Relationships between specific ultraviolet absorbance and trihalomethane precursors of different carbon sources

Alex T. Chow, Randy A. Dahlgren, Qian Zhang and P. K. Wong

ABSTRACT

A rapid and effective detection method is essential for water utilities to monitor variability of dissolved organic carbon (DOC) in source waters in order to apply strategies to minimize formation of disinfection by-products in treated waters. Ultraviolet absorbance at 254 nm (UVA_{254}) and specific UVA_{254} ($SUVA_{254}$) have been widely used as surrogates of concentration and reactivity of DOC, respectively. However, poor correlations between $SUVA_{254}$ and specific trihalomethane formation potential (STHMFP) have been occasionally reported and the reliability of using $SUVA_{254}$ to predict trihalomethane (THM) formation has been questioned. In this study, the correlations of $SUVA_{254}$ and THM reactivity of three different DOC sources commonly found in water treatment facilities (aquatic carbon, soil carbon, and fecal matter) were evaluated. A 0.22 μm filter, instead of 0.45 μm filter, was used for water filtration to minimize the effects of colloidal materials on UVA_{254}. UVA_{254} and DOC after chlorination were also examined and differential UVA_{254} and $SUVA_{254}$ ($\Delta SUVA_{254}$) were compared to THM reactivity. Results showed correlations between UVA_{254} and DOC were source dependent suggesting natural humification and degradation processes did not alter DOC characteristics from its original sources. The STHMFP of river and soil DOC samples were comparable, whereas their UVA_{254} normalized THMFP were different ($p < 0.05$), suggesting that UVA_{254} is a better indicator in predicting THM formation potential than DOC concentrations. $\Delta SUVA_{254}$ showed a stronger correlation with STHMFP than the conventional surrogate—$SUVA_{254}$.

Key words | chlorination, differential UV absorbance, disinfection by-products, Sacramento-San Joaquin Delta

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ABBREVIATIONS

DBPs	disinfection by-products
DOC	dissolved organic carbon
$SUVA_{254}$	specific ultraviolet absorbance at 254 nm
STHMFP	specific trihalomethane formation potential
THM	trihalomethanes
THMFP	trihalomethane formation potential
UVA_{254}	ultraviolet absorbance at 254 nm
$\Delta SUVA_{254}$	differential specific ultraviolet absorbance at 254 nm
ΔUVA_{254}	differential ultraviolet absorbance at 254 nm

INTRODUCTION

Dissolved organic carbon (DOC) in drinking water sources has been a great concern. Not only does DOC cause color and odor in water, but it also is a precursor for a variety of carcinogenic disinfection byproducts (DBPs), such as trihalomethanes (THMs), in water chlorination (Singer 1999; Xie 2004). A source water often contains organic carbon from a variety of sources, such as algal biomass and agricultural returns, which may have different reactivity (quality) in forming DBPs (Croue et al. 2000; Chow et al. 2005a). The contribution from different carbon sources in a

given source water frequently changes over time and DOC quantity and quality can be seasonal and climate dependent (Tranvik & Jansson 2002; Chow *et al.* 2006). The THM formation potential (THMFP) tests for evaluating the reactivity of DOC in forming THMs are usually labor-intensive and costly (Xie 2004; Chow *et al.* 2005*a*). Thus, a rapid and effective detection method is essential for water utilities to monitor the variability of DOC in source waters in order to apply corresponding strategies to minimize the formation of DBPs in treated waters.

The amount of DBPs in treated waters is usually proportional to the concentration of DOC in raw waters (Owen *et al.* 1993; Singer 1999; Croue *et al.* 2000; Xie 2004). Among the functional moieties, aromatic carbon is considered one of the most reactive molecular moieties with respect to THM formation during water chlorination (Norwood *et al.* 1987; Westerhoff *et al.* 2004). Ultraviolet absorbance at 254 nm (UVA$_{254}$) is proportional to the aromatic carbon content and has been used as a surrogate for DOC concentrations in natural waters for more than 35 years (Dobbs *et al.* 1972; Traina *et al.* 1990). In general, UVA$_{254}$ is considered a good indicator for the amount of DBP precursors in waters (Owen *et al.* 1993; Korshin *et al.* 1997). Specific UVA$_{254}$ (SUVA$_{254}$), which is equal to carbon normalized UVA$_{254}$, has also been used as a measurement of DOC propensity to form THM (Korshin *et al.* 1999; Chow *et al.* 2005*a*). Similarly, specific THMFP (STHMFP), which is equal to the THMFP divided by the DOC concentration, is used as a measurement of the reactivity of DOC in forming THMs and is generally proportional to the SUVA$_{254}$ (Singer 1999; Croue *et al.* 2000; Xie 2004). All these parameters have been widely used by the water industry and in academic research.

Several recent studies have questioned the reliability of using SUVA$_{254}$ to predict reactivity of DOC in natural waters (Weishaar *et al.* 2003). Poor correlations between SUVA$_{254}$ and STHMFP have been occasionally reported (Fujii *et al.* 1998; Fram *et al.* 1999). Indeed, not all organic carbon having absorbance at 254 nm is reactive in THM formation (Korshin *et al.* 1999; Weishaar *et al.* 2003). Slight changes in the position and number of substituted functional groups in the attached aromatic carbons can significantly alter the reactivity of organic carbons in THM formation (Norwood *et al.* 1980; Ichihashi *et al.*

1999). To further complicate the issue other common water constitutes, such as nitrate and bromide, can cause absorbance at 254 nm (Croue *et al.* 2000). However, the measurements of SUVA$_{254}$ are much more rapid and economical than for THMFP. Thus, improving the predictability of SUVA$_{254}$ as a proxy for DOC in raw waters and THM formation in treated waters is desirable.

The major limitation to using SUVA$_{254}$ to predict DBP formation in drinking water treatment is probably the involvement of non-reactive components in DOC. A better correlation could result if only the reactive carbon is measured. It has been proposed that differential ultraviolet absorbance, the difference between ultraviolet absorbance before and after chlorination, is proportional to DBP formation and is a better measure of THM formation in treated waters (Korshin *et al.* 1997; Li *et al.* 1998, 2000). In addition, the 0.45 μm pore size filters used in most water research cannot remove all colloidal materials that cause abnormally high UVA$_{254}$ in tested waters (Karanfil *et al.* 2003; Chow *et al.* 2005*b*). The use of a smaller pore size filter may improve the use of SUVA$_{254}$ for predicting THM formation in treated waters. We hypothesize that the use of differential UVA$_{254}$ (ΔUVA$_{254}$) and a smaller pore size filter may improve the reliability of using SUVA$_{254}$ for predicting DOC reactivity and THM formation in treated waters.

To test our hypothesis, we conducted a laboratory test on three major DOC sources that are commonly found in drinking water sources: soil humic substances, aquatic carbon, and fecal matter. The specific objectives of this study were to 1) establish correlations between UVA$_{254}$-DOC concentrations and SUVA$_{254}$-STHMFP when smaller pore size filters were used, and 2) evaluate the use of differential SUVA$_{254}$ for predicting STHMFP.

MATERIALS AND METHODS

Soil samples

Soil samples were collected from agricultural fields of Bacon Island (Kingile-Ryde Complex), Bouldin Island (Rindge Muck), Twitchell Island (Scriber Clay Loam) and Webb Tract (Rindge Muck) in the Sacramento-San Joaquin Delta, California. Soils in the region contain high concentrations of

humic substances and have been identified as major THM precursors in Delta waterways, a water source for 22 million people in California (Fujii *et al.* 1998; Chow *et al.* 2003). The carbon content of tested soils ranged from 3–20%, covering the range of typical organic and inorganic soils in the region. All soil samples were collected from the 0–0.3 m depth and were fully mixed in a plastic bag. Soils were transferred to sealed glass jars and frozen until used. The dry mass of each soil was determined after drying a sub-sample at 105°C for 24 hr. Ten grams of soil were mixed in a large glass container with 1000 mL deionized water or synthesized Na$^+$ or Ca^{2+} solutions (as chloride salts) with a specific conductivity of 1 or 4 dS m^{-1}; these ionic strengths represent the median and maximum salinity of irrigation waters. These different extracting solutions were used to simulate the DOC leaching under different irrigation water quality (Chow 2006). The soil-solution mixture was stirred for two hours at room temperature (20 ± 1°C). The mixture was then transferred to glass centrifuge tubes and centrifuged for 20 min at 250 g relative centrifugal force. The supernatants were saved for further processing and analyses. A total of 40 soil extracts were evaluated: 4 soils with 5 different extracting solutions and replication for each treatment.

River water samples

Two-litre grab samples were collected from the upper 50 to 75% of the water column at mid-channel from 35 sites of the Sacramento (19 sites) and San Joaquin (16 sites) Rivers every two weeks from October 1, 2002 to September 30, 2003. Locations were selected to represent the wide range of diversity in the physical environment and land use/land cover (e.g. wetland, rangeland, reservoir, agricultural field, etc.) in the watersheds of the two rivers. The sampling design resulted in 26 samples per site per year. Water samples were stored on ice and returned to the laboratory for further processing and analyses. A total of 910 river samples were collected for DOC and UVA$_{254}$ analyses. A subset of 50 samples was selected for THMFP and UVA$_{254}$ analysis after chlorination.

Fecal materials

Fecal materials are usually the major carbon source in waters from aquariums and municipal wastewater treat-

ment facilities. Feces and scats of pinnipeds were collected from the floor of animal cages or drainage screen of water treatment systems in the Marine Mammal Center at Sausalito, California. Volunteers collected feces using a forceps, placed it in a 50 mL plastic tube immediately after excretion, and samples were immediately frozen. Scats from the drainage screen were collected daily after the water tanks were emptied and frozen immediately. To extract a DOC fraction from these fecal samples, one gram of feces or scat was placed into a 50 mL plastic tube and 50 mL of deionized water was added. The samples were mixed by vortex for 5 min and then centrifuged for 20 min at 250 g relative centrifugal force. The supernatants were saved for further processing and analyses. There were a total of 20 samples, including 10 feces and 10 scats.

DOC, UVA$_{254}$ and THMFP analyses

All extracted and collected samples were filtered through a pre-rinse 0.22 μm (Isopore Polycarbonate, Millipore) membrane filter. The filtrates were analyzed for DOC and UVA$_{254}$. DOC was measured using a Dohrmann ultraviolet enhanced-persulfate total organic carbon analyzer (Phoenix 8000) with a detection limit of 0.05 mg L^{-1}. UVA$_{254}$ was determined using a diode array spectrophotometer (Hewlett Packard P8452A). Samples were diluted to a DOC of 10 mg L^{-1} or less before UVA$_{254}$ measurement. All soil and fecal sample extracts, and selected river water samples were analyzed for THMFP using the dose-based THMFP method developed by the Bryte Laboratory of the California Department of Water Resources (CDWR 1994). Briefly, samples were chlorinated with a freshly prepared NaOCl/H$_3$BO$_3$ buffer at pH 8.3 ± 0.1. An excess chlorine dosage (120 mg L^{-1}) was added to each sample with a DOC of 10 mg L^{-1} less. Samples were stored in a 40 ml borosilicate amber vial and sealed without headspace. The vials were incubated for 7 d at room temperature (20 ± 1°C). Following incubation, 0.15 mL of 10% sodium sulfite solution was added to quench residual chlorine. THM was quantified using a Hewlett Packard 5890 II gas chromatograph equipped with an electrolytic conductivity detector and a purge and trap condenser (modified US-EPA Methods 524.2). In addition, DOC and UVA$_{254}$ were determined on the chlorinated samples after quenching.

The change in UVA$_{254}$ was less than $0.001\,\mathrm{cm}^{-1}$, which was less than 1% of typical UVA$_{254}$ values, when both chlorine buffer and quenching solutions were added to a deionized water blank.

RESULTS AND DISCUSSION

UVA$_{254}$ and DOC concentration

UVA$_{254}$ has long been used as a surrogate for DOC concentrations in natural waters (Dobbs *et al*. 1972; Edzwald *et al*. 1985). The UVA$_{254}$ of our tested carbon sources increased linearly with increasing DOC concentrations. However, the correlation between UVA$_{254}$ and DOC concentration was source dependent and each carbon source showed a distinctly different linear regression (Figure 1). At a given DOC concentration, the relative UVA$_{254}$ followed: soil > aquatic > fecal carbon. Linear regressions calculated for each data set displayed strong correlations ($r^2 > 0.90$) for river and soil DOC samples (Figure 1). In contrast, there was a weaker correlation ($r^2 = 0.65$) for fecal matter, although UVA$_{254}$ also increased in a linear manner with increasing DOC concentrations.

Particularly, the correlation coefficients of aquatic DOC samples collected at the same study region were somewhat
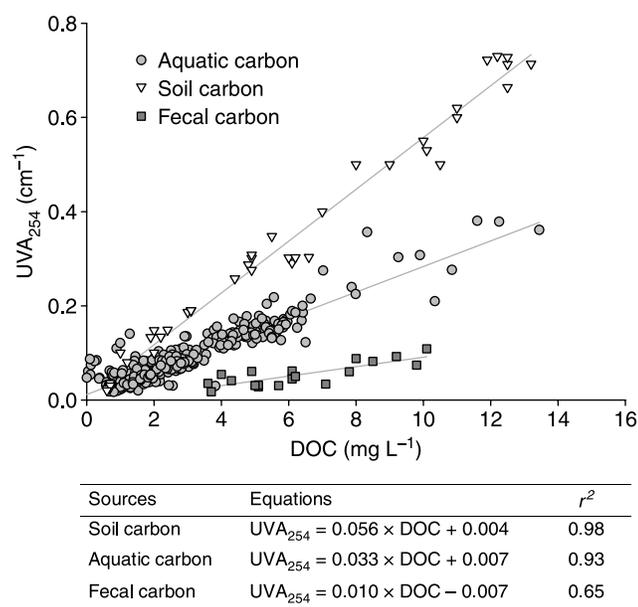

Sources	Equations	r^2
Soil carbon	UVA$_{254}$ = 0.056 × DOC + 0.004	0.98
Aquatic carbon	UVA$_{254}$ = 0.033 × DOC + 0.007	0.93
Fecal carbon	UVA$_{254}$ = 0.010 × DOC − 0.007	0.65

Figure 1 | Correlations of UVA$_{254}$ and DOC from aquatic, soil and fecal carbon sources.

greater than those in other studies, which used $0.45\,\mu\mathrm{m}$ filter for isolating DOC (CDWR 1994; Fram *et al*. 1999; CDWR 2003). The slopes of our linear correlations are also smaller than what they found. For example, National Water Quality Assessment Program found UVA$_{254}$ = 0.041 × DOC − 0.043 with a correlation coefficient of 0.71. Studies had indicated that $0.45\,\mu\mathrm{m}$ filtrates may contain a significant portion of colloidal materials, resulting in abnormally high UV absorbance (Chow *et al*. 2005*b*). In fact, the choices of filters could affect the DOC and UVA$_{254}$ measurement (Karanfil *et al*. 2003). Our study using $0.22\,\mu\mathrm{m}$ pore size filter eliminated colloidal materials and minimized its interference on UVA$_{254}$ measurement.

The three distinct linear regressions between UVA$_{254}$ and DOC concentrations imply that soil humic substances, aquatic carbon, and fecal matter have different chemical characteristics. The slope of the linear regressions between UVA$_{254}$ and DOC concentrations is equal to SUVA$_{254}$, which is defined as UVA$_{254}$ divided by the concentration of DOC. SUVA$_{254}$, in general, is proportional to the aromaticity of DOC and has been widely used as a surrogate for THM precursors (Traina *et al*. 1990; Chow *et al*. 2005*a*). Statistical analyses indicated that the slope of each regression line (SUVA$_{254}$ value) was significantly different from each other ($p < 0.05$), suggesting differences in aromatic carbon contents among the three carbon sources. The aromatic carbon content followed: soil > aquatic > fecal matter (Figure 1). These results are in agreement with conventional theory that soil humic substances are mainly large polymers with high aromatic carbon content and fecal matter contains mostly low molecular weight compounds with lower aromatic carbon content (Stevenson 1994; Jenner *et al*. 2005).

The UVA$_{254}$ and DOC concentrations of river samples were replotted using different symbols for the corresponding dominant land use/land cover for each sample site's watershed (Figure 2). The relationship between UVA$_{254}$ and DOC was remarkably consistent for the 35 river sites in spite of the wide range of watershed conditions affecting DOC chemistry. Statistical analysis showed no differences ($p > 0.05$) among the slopes if a linear regression was constructed for each dominant land use/land cover type. The similarities in slopes suggest that DOC in the Sacramento-San Joaquin Rivers have similar SUVA$_{254}$ or
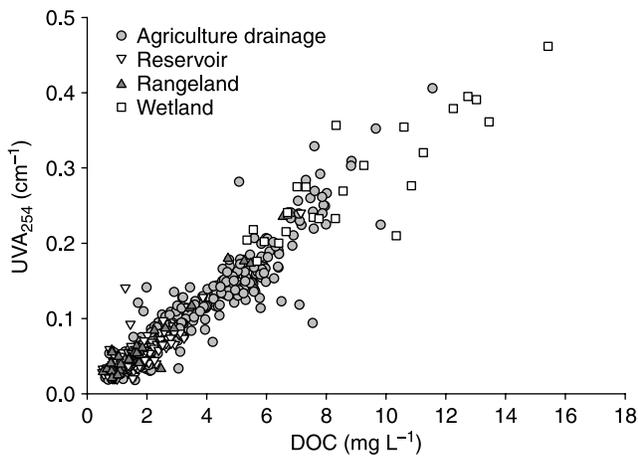
Figure 2 | Correlations of UVA$_{254}$ and DOC from river waters in the Sacramento-San Joaquin Watersheds.

similar aromatic carbon content regardless of the original DOC source. This observation may appear to conflict with our previous finding that the carbon sources (e.g. soil, river, fecal) have different UVA$_{254}$-DOC characteristics. The UVA$_{254}$-DOC data collected from different river sites had the same UVA$_{254}$-DOC relationship because the chemical nature of aquatic carbon has been altered through microbial degradation and humification processes in the river water (Stevenson 1994; Kalbitz *et al.* 2003). Thus, the DOC in rivers appears to be altered from its original chemical characteristics. In contrast, the extracted carbon from soils

and fecal matter was "fresh" from their sources and was not altered by processing during river transport. Thus, the unique characteristics of soil humic substances and fecal materials can be easily detected by UVA$_{254}$-DOC relationships and these two carbon sources have distinctly different characteristics from altered aquatic carbon.

SUVA$_{254}$ and THM reactivity

Generally, DOC concentration was linearly correlated with THMFP for all DOC sources (Figure 3(a)). By definition, the slope of the linear regression line of THMFP versus DOC is equal to the STHMFP. The STHMFP of aquatic carbon was slightly higher than soil carbon, with an average of 127.5 μg-THM mg-C^{-1} and 103.6 μg-THM mg-C^{-1}, respectively, although the difference was not significant ($p > 0.05$). THM formation increased with increasing DOC from fecal matter, but this DOC was the least reactive. The average STHMFP of fecal DOC was 35.0 μg-THM mg-C^{-1}, which was significantly lower ($p < 0.05$) than both aquatic and soil DOC. The THM reactivity of DOC for soil carbon was similar to aquatic carbon in spite of the significantly higher SUVA$_{254}$ values for soil DOC samples. These results further demonstrate that SUVA$_{254}$ is not always a reliable indicator for the reactivity of DOC in nature waters (Weishaar *et al.* 2003).
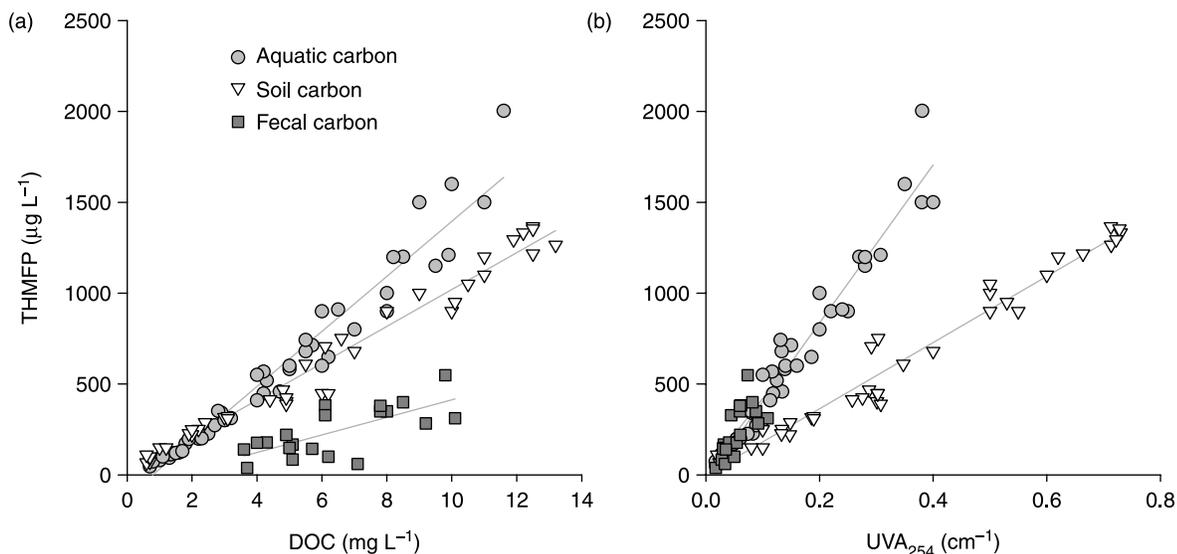
Figure 3 | Correlations of THMFP-DOC and THMFP-UVA254 for aquatic, soil, and fecal carbon sources.

Plots of UVA$_{254}$ versus THMFP were distinctly different from the DOC versus THMFP plots (Figure 3(b)). Linear regressions of river and soil DOC samples were different ($p < 0.05$) with slopes of 4322 and 1828 μg-THM cm^{-1}, respectively. According to the Beer-Lambert law, UVA$_{254}$ is proportional to the concentration of chromophores in solution, a group of atoms in DOC producing UV absorption. This UVA$_{254}$-active group usually contains unbonded electrons on oxygen and sulfur atoms, conjugated C=C double bonds and aromatic carbon (Stevenson 1994). The concentration of chromophores or aromatic carbon should be the same at a given UVA$_{254}$, assuming no interference from bromide, nitrate or other UVA$_{254}$ absorbing compounds. Therefore, higher THM formation for a given UVA$_{254}$ value implies that the chromophores or aromatic carbons have different reactivity in terms of forming THM during chlorination. A greater slope for the UVA$_{254}$ versus THMFP linear regression line of river DOC indicates that the chromophores and aromatic carbon from river water were more reactive in forming THM than those originating from soil samples. Fecal matter DOC had a similar slope to aquatic DOC and its chromophores were more reactive than soil DOC during chlorination. Results suggested that soil humic substances contained a relatively larger portion of aromatic carbons which were active in UVA$_{254}$, but not reactive in DBP formation during chlorination.

The linear correlation between UVA$_{254}$ and THMFP indicated that THM formation was proportional to the amount of chromophore or aromatic carbon. However, chromophores from different sources may have different reactivity with respect to THM formation, causing an error if SUVA$_{254}$ is used as a surrogate for THM precursors. In addition, other non-UV active carbons, such as aliphatic carbons, may contribute THM formation and could scatter or disperse the linear relationship between UVA$_{254}$ and THMFP. The STHMFP versus SUVA$_{254}$ plot (Figure 4) illustrates the potential errors associated with using SUVA$_{254}$ to predict STHMFP. SUVA$_{254}$ is equal to UVA$_{254}$ normalized by DOC concentration. It is equivalent to the amount of chromophore or aromatic carbon per unit of DOC. Similarly, STHMFP is equal to THMFP normalized by the DOC concentration. It represents the amount of THM formation per unit of DOC. The units for STHMFP in Figure 4 were converted from a mass (μg-THM mg-C^{-1}) to

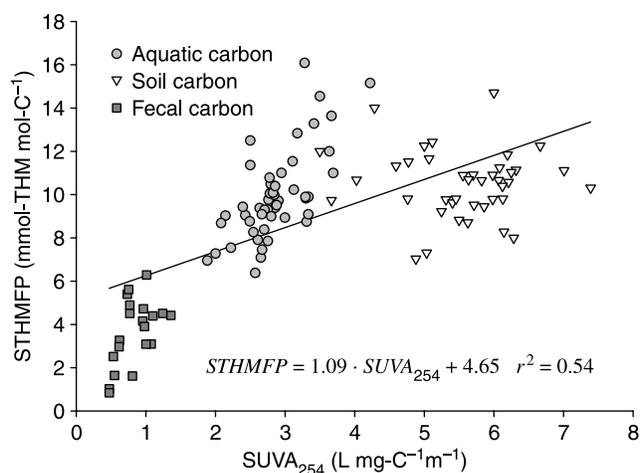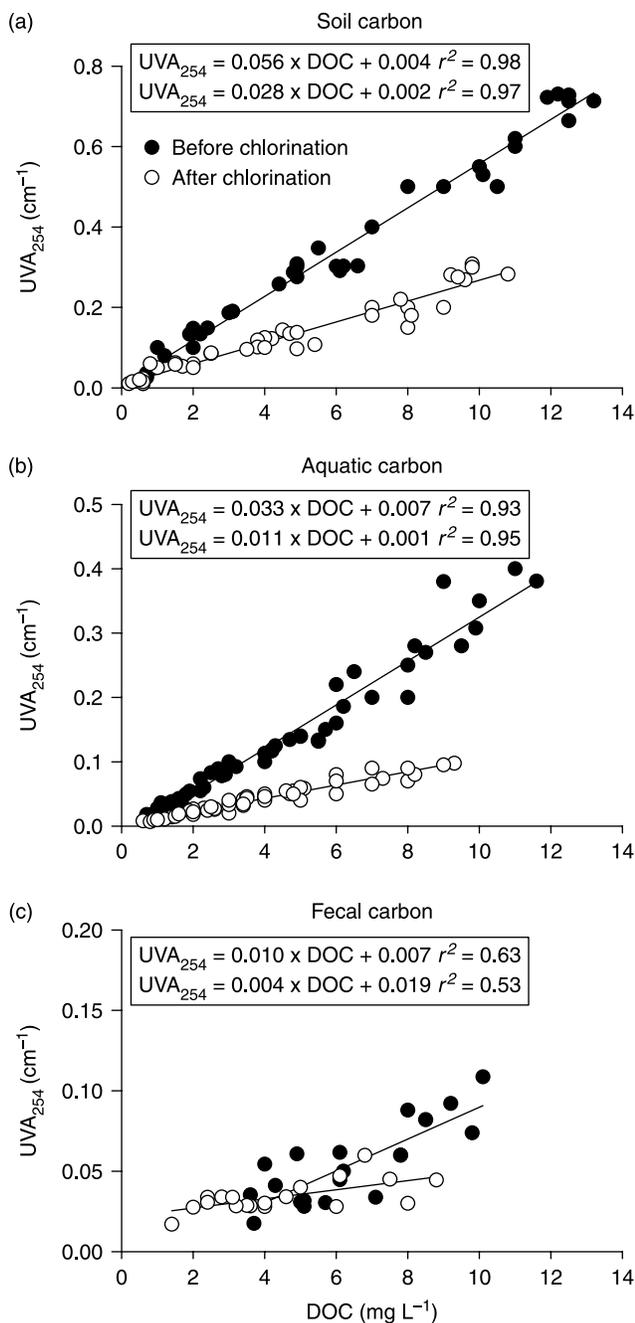**Figure 4** | Correlation between STHMFP and SUVA$_{254}$ for aquatic, soil and fecal carbon sources.

molar (mmol-THM mol-C^{-1}) basis in order to eliminate the enhanced mass yield due to elevated bromide DBPs from confounding the carbon reactivity evaluation.

STHMFP increased linearly with an increase of SUVA$_{254}$ in a range of 0 to 3 L mg-C^{-1} m^{-1}, but leveled off when SUVA$_{254}$ was greater than about 4 L mg-C^{-1} m^{-1} (Figure 4). The increased response indicates greater THM formation for DOC having a greater content of chromophores or aromatic carbon; however, the relationship was not linear with a weak correlation coefficient ($r^2 = 0.54$). Notably, our results using 0.22 μm filtrates did not show significantly improvement in the linear correlations, comparing to the results from CDWR and U.S. Geological Suvey which used 0.45 μm filters. A higher SUVA$_{254}$ value for DOC means that more conjugated double bonds and aromatic carbon existed per unit carbon than DOC with a lower SUVA$_{254}$. Chromophores or aromatic carbons embedded within a large complex structure are probably sterically hindered and protected by the outer molecular structure limiting their interaction with chlorine. Our data basically segregated into three distinct regions, depending on the DOC source (Figure 4). This segregation illustrates that the THM reactivity of aromatic carbon in DOC is source dependent.

Differential UVA$_{254}$ and differential DOC

As shown above, not all DOC or aromatic carbon is equally reactive in producing THM during chlorination. A better

correlation between STHMFP and SUVA$_{254}$ may result if the unreactive components are eliminated from consideration. This approach was investigated by examining the relationships between DOC and UVA$_{254}$ before and after chlorination (Figure 5). A strong linear relationship ($r^2 \geq 0.97$)

(a)

Soil carbon

$$UVA_{254} = 0.056 \times DOC + 0.004 \; r^2 = 0.98$$
$$UVA_{254} = 0.028 \times DOC + 0.002 \; r^2 = 0.97$$

● Before chlorination
○ After chlorination

(b)

Aquatic carbon

$$UVA_{254} = 0.033 \times DOC + 0.007 \; r^2 = 0.93$$
$$UVA_{254} = 0.011 \times DOC + 0.001 \; r^2 = 0.95$$

(c)

Fecal carbon

$$UVA_{254} = 0.010 \times DOC + 0.007 \; r^2 = 0.63$$
$$UVA_{254} = 0.004 \times DOC + 0.019 \; r^2 = 0.53$$

Figure 5 | Linear regression of DOC versus UVA$_{254}$ for aquatic, soil and fecal carbon sources before and after chlorination.

between DOC and UVA$_{254}$ still existed after chlorination in soil and river DOC samples. The SUVA$_{254}$ of chlorinated water was less than that of non-chlorinated samples, indicating a decrease in the amount of chromophore or aromatic carbon per unit DOC after chlorination. The positive linear regression following chlorination in both soil and aquatic DOC indicates that a certain fraction of the aromatic carbon or chromophores is not reactive during chlorination. For example, the decrease in SUVA$_{254}$ of soil carbon was 50%, suggesting that half of the chromophores or aromatic carbon was non-reactive during chlorination. Although new chromophores can be created during chlorination, residual SUVA$_{254}$ should be proportional to the unreactive chromophores in the DOC. The amount of new chromophores is believed to be minimal compared to the amount of original unreactive chromophores (Li *et al.* 2000).

The changes in UVA$_{254}$ (ΔUVA$_{254}$) due to chlorination were calculated and the negative values were converted to positive values for easier comparison. Among the three sample types, aquatic DOC had the greatest change in UVA$_{254}$, followed by soil and fecal matter, with an average change of 67%, 58%, and 24%, respectively (data not shown). This order was consistent with the STHMFP of the three sample types, which were 127.5, 103.6, and 35 μg-THM mg-C^{-1} for soil, aquatic and fecal DOC, respectively. Several studies have reported that differential UV spectroscopy can be an effective tool for monitoring the amount of DBPs formed by chlorination (Li *et al.* 1998; Croue *et al.* 2000). The differential spectrum detects both the chromophores that are destroyed and generated by the reaction. In contrast, any non-reacting chromophores contribute the same absorbance to the original and chlorinated samples and therefore do not appear in the differential spectrum. Thus, by its nature, differential spectroscopy focuses strictly on the UV-absorbing sites involved in the reaction (Li *et al.* 1998).

While SUVA$_{254}$ has long been used as a surrogate for aromatic carbon and THM precursors, it does not always correlate well with STHMFP because it incorporates both reactive and unreactive aromatic carbon. As shown here, ΔUVA$_{254}$ can be an effective tool to measure reactive carbon and predict THM formation. Therefore, ΔSUVA$_{254}$, which is defined as the differences in SUVA$_{254}$ before and after chlorination, may be a better surrogate for predicting

the reactivity of DOC in THM formation compared to SUVA$_{254}$ alone. We define the differential SUVA (ΔSUVA) as the difference in SUVA before chlorination (SUVA$_{(-Cl)}$) and SUVA after chlorination (SUVA$_{(+Cl)}$). SUVA$_{(-Cl)}$ was calculated as UVA before chlorination normalized by DOC before chlorination. SUVA$_{(+Cl)}$ was calculated by UVA after chlorination normalized by DOC after chlorination. SUVA is proportional to the aromaticity and is a surrogate of aromatic content in DOC (Traina *et al.* 1990). SUVA$_{(-Cl)}$ represented the aromaticity of DOC in raw water, while SUVA$_{(+Cl)}$ represented the aromaticity of DOC after chlorination. ΔSUVA should represent the change in aromaticity due to chlorination. The correlation of STHMFP with ΔSUVA$_{254}$ (Figure 6) displays a slightly improved correlation coefficient ($r^2 = 0.69$) compared to SUVA$_{254}$ versus STHMFP ($r^2 = 0.54$).

The limited improvement in the correlation is probably due to the change in DOC concentration due to chlorination (ΔDOC). The ΔDOC is equal to the amount of DOC oxidized to form CO_2 and volatile compounds such as THM, and we hypothesized that it should be proportional to the amount of THM reactive carbon in the complex heterogeneous mixture of DOC. Among the three sample types, fecal carbon had the greatest change in ΔDOC with an average of 36%. The soil and aquatic DOC have a lower ΔDOC with average values of 19% and 16%, respectively. Interestingly, the results are completely opposed to the

ΔUVA$_{254}$ discussed in the previous paragraph. Fecal carbon had the greatest loss in DOC but the least THM reactivity, suggesting that significant portions of DOC were oxidized to CO_2 or other volatile compounds rather than to THMs. In contrast, the smallest loss in DOC but the greatest THM reactivity occurred in river DOC samples indicating a larger oxidized portion of aquatic DOC was converted to THMs during chlorination. This result rejects our hypothesis that there is a relationship between the amount of oxidized DOC and THM formation. The result further suggests that chlorination is an unselective process and it does not discriminate among the different types of carbon. In other words, chlorine can oxidize any form of carbon in the DOC molecule resulting in destruction of both reactive and unreactive THM sites (Nicholson *et al.* 2003).

SUMMARY

The relationship of STHMFP with SUVA$_{254}$ and ΔSUVA$_{254}$ was examined for DOC originating from soils, rivers and fecal carbon. Results showed that correlations between UVA$_{254}$ and DOC could be source dependent; however, natural humification and degradation processes can alter the characteristics of DOC from its original sources. The carbon normalized THMFP of soil and aquatic DOC was similar, whereas UVA$_{254}$ normalized THMFP was significantly different, suggesting that UVA$_{254}$ is a more sensitive indicator of THM formation potential. The ΔSUVA$_{254}$ was a somewhat better predictor for SUVA$_{254}$ on the reactivity of DOC in THM formation, but the correlation is still considered weak. Further research is needed to improve the reliability of this technique with the THM production in treated waters.
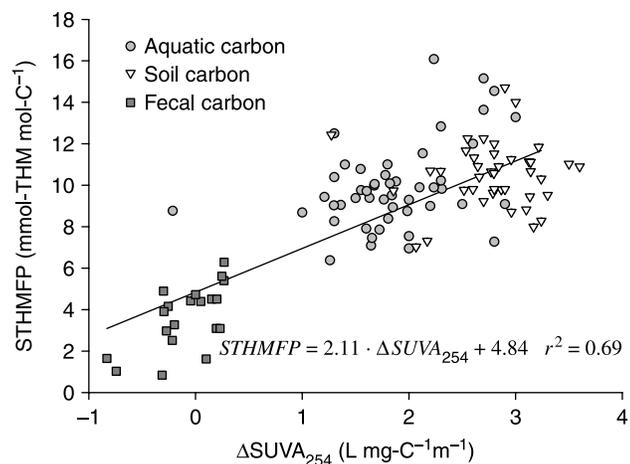
Figure 6 │ Linear regression of STHMFP versus ΔSUVA$_{254}$ combining data from aquatic, soil and fecal DOC sources.

$$STHMFP = 2.11 \cdot \Delta SUVA_{254} + 4.84 \quad r^2 = 0.69$$

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