-pressure conditions, whereas mass spectrometry determines molecular weights, molecular formulas, and generated charged molecules (Cyprianus & Muzakky, 2010). This method can separate individual chemical components and identify them based on their mass spectra, making it particularly suitable for detecting POPs in sediments.

Separated samples are put in an evaporator flask and allowed to evaporate. The results of the evaporation were put into a 3 ml vial flask and filtered using a syringe filter. Filtered samples are then inserted into the GC-MS to analyse POPs organic compounds using GC-MS QP2010 Shimadzu Ultra. The carrier gas used is nitrogen. GC-MS will analysed each organic sample for 1 hour.

Data Analysis

The data were analysed descriptively by comparing them with data from previous studies conducted by several researchers in several waters and sediments and categorising each source of compounds according to the Stockholm Convention on Persistent Organic Compounds.

Result and Discussion

Table 1 shows the results of the identification of POP compounds in sediments. The table shows that the POP compounds identified in the Cisangkuy Watershed are Benzene1,2,4-trimethyl-, 1,2-benzenedicarboxylic acid, mono(2-ethylhexyl) ester, 4,8,12-tetradecatrienenitrile 5,9,13-trimethyl, and 2-hexyl-1-octanol.

Benzene, 1,2,4-trimethyl-

Benzene, 1,2,4-trimethyl- is a compound that 1,2,4-trimethyl benzene (C_9H_{12}) is a compound known as POPs because it persists in the environment for a long time due to the difficulty of this compound to be degraded through chemical, biological, and photolysis processes. This compound is difficult to dissolve in water but tends to dissolve in fat, so it accumulates and is always present in the environment. Benzene, 1,2,4-trimethyl compounds are produced by chemical industry waste activities around the Cisangkuy Watershed. Benzene, 1,2,4-trimethyl-compounds were detected at sampling points CS-1 and CS-11.

Benzene, 1,2,4-trimethyl, is most generally found in fuel oil, where benzene is released into the environment during the final combustion process (Aldi, 2024). Organic compounds in the aquatic environment may come from natural activities (oil seepage, forest fire smoke, volcanic eruptions) and human or anthropogenic activities such as industry, transportation, and households (Zakaria, 2013).

According to land use activities, sampling point CS-11 is adjacent to the textile industry, and POPs compounds may originate from the textile industry. In the textile and leather dyeing process, the textile industry can produce POPs using chlorinated chemicals, such as pentachlorophenol and chloronitrophen (Wulandari, 2020). Based on the Stockholm Convention, Benzene compounds, 1,2,4-trimethyl- are categorised as POPs with the type of industrial chemicals.

Table 1. POPs Identification

Compound	Sources	Bjn		Pnj		Pmk				Cpy	Bld		Dyk			Bjs		Ktp	Mgu		
		CS 1	CS 2	CS 3	CS 4	CS 5	CS 6	CS 7	CS 8	CS 9	CS 10	CS 11	CS 12	CS 13	CS 14	CS 15	CS 16	CS 17	CS 18	CS 19	CS 20
Benzene, 1,2,4-trimethyl-	chemical industrial waste	✓										✓									
1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester	industrial and domestic waste	✓	✓	✓			✓	✓	✓	✓		✓	✓	✓	✓	✓	✓				
4,8,12-Tetradecatrienenitrile, 5,9,13-trimethyl-	Chemical industry waste and fossil fuel combustion	✓		✓										✓							
2-Hexyl-1-octanol	agricultural organic waste										✓				✓	✓	✓				

Description

Bjn = Banjaran   Pnj = Pananjung   Pmk = Pamengpeuk   Cpy = Ciparay   Dyk = Dayeuhkolot
Ktp = Katapang   Mgu = Margahayu   Bjs = Bojongsoang   Bld = Baleendah

1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester

The compound 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester is also known as Monoethylhexyl phthalate (MEHP); this MEHP compound can last a very long time in the environment because of the difficulty of this compound to be degraded through chemical, biological, and photolysis processes (Senaen et al., 2022). Based on the analysis, the compound 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester was detected at 13 points along the Cisangkuy Watershed; its presence was in CS-1, CS-2, CS-3, CS-6, CS-7, CS-8, CS-9, CS-11, CS-12, CS-13, CS-14, CS-15 and CS-16. According to the results of the analysis, the compound 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester, is sourced from several industrial activities, such as the asphalt and textile industries. This compound can enter the water using water solvents, extract fractions, or identification in methanol extracts. This compound was detected in the water fraction of some drinks and had the same polarity level as water. Thus, it can dissolve in water (Stocks, 2016)

To state the source was determined based on the land use map of the Cisangkuy watershed.

According to the Stockholm Convention on Persistent Organic Compounds, the compound 1,2-benzene dicarboxylic acid, mono(2-ethylhexyl) ester, is classified as a POP with the type of industrial chemical.

4,8,12-Tetradecatrienenitrile, 5,9,13-trimethyl-

The compound 4,8,12-tetradecatrienenitrile, 5,9,13-trimethyl belongs to the Aldehydes category. Aldehydes are a class of chemical compounds that have an aldehyde group. Aldehydes fall under the category of POPs because they have several properties that are hazardous to the environment and human health. Aldehydes can persist for a relatively long time in the environment, accumulating and being transported through the food chain. They can spread through air, water, and species and accumulate in fats and soil (Ratnaningsih, 2010).

This study analysis has identified 4,8,12-Tetradecatrienenitrile, 5,9,13-trimethyl compounds at several points, including CS-1, CS-3, and CS-13 along the Cisangkuy Watershed. These compounds, which are associated with chemical and textile industry activities, warrant further investigation into their potential sources.

The primary source of 4,8,12-tetradecatrienenitrile and 5,9,13-trimethyl compounds comes from chemical industry waste at CS-1 and CS-3. Under the Stockholm Convention on Persistent Organic Pollutants, this compound belongs to the POPs category of industrial chemicals with the type of antibiotic drugs.

2-Hexyl-1-octanol

The compound 2-Hexyl-1-octanol is essential in agriculture, especially regarding antioxidant activity in Sargassum hystrix powder (Afgatiani et al., 2020). Based on the analysis, the compound 2-Hexyl-1-octanol was detected at 4 points of the Cisangkuy Watershed, namely CS-10, CS-14, CS-15 and CS-16. Moreover, based on land use activities at point CS-10 dominated by agricultural activities, 2-Hexyl-1-octanol compounds can protect plants from oxidation damage. This compound has antioxidant activity that can help inhibit plant oxidation reactions, thus preventing oxidation damage to plant structure and function. Based on its role in agriculture to protect plants from damage (Afgatiani et al., 2020).

Based on the land use activities in CS-14, CS-15 and 16, it is dominated by textile industry activities, where 2-Hexyl-1-octanol compounds can also originate from the textile industry, especially as part of surfactant formulations or lubricants used in textile processes for cleaning or machine lubrication. The production of 2-Hexyl-1-octanol involves chemical processes with potential environmental impact, such as hydroformylation (oxo synthesis) of the relevant olefins. 2-Hexyl-1-octanol enters river water through various pathways, including industrial and household waste disposal, spills or leakage, and discarded products (Effendi, 2021).

From the analysis, there are several sampling points where POPs compounds were not identified, including CS-4, CS-5, CS-17, CS-18, CS-19 and CS-20. The spread of POPs through the air occurs through evaporation, atmospheric transport, global transport, and pesticide use; POPs can move through the air by evaporation and deposition across long-distance atmospheric boundaries. This is due to the semi-volatile nature of POPs. Therefore, the spread of POP compounds may be only sometimes at the closest point to the pollutant source due to its volatile nature, which indicates why no POP compounds were detected at sampling points 4,5,17,18,19 and 20.

Conclusions

The measurement result of 20 sampling points in Cisangkuy Watershed, 16 points were identified as containing Persistent Organic Pollutants (POPs) compounds. The content of POPs compounds found were:

- Benzene, 1,2,4-trimethyl-: Derived from chemical industry waste, according to the Stockholm Convention.
- 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester: Derived from industrial waste, under the Stockholm Convention.
- 4,8,12-Tetradecatrienenitrile, 5,9,13-trimethyl-: Derived from chemical industry waste and fossil fuel combustion, according to the Stockholm Convention.
- 2-Hexyl-1-octanol: Derived from agricultural organic waste, under the Stockholm Convention.

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