



Trihalomethane, haloacetonitrile, and chloral hydrate formation potentials of organic carbon fractions from sub-tropical forest soils

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ABSTRACT

Forest landscapes represent the major land-cover type for the watersheds of the East River, which is the source of water for 40 million people in South China. Forest soils with high levels of organic carbon are a potential terrestrial source of dissolved organic carbon (DOC) into the East River. DOC is of great concern, since it can form carcinogenic disinfection byproducts (DBPs) during drinking water treatment. In this study, soils from three altitudes (200, 450 and 900 m) in the Xiangtuo Mountain Nature Reserve in South China, representing soils from evergreen moon forest, transitional evergreen broadleaf forest, and evergreen broadleaf forest, respectively, were evaluated for their potential contributions of DBP precursors into the East River. The water extractable organic carbon (WEOC) in three forest soils was physically and chemically fractionated into particulate organic carbon (1.2–0.45 μm), colloidal organic carbon (0.45–0.22 μm), and dissolved organic carbon (DOC) (<0.22 μm), hydrophobic acid (HPOA), transphilic acid and hydrophilic acid and were analysed for the formation potentials of trihalomethanes (THMs), haloacetonitriles (HANs), and chloral hydrate (CHD). Also, soils were incubated at 15, 25 and 35 °C for 14 d in darkness to examine the impact of temperature effects on the availability and characteristics of WEOC. The extraction study showed that the amount of WEOC was proportional to soil organic carbon content, of which about 1% was water extractable. Regardless of soil type, DOC and HPOA were the most reactive fractions in forming THMs, CHD, and HANs. Production of DOC and HPOA in WEOC increased over 14 d incubation as incubation temperature increased, but the temperature did not alter the distribution of physical and chemical fractions and their reactivity in DBP formation. Results suggest higher inputs of DOC and DBP precursors from forest watersheds into source water may result in a warmer environment.

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1. Introduction

Forest landscapes have been identified as one of the major watershed sources of dissolved organic carbon (DOC) in surface water [1]. Forest soil in particular is characterized by high organic matter content [2]. Water draining from forest catchments can contain high levels of DOC [3]. DOC in source water is of great concern, since it is a precursor of carcinogenic disinfection byproducts (DBPs), such as trihalomethanes (THMs) and haloacetonitriles (HANs), during drinking water treatment [4]. The upstream basin of the East River (known as Dongjiang in China) is mainly covered by broadleaf forest. The soil layer in this broadleaf forest has an average depth of

50 cm. In some areas, this organic soil is up to 100 cm thick and consists of 20–50% organic matter [5]. Surface runoff from this forest could contribute large amount of organic matter into the East River. In fact, the terrestrial input has been considered as the major source of DOC in the upper reaches of the East River [6]. Few studies have evaluated the characteristics of DOC from forest soil in terms of DBP formation and drinking water quality. Notably, the East River is the major drinking water source for 40 million residents in South China. High level of DOC and its potential to form DBPs raise a health concern and a challenge to manage this important drinking water source.

Increases in DOC concentration in riverine water over the past two decades have been reported [7]. The increase was partially attributed to the increase in DOC production from soil responding to an increase in temperature due to global warming [8]. An upward temperature trend has also been observed in China [9].

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In particular, an increasing temperature trend of 0.1 °C per decade has been observed in South China [10]. Sub-tropical weather in South China belongs to the typical monsoon humid climate of sub-torrid zone and is characterized with hot (>35 °C) and humid summer but relatively warm winter time (>5 °C). Temperature is expected to increase in the next decade to 38 °C in summer time (average) [10]. DOC release from soils is temperature dependent [11]. Thus, the increase in temperature can significantly affect the biogeochemistry and the carbon cycling in forest soil and eventually could lead to deterioration of the water quality in the East River.

Not all organic carbons in surface water are equally reactive in forming DBPs during chlorination. Hydrophobic and high molecular weight organic carbons produce more total organic halogen than hydrophilic and low molecular weight carbon fractions during chlorination [12,13]. Information about the distribution of organic carbon fractions in source water could provide useful information for water utilities to implement suitable flocculation and coagulation processes to remove DBP precursors in water treatment. In addition, information about the reactivity of terrestrial organic carbon source in forming nitrogenous and oxygenous DBPs such as haloacetonitriles (HANs) and chloral hydrate (CHD) is relatively limited. Notably, these DBPs are more toxic than well-studied THMs such as the chloroform or the bromoform, even though their concentrations are significant lower [14].

With the continuous increase in water demand in South China, knowledge about the distribution and reactivity of soil-derived organic carbon from the water basin of the East River is particularly important for making long-term water management plans. In this study, we extracted water soluble organic carbon from three forest soils from Xiangtuo Mountain Nature Reserve in South China and separated these into different fractions by membrane filtration and an XAD-8/XAD-4 fractionation scheme. Soils were also incubated at 15, 25 and 35 °C to evaluate the impacts of temperature on the availability of water soluble organic carbon. The goal of this study is to determine the characteristics of DBP precursors from sub-tropical forest soil.

2. Materials and methods

2.1. Site description and soil sampling

Xiangtuo Mountain, which is a national nature reserve in South China, represents a typical landscape of the upstream basin of the East River (Fig. 1). Xiangtuo Mountain Nature Reserve has a total area of 10,697 km², with 88.4% forested. The evergreen broadleaf forest is the major forest type and represents 56.1% of the total forest area. The annual precipitation in the reserve averages 2319 mm. Average temperature in summer and winter is 28 and 8 °C, respectively [5].

Soil samples were collected from two locations at three altitudes: 200, 450 and 900 m, within the Xiangtuo Mountain Nature Reserve, representing soils from evergreen moon forest, transitional evergreen broadleaf forest, and evergreen broadleaf forest, respectively [5]. Evergreen moon forest is found from 300 m or lower and *Sterculia lanceolata* and *Altingia chinensis* are the dominant plant species. Three hundred to eight hundred meters is transitional evergreen broadleaf forest and *Rhodoleia championii*, *Castanopsis fabri* and *Castanopsis fissa* dominate in this range. Evergreen broadleaf forest can be only found at altitudes over 800 meters and it mainly has *Lithocarpus calophyllus*, *Castanopsis eyrei* and *Machilus thunbergii*. According to the Chinese Soil Taxonomy, soils in evergreen moon forest, transitional evergreen broadleaf forest, and evergreen broadleaf forest are classified as Crimson soil, Red soil, and Yellow soil, respectively [5]. In this study, soils were labeled according to the altitudes of the sam-

pling location in the three forest types: soil at 200 m (S200), soil at 450 m (S450), and soil at 900 m (S900). The coordinates of sampling sites are S200 [23°14'31.9"N, 114°23'57.6"E] and [N3°16'24"N, 114°25'16.1"E], S450 [N23°15'84.1"N, E114°21'84.3"E] and [23°15'54.6"N, 114°21'57.2"E], and S900 [23°16'80.1"N, 114°20'64.3"E] and [N23°15'74.6"N, 114°21'65.3"E] (Fig. 1). Samples were taken from the surface layer between 0 and 0.3 m. Rocks, non-decomposed roots, and leaves residue were physically removed. Soils of the same type were fully mixed and placed into glass jars. All samples were stored at 4 °C before further processing.

2.2. Soil characterization

Samples were air-dried and sieved through a 0.25 mm sieve before further processing. The specific conductivity and pH of soils were determined from a suspension with a 1:1 (w/v) soil:water ratio according to U.S. Environmental Protection Agency (EPA) Methods 9050 and 9045C, respectively. Soil organic carbon was measured with a total organic carbon analyser with a solid module (TOC-V with SSM-5000A, Shimadzu, Japan). Major cations (Na⁺, K⁺, Ca²⁺, and Mg²⁺) were determined by an inductively coupled plasma-atomic emission spectrometry. Major anions (Cl⁻, NO₃⁻, HCO₃⁻, and SO₄²⁻) were determined using a Shimadzu high performance liquid chromatograph (Shimadzu Scientific Instruments, Inc., Columbia, MD) with an AS4A separator columns and conductivity detector. Bromide was measured using an AS18 analytical column in a Dionex ICS-2000 ion chromatograph.

2.3. Water extraction

A water purifier (Millipore Elix 70) was used to generate de-ionized H₂O for extracting water soluble organic carbon from soil. De-ionized H₂O, instead of conventional alkaline solution, was used to mimic the effect of surface runoff and minimize oxidation during alkaline extraction [15]. A 1:10 soil–water extraction was prepared by mixing a 125 g air-dried sample with 1250 mL de-ionized H₂O in a large glass beaker. The mixture was stirred using a magnetic stirrer for 30 min at room temperature (20 ± 2 °C), and then centrifuged at 1788 × g relative centrifugal force for 10 min. The supernatant was withdrawn for physical and chemical fractionation. All extracted samples were refrigerated at 4 °C and were processed within two weeks.

2.4. Soil incubation

A batch incubation experiment was conducted to determine the effects of temperature on production in water soluble organic carbon. Each soil type was incubated at 15, 25 and 35 °C at water content (θ_g) of 1.0 g water g soil⁻¹ for 14 d. The selected θ_g represented typical soil moisture content after heavy rainfall during the monsoon season, at which time the surface soil was completely saturated but not inundated. A total of four 1 L glass jars were used for each soil type at each temperature treatment (4 replicates × 3 soils × 3 temperatures). Each jar contained 150 g (dry weight) of forest soil. De-ionized water was sprinkled onto the soils to reach the desired θ_g . After water content adjustment, all jars were placed in constant temperature chambers in the dark. Each jar was covered by a lid with a 2 mm opening to allow for gas exchange. The θ_g in each jar was monitored every other day by gravimetric measurement. De-ionized water was added when a 5% or more change in θ_g occurred. De-ionized water was used to avoid salt accumulation and maintain constant salinity in each treatment. At the end of 14 d of incubation, 125 g of soil was withdrawn from each jar for water extraction.

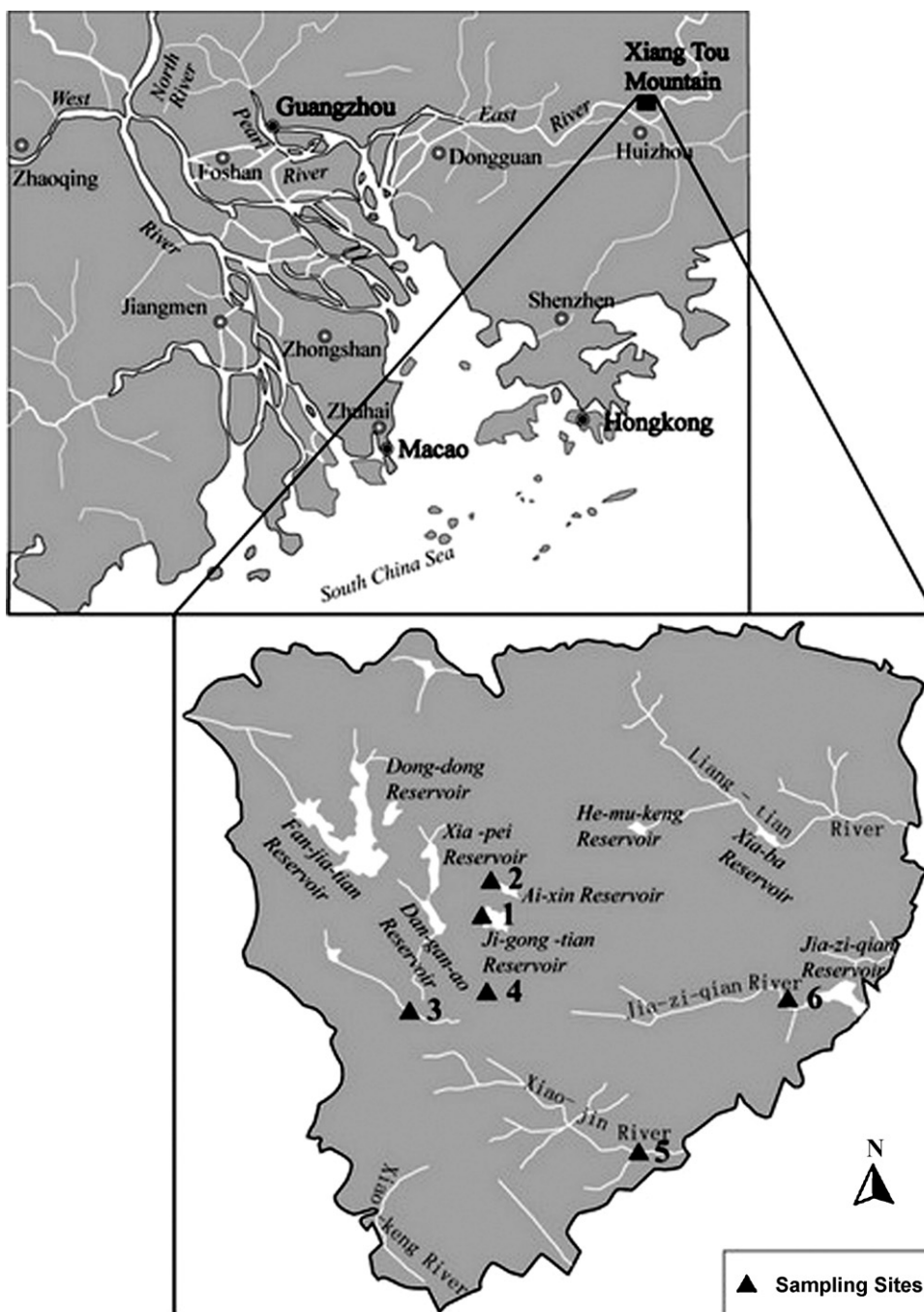


Fig. 1. Locations of Xiangtou Mountain Nature Reserve and sampling sites. Sampling sites of S900 were at (1) [23°15'74.6"N, 114°21'65.3"E] and (2) [23°16'80.1"N, 114°20'64.3"E], S450 were at (3) [23°15'54.6"N, 114°21'57.2"E] and (4) [23°15'84.1"N, 114°21'84.3"E] and S200 were at (5) [23°16'24"N, 114°25'16.1"E] and (6) [23°14'31.9"N, 114°23'57.6"E].

2.5. Physical fractionation

The supernatant was withdrawn from the soil and water mixture and filtered through a series of MF-Millipore mixed cellulose ester membrane filters: 1.2 μm , 0.45 μm and finally through 0.2 μm membrane. Each filter membrane was rinsed with 1000 mL of de-ionized H_2O to remove residual organic contaminants before use. During filtration with 1.2 and 0.45 μm membranes, filter fouling presented some difficulty. To avoid filter fouling, a new pre-rinsed membrane was installed as soon as visible water pileup occurred. Each extraction was run in triplicate.

In this study, water extractable organic carbon (WEOC) was defined as organic carbon that passed through a 1.2 μm membrane.

Particulate organic carbon (POC) was organic carbon that passed through a 1.2 μm membrane but was retained by a 0.45 μm membrane. Colloidal organic carbon (COC) represented organic carbon that passed through a 0.45 μm membrane but was retained by a 0.22 μm membrane. Dissolved organic carbon (DOC) was organic carbon that passed through a 0.22 μm membrane. By these operational definitions, WEOC contained POC, COC, and DOC.

2.6. Chemical fractionation

Filtrates that passed through 0.45 μm membranes were further characterized by XAD-8/XAD-4 fractionation scheme [12]. In the XAD-fractionation, 20 mL capacity columns were used and these

columns processed sample volumes of 500 mL with a WEOC concentration of not more than 20 mg L⁻¹ for maximum adsorption efficiency. The samples were acidified to pH 2 by the addition of 12.1 M HCl. After acidification, the samples were passed through the XAD-8 column, and the effluent was collected in an Erlenmeyer flask. The XAD-8 effluent was then run through a XAD-4 column and the effluent collected in an Erlenmeyer flask. These samples were run through both columns at a rate of 4 mL min⁻¹. After all the samples were run through the columns, each column was separately back eluted with 100 mL of 0.1 M NaOH at the rate of 2 mL min⁻¹. The eluates were collected in volumetric flasks and acidified to pH 2 with 12.1 M HCl. The eluate from XAD-8 is defined as hydrophobic acid (HPOA) and the eluate from XAD-4 is defined as transphilic acid (TPHA). The hydrophobic neutral (HPON) and transphilic neutral (TPHN) fractions are those compounds that adsorb onto XAD-8 and XAD-4 resins, respectively, but are not dissolved during back elution with 0.1 M NaOH. The hydrophilic acid (HPHA) fraction is the carbon in the XAD-4 effluent [12]. Supelite™ DAX-8 resin (Supelco–Sigma–Aldrich Co.) was used in the fractionation instead of Amberlite® XAD-8 resin (Rohm & Haas Co.) since XAD-8 resin was no longer commercially available. The efficiency of DAX-8 resin in isolating DBP precursors is comparable to that of XAD-8 resin [16].

2.7. Organic carbon concentration

Organic carbon concentration was measured by high-temperature catalytic oxidation using a Shimadzu TOC-V analyser. Organic carbon standards were prepared in 18 MΩ de-ionized water using potassium hydrogen phthalate. All standards and samples were acidified (300 μL concentrated HCl into 20 mL) prior to injection into the analyser.

2.8. Chlorination and DBP analyses

The chlorination procedure employed uniform formation conditions (UFC) as described by Summers et al. [17]. The protocols were a modification of procedures published by the United States Environmental Protection [18] and the American Water Works Association [19]. Briefly, all water samples were diluted to about 3–5 mg L⁻¹ DOC prior to chlorination. A ≥ 4% NaOCl solution (Sigma–Aldrich, USA) was used for all chlorination experiments. The UFC were those conditions that yielded a 1 mg L⁻¹ free chlorine residual at pH 8 after 24 h of incubation in the dark at 20 °C. Before every chlorination experiment, a 1000–3000 mg L⁻¹ chlorine working solution

was prepared and standardized with a Hach chlorine pocket colorimeter (Hach Co., Loveland, CO) in accordance with Standard Method 4500-Cl B (APHA, 2005). All glassware used in chlorination experiments was made chlorine demand-free in accordance with Standard methods [19].

For the chlorine demand experiments, five doses of chlorine in the range of 0.8–2.5 mg Cl₂ per mg DOC were evaluated per water to determine the chlorine dose necessary to yield a free chlorine residual of 1 mg L⁻¹ as Cl₂ at pH 8 after 24 h. After determining the requisite chlorine dosage, samples chlorinated under UFC for DBP analysis were filled headspace-free to 60 mL glass vials with screw caps and polytetrafluoroethylene-lined silicone septa. A 5 mL sample was withdrawn after 24 h to ensure a level of residual chlorine prior to further process. 10 mg of ammonium chloride was added to quench the chlorine residual after incubation. A total of 50 mL of chlorinated water samples was extracted by HPLC grade methyl tert-butyl ether (Fluka, Switzerland) immediately after 24 h chlorination. All samples were analysed for the four bromine- and chlorine-containing trihalomethanes species (THMs), chloroform, bromodichloromethane, bromoform and dibromochloromethane; three haloacetonitriles species (HANs), dibromoacetonitrile, dichloroacetonitrile and trichloroacetonitrile; and chloral hydrate (CHD), using gas chromatography with electron capture detection (Hewlett Packard 5890 Series II gas chromatograph) according to USEPA method 551.1. The minimum reporting level (MRL) for all DBP species was approximately 1 μg L⁻¹. Standards for the nine DBPs were obtained from Supelco (Bellefonte, PA, USA). DBP analysis was conducted within a week of chlorination.

3. Results and discussion

3.1. General soil properties

Soil types and some physicochemical properties of soil samples are summarized in Table 1. In particular, soil organic carbon (SOC) decreased with increasing altitude. Soil at 200 m (S200), 450 m (S450) and 900 m (S900) contained 10.8, 8.7 and 8.0 mg C g soil⁻¹, respectively. The S200 was more acidic and saline than soils at higher altitudes. Sand and silt were the dominant fractions of the three soil samples. The clay fraction was minor, consisting of 15% or less. The levels of Na⁺, Ca²⁺ and Mg²⁺ in S200 were the highest whereas its level of NH₄⁺ was the lowest of the three soil samples. The levels of K⁺ and NH₄⁺ in S450 were the highest with values of 0.42 and 0.48 mg g⁻¹, respectively. Sulfate was the dominant anion in all soils, following by nitrate, chloride, and

Table 1
Physical and chemical properties of soils in the study.

Parameters	S200	S450	S900
Altitude (m)	200	450	900
Soil type ^a	Crimson	Red	Yellow
pH	5.21 ± 0.42	6.05 ± 0.45	6.45 ± 0.24
Specific conductivity (dS m ⁻¹)	1.50 ± 0.17	1.20 ± 0.20	1.12 ± 0.15
Soil organic carbon (mg g ⁻¹)	108.2 ± 8.0	87.1 ± 10.1	79.5 ± 9.2
Sand (%)	52.8 ± 3.7	50.3 ± 1.5	49.2 ± 0.5
Silt (%)	32.9 ± 2.3	35.9 ± 2.0	39.8 ± 1.3
Clay (%)	14.3 ± 1.5	13.8 ± 1.3	11.0 ± 0.7
Na ⁺ (mg g ⁻¹)	0.85 ± 0.18	0.76 ± 0.14	0.69 ± 0.15
K ⁺ (mg g ⁻¹)	0.39 ± 0.19	0.32 ± 0.16	0.28 ± 0.09
NH ₄ ⁺ (mg g ⁻¹)	0.42 ± 0.18	0.46 ± 0.19	0.44 ± 0.12
Ca ²⁺ (mg g ⁻¹)	6.20 ± 0.78	5.51 ± 0.80	4.55 ± 0.93
Mg ²⁺ (mg g ⁻¹)	2.73 ± 0.94	2.11 ± 0.81	1.62 ± 0.55
Br ⁻ (mg g ⁻¹)	<0.01	<0.01	<0.01
Cl ⁻ (mg g ⁻¹)	6.55 ± 0.95	6.21 ± 0.83	5.80 ± 0.73
NO ₃ ⁻ (mg g ⁻¹)	9.82 ± 0.76	7.50 ± 0.85	5.01 ± 0.63
SO ₄ ²⁻ (mg g ⁻¹)	11.01 ± 0.82	8.52 ± 0.72	4.37 ± 0.91
HCO ₃ ⁻ (mg g ⁻¹)	3.17 ± 0.49	2.95 ± 0.61	2.71 ± 0.87

^a Soil type was classified according to the Chinese Soil Taxonomy [5].

bicarbonate. The Br level of the three soil samples was below 0.01 mg g^{-1} , suggesting the effect of Br on DBP formation was minimal.

3.2. Distribution of organic carbon fractions

Only a small portion of SOC was water extractable. Take S200 and S900 for examples. S200 had the highest SOC content and contained $108 \pm 8 \text{ mg C g soil}^{-1}$, of which only $1.29 \pm 0.19 \text{ mg C g soil}^{-1}$ was extracted (Fig. 1). Only 1.2% of SOC was extractable. Similarly, $1.04 \pm 0.13 \text{ mg C g soil}^{-1}$ was extracted from S900, representing only 1.3% of SOC. Other studies have also found a comparable yield from other soils, ranging from 0.5 to 4% [16,20]. This water extraction process, which simulates the surface runoff process, extracts the quick release fraction in the carbon bed. The release of other soil carbon fractions is a microbe-driven process and only a small portion of SOC will be released over time [20].

WEOC from forest soils at different altitudes had similar distributions in POC, COC, and DOC fractions (Fig. 2). DOC ($<0.22 \mu\text{m}$) was the dominant fraction, representing 63 to 71% of WEOC. POC ($1.2\text{--}0.45 \mu\text{m}$) comprised 25 to 28% of WEOC. COC was the smallest fraction and was less than 10% of WEOC.

This distribution pattern is common in forest soils [21]. The physical fractionation results also suggest the WEOC of forest soils have similar characteristics to that of peat soil, which has over 20% of soil organic matter and has been identified as a source of DBP precursors in drinking water sources [22]. The amount of DBP formation is essentially proportional to the concentration of organic carbon in chlorinated water [4,23], while the amount of WEOC is proportional to SOC content. Thus, a forest soil with a higher SOC content potentially contributes more DBP precursors to surface water than a forest soil with a lower SOC content.

The filtrate passing a $0.45 \mu\text{m}$ filter was also chemically fractionated into five operational fractions: HPOA, HPON, TPHA, TPHN and HPIA (Fig. 3). More than half of the organic carbon in $0.45 \mu\text{m}$ filtrate was HPOA. TPHA and HPIA were relatively minor constituents, ranging from 11 to 29%. The sums of HPON and TPIN were less than 16%. HPOA is considered to be major precursor for total organic halogen and THMs [12,13]. The results of chemical fractionation also indicate the similarity in WEOC between peat soil and forest soil [14]. Also, S200 had significantly higher HPOA and DOC contents than S900. HPOA and DOC are major DBP precursors. Results suggest that soil in Evergreen moon forest could be an important source of DBP precursors in the East River in South China.

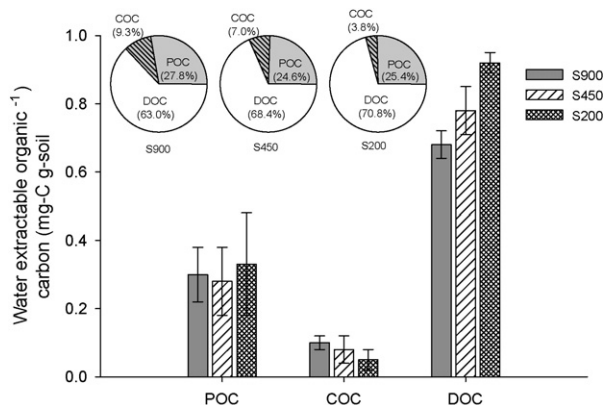


Fig. 2. Physical fractionation by membrane filtration of the forest soils at three altitudes: 200 m (S200), 450 m (S450) and 900 m (S900). The three pie diagrams indicate the distributions of carbon fractions in the water extracts. POC, COC and DOC are abbreviations for particulate, colloidal, and dissolved organic carbon, respectively. An error bar represents the standard deviation of triplicates.

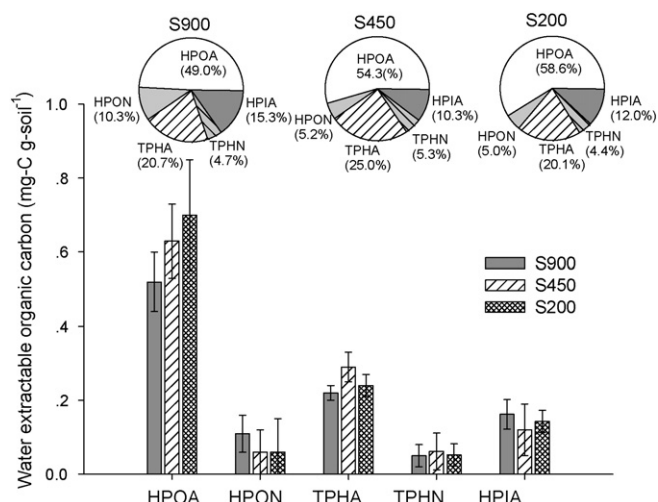


Fig. 3. Chemical fractionation by XAD-8-XAD-4 scheme of the forest soils at three altitudes: 200 m (S200), 450 m (S450) and 900 m (S900). The three pie diagrams indicate the distributions of carbon fractions in the water extracts. HPOA, HPON, TPHA, TPHN and HPIA are abbreviations for hydrophobic acid, hydrophobic neutral, transphilic acid, transphilic neutral, and hydrophilic acid, respectively. An error bar represents the standard deviation of triplicates.

3.3. Formation potentials of trihalomethane, haloacetonitriles and chloral hydrate

Different carbon fractions can have different reactivity in forming DBPs [12,13]. Specific DBP formation potential (SDBPFP), including specific THM formation potential (STHMFP), specific HAN formation potential (SHANFP), and specific CHD formation potential (SCHDFP) are operationally defined parameters reflecting the propensity of organic carbon to form THMs, HANs and CHD when the carbon is chlorinated, respectively. The SDBPFP of POC, COC and DOC were calculated by the differences of DBP formation potentials of 1.2, 0.45 and $0.22 \mu\text{m}$ filtrates and normalized to the concentrations of POC, COC and DOC, respectively. First, no differences were found among the STHMs of these fractions from different soils. Individual carbon fractions from different soils were insignificantly different ($p > 0.05$) in their THMs formation potentials. For SHANFP and SCHDFP of three carbon fractions, S450 and S900 were higher than that of S900 (Fig. 4). Also, DOC was more reactive in forming THMs than POC and COC. The STHMFP of DOC ranged from 10.4 to 12.1 mmol THMs mol C^{-1} and was significantly higher ($p < 0.05$) than that for POC and COC, which were 5.1 to 5.5 and 7.7 to 8.2 mmol THMs mol C^{-1} , respectively (Fig. 4a). The results suggest that 10–12/1000 carbon atoms in the DOC fraction form THMs after chlorination. In addition, DOC was more reactive in forming HANs and CHD than POC and COC. The SHANFP and SCHDFP of DOC were 0.93 to 1.05 mmol HANs mol C^{-1} and 0.48 to 0.62 mmol CHD mol C^{-1} , respectively, suggesting that only 1/1000 carbon atoms form HAN and 1/2000 carbon atoms form CHD after chlorination (Fig. 4b and c).

Similar to the results for physical fractionation, the reactivity of the chemical fractions from the three soils were not significantly different ($p > 0.05$). Noticeably, all chemical fractions had comparable or even higher SDBPFP than the physical fractions. The higher reactivity in chemical fractions was partially due to the oxidation by NaOH during the chemical fractionation. This is inherent to XAD-8/XAD-4 fractionation [15]. Among the three chemical fractions, HPOA had the highest STHMFP, ranging from 15.3 to 19.2 mmol THM mol C^{-1} (Fig. 4a). The STHMFP of TPHA and HPIA were 10.8 to 12.3 and 7.2 to 8.6 mmol THMs mol C^{-1} , respectively, and were significantly lower ($p < 0.05$) than that of HPOA. These

results agree with previous studies and showed that HPOA is a major THM precursor and the trend of relative reactivity among fractions is HPOA > TPHA > HPIA [4,12,13].

In contrast, minor difference was found between the three chemical fractions in forming HANs (Fig. 4b). Although the difference of SHANFP of these three chemical fractions, i.e. HPOA, TPHA and HPIA, were statistically insignificant ($p < 0.05$), HPOA had a greater average of SHANFP than TPHA and HPIA. Dissolved organic nitrogen has been identified as a precursor of HANs [24] and HPOA generally has greater N content than other fractions [25,26], thus, it has the greater potential to react as the HANs precursors during the chlorination. Our results confirm this possibility. On the other hand, HANs is unstable and can serve as the precursors of haloacetic acid and THMs. Besides, the C-to-N ratio of dissolved organic matter, as well as the N content, can affect HAN formation. In fact, a greater N content in HPOA but similar C-to-N ratio among HPOA, TPHA, and HPIA was observed [25,26]. And on the contrary, no difference in SHANFP was found between hydrophobic, transphilic, and hydrophilic fractions in another study [24]. The effect of N content and C/N ratio on HAN formation is still unclear.

A significantly higher ($p < 0.05$) SCHDFP was found in HPOA, with an average of 0.41 to 0.58 mmol CHD mol C⁻¹. CHD is a halogenated alcohol containing two attached hydroxyl groups and it is relatively unstable. At a pH of 8 and temperature of 35 °C, it decomposes to chloroform and trichloroacetic acids with a half-life of 2 d [27]. A linear correlation between concentrations of CHD and THMs in chlorinated waters was reported [28]. CHD can also be produced from the chlorination of humic acid and nitrogen-containing organic compounds [27]. Our results suggest HPOA is the major precursor of CHD and produced twice as much CHD as TPHA and HPIA (Fig. 4c).

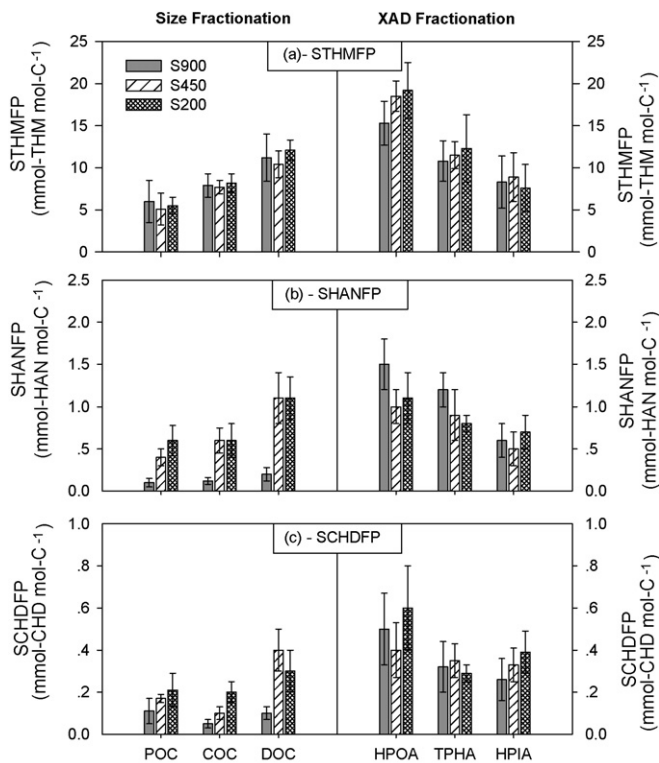


Fig. 4. Specific DBP formation potential of different water extractable organic carbon fractions from three forest soils. An error bar represents the standard deviation of triplicates.

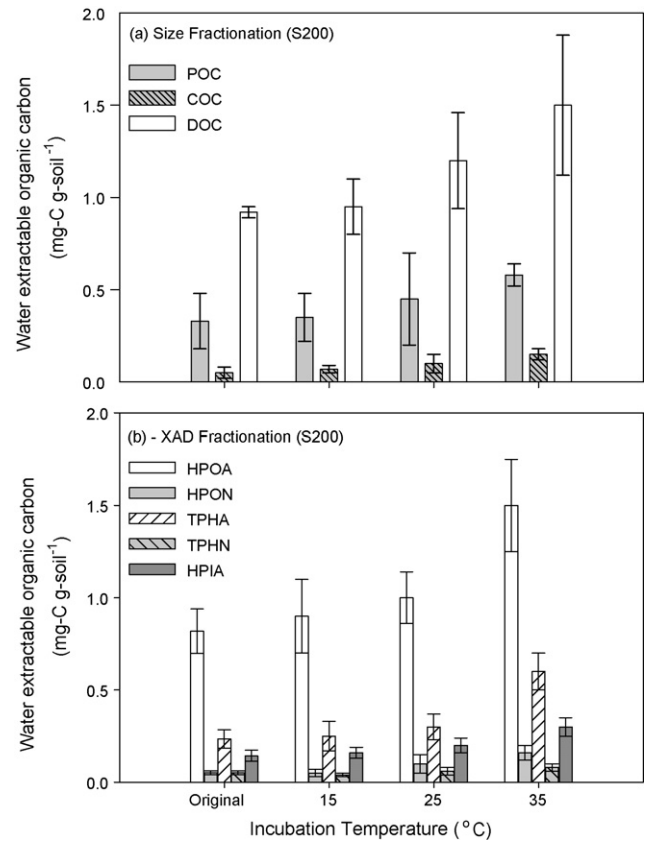


Fig. 5. Temperature effects on the physical and chemical fractionation of water extractable organic carbon from soils at 200 m. Soils were incubated at 15, 25 and 35 °C with water content at 10 g g⁻¹ for 14 d. An Error bar represents the standard deviation of triplicates.

3.4. Temperature effect on productions of DOC and DBP precursors

Increasing incubation temperature increased the production of the reactive DBP precursors (DOC and HPOA) in all soils. The changes were similar in all three soils and the results for S200 are plotted in Fig. 5 as an example. Temperature is one of the main factors determining microbial activity and DOC production in soil environments [11]. As temperature increases, the rate of microbial utilization of SOC increases, as well as the physicochemical dissociation of organic carbon from solid, resulting the increase in DOC in the water extraction organic carbon [20,29,30]. A total of 2.53 ± 0.28 mg C g soil⁻¹ was extracted at 35 °C and was twice as much as the WEOC from the original soil (1.29 ± 0.19 mg C g soil⁻¹). In fact, terrestrial export of DOC to surface water is highly season and temperature dependent [11,31]. Results imply that the DOC production from forest soils is increased in a warmer environment, resulting in higher DOC inputs into surface waters. In particular, soils at higher temperatures preferentially produce DOC and HPOA. A greater effort is required to provide safe drinking water when treating waters with a high portion of reactive DBP precursors in the source water.

In spite of the increases in WEOC production, higher temperature did not alter the distribution and the chemical characteristics of the carbon fractions. DOC remained the dominant physical fraction and COC was the minor fraction, accounting for about 70 and 10% of WEOC, respectively. HPOA was the major fraction and representing over 50% of WEOC. The results of both physical and chemical fractionations were similar to those for the original soils. Moreover, there are no significant differences ($p > 0.05$) in STHMFP,

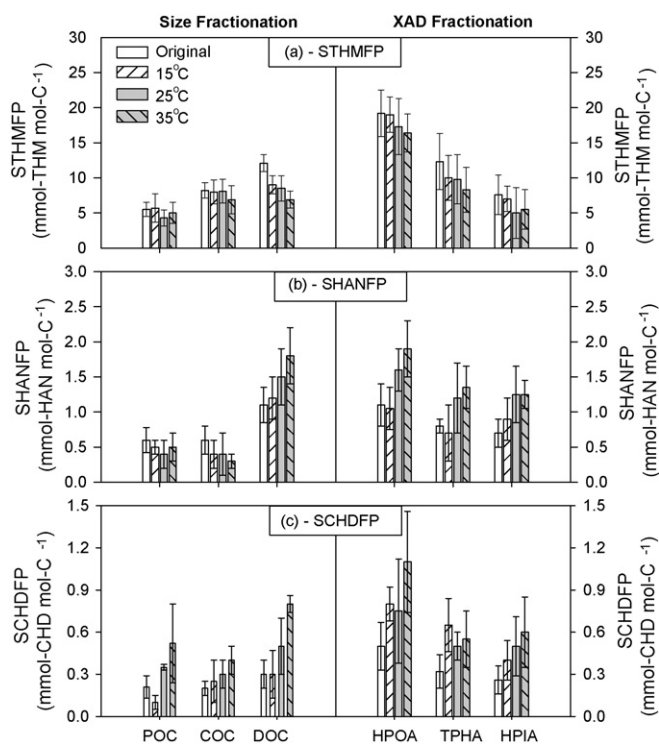


Fig. 6. Specific DBP formation potential of different carbon fractions from soil at 200 m after 14 d incubation. Soils were incubated at 15, 25 and 35 °C with water content at 10 g g⁻¹. An error bar represents the standard deviation of triplicates.

SHANFP, and SCHDFP at different temperatures treatment, compared to those for the original soils (Fig. 6). Although a downward trend in the STHMFP of HPOA and an upward trend in SHANFP were observed when incubation temperature increased, the changes were not statistically significant ($p > 0.05$).

4. Conclusions

The WEOC from three representative forest soils in South China were physically fractionated into POC, COC and DOC and chemically fractionated into HPOA, TPHA and HPIA. These extracted fractions were examined for the formation potentials of THMs, HANs and CHD upon chlorination. The extraction study indicated that DOC and HPOA were the major physical and chemical fractions in soil samples, respectively. These two fractions contained most of the reactive carbon forming THMs, CHD, and HANs. A temperature incubation study also revealed that production of these two reactive fractions was increased when temperature was increased. The results suggest that forest soils may contribute a greater amount of DBP precursors in surface water in a higher temperature environment.

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