



The Presence of Trihalomethanes and Haloacetic Acids in Tropical Peat Water

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Highlights:

- The presence of trihalomethanes and haloacetic acids in natural tropical peat water was investigated.
- Chlorinated THM4 predominated the THM4 content at all sampling points.
- Brominated HAA5 predominated the HAA5 content at the river sampling points.

Abstract. The presence of dissolved organic matter (DOM) in tropical peat water affects the appearance of trihalomethanes (THMs) and haloacetic acids (HAAs) in natural water sources. However, information about the presence of THM and HAA in tropical peat water is still limited. This study was conducted to determine the presence of THMs and HAAs in tropical peat water taken from a canal and a river in Riau Peatland, Indonesia, influenced by the seasons and the tides. DOM was measured by dissolved organic carbon (DOC) and UV₂₅₄ absorbance. The presence of THMs and HAAs was determined based on total THM4 and HAA5 and correlated with chloride and bromide concentrations. The concentrations of chloride and bromide in the river water were higher than in the canal water because of tidal influence. Total THM4 in canal water reached 22.70 ± 0.90 and 10.78 ± 0.71 $\mu\text{g/L}$ in the dry and rainy seasons, respectively, but only reached 16.64 ± 1.93 and 5.52 ± 0.05 $\mu\text{g/L}$ in the river water. In contrast to THM4, total HAA5 in the river water was higher than in the canal water and reached 104.01 ± 4.67 and 106.39 ± 9.53 $\mu\text{g/L}$ in the dry and rainy seasons, respectively, but only reached 9.83 ± 0.48 and 56.87 ± 6.11 $\mu\text{g/L}$ in the river water. THM4 predominated in the dry season while HAA5 predominated in the rainy season.

Keywords: *dissolved organic matter; haloacetic acids; seasonal and tidal effects; trihalomethanes; tropical peat water.*

1 Introduction

Peat water is a raw water source used as primary water source in Indonesian peatland, especially on the island of Sumatra [1]. In the rainy season, rainwater

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is used as a drinking water source, but in the dry season, peat water is used as an alternative source because of the lack of clean water sources [1]. Natural peat water contains a high concentration of dissolved organic matter (DOM) in the form of humic acids dissolved from the peatland [2,3]. The presence of humic acids causes an acidic pH and a brownish color of the peat water [3]. Dissolved organic matter can lead to the formation of carcinogen disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) because of the presence of chemical oxidants [4] in natural water.

The four THMs (THM4), i.e., chloroform (TCM), bromodichloromethane (BDCM), dibromochloro-methane (DBCM), and bromoform (TBM), have been reported as carcinogens in humans [5,6]. It has also been reported that THM4 can damage the heart, lungs, kidneys, liver, and central nervous system [7]. The five HAAs (HAA5), i.e., monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA) monobromo-acetic acid (MBAA), and dibromoacetic acid (DBAA), are classified as probable and possible human carcinogens (Group-C) [8]. The United States Environmental Protection Agency (USEPA) has set a maximum pollution level of 80 µg/L for total THM4 and 60 µg/L for total HAA5 [9,10].

The DOM content in water depends on the condition of the peatland, climatic conditions, and outside intrusion, for example through the tidal effect [11]. The presence of chloride and bromide ions from seawater can affect the disinfection by-product variation and concentration in natural peat water [12]. Previous research [13] has reported that the presence of THM in African raw water could reach 3-18 µg/L depending on the season. The presence of chlorinated HAA5 in river water has been reported to reach 41.2-308 µg/L in Portugal, with the presence of total organic carbon (TOC) and bromide ion at 6 and 0.7 mg/L, respectively [14]. The presence of HAAs and bromide ions has been reported to be below the detection limit in water from the Quebec River [15]. Notodarmojo, *et al.* in [3] reported that DOC in tropical peat water from Kalimantan, Indonesia reached 32.98 mg/L. A major study on the influence of seasonal changes and the tidal effect on DOM was done in a non-tropical region and found low DOC content [16].

The information about DOM in tropical waters is still limited, especially for tropical peat water. The present study aimed to determine the presence of THM4 and HAA5 in natural peat water. As a result of this work, we hoped to determine the seasonal and tidal effects on THM4 and HAA5 formation in natural peat water in view of delivering suggestions related to peat water treatment to control THM4 and HAA5.

2 Materials and Methods

2.1 Samples, Reagents, and Solutions

Figure 1 shows the peat water sampling location. Peat water samples were collected from a peat water canal and the Peria river in Riau Province's peatland, in the dry and rainy seasons. The Peria river is close to an estuary area, which is affected by the tides. The peat water canals were made for log transportation activities and are not connected to the sea.

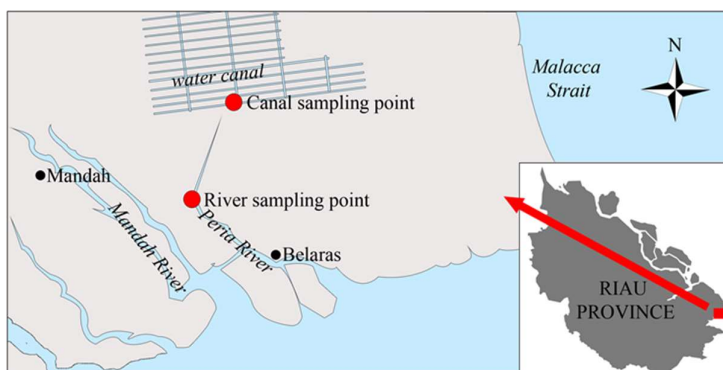


Figure 1 Sampling locations.

The samples consisted of about 1.5 L water and were taken at a depth of 0.5 m from the canal in the dry season (CWD), from the river in the dry season (RWD), from the canal in the rainy season (CWR), and from the river in the rainy season (RWR). All samples were taken and analyzed in triplicate for accuracy. All reagents and solutions used in this research were based on our previous studies [3,10].

2.2 Analytical Methods

UV254, E465, and E665 were measured using a UV-Vis spectrophotometer (Shimadzu UV-1700). Dissolved organic carbon (DOC) was analyzed using a TOC analyzer (Shimadzu TOC VCSH) using the EPA 415.3 method [17]. The Bromide APHA 4500 Br-B and APHA 4500 Cl-B [18] methods were used for measuring bromide and chloride. THM and HAA were analyzed using an Agilent 7890A Gas Chromatographer (GC) coupled with an Agilent 5975C Mass Selective Detector (MSD). The EPA 551.1 method was used for THM4 extraction and analysis [19] with minor modification for GC-MS [20]. HAA extraction and analysis were carried out based on the EPA 552.2 method [21] modified according to Xie, *et al.* [22] for GC-MS analysis.

3 Results and Discussions

3.1 Peat Water Properties

Table 1 shows the characteristics of peat water. Total dissolved solids and electrical conductivity are quality parameters of water sources. These were high in the river water samples. This may be because of the influence of tidal water, which is marked by a large concentration of chloride ions in the river water. Bromide ions are also only found in river water due to seawater impact [16]. The color content of the water varied from 250 to 500 Pt/Co, where CWR had higher content than RWR. The color content of the peat water was higher than the results of Mahmud, *et al.* [23] (South Kalimantan peat water) but lower than the results of Sismiarty, *et al.* in [24] (West Kalimantan peat water). The high color content during the rainy season occurs due to leaching of organic material from peat soil by acidic rainwater.

According to Notodarmojo, *et al.* in [3], peat water has unique characteristics, such as acidic pH, a brownish color, and high organic content. The degree of acidity (pH) of the peat water varied from 3.7 to 5.7 (acidic). A high concentration of DOM is supported by a high value of COD. The presence of chloride ions in the peat water from the river was more significant than in the peat water from the canal due to the influence of the tides. Bromide ions were only found in the peat water from the river.

Table 1 Peat water characteristics.

Parameters	CWD \pm SD	RWD \pm SD	CWR \pm SD	RWR \pm SD
DOC (mg.C/L)	43.734 \pm 1.03	21.1 \pm 1.55	54.6 \pm 2.62	46.23 \pm 1.74
UV ₂₅₄ (l/cm)	2.55 \pm 0.07	1.18 \pm 0.08	3.03 \pm 0.19	2.55 \pm 0.07
SUVA ₂₅₄ (L/mg.m)	5.85 \pm 0.06	5.62 \pm 0.03	5.53 \pm 0.09	5.52 \pm 0.03
E ₄₆₅ /E ₆₆₅ (E ₄ /E ₆)	7.75 \pm 0.07	8.29 \pm 0.009	5.01 \pm 0.13	5.53 \pm 0.05
TDS (mg/L)	167.50 \pm 3.53	2186.5 \pm 9.19	82.5 \pm 7.78	1456.59.19
Turbidity (NTU)	8.65 \pm 0.49	9.35 \pm 0.91	13.10 \pm 0.84	14.85 \pm 0.21
COD (mg/L)	275.00 \pm 2.82	147.00 \pm 4.24	172.00 \pm 5.65	131.50 \pm 4.94
pH	4.29 \pm 0.01	4.77 \pm 0.10	3.60 \pm 0.14	5.60 \pm 0.14
Color (Pt/Co)	356.87 \pm 9.72	348.75 \pm 1.76	529.67 \pm 3.77	111.45 \pm 3.46
Chloride (mg/L)	91.00 \pm 4.24	188.50 \pm 4.94	83.50 \pm 6.36	194.50 \pm 7.77
Bromide (mg/L)	bdl*	169.23 \pm 8.81	bdl*	97.50 \pm 3.53

*bdl = below the detection limit, n = 3

The concentration of dissolved organic carbon (DOC) in the peat water ranged from 21.1 \pm 1.55 to 54.6 \pm 2.62 mg.C/L, where the highest concentration was found in CWR and the lowest comes in RWD. The DOC values resembled the UV₂₅₄ absorbance values. The highest UV₂₅₄ absorbance was found in CWR, which was 3.175/cm, and the lowest in RWD. The SUVA₂₅₄ values ranged from

5.53 ± 0.09 to 5.85 ± 0.06 L/mg.m, indicating that the natural organic compounds in the peat water were mostly humic substances with high aromaticity and were strongly hydrophobic. The presence of humic substances with a large molecular structure derived from peat soils comes from the decomposition of dead plants and animals in the peatland [3,10,21,23,24].

The high concentration of DOC in the rainy season is caused by peat soil leaching [25-27]. Previous studies [28,29] have reported that the DOC concentration in natural water was higher in the dry season. On the other hand, another study [12] found that the dilution process during the rainy season in an urban area decreased the DOC concentration. The existence of a secondary forest around the sampling location can also influence the concentration of DOC [28]. The E_4/E_6 ratio represents the dominance of large NOM molecules in water [30,31]. The highest E_4/E_6 ratio was found in the peat water originating from the river during the dry season, reaching 8.29 ± 0.009 , which indicates that RWD was dominated by large molecular NOM (i.e., humic acid), also indicated by the higher color ratio (356.87 ± 9.72 Pt/Co) [3,30,31]. The smallest E_4/E_6 ratio was found in the peat water coming from the canal during the rainy season (5.01 ± 0.13). The higher the E_4/E_6 ratio, the greater the disinfection byproduct formation [31].

3.2 Presence of Trihalomethanes in Peat Water

Figure 2 shows the THM content in the peat water. Chloroform (TCM) predominated the THM4 content in the peat water in all seasons and under all conditions (Figure 2(a)). This is consistent with the study of Guyo *et al.* [13], who reported that TCM predominated THM in Zimbabwean raw water, reaching 3.93 ± 0.05 $\mu\text{g/L}$. The presence of brominated THM4 was higher in the dry season. This probably occurs due to fewer dilution in the water body [10,12,13]. The presence of THM4 in the dry season is higher than in the rainy season due to the natural dilution that occurs in the rainy season [10,12]. It has been reported that the presence of THMs in sub-tropical waters significantly decreases during winter, is moderate in spring and fall, and increases to its maximum level during summer [32].

The highest total THM4 was found in CWD (22.70 ± 0.90 $\mu\text{g/L}$), which had a high DOC concentration and color content, while the lowest value was found in RWR (5.52 ± 0.05 $\mu\text{g/L}$) (Figure 2(b)). The highest presence of total THM4 in the tropical peat water was smaller than the total THM4 found in West Scotland raw water (142.5 $\mu\text{g/L}$) [33]. In contrast with its presence in natural water, the THM4 formation potential was higher in the rainy season, reaching 1167.80 ± 5.84 $\mu\text{g/L}$ by our latest research [10]. The formation potential of THM4 in non-peat tropical river water also showed comparable results, reaching its highest concentration (>2000 $\mu\text{g/L}$) in the rainy season [12].

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The inorganic parameters (i.e., pH, turbidity, TDS, chloride, bromide) did not have a direct correlation with the presence of THM4 and inorganic parameters. The presence of chloride and bromide ions did not have a significant effect on the presence of chlorine based THM4, which can be seen from the low TCM concentration in the river water, which had higher chloride and bromide ion levels than the water from the canal. The higher concentration of THM4 in the dry season was directly proportional to DOC, SUVA, and E_4/E_6 ratio, and the color content indicated a higher concentration of high molecular NOMs in the peat water [31,34].

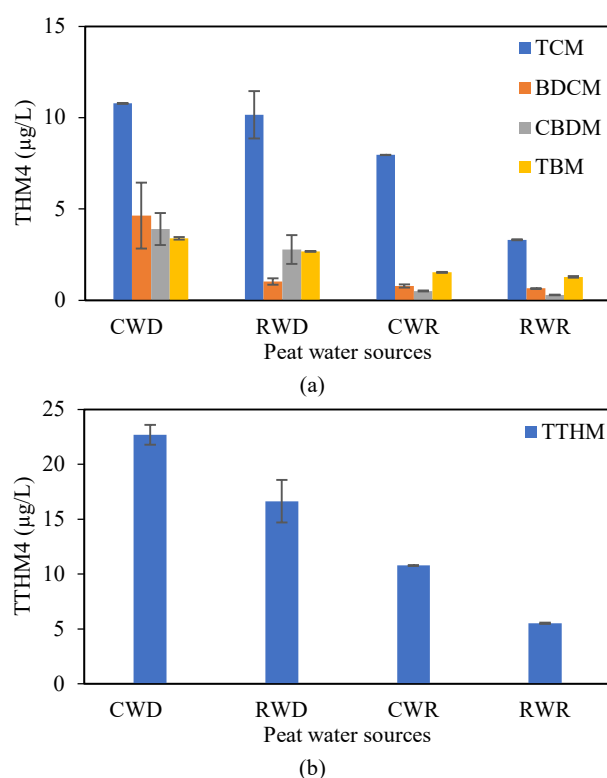


Figure 2 Presence of trihalomethanes in peat water: (a) THM4 and (b) total THM4.

3.3 Presence of Haloacetic Acids in Peat Water

Figure 3 shows the presence of HAA5 in the peat water. The HAA5 content in the peat water was higher than that of THM4 because of the high volatility of THM4 compared to HAA5 [13]. Figure 3a shows that the highest brominated HAA5 content was found in the peat water from the river, where there was a high

content of bromide ions (169.23 ± 8.81 mg/L in RWD and 97.5 ± 353 mg/L in RWR), which is consistent with previous research [34], which examined the state of HAA in water containing bromide ions.

The presence of bromide ions has a significant impact on the high presence of brominated HAA5 (MBAA and DBAA). The content of MBAA in the river water samples reached 34.80 ± 3.98 $\mu\text{g/L}$ in RWD and increased to 36.737 ± 3.17 $\mu\text{g/L}$ in RWR. The presence of chloride ions, reaching 91 ± 4.24 mg/L in CWD and 83.5 ± 6.36 mg/L in CWR, significantly influenced the presence of MCAA in the canal water. MCAA dominated chlorinated HAA5 in CWD, reaching 3.56 ± 0.073 $\mu\text{g/L}$, and DCAA predominated in CWR (19.28 ± 1.95 $\mu\text{g/L}$). In contrast to THM4, the existence of HAA5 increased during the rainy season.

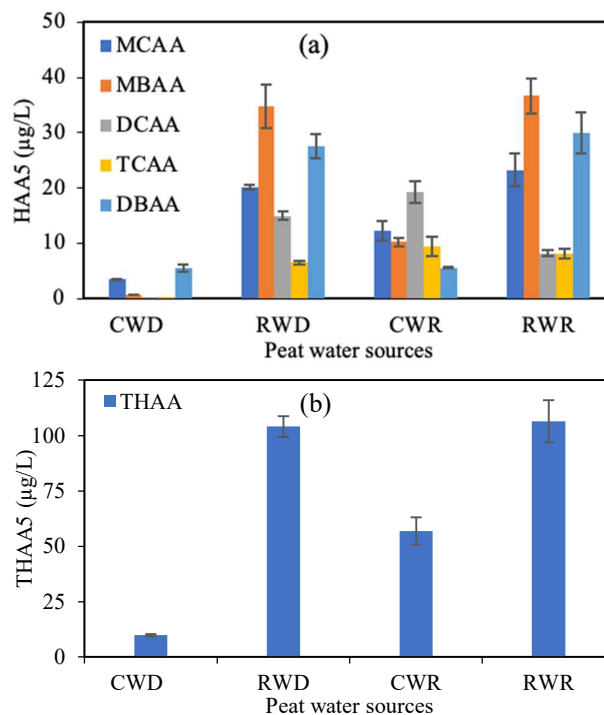


Figure 3 Presence of haloacetic acids in peat water: (a) HAA5, (b) total THAA5.

Compared to the dry season, HAA5 had a higher concentration in the rainy season, which can be related to several factors, including the concentrations of TDS, chloride, bromide, and NOMs speciation indicator (DOC, SUVA, and E_4/E_6 ratio) [10,23,34]. A smaller E_4/E_6 ratio and lower color content indicate higher HAA5 formation, because of which low molecular NOMs predominated the

HAA5 precursors [10,23]. The highest total HAA5 was found in the river water samples taken during the rainy season ($106.397 \pm 9.53 \mu\text{g/L}$). Unlike THM4, which had the highest total THM4 content, the canal water samples taken in the dry season had the lowest total HAA5 content ($9.837 \pm 0.48 \mu\text{g/L}$) (Figure 3b). The lower level of total HAA5 and the higher level of total THM4 could be caused by the lack of HAA5 precursors in the form of low molecular NOMs diluted from peatland, indicated by the higher SUVA values [10,34].

3.4 Specific THM4 and HAA5 Formation in Peat Water

DOM in peat water is formed when organic-rich peat soils create a large water reservoir [11]. Surface tropical peat water containing a high NOM concentration has a high color intensity [3]. Climate change may have a large effect on NOM content in peat water as an acidic water source [10,11]. Tropical peat water can have up to 61.8% molecular weight and can be strongly hydrophobic, with up to 13.2% of charged hydrophobic DOM fraction, which is a precursor to THM4 and HAA5 formation [10,23]. Specific THM4 and HAA5 formation can be used to relate DOC reactivity with disinfectant agents forming THM4 and HAA5 [30].

3.4.1 Specific THM4 and HAA5 formation

Figure 4 shows the specific THM4 and HAA5 formation in the natural peat water. The dry season contributed to the greatest formation of THM4 in the natural peat water (Figure 4(a)). RWD had the highest THM4 yield from DOC in the natural peat water, with a specific total trihalomethane formation (STTHMF) of $0.747 \pm 0.08 \mu\text{g/mg.C}$. This occurred because RWD had a low DOC concentration but high THM formation. The smallest STTHMF was found in RWR with a total of $0.117 \pm 0.001 \mu\text{g/mg.C}$. The dilution process in the rainy season and the tidal effect can reduce the presence of THM4, while the leaching process can raise the DOC concentration in river water in the rainy season [12,27,28]. CWD had the highest THM4 contamination and the second highest STTHMF with $0.517 \pm 0.02 \mu\text{g/mg.C}$, caused by the yield of THM from DOC being smaller than RWD.

Compared with DOC, the formation of THM4 in natural peat water is much lower than in disinfectant added natural water. Gough, *et al.* in [35] reported that STHMFP in water during algal blooming reaches $66 \mu\text{g/mg.C}$. All the THM4 formation in the natural peat water was dominated by chloroform (TCM). RWD had higher specific TCM formation, although the TCM concentration in CWD was greater than in RWD, because of the higher TCM ratio and DOC concentration. This is because the DOC concentration in RWD was lower than in CWD. The higher specific TCM formation could be caused by a higher source of TCM precursors (i.e., humic acid) [5,11,35].

River water had the highest specific total haloacetic acid formation (STHAAF) (Figure 4(b)) at $4.687 \pm 0.21 \mu\text{g}/\text{mg.C}$ in RWD and $2.247 \pm 0.20 \mu\text{g}/\text{mg.C}$ in RWR. Although CWR had high DOC concentrations, it had very low specific total haloacetic acid formation, at $1.017 \pm 0.10 \mu\text{g}/\text{mg.C}$. CWD had lower STHAAF and lower DOC concentrations than CWR ($0.227 \pm 0.01 \mu\text{g}/\text{mg.C}$). MBAA predominated HAA5 in the river water with specific formation at $1.567 \pm 0.17 \mu\text{g}/\text{mg.C}$ in RWD and 0.77 ± 0.06 in RWR. Chlorinated HAA5, DCAA predominated HAA in CWR as a result of the absence of bromide ions, but CWD was predominated by DBAA. The specific formation of HAA in RWD was greater than in RWR because of the lower DOC concentrations in RWD. The lower SHAAF could be caused by fewer disinfectants and pollutants introduced into the peat water [9,35]. The SHAAF in the natural peat water was lower than in chlorine added SHAAFP in Thailand raw water, which reached $57.9 \mu\text{g}/\text{mg.C}$ [35] because of fewer pollutants discharged into the river.

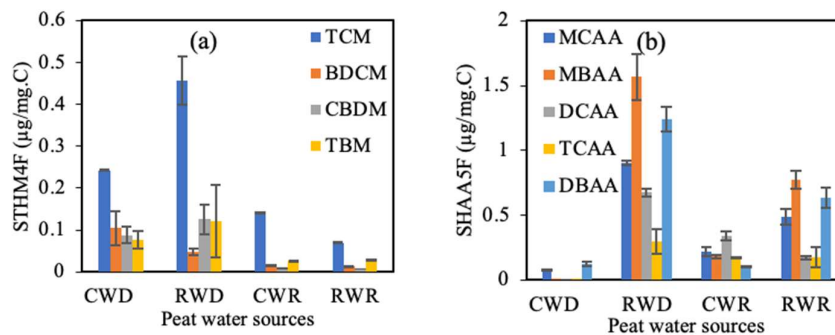


Figure 4 Specific disinfection by-product formation in natural peat water: (a) THM4 and (b) HAA5.

4 Conclusions

The highest DOC concentration was found in the CWR sample. The high SUVA₂₅₄ value indicates that the natural organic compounds in the peat water consisted mostly of humic substances. In the dry season, THM predominated in the natural peat water, while HAA predominated in the river water. The THM content in the natural peat water was predominated by chloroform (TCM) and the total concentration of THM in the dry season was higher than in the rainy season due to the natural dilution process that occurs in the rainy season. Brominated HAA (MBAA) predominated total HAA in the river, where a high content of chloride and bromide ions was found. Since peat water contains a high concentration of NOM, several water-treatment processes are needed to remove

DBP contamination and DOC, which is the primary precursor of THM4 and HAA5. Raw peat water without any treatment is not recommended for daily use.

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