TRIHALOMETHANE AND HALOACETIC ACID FORMATION POTENTIAL OF TROPICAL PEAT WATER: EFFECT OF TIDAL AND SEASONAL VARIATIONS

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ABSTRACT: The existence of humic substances in peat water impacts the presence of the dissolved organic matter (DOM) which is the precursor of trihalomethanes (THMs) and haloacetic acids (HAAs). However, information on DOM characteristics, THMs and HAAs Formation Potential (THMFP and HAAFP) in tropical peat water are still limited. This study aimed to determine the correlations between DOM, THMFP, and HAAFP during dry and rainy seasons in tropical peat water in Indonesia. Samples of peat water are taken from the water canal and tidally affected river on Sumatera’s peatland during the rainy season and dry season to determine the effects of the seasons and tides. DOM measured by dissolved organic carbon (DOC), specific ultraviolet absorbance and the ratio of E465/E665 while THMFP determined from a total of THMFP4 measurements and HAAFP determined from measurement of total HAAFP5. Compared to dry season, values of all organic parameters on rainy season were higher but fewer in river. Canal water has a higher DOC while river water has a higher chloride and bromide content. Increasing of DOC in the rainy season correlates with increasing of THMFP4 and HAAFP5. THMFP4 is dominated by chloroform on canal while brominated THMs predominate in river water which correlates with the presence of bromide. Chlorinated HAAs dominate HAAFP5 in canal water while brominated HAAs increases in the river. Seasons and tides affect the appearance of bromide contaminants in water that affects the form of THMFP and HAAFP.

Keywords: Trihalomethanes, Haloacetic acids, Dissolved organic matter, Tropical peat water, Tides and seasons effect

1. INTRODUCTION

Peat water is colored and acidic and has a nutrient content [1]. Peat water is acidic with a pH of <5.2 due to dissolved organic matter (DOM) in the form of humic acid [2]. Humic acid contained in soil and peat water comes from the decomposition of animals and plants from microbial activity. Humic acid is a weak acid that gives brownish color to peat water. The content of organic compounds in peat water depends on the condition of peat soils and the climatic conditions of peat swamps [3]. Peat water is raw water that is not suitable for drinking water. Compared to other better surface water, peat water requires special processing to be used as a source of drinking water.

The composition of DOM in raw water can be different due to the land use pattern [4]. The source of organic compounds present in peat water comes from soil peat itself because peatlands are wetlands where the land will be flooded throughout the year so that there are considerable water reserves [5]. Peat soil itself is soil derived from the accumulation of decomposition of plants that are rich in organic matter. Distribution of land or peatland in Indonesia covers all regions in Indonesia. Some of them are in Sumatra, Papua, and Borneo. The peatland which located in each of these regions has different thicknesses [6].

Humic acid is not a hazardous material and has many beneficial environmental effects [7]. However, humic acid is a precursor for the formation of potentially hazardous carcinogen disinfection by-products (DBPs) during the chlorination of water. Besides containing DOM, peat water also contains pathogenic bacteria and halogenated ions (Cl, Br, F, I) [8]. The process of chlorine disinfection produces DBPs in the form of THMs and HAAs [9].

The use of chlorine as disinfection has the advantage because the remaining chlorine in water can disinfect introduced pollutants into the water during the storage and distribution process [10]. However, carcinogen disinfection by-products (DBPs) simultaneously generated during the chlorination process including trihalomethanes and haloacetic acids, formed from reactions between chlorine and natural organic matter in water [11,12]. In general, trihalomethane and haloacetic acid concentrations are substantially greater than other
By-products [12].

Trihalomethane is a halogenated organic compound in which three of the four hydrogen methanes (CH$_4$) atoms are replaced by halogen atoms. THM is also a large pollutant that is considered carcinogenic [13]. THM$_4$ (chloroform/TCM, bromodichloromethane/BDCM, dibromochloromethane/BDCM, and bromoform/TBM) are carcinogens of Cancer Group B (proven to cause cancer in laboratory animals). The United States Environmental Agency (USEPA) established a maximum pollution level of 80 μg/L for total THM$_4$.

The second most important DBPs, haloacetic acids is a carboxylic acid in which halogen atoms replace hydrogen atoms in acetic acid. The United States Environmental Agency (USEPA) sets a maximum pollution level of 60 μg/L of total HA$_A$ including dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monochloroacetic acid (MCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA), while four other HAAs including tribromoacetic acid (TBA), bromochloro-acetic acid (BCAA), bromodichloro-acetic acid (BDCAA) and chlorodibromoacetic acid (CDBAA) were not included in the regulation [13].

The effect of chloride and bromide ions on THM and HAA formation in the chlorination process was investigated, and it was found that brominated DBP concentrations (Br-DBP) increased with increasing bromide concentration [14,15]. Experiments show that with increasing bromide concentration, the total THM and HAA results in an increase [16]; The formation of brominated THM and HAA species are increased during chlorination with an increase in bromide concentration [16].

The purpose of this study was to determine the THM and HAA formation potential of peat water based on tidal and seasonal influences that have an impact on the presence of bromide and chloride ions in peat water. As a result of this work, we hope to identify the information on the relationship between tides and seasons in THM and HAA generation characteristics in treatment processes, and finally, to provide suggestions for the control of THM and HAA in water treatment processes.

2. MATERIAL AND METHODS

2.1 Samples

Sampling was carried out in the Peria River and water canal found in Indragiri Hilir Regency’s peatland, Riau Province, Indonesia to see the effects of tides. Samples were taken in two different places, in the rainy and dry season. River water that affected by tides and canal water that was not affected by tides. the water samples are canal water at dry season (CWD), river water at dry season (RWD), Canal water at rainy season (CWR) and river water at rainy season (RWR). All the samples prepared and analyzed in Integrated Laboratory of Poltekkes Kemenkes Bandung, Indonesia. The sampling location shows in Fig. 1.

2.2 Chemicals

A standard mixture of trihalomethanes contain of THM$_4$ (chloroform/TCM, bromodichloromethane /BDCM, dibromochloromethane /DBCM, and bromoform/TBM) in methanol and haloacetic acids containing HAA$_9$ (dichloroacetic acid/DCAA, dichloroacetic acid/TCAA, monochloroacetic acid/MCAA, monobromoacetic acid/MBAA, dibromoacetic acid/DBAA, tribromoacetic acid /TBA), bromochloro-acetic acid/BCAA, bromodichloroacetic acid/BDCAA, and chlorodibromoacetic acid/CDBAA) in methyl tert-butyl ether (MTBE) were purchased from Sigma Aldrich (USA). GC solvent grade of methyl tert-butyl ether (MTBE), sodium sulfate, sodium bicarbonate, copper II sulfate pentahydrate, sodium sulfite, phosphate buffer, methanol, and sulfuric acid were purchased from Merck (Germany). Chlorine solution (sodium hypochlorite 25%) was purchased from Pudak Scientific (local). All solutions were diluted with milli-Q grade water.

2.3 Instrumentations

UV-Vis absorbance (UV$_{254}$, E$_{465}$, and E$_{665}$) was measured using a UV-Vis Spectrophotometer (Shimadzu UV-1700). TOC Analyzer (Shimadzu TOC VCSH) is used to measure DOC (dissolved organic carbon) using EPA 415.3 method. Bromide was determined with APHA 4500 Br-B using phenol red colorimetric method. Chloride was determined by APHA 4500 Cl-B using argentometric method.

Gas Chromatography (GC) Agilent 7890A and Agilent 5975C Mass Selective Detector (MSD) were used to analyze HAA and THM. Agilent 7693 Series Automatic Liquid Sampler is used for sample injection and Agilent MSD ChemStation software is used to process data.
2.3.1 Trihalomethane Analysis

In the THM analysis, 1.0 µl of the sample was entered into GC by splitless injection and completed in the HP-5MS capillary column 30 m × 0.25 mm, 0.25 mm thick. The gas carrier (helium) rises at a constant inlet pressure of 15 kPa with a flow rate of 1.5 ml/minute. The injector temperature is 93 °C. The oven temperature is set to 90 °C, and the setting temperature is set to 300 °C.

2.3.2 Haloacetic acids Analysis

In the HAA analysis, setting GC conditions was carried out based on EPA 552 modified with Xie et al [17] for GC-MS analysis. 40 mL water sample was extracted using 4 mL MTBE after acidified to pH 2 using concentrated sulfuric acid and the addition of 16 g sodium sulfate and 3 g of copper II sulfate pentahydrate. Approximately 3 mL of the organic phase was methylated with acidic methanol in 50 °C ±2 for 2 hours. 1.0 µl of the sample was entered into GC by splitless injection and filled in the HP-5MS capillary column thickness 30m × 0.25mm, 0.25mm. The flow rate of the carrier gas (helium) is 1.0 mL/minute (constant flow). The oven temperature is set at 35 °C for 10 minutes and then raised to 75 °C with 5 °C/minute for 15 minutes, then raised to 100 °C with 5 °C/minute for 5 minutes, 135 °C with 5 °C/minute for 2 minutes, and 185 °C by increasing 25 °C/minute for 2 minutes. The injector temperature is 200 °C and the line transfer is received at 280 °C. MSD is operated in Electron Impact (EI) mode. The ion source temperature is regulated by 230 °C with electron energy being 70 eV.

2.4 Trihalomethane and Haloacetic Acids Formation Potential

The trihalomethane and haloacetic acid formation potential (THMFP and HAAFP) is the quantity of THMs and HAAs formed where the water sample is dosed with excess chlorine for 7 days at 25 °C and pH 7. The chlorine dosage was determined so that the remaining chlorine was 3-5 mg/L after 7 days of incubation. The method was adapted from the standard method 5710B procedure [18]. In this method, 97.5 mL samples were dosed with 2 ml 0.5 M phosphate buffer solution to buffer the sample at pH 7 and 0.5 mL NaOCl. The sample was incubated for 7 days in a dark at 25 °C. After 7 days, 0.5 mL of cooling solution (sodium sulfite 10%) was added to prevent further reaction and the sample was cooled until analysis.

2.5 Sample Extraction

2.5.1 Trihalomethane extraction

The sample extraction procedure for THM analysis was carried out based on the EPA 551.1 Method [19] with minor modification. 50 mL of sample water was extracted with 3 mL MTBE by adding 20 gr of sodium sulfate anhydrous to increase the strength of the aqueous phase ion. After an organic phase (MTBE) and the water phase were separated, a micro pipette used to remove approximately 1µL MTBE to autosampler vial for GC/MS analysis.

2.5.2 Haloacetic acid extraction

The sample extraction procedure for HAA analysis was carried out based on the EPA 552.2 Method. [20]. After adding 1 mL of concentrated sulphuric acid, 16gr of sodium sulfate anhydrous, 2gr of copper II sulfate pentahydrate and surrogate (2,3-dibromopropionic acid), 40 mL of water sample was extracted with 4 mL MTBE and added internal standard, 1,2,3-trichloropropane, manual for 2 minutes. 2.5mL of the extract was methylated by adding 1.0 mL of 10% sulphuric acid solution in methanol and heated at 50°C for 2 hours. After neutralization with 4mL of saturated sodium bicarbonate solution, the extract was analyzed using GC/MS.

3. RESULTS AND DISCUSSIONS

3.1 Properties of Peat Water

Table 1 shows that the DOC values are ranging from 22.2 mg.C/L-56.2 mg.C/L where the highest concentration is found in peat water originating from CWR and the lowest comes from RWD. The DOC value corresponds to the UV 254 absorbance. The highest UV 254 absorbance was found in canal water during the rainy season which was 3.175/cm and the lowest was in river water during the dry season which was 1.246/cm. The SUVA values range from 5.5 L/mg.m-5.9 L/mg.m which indicates that the compounds of DOM in peat water consist mostly of humic compounds that have high aromaticity and are strongly hydrophobic. Increasing of DOC in the rainy season can occur due to the leaching process that dissolves natural organic matter (NOM) from peat soil [21].

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<td>88</td>
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Table 1 Properties of peat waters
The E4/E6 ratio illustrates the presence of high molecular weight NOM in water [22]. The smaller E4/E6 ratio is found in peat water originating CWR, which is 4,914, whereas a large E4/E6 ratio is found in peat water originating from rivers in the dry season (= 8,286). The presence of chloride ions in the river greater than canal due to the tidal influence. Bromide ions are only found in river peat water.

3.2 Trihalomethane Formation Potential

THMFP was determined from the total formation of THM4 after chlorination for seven days due to variations in the dominant compounds formed shows in Fig. 2. THMFP on peat water increase in the rainy season because increasing of DOC [23] during the rainy season due to NOM leaching from peat soil [22]. THMFP in peat water originating from canals dominated by TCM formation. According to Stuart et al. [23], Garrido and Ponseca [24], Panyapinyopol et al. [25], Sururi et al [4] TCM was the largest THM formed during chlorination. TCM concentration in the dry season from 653.37±6.92 µg/L in dry season becomes 1020.52±6.07 µg/L during the rainy season (Fig. 2a).

The total THM4 which was THMFP was also increased in the rainy season from 928.1±11.9 µg/L to 1167.8±5.84 µg/L. In the river, THMFP is dominated by BDCM and CBDM in accordance with the Rajamohan [26] study. The presence of TBM is a significant difference between canal water and river water where the presence of TBM has a higher concentration in river water. This is in accordance with Marhaba et al [27] and Padhi et al [28] that bromide-containing water produces higher brominated THM. The pattern of THM formation in river water has the same pattern in peat canal water where the concentration of each THM increases during the rainy season. The THMFP increased from 250.67±0.07 µg/L to 1167.8±5.84 µg/L (Fig. 2b).

3.3 Haloacetic acid Formation Potential

HAAFP was determined from the total formation of HAA5 after chlorination for seven days due to variations in the dominant compounds
formed (Fig.3). HAAFP in the canal water is dominated by DCAA and TCAA that corresponds to the results of He, et al. [29] which indicate chlorine reactivity with low molecular weight compounds during the disinfection process. The DCAA and TCAA concentrations increased from 3389.23±3.29 µg/L and 339.51±14.59 µg/L to 6883.35±21.14 µg/L and 5895.45±1.75 µg/L during the rainy season (Fig. 3a).

Fig. 3 Haloacetic acid formation potential of peat water based on: (a) HAA5 formation, and (b) Total HAA5 formation

Increased concentrations of DCAA and TCAA resulted in an increase in total HAA5 which was HAAFP from 6806.39±20.55 µg/L to 12973.96±26.64 µg/L (Fig. 3b). The same pattern occurs in peat water originating from rivers but HAAFP is only dominated by DCAA. This result corresponds to Yu et al. [30] and Yue et al. [31] where the low concentration of TCAA is influenced by the high concentration of bromide ions originating from the sea, so the presence of TCAA is replaced by bromine-based HAA (DBAA). Total HAAFP in river water increases in the rainy season from 401.44±3.66 µg/L to 2435.08±6.85 µg/L.

3.4 Specific Formation Potential

Figure 4 shows the Specific Trihalomethane Formation Potential (STHMFP) and Specific Haloacetic Acid Formation Potential (SHAAFP). Compared with DOC values, the STHMFP of peat water ranged from 11.29±0.003-76.72±0.14 µg/mg.C. There was no big difference in HAAFP on canal water between dry and rainy seasons. On the other hand, STHMFP of river water in the dry season rise significantly compared to the rainy season that related to E4/E6 ratio. The ratio of E4/E6 of river water in the dry season was higher than a rainy season but the DOC value was smaller that relates to the appearance of low molecular weight NOM-THMs precursor.

SHAAFP of peat water range from 18.08±0.16-230.85±0.47 µg/mg.C where the highest value is found in canal water during the rainy season and related to a higher E4/E6 ratio. This value is not much different from raw water originating from Bangkhan Water Treatment at 288 µg / mg.C [32]. Canal water has a higher E4/E6 ratio indicated that canal water has more humic content that major
precursors to HAAs. SHAAFP of river water was raised but has a smaller ratio than canal water indicated that low molecular weight was not a major precursor of HAA compared to humic substances.

Fig. 4 Specific Trihalomethane and Haloacetic acid formation potential of pat water

4. CONCLUSIONS

This work is conducted to identify the information on the relationship between tides and seasons in THM and HAA generation characteristics in tropical peat water during the chlorination process. The peat water has high DOC values ranged from 22.2-56.2 mg/L that the highest value found in canal water in the rainy season. THMFP and HAAFP are higher in the canal water and the rainy season. Bromide ion contains in river water influence the formation of brominated THM and HAA during chlorination. THMFP is dominated by TCM in canal water and dominated by BDCM and CBDM in river water. HAAFP in the canal water is dominated by DCAA and TCAA then in river water only dominated by DCAA.

5. ACKNOWLEDGMENTS

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6. REFERENCES


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