4. Research Report

Title of Research Project:
Assessment of the Occurrence, Distribution and Ecological Risk of Bisphenol Analogues in the Surface Water from Citarum Watersheds

Project Members:

- Dr. Agus Sudaryanto (PI)
  Research Center for Environmental and Clean Technology, National Research and Innovation Agency – BRIN, Kawasan Puspiptek Gedung 720, Tangerang Selatan 15314, Indonesia
- Dr. Dwindrata B Aviantara (Member)
  Research Center for Environmental and Clean Technology, National Research and Innovation Agency – BRIN, Kawasan Puspiptek Gedung 720, Tangerang Selatan 15314, Indonesia
- Fuzi Suciati
  Research Center for Environmental and Clean Technology, National Research and Innovation Agency – BRIN, Kawasan Puspiptek Gedung 720, Tangerang Selatan 15314, Indonesia
- Dr. Budi Kurniawan
  Research Center for Environmental and Clean Technology, National Research and Innovation Agency – BRIN, Kawasan Puspiptek Gedung 720, Tangerang Selatan 15314, Indonesia
- Dr. Rumi Tanoue
  Center for Marine Environmental Studies (CMES), Ehime University, Bunkyo-cho 2-5, Matsuyama 790-8577, Japan
- Prof. Tatsuya Kunisue (Member)
  Center for Marine Environmental Studies (CMES), Ehime University, Bunkyo-cho 2-5, Matsuyama 790-8577, Japan

Research Background and Purposes:
Water contamination by endocrine disrupting bisphenol-A (2,2-bis(4-hydroxyphenyl) propane, BPA) has been a matter of global concern. This is because of BPA has shown varying different adverse effects, including to fish (Suzuki et al., 2003), rats (Liu et al., 2019) and human health (Rochester, 2013). Therefore, in response to the adverse effects of BPA, several countries and regions, including China (Jin and Zhu, 2016), San Francisco (Chen et al., 2016), Canada, and the European Union (Negev et al., 2018), have issued policies banning BPA in products. However, in order to meet the market demand for products, various alternatives to BPA were widely used in industrial production (Zheng et al., 2019), such as bisphenol-S (4,4′-sulfonyldiphenol; BPS), which is widely used in the manufacture of epoxy resins, bisphenol-E (bis(4-hydroxyphenyl) ethane, BPE) for cyanate resin, bisphenol-F (bis(4-hydroxypheny)methane; BPF) for epoxy resin reinforced with nano polyanilines, and bisphenol-AF (4,4′-(hexafluoroisopropylidene) diphenol, BPAF) and bisphenol-Z (4,4′-(cyclohexane-1,1-diyl) diphenol, BPZ) for the manufacture of epoxy resins and polycarbonate plastics. Indeed, recent studies have shown that BPS, BPF, and other BPA analogues were widely detected in the water environment, and the pollution levels have an increasing trend (Chen et al., 2016). In addition, current research studies have indicated that BPS, BPAF, and BPF can be accumulated by aquatic organisms, and pose a serious threat to the whole ecosystem as BPA (Yan et al., 2017). Research is still needed to better elucidate the environmental sources, distribution, and fate of bisphenol analogues (BPs).

The Citarum is the largest river in the West Java, Indonesia stretches for 297 km across 13 regencies/cities with its upstream in Bandung Regency and empties into the Java Sea, at Muara Gembong, Bekasi Regency (Figure 1). Every day, the Citarum watersheds receives no less than 20,000 tons of waste and 340,000 tons of wastewater from more 2,000 factories. Thus, the Citarum watershed is experiencing pollution and environmental damage due to high domestic and industrial activities on the riverbanks. Pollution to the Citarum River is due to includes industrial pollution, agricultural waste, livestock waste, fishery waste, and both domestic wastewater and domestic waste (West Java Province task force for pollution control and damage to the Citarum watershed, 2018). As the result, aquatic environment of Citarum is under threat. For example, since 2002, lead, aluminum, manganese, and iron in the Citarum has never met the water quality standards of Government Regulation No. 82 of 2001 and levels of lead reached 1,000 times worse than the U.S. standards for drinking water (Blacksmith Institute, 2013). Citarum River considered as the “world’s most polluted river” and thus government paid attention to restore the ecosystem through “Citarum Harum National Project”. Despite improving visual environment of Citarum River after "Citarum Harum" was launched at 2018, there is limited or no available information on trace toxic contaminants including bisphenol analogues in Citarum watershed.

The purpose of this study is to determine bisphenol analogues in surface waters of Citarum Watershed in order: (a) to understand their occurrence, distribution and sources, and (b) to estimate their potential health risk to aquatic ecosystems.

Methods

Sampling and Sample

The study combined of sampling survey to acquire the samples and chemicals analysis at laboratory. Sampling locations were selected along Citarum River generally according to water quality monitoring point from the Ministry of Environment and Forestry of Republic Indonesia started from upstream (upper), middle to downstream (lower) Citarum. This river crosses to several city and regency such in Bandung, Purwakarta, Kerawang, and Bekasi (Figure 1). Samples are surface river water consisting of a total of 61 sampling sites along the main Citarum River and its tributaries (Figure 1). The sampling program was conducted during 29 October – 2 November 2022 and 1 - 20 June 2023. Surface water were sampled using a stainless steel containers. The surface water then transferred to 100 ml of bottle sample, preserved with keep in cool box, and transferred to Center for Marine Environmental Studies (CMES), Ehime University, Japan for chemicals analysis.

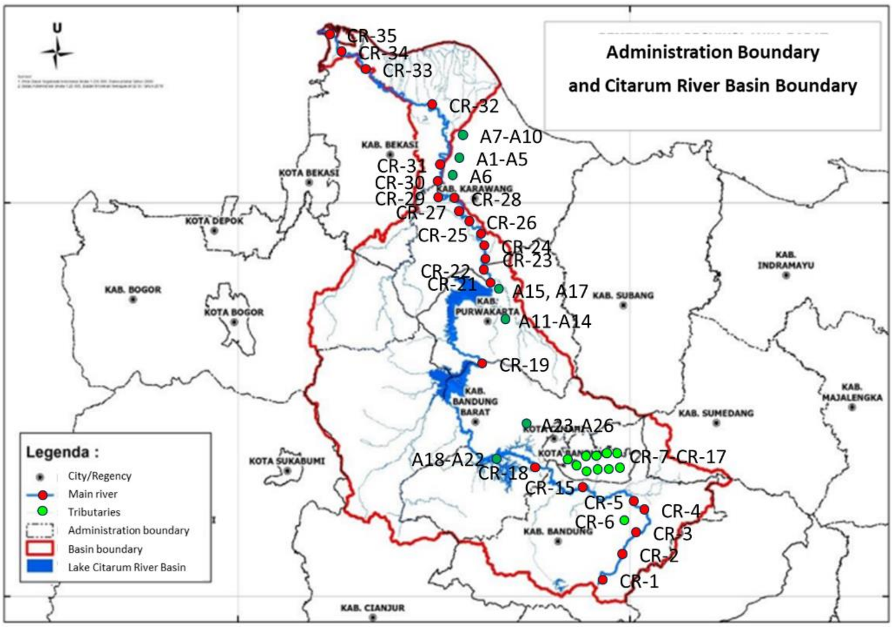

Figure 1. Sampling locations of surface water at Ciliwung River and its tributaries from upstream to downstream.

Chemicals Analysis

Ten commonly used BPs such as BPA, BPAF, BPF, BPS, BPB, BPC, BPC12, BPE, BPZ and TBBPA were selected as target analytes. The target of bisphenol analogues in this study include ten commonly used BPs such as bisphenol-A (2,2-bis(4-hydroxyphenyl) propane; BPA), bisphenol-AF (4,4′-(hexafluoroisopropylidene) diphenol, BPAF), bisphenol-F (bis(4-hydroxypheny)methane; BPF), bisphenol-S (4,4′-sulfonyldiphenol; BPS), bisphenol-B (4,4'-(1-methylpropylidene)bisphenol; BPB), bisphenol-C (4,4′-isopropylidenedi-o-cresol; BPC); bisphenol-C12 (4,4'-(dichlorovinylidene)diphenol; BPC12), bisphenol-E (bis(4-hydroxyphenyl) ethane, BPE), bisphenol-Z (4,4′-(cyclohexane-1,1-diyl) diphenol, BPZ), and Tetrabromobisphenol A [4,4’-isopropylidenebis(2,6- dibromophenol)] (TBBPA). The bisphenol analogues analysis were conducted at Laboratory of Environmental Chemistry and

Ecotoxicology, Center for Marine Environmental Studies (CMES), Ehime University, Japan. Surface water samples were analysed according to the method published elsewhere11) . Briefly, extraction of the sample was carried out by filtering water samples (20 mL), added with internal standard (IS) and then inserted into the Oasis HLB Plus Light cartridge as a solid phase extraction for the clean-up procedure. The target BPs retained in the cartridge was 5 / 9 eluted with a solution of methanol/MTBE (3 mL, by volume ratio 7:3), and the eluate was concentrated to 0.2 mL under a stream of N2. For identification and quantification of BPs, the residue was dissolved in acetonitrile/methanol/Milli-Q (1 mL, volume ratio 1:2:7). Identification and quantification of target BPs was carried out using a Prominence Ultra-Fast Liquid Chromatograph equipped with a mass spectrometer. This equipment operates in positive and negative electrospray ionization (ESI) mode with dual reaction monitoring (MRM).

Results

Occurrence, Distribution and Sources

A total of 61 surface water samples collected along Citarum River and its watersheds comprising three segments of upper, middle and lower Citarum River has been analyzed for ten bisphenol analogous (BPs). Figure 1 shows the concentration of BPs analogous in surface water from main Citarum River and its watersheds from upper part to lower Citarum. BPs were detected at 35 locations which accounted 57% of the total locations (61 locations). Among the 10 BPs, only 2 BPs i.e BPA and BPS were generally detected at relatively in wide range of Citarum River, 1 BPs was detected in only 1 location i.e TBBPA and the rest BPs were not detected in any locations. BPS (57% of the locations) showed a more detection frequency than BPA (43%). Among the detected BPs, BPA had the highest level in surface water with a concentration up to 5800 ng/L, whereas maximum concentration of BPS was 4100 ng/L. The detectable TBBPA in one location was 19 ng/L.

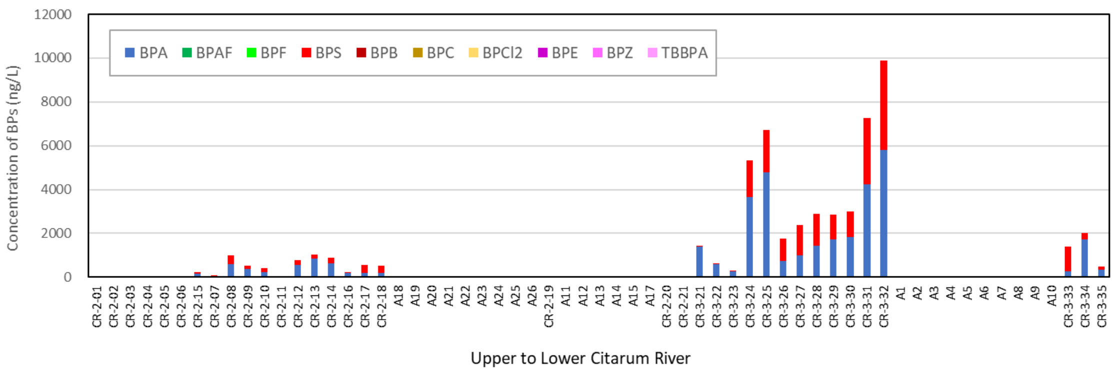

Figure 2. Concentration of BPs analogous in surface water from main Citarum River and its watersheds from upper part to lower Citarum.

Even though it has been replaced by other BPA analogues in recent years, BPA is still the most dominant compound in the surface water of the Citarum River. Although there is very little information on BP use data, the results of this study show that there is common use of BPA and BPS in several areas around the Citarum River. The distribution of BPs at each observation station shows that BPA and BPS were detected in the Citarum River, especially in the lower Citarum segment which crosses Kerawang City and Bekasi Regency, namely detected at all stations from CR-21 to CR-35, especially in Kerawang City, Bekasi. Meanwhile, the concentration of BPs in the upper and middle segments of Citarum is much lower and is not even detected in many locations, including in its tributaries. However, BPs were also detected in several Citarum river tributaries, especially in rivers that cross the city of Bandung (CR-7 to CR-17). Kerawang City, Bekasi Regency and Bandung City have higher population numbers and industrial activity, resulting in the widespread presence of BP in rivers.

Potential Health Risk to Aquatic Ecosystems.

The risk quotient (RQ) method was used to assess the ecotoxicity of the selected BPs namely BPA and BPS which generally detected in the water bodies of Citarum River. This approach has been used elsewhere (Wang et al. 2022). For each compound of BPs, RQi value is the proportion of the maximum measured environmental concentration (MECi) to the predicted no-effect concentration (PNECi). The total RQ (TRQ) of BPs was calculated based on the following equation.

∑RQ (TRQ)= ∑RQi = ∑MECi / PNECi

The TRQ was the sum of RQ of each separately measured contaminant (RQi) at each sampling site. Generally, environmental risks are classified as high risk (RQ>1.0), medium risk (0.1<RQ<1), and low risk (0.01<RQ). In this study, the PNEC values are obtained from dividing the minimum toxicity value (i.e., lowest short-term EC50 for BPS and long-term NOEC value for BPA) in the literature by an assessment factor (AF) of 1000 and 100, respectively (Wang et al. 2022). The toxicity values of BPA and BPS used in the present study were derived from literature published study (Yan et al., 2017).

The range of Total RQ for the detectable of BPA and BPS in Citarum River was 0.000068 – 0.99 (Figure 3). The result indicates that none of the sampling site had high risk to aquatic organism (RQ<1). At all site, only 16 % of the river water bodies had moderate risk to river ecosystem and at locations where BPs were detected (35 sites), 29 % of them represent moderate risk. However, at one location in CR-3-32, the TRQ was close to 1 (0.99) which a border of the value for high risk. Among BPs, BPA was the most contributor to total RQ of which the all-moderate risk was contributed by BPA than BPS.

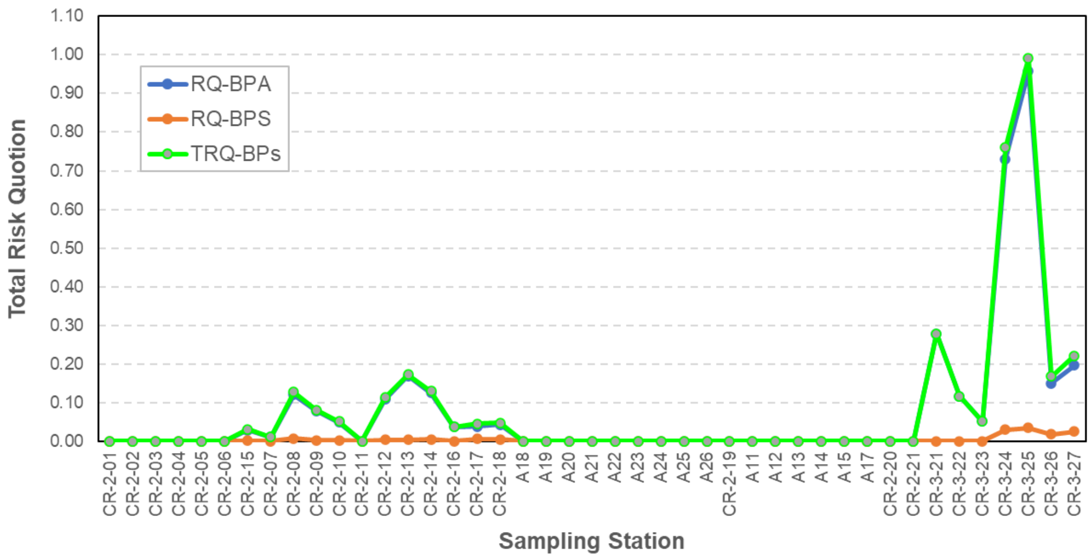

Figure 3. Calculated of risk quotient (RQ) for BPA and BPS as well total RQ (TRQ) for BPs.

Future Challenges.

This study highlights hot spot BPs contamination in specific locations of river bodies at Citarum River. In particular, current study found BPA and BPS were the only detected BPs and indicate common use of BPA and BPS in several areas around the Citarum River. BPA was the most contributor to total RQ of which the all-moderate risk was contributed by BPA than BPS. However, in order to meet the market demand for products, currently and time to come, various alternatives to BPA are widely used in industrial production. Thus, future contamination of BPs other than BPA may will increase. Since some BPs, i.e., BPF, BPS, and BPAF, etc., had similar estrogenic effects and anti-androgenic effects to that of BPA, thus risks may be significantly enhanced due to their elevated combined effects of complex estrogenic contaminants. Therefore, it is necessary to take more effective actions to decrease the discharge of BPs as well as long-term monitoring study of these compounds.

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