

Comparison of DAX-8 and XAD-8 resins for isolating disinfection byproduct precursors

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ABSTRACT

XAD fractionation has been widely used for isolating natural organic carbon into different fractions for disinfection by-product (DBP) formation tests. The widely used Amberlite® XAD-8 resin is no longer commercially available and Supelite™ DAX-8 resin has been substituted in recent research. The objective of this study was to evaluate the differences, in terms of reactivity in DBP formation, among the dissolved organic carbon (DOC) fractions isolated by these two resins. DOC collected from two rivers and two soils in the Sacramento–San Joaquin Watershed was fractionated in parallel by the non-ionic macroporous DAX-8 and XAD-8 resins into hydrophobic and hydrophilic fractions. Four parameters used to predict DBP formation in the water industry were evaluated: specific ultraviolet absorbance at 254 nm (SUVA₂₅₄), differential ultraviolet absorbance at 272 nm (Δ UVA₂₇₂), specific trihalomethane formation (STHMFP) and specific haloacetic acid formation (SHAAFP). Results indicated that the sorption efficiency of DAX-8 resin was systematically greater than that of XAD-8 resin in our testing conditions and separated an average of 4% more humic substances. Hydrophobic and hydrophilic fractions isolated by XAD-8 and DAX-8 resins showed no significant difference in DBP reactivity ($p > 0.05$), except for the hydrophilic fraction of the peat soil extracts. Our results indicated their comparability in general use for isolating DBP precursors from bulk aquatic humic substances. However, the fractions of soil humic substances, particularly organic-rich soil, isolated by these two resins may have different chemical characteristics.

Key words | Dissolved organic carbon, haloacetic acids, humic substances, Sacramento–San Joaquin Delta, SUVA, trihalomethanes

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ABBREVIATIONS

DBPs	disinfection byproducts
DOC	dissolved organic carbon
EC ₂₅	electrical conductivity at 25°C
HAA	haloacetic acid
SHAAFP	specific haloacetic acid formation potential
STHMFP	specific trihalomethane formation potential
SUVA ₂₅₄	specific ultraviolet absorbance at 254 nm
THM	trihalomethane
Δ UVA ₂₇₂	differential ultraviolet absorbance at 272 nm

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INTRODUCTION

Dissolved organic carbon (DOC) has been identified as a precursor in forming carcinogenic disinfection by-products (DBPs) during drinking water treatment, such as chlorination and ozonation (Nawrocki & Kalkowska 1999; Rook 1976). Not all organic carbon is equally reactive in forming DBPs (Croue *et al.* 2000; Swietlik *et al.* 2004; Chow *et al.* 2005b). Identifying the reactive fractions of DOC is important for water utilities to develop effective treatment strategies to minimize DBP formation. Various

fractionation techniques have been used to isolate and identify the reactive fractions from natural waters (Owen *et al.* 1993; Croue *et al.* 2000; Chow *et al.* 2005a). The most frequently applied procedures for isolating DOC fractions for DBP formation potential tests is XAD fractionation using Amberlite® XAD-8 resin (Rohm & Haas Co.). However, the manufacture of this non-ionic adsorbent ended some years ago and XAD-8 resin is no longer commercially available. Supelite™ DAX-8 resin (Supelco – Sigma-Aldrich Co.) which has similar physical and chemical structures has been substituted for XAD-8 resin in many DOC fractionation schemes. Without knowing the chemical characteristics of fractions separated by these two resins, comparing data from prior studies using XAD-8 resin to recent and future studies using DAX-8 resin will be questionable.

XAD fractionation is based on column sorption techniques which simultaneously concentrate and fractionate specific organic solutes from most other dissolved constituents (Aiken *et al.* 1992). The hydrophobic effect for sorption on the XAD-8 or DAX-8 resin is the principal driving force for the fractionation (Aiken 1985). Hydrophobic fraction is that portion of DOC that sorbs to the resin at pH 2 with a capacity factor (k') of 50, where k' is defined as the mass of a solute sorbed on the XAD-8 or DAX-8 resin divided by the mass of the solute in column void volume (Aiken *et al.* 1992). The portion of DOC that passed through the XAD-8 or DAX-8 resin at pH 2 is generally termed as the hydrophilic fraction. The hydrophilic fraction can be further fractionated into transphilic and truly hydrophilic fractions by using XAD-4 resin, which are the eluate and the effluent of the XAD-8/DAX-8 effluent running through a XAD-4 column, respectively (Krasner 1999; Leenheer & Croue 2003). The hydrophobic fraction can be further fractionated into acidic, basic and neutral fractions by using different eluting solvents. Hydrophobic

acid and hydrophobic base are the portions of DOC that are eluted with 0.1 M NaOH and 0.1 M HCl from the XAD-8 or DAX-8 resins, respectively. The hydrophobic neutral fraction is those compounds that adsorb onto the resin, do not dissolve during elution with NaOH nor HCl, but can be extracted by organic solvents such as acetonitrile (Aiken *et al.* 1992). The hydrophobic fraction has a higher aromatic and phenol content, while the hydrophilic fraction contains less aromatic character but a higher content of oxygen, sulfur and nitrogen. Generally, the hydrophobic fraction is more reactive in trihalomethane formation than the transphilic and truly hydrophilic fractions (Owen *et al.* 1993; Croue *et al.* 2000).

Both XAD-8 and DAX-8 resins are made of poly(methyl methacrylate). In spite of their similarities in physical and chemical structures (i.e. non-ionic macroporous copolymer with large surface area), the technical specifications such as pore size and surface area of DAX-8 resin are slightly different from those of XAD-8 resin (Table 1). Studies using pyrolysis gas chromatography and synchronous scanning fluorescence spectroscopy showed that sorption by the DAX-8 resin was systematically greater compared to that of XAD-8 resin (Peuravuori *et al.* 2002a, b). Importantly, the content of aliphatics is slightly greater in DAX-8 isolates, although there was no significant difference between the major elemental compositions of the parallel humic solutes obtained by these two resins (Peuravuori *et al.* 2001). The differences in sorption efficiency and aliphatics content imply that isolates from the two resins may have different propensity in forming DBPs.

In addition to isolating aquatic humic substances, XAD fractionation has been widely used in isolating fulvic acid from soils (Swift 1985; Stevenson 1994). However, studies comparing XAD-8 and DAX-8 resins only examined samples from aquatic environments (Peuravuori *et al.* 2001, 2002b). The differences between XAD-8 and DAX-8 resins in isolating DOC fractions from terrestrial

Table 1 | Specifications of Amberlite® XAD-8 and Superlite™ DAX-8 resins

Resins	Particle size (mesh)	Pore diameter (Å)	Surface area (m ² g ⁻¹)	Specific pore volume (cm ³ g ⁻¹)
Amberlite® XAD-8 resin	20–50	250	140	0.82
Superlite™ DAX-8 resin	40–60	225	160	0.79

environments have not been fully examined. Importantly, soil humic substances are an important source of DBP precursors in drinking water (Amy *et al.* 1990; Fujii *et al.* 1998; Chow *et al.* 2003; Li *et al.* 2003). The objective of this study was to compare the reactivity in DBP formation of DOC fractions isolated by XAD-8 and DAX-8 resins and to provide a linkage between the data using different resins. Four parameters commonly used to predict DBP formation in the water industry were evaluated: specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), differential ultraviolet absorbance at 272 nm (ΔUVA_{272}), specific trihalomethane formation (STHMFP) and specific haloacetic acid formation (SHAAFP) (Summers *et al.* 1996; Korshin *et al.* 1997; Li *et al.* 1998, 2000; Weishaar *et al.* 2003). Both soil and aquatic humic substances collected from the Sacramento–San Joaquin Watershed were examined in this study.

MATERIALS AND METHODS

Origin of samples

DOC was collected from two riverine waters and two soils in the Sacramento–San Joaquin Delta, California. Samples were chosen as they were representative of many aquatic and soil humic substances found in this region. The Sacramento–San Joaquin Delta is a drinking water source for 22 million people in California and soil and riverine DOC have been identified as major sources of DBP precursors (Amy *et al.* 1990; Brown 2003). Water samples were collected in summer 2003 from the Tuolumne River and the San Joaquin River at Mossdale. The San Joaquin River at Mossdale contains drainage waters from irrigated agriculture throughout the San Joaquin Valley, whereas the Tuolumne River (a tributary of the San Joaquin River) contains runoff from mixed sources, including rangeland, reservoir and agricultural drainage. These two rivers contain typical DOC materials entering the Sacramento–San Joaquin Delta (Saleh *et al.* 2003). Ten liters of water sample were collected in a high density polyethylene carboy and were transported to our laboratory for immediate processing. Waters were filtered through a 0.45 μm membrane filter (Pall, Supor[®]-450) and filtrates were acidified by adding 12.1 M hydrochloric acid (Fisher

Scientific, trace metal grade) to pH 2. Acidified samples were stored at 4°C prior to fractionation and analysis.

Soil samples were collected from Twitchell Island and Webb Tract in the Sacramento–San Joaquin Delta. The soil from Twitchell Island is classified as a Scribner Clay Loam (*Cumulic Endoaquoll*) and the soil from Webb Tract is classified as a Rindge Muck (*Typic Haplosaprist*) (USDA, 1977, 1993). These two soils were selected because they are representative of major mineral and organic soils in the Delta. Soil samples were collected from the surface at 0–0.3 m depth. Surface soil was used because it has been identified as the major sources of THM precursor in the soil profile (Chow *et al.* 2003). Soils were fully mixed in a plastic bag, transferred to a 1 L Mason jar and frozen until further use. Ten grams of dry soil was mixed with 1 L of 0.1 M NaOH in a Nalgene[®] high density polypropylene container. The container was flushed with ultra high purity grade N₂ before closing. The containers were shaken for 16 h at room temperature (20 \pm 2°C). The mixture was transferred to glass centrifuge tubes and centrifuged at 250g relative centrifugal force for 20 min. The supernatant was withdrawn and filtered through a 0.45 μm membrane filter (Pall, Supor[®]-450). Filtrates were acidified to pH 1 with 12.1 M hydrochloric acid (Fisher Scientific, trace metal grade). After refrigeration at 4°C overnight, the extracts were filtered again through a 0.45 μm membrane filter. The filtrate was collected and readjusted to pH 2 by adding 6 M NaOH for XAD/DAX fractionation. Organic material not passing through the 0.45 μm membrane filter, by definition, was humic acid (Swift 1985; Stevenson & Cole 1999). Briefly, soil extracts were passed through a 0.45 μm filter twice and soil humic acid was removed prior to fractionation. Only fulvic acid was isolated from the XAD-8 or DAX-8 column.

XAD-8 and DAX-8 fractionation

The resins were cleaned by first washing the beads in 0.1 M NaOH and then rinsing the resin with distilled water. The resin was placed in a soxhlet extractor and sequentially extracted for 48 h each with methanol and acetonitrile. This sequence was repeated twice. Clean resin was stored in methanol. Glass columns were packed with a H₂O–resin slurry and rinsed with distilled water to remove methanol. The resin was further cleaned with 3 successive 0.1 M

NaOH–0.1 M HCl rinses immediately before use. Both acidic and basic effluents in the last rinse were collected for DOC analysis to ensure no bleeding from the resins ($< 0.1 \text{ mg L}^{-1}$). For the fractionation, 20 mL capacity columns were used and these columns can process sample volumes of 1 L with a DOC concentration of no greater than 20 mg L^{-1} for maximum adsorption efficiency (Aiken *et al.* 1992). In each run, 500 mL of acidified water samples at pH 2 with $10 \pm 2 \text{ mg-C L}^{-1}$ were run from the top of the column at 4 mL min^{-1} . The effluent was collected at the bottom of the column. Then, 100 mL of 0.1 M NaOH was back-flushed from the bottom of the column at 2 mL min^{-1} . This eluate was immediately acidified to pH 2 with 12.1 M HCl and stored at 4°C . New resin was replaced after four runs (2 L of water samples) to avoid retention of hydrophobic neutrals, which cannot be eluted with NaOH. Resin was also replaced when different samples were used to avoid cross-contamination.

Chemical and statistical analyses

All samples were analyzed for DOC, UV/VIS absorbance at 200–800 nm (UVA), THM formation potential (THMFP) and haloacetic acid formation potential (HAAFP). DOC was determined by heat-promoted persulfate oxidation, using a total organic carbon analyzer (O.I. Analytical 1010). UVA was determined by a diode array spectrophotometer (HP8452A). Samples were diluted to a DOC of 10 mg L^{-1} or less before UVA measurement. The dose-based THMFP method developed by Bryte Laboratory at the California Department Water Resources (CDWR) was used in this study (CDWR 1994). Briefly, samples were chlorinated with a freshly prepared NaOCl/ H_3BO_3 buffer with pH 8.3 ± 0.1 . A constant chlorine dosage (120 mg L^{-1}) was added to each sample with a DOC of 10 mg L^{-1} or less. Samples were stored in a 40 mL borosilicate amber vial and sealed without headspace. All the vials satisfied the requirements of USEPA Publication #9240.0-05A specifications and guidance for contaminant-free containers. The vials were incubated for 7 d at room temperature ($20 \pm 2^\circ\text{C}$). A volume of 0.15 mL of 10% sodium sulfite solution was added to quench residual chlorine. DOC and UVA were measured again after chlorination. Quantification of THM was accomplished using a Hewlett Packard 5890 II gas chromatograph with electrolytic conductivity detector, according to the

modified USEPA Method 524.2, in which a purge and trap condenser was utilized. Samples for HAA were extracted by liquid–liquid extraction immediately after quenching, based on USEPA Method 552.2. Methyl-tertiary-butyl-ether was used as the extracting solvent. 1,2,3-trichloropropane was used as an internal standard and 2,3-dibromopropionic acid was used as a surrogate to monitor the derivatization efficiency. Six haloacetic acid (HAA) species (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, dibromoacetic acid and tribromoacetic acid) were determined. Quantification of HAA was accomplished using a Hewlett Packard 5890 II gas chromatograph with electron capture detector, according to the USEPA Method 522.2. All THM and HAA samples were refrigerated at 4°C for no more than 2 weeks prior to analysis.

Specific UVA absorbance at 254 nm (SUVA_{254}), specific THMFP (STHMFP) and specific HAAFP (SHAAPF) were determined by normalizing UVA at 254 nm, THMFP and HAAFP with the concentrations of DOC in tested waters. ΔUVA_{272} was determined as the difference of UVA at 272 nm before and after chlorination. There were 4 replicates for each sample and the *t*-statistic with equal variances assumption was employed to test for the differences in isolates between XAD and DAX resins. The statistical function in Microsoft Excel was used to perform the statistical analyses and the results were considered statistically significant if the two-tailed chance probability (*p* value) was less than 0.05. Sample means and standard deviation of each measured parameter were listed in the corresponding tables.

RESULTS AND DISCUSSIONS

General properties of riverine and soil samples

Table 2 provides selected chemical characteristics of water samples collected at the Tuolumne and San Joaquin Rivers. A higher level of salinity was observed in the San Joaquin River. Electrical conductivity at 25°C (EC_{25}) of water from the San Joaquin River was 553 S cm^{-1} and was almost 4 times greater than that from the Tuolumne River. Importantly, the San Joaquin River had 8 times more bromide, an inorganic DBP precursor, than the Tuolumne River, containing 0.31 and 0.04 mg L^{-1} , respectively. A higher level of bromide in the San Joaquin River resulted in a

Table 2 | General characteristics of water samples from Tuolumne River and San Joaquin River at Mossdale

Parameters	Tuolumne River	San Joaquin River
<i>Cations</i>		
Na ⁺ (mg L ⁻¹)	10.8	87.0
K ⁺ (mg L ⁻¹)	2.0	2.6
Ca ²⁺ (mg L ⁻¹)	12.0	38.3
Mg ²⁺ (mg L ⁻¹)	5.9	24.4
<i>Anions</i>		
HCO ₃ ⁻ (mg L ⁻¹)	63.8	133.0
NO ₃ ⁻ (mg L ⁻¹)	4.3	7.7
SO ₄ ²⁻ (mg L ⁻¹)	4.9	83.3
Cl ⁻ (mg L ⁻¹)	9.7	105.4
Br ⁻ (mg L ⁻¹)	0.04	0.31
<i>Other properties</i>		
pH	8.06	8.14
EC ₂₅ (S cm ⁻¹)	141	553
DOC (mg L ⁻¹)	2.8 ± 0.1 [‡]	2.2 ± 0.1 [‡]
SUVA ₂₅₄ (L mg-C ⁻¹ m ⁻¹)	3.2 ± 0.1 [‡]	2.9 ± 0.1 [‡]
STHMFP (μg-THM mg-C ⁻¹)	116 ± 2 [‡]	167 ± 5 [‡]
SHAAFP (μg-HAA mg-C ⁻¹)	90 ± 8 [‡]	79 ± 24 [‡]

[‡]: average and standard deviation, *n* = 4

higher STHMFP, although DOC from the Tuolumne River may contain more organic DBP precursor, as indicating by a higher SUVA₂₅₄. For a milligram of carbon from the San Joaquin River, 167 μg-THM is potentially formed with 35% in chloroform and 65% in brominated THM species. In contrast, 116 μg-THM mg-C⁻¹ is potentially produced from Tuolumne River water, with 86% in chloroform and 14% in brominated THM species. Also, 79 μg-HAA mg-C⁻¹ was

recorded in San Joaquin River water with 43% in brominated HAA species, while 90 μg-HAA mg-C⁻¹ was found in Tuolumne River water with 13% in brominated HAAs. The statistical analysis indicated that there was significant difference in STHMFP (*p* < 0.05), but not in SHAAFP (*p* > 0.05). The hydrolysis and degradation of HAA, particularly as sulfite was used as quenching agents at the end of incubation periods, is a possible explanation (Xie & Reckhow 1996; Zhang & Minear 2002; Xie 2004).

Table 3 presents some general physical and chemical properties of soils collected from Webb Tract and Twitchell Island. Significant differences (*p* < 0.05) in soil organic carbon and soil salinity were noted between the two soils. The Clay Loam contained 4% soil organic carbon and had an EC₂₅ of 0.35 dS m⁻¹. In contrast, the Rindge Muck had much higher soil organic carbon and EC₂₅, 23% and 2.10 dS m⁻¹, respectively. In spite of the differences in carbon content, the extractable organic carbon between the two soils contained comparable aromatic carbon content, in terms of SUVA₂₅₄ measurements (Traina *et al.* 1990; Novak *et al.* 1992). The STHMFP and SHAAFP were not significantly different (*p* > 0.05) between the two soils. Also, the bromide levels of the two soils were below the detection limit and the effects of bromide on DBP formation can be neglected.

Sorption efficiency

The sorption efficiency of DAX-8 resin was systematically greater compared to that of the XAD-8 resin for both aquatic and soil humic substances, although the differences of DOC in isolated fractions were not significant (*p* > 0.05) (Tables 4 and 5). For each riverine or soil sample, XAD-8 effluent contained a higher percentage of DOC than DAX-8 effluent. Equivalently, a higher percentage of DOC in eluates, as back-flushed with 0.1 M NaOH, was recovered from DAX-8 resins. Considering the water sample from the Tuolumne River as an example (Table 4), 38% of DOC was not sorbed and was collected as effluent from a XAD-8 column; meanwhile, 55% of DOC was collected as eluate from the same XAD-8 column. Also, 7% of DOC was retained in the column as hydrophobic neutral fraction after elution with 0.1 M NaOH. By comparison, 35% of DOC passed through the DAX-8 column, 59% of DOC was back-flushed with NaOH and 6% of DOC was retained. On average, with all our tested samples,

Table 3 | General soil properties of Clay Loam from Twitchell Island and Rindge Muck from Webb Tract

Parameters	Webb Tract Rindge Muck	Twitchell Island Clay Loam
<i>Water soluble cations</i>		
Na ⁺ (mg g ⁻¹)	2.72	0.88
K ⁺ (mg g ⁻¹)	1.64	3.68
Ca ²⁺ (mg g ⁻¹)	60.96	19.48
Mg ²⁺ (mg g ⁻¹)	14.00	26.88
<i>Water soluble anions</i>		
HCO ₃ ⁻ (mg g ⁻¹)	ND	ND
NO ₃ ⁻ (mg g ⁻¹)	2.90	1.10
SO ₄ ²⁻ (mg g ⁻¹)	12.6	<0.02
Cl ⁻ (mg g ⁻¹)	2.80	1.80
Br ⁻ (mg g ⁻¹)	<0.01	<0.01
<i>Other properties</i>		
pH	5.25	6.41
EC ₂₅ (dS m ⁻¹)	2.10	0.35
Soil CEC (meq 100g ⁻¹)	148.7	36.6
Sand (%)	51.2	48.1
Silt (%)	34.7	41.8
Clay (%)	14.1	10.1
SOC (%)	22.9	3.7
SUVA ₂₅₄ (L mg-C ⁻¹ m ⁻¹)	7.0 ± 0.1 [‡]	7.2 ± 0.1 [‡]
STHMFP (μg-THM mg-C ⁻¹)	98 ± 4 [‡]	92 ± 9 [‡]
SHAAFP (μg-HAA mg-C ⁻¹)	109 ± 11 [‡]	99 ± 20 [‡]

ND: Not determined

‡: average and standard deviation, *n* = 4

DAX-8 adsorbed 4% more DOC than the XAD-8 resin in our columns with a *k'* of 50. Stronger sorption power has been observed in other studies using different soil and aquatic humic substances. DAX-8 resin retained 19% more aquatic humic substances from lakes and reservoirs than did the XAD-8 resin (Peuravuori *et al.* 2002a). Also, Franworth (1995) reported that DAX-8 resin adsorbed almost three times as much soil humic acids isolated from a sapric Histosol as was adsorbed with the XAD-8 resin. Greater sorption efficiency is probably attributed to a greater surface area in DAX-8 resin than XAD-8 resin, which is 160 m² g⁻¹ and 140 m² g⁻¹, respectively (Table 1). Although our tested samples are not statistically different (*p* > 0.05) from each other, greater sorption efficiency in DAX-8 resin has been observed from several studies using various sources of natural organic matter. Thus, the sorption efficiency of DAX-8 for DOC from natural sources is somewhat greater than XAD-8 resins.

Specific and differential UV absorbance

Except for the effluent of the peat soil extracts, eluates or effluents in each sample isolated by XAD-8 resin showed no significant difference (*p* > 0.05) in contents of DBP precursors, in terms of SUVA₂₅₄ and ΔUVA₂₇₂, compared to that isolated by DAX-8 resin. SUVA₂₅₄ has been widely used as a surrogate for aromatic carbon content and DBP precursors in aquatic humic substances (Traina *et al.* 1990; Novak *et al.* 1992; Weishaar *et al.* 2003). ΔUVA₂₇₂ is also an excellent indicator of total organic halogen and DBP formation (Korshin *et al.* 1997; Li *et al.* 1998, 2000). No differences in SUVA₂₅₄ and ΔUVA₂₇₂ of aquatic humic isolates between DAX-8 and XAD-8 resins indicated their comparability in general use for isolating DBP precursors from bulk aquatic humic substances. However, the fractions of soil humic substances, particularly organic-rich soil, isolated by these two resins may have different chemical characteristics. In general, soil humic substances are greater in aromatic carbon content and molecular size than aquatic humic substances (Senesi *et al.* 1989; Malcolm 1990), implying that soil humic substances have a stronger hydrophobic character than aquatic humic substances. In our tested samples, greater aromatic carbon content as measured by SUVA₂₅₄ was observed in soil humic substances (Tables 2 and 3).

Table 4 | Percentages of DOC adsorbed, specific and differential UV absorbance, and disinfection by-production formation potentials of aquatic humic substances isolated by XAD-8 and DAX-8 resins (mean \pm standard deviation, $n = 4$). All differences between XAD-8 and DAX-8 are insignificant ($p > 0.05$)

Sources	Parameter	Unit	Eluate		Effluent	
			XAD-8	DAX-8	XAD-8	DAX-8
Tuolumne River	DOC	%	55 \pm 4	59 \pm 2	38 \pm 2	35 \pm 3
	SUVA ₂₅₄	L mg-C ⁻¹ m ⁻¹	3.9 \pm 0.3	3.5 \pm 0.1	1.9 \pm 0.1	2.0 \pm 0.2
	Δ UVA ₂₇₂	m ⁻¹	-2.4 \pm 0.1	-2.1 \pm 0.1	-1.0 \pm 0.1	-1.1 \pm 0.1
	STHMFP	μ g-THM mg-C ⁻¹	190 \pm 7	178 \pm 4	112 \pm 7	116 \pm 13
	SHAAFP	μ g-HAA mg-C ⁻¹	119 \pm 20	126 \pm 24	97 \pm 23	112 \pm 4
San Joaquin River	DOC	%	42 \pm 1	43 \pm 2	48 \pm 2	44 \pm 2
	SUVA ₂₅₄	L mg-C ⁻¹ m ⁻¹	3.8 \pm 0.2	3.5 \pm 0.2	2.2 \pm 0.1	2.4 \pm 0.1
	Δ UVA ₂₇₂	m ⁻¹	-2.1 \pm 0.1	-1.9 \pm 0.1	-1.0 \pm 0.2	-0.9 \pm 0.4
	STHMFP	μ g-THM mg-C ⁻¹	140 \pm 8	164 \pm 18	134 \pm 15	151 \pm 19
	SHAAFP	μ g-HAA mg-C ⁻¹	128 \pm 10	114 \pm 12	77 \pm 14	84 \pm 11

Table 5 | Percentages of DOC adsorbed, specific and differential UV absorbance, and disinfection by-production formation potentials of soil humic substances isolated by XAD-8 and DAX-8 resins (mean \pm standard deviation, $n = 4$). The asterisk (*) indicates significant differences with $p < 0.05$

Sources	Parameter	Unit	Eluate		Effluent	
			XAD-8	DAX-8	XAD-8	DAX-8
Webb Tract	DOC	%	43 \pm 2	47 \pm 4	44 \pm 4	39 \pm 2
Rindge Muck	SUVA ₂₅₄	L mg-C ⁻¹ m ⁻¹	6.1 \pm 0.3	6.1 \pm 0.2	4.4 \pm 0.3 *	3.9 \pm 0.2 *
	Δ UVA ₂₇₂	m ⁻¹	-3.5 \pm 0.2	-3.4 \pm 0.2	-2.4 \pm 0.2 *	-1.6 \pm 0.3 *
	STHMFP	μ g-THM mg-C ⁻¹	122 \pm 10	140 \pm 17	78 \pm 10 *	60 \pm 5 *
	SHAAFP	μ g-HAA mg-C ⁻¹	170 \pm 18	177 \pm 6	113 \pm 24	103 \pm 7
Twitchell Island	DOC	%	55 \pm 3	55 \pm 4	42 \pm 5	38 \pm 3
Clay Loam	SUVA ₂₅₄	L mg-C ⁻¹ m ⁻¹	5.2 \pm 0.4	5.9 \pm 0.5	4.3 \pm 0.3	3.9 \pm 0.3
	Δ UVA ₂₇₂	m ⁻¹	-3.1 \pm 0.4	-3.3 \pm 0.6	-1.4 \pm 0.5	-1.8 \pm 0.2
	STHMFP	μ g-THM mg-C ⁻¹	117 \pm 15	152 \pm 11	82 \pm 10	64 \pm 12
	SHAAFP	μ g-HAA mg-C ⁻¹	150 \pm 12	160 \pm 20	120 \pm 8	130 \pm 15

As mentioned, DAX-8 resin has a better hydrophobic–hydrophilic sorption–desorption property (Peuravuori *et al.* 2002a) and can adsorb 3 times more soil humic acid than XAD-8 resin (Franworth 1995). XAD-8 effluents from both Rindge Muck and Clay Loam soils had greater $SUVA_{254}$, further supporting the fact that DAX-8 may have a better discriminating capacity for hydrophobic organic matter or soil humic substances. The differences for soil humic substances, but not for aquatic humic substances, are probably due to a greater hydrophobic characteristic in soil humus; therefore, the results were observable and significant. Particularly, even though humic acid was removed before passage through the XAD-8/DAX-8 column in this study, the acid soluble fraction, which contained fulvic acid and non-humic substances, still had a $SUVA_{254}$ of 5.0 ± 0.2 , significantly greater than aquatic humic substances obtained in the two rivers.

The specific UVA (SUVA) and differential UVA (ΔUVA) of all tested samples from wavelength 230 nm to 500 nm is shown in Figures 1 and 2. The wavelengths below 230 nm and beyond 500 nm are not shown because inorganic constituents such as bromide and nitrate absorb at wavelengths up to

230 nm (Ogura & Hanya 1966; Croue *et al.* 2000), and wavelengths greater than 500 nm are usually featureless (Stevenson 1994). For each tested sample, the SUVA and ΔUVA of eluates or effluents from both resins had similar patterns and closely matched each other. Statistical comparisons for SUVA and ΔUVA at 254, 272 and 280 nm, which are three common wavelengths in water and DBP research, showed no differences between the two resins, except the effluents in peat soil extracts. Furthermore, the eluates from both resins had a greater SUVA and a greater ΔUVA than the original samples in riverine samples, whereas the SUVA and ΔUVA of effluents were lower and smaller than that of the original samples, respectively (Figures 1(a, b) and 2(a, b)). The segregations in SUVA and ΔUVA of eluates and effluents and similarities in the shapes of curves from the original samples indicated that both XAD-8 and DAX-8 resins effectively fractionated aquatic humic substances into hydrophobic and hydrophilic fractions without significantly altering their chlorine reactive moieties. The hydrophobic fraction (eluate) has a higher aromaticity than the hydrophilic fraction (effluent). For soil humic substances, both resins effectively isolated soil fulvic acid from the acid

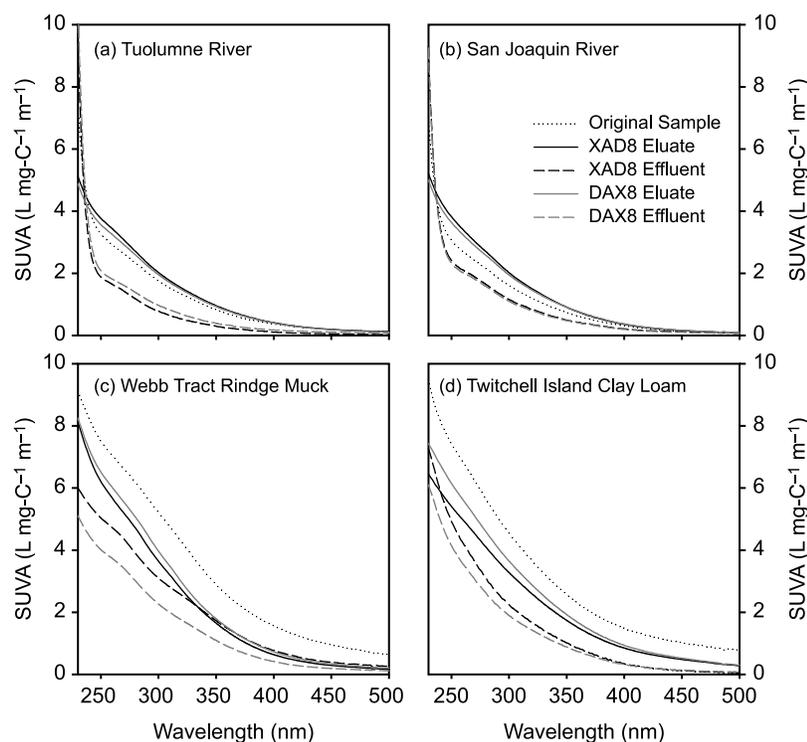


Figure 1 | SUVA spectrum of eluates and effluents isolated by XAD-8 and DAX-8 resins. The eluates in the soil extracts, as shown in (c) and (d), only contained fulvic acid.

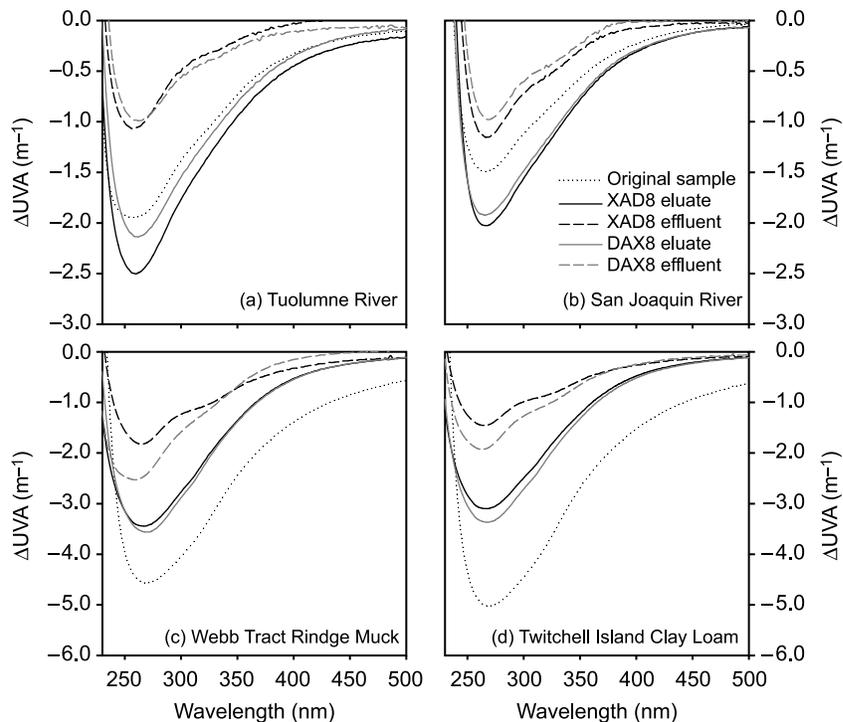


Figure 2 | Differential UV spectrum of chlorinated water samples. The eluates in the soil extracts, as shown in (c) and (d), only contained fulvic acid.

soluble fraction. Obvious segregations in SUVA and ΔUVA between fulvic acid and non-humic substances were found (Figures 1(c, d) and 2(c, d)). The SUVA and ΔUVA of fulvic acid and non-humic substances were lower than the original samples because humic acid, which had the highest aromatic carbon content, was removed by acid precipitation prior to XAD-8/DAX-8 fractionation. Importantly, DAX-8 and XAD-8 can effectively fractionate both soil and aquatic humic substances and the effluents and eluates from both resins had similar chemical characteristics, in terms of SUVA and ΔUVA measurements.

Disinfection byproduct formation

Statistically significant differences in STHMFP between XAD-8 and DAX-8 resins were only observed in effluents of the peat soil extracts, consistent with the significant differences in $SUVA_{254}$ and ΔUVA_{272} . A higher $SUVA_{254}$ and a greater ΔUVA_{272} in XAD-8 effluent indicated that it contained a greater content of DBP precursors than DAX-8 effluent (Korshin *et al.* 1997; Li *et al.* 2000; Weishaar *et al.* 2003). Results of the DBP formation test agreed with these

findings. The STHMFP of XAD-8 effluent was $76 \mu\text{g-THM mg-C}^{-1}$ and was significantly higher ($p < 0.05$) than DAX-8 effluents, which was $60 \mu\text{g-THM mg-C}^{-1}$. The SHAAFP of XAD-8 effluent was also higher than DAX-8 effluent, but the differences were not statistically significant ($p > 0.05$). The greater $SUVA_{254}$, ΔUVA_{272} and STHMFP of XAD-8 effluents indicated that the soil humic isolates fractionated by the two resins may have different reactivity in DBP formation. In particular, XAD-4 resin in tandem is used to isolate XAD-8 effluents and it may pose a potential artifact for further fractionation by XAD-4 resin. Also, there were no statistically significant differences in the distribution of THM and HAA species in the isolates of both XAD-8 and DAX-8 resins. Chloroform and chlorinated haloacetic acids were the only species in soil extracts. For the HAA speciation, roughly equal amounts of dichlorohaloacetic acid and trichlorohaloacetic acid represented 80% of total HAA.

XAD-8/DAX-8 resins may have effects on DBP speciation if bromides existed in the original samples. Both XAD-8 and DAX-8 resins, which are non-ionic adsorbents, do not retain or fractionate anions. All the anions pass through the column and are collected in

the effluents. Thus, the effluent isolated by the XAD-8/DAX-8 column contains the majority of bromide from the raw water, whereas the eluate isolated from the column does not contain any. Thus, the eluate only forms chlorinated species in the formation potential test unless bromide is added. The speciation of DBP in effluent depends on the bromide concentration in the isolates and the reaction condition in the formation test. Also, the reactivity of effluent (transphilic and truly hydrophilic fractions) in DBP formation would be increased because of the existence of bromide (Symons *et al.* 1987). Consider the San Joaquin River water as an example, which had 0.31 mg L^{-1} Br. The major species of eluates was chloroform (>90%), whereas brominated species were dominant in the effluents. Moreover, the reactivity in forming THM and HAA of both eluate (hydrophobic fraction) and effluent (transphilic and truly hydrophilic fractions) showed no significant differences ($p > 0.05$). The result was different from the general observation that the hydrophobic fraction had a higher reactivity in DBP formation than the transphilic and hydrophilic fractions (Owen *et al.* 1993; Croue *et al.* 2000; Chow *et al.* 2005a). High reactivity of the effluent in the San Joaquin River was probably due to the existence of bromide.

CONCLUSION

Two river waters and two soil extracts were fractionated into hydrophobic and hydrophilic fractions by XAD-8 and DAX-8 resins for DBP formation tests. Results indicated that the sorption efficiency of DAX-8 resin was systematically greater than XAD-8 resin, although the differences were not statistically significant ($p > 0.05$). The hydrophilic fraction of soil extracts isolated by XAD-8 resin had significantly greater ($p < 0.05$) values in SUVA_{254} , ΔUVA_{272} and STHMFP than those isolated by DAX-8 resin. In general, DAX-8 and XAD-8 resins are comparable for isolating DBP precursors from bulk aquatic humic substances, but caution should be taken for isolating DBP precursors from bulk soil humic substances or DOC having stronger hydrophobic characteristics.

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REFERENCES

- Aiken, G. R. 1985 Isolation and concentration techniques for aquatic humic substances. In: Aiken, G. R., McKinght, D. M., Wershaw, R. L. & MacCarthy, P. (eds) *Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization*. John Wiley & Sons, New York, pp. 363–385.
- Aiken, G. R., McKnight, D. M., Thorn, K. A. & Thurman, E. M. 1992 Isolation of hydrophilic organic acids from water using nonionic macroporous resins. *Org Geochem* **18**(4), 567–573.
- Amy, G. L., Thompson, J. M., Tan, L., Davis, M. K. & Krasner, S. W. 1990 Evaluation of THM precursor contributions from agricultural drains. *J. AWWA* **82**(1), 57–64.
- Brown, L. R. 2003 Potential effects of organic carbon production on ecosystems and drinking water quality. *San Francisco Estuary Watershed Sci.* **1**(1), Article 3.
- CDWR 1994 *Five-Year Report of the Municipal Water Quality Investigations Program – Summary and Findings During Five Dry Years: January 1987 – December 1991*. California Department of Water Resources, Sacramento, CA.
- Chow, A. T., Gao, S. D. & Dahlgren, R. A. 2005a Physical and chemical fractionations of DOM and THM precursors - a review. *J. Wat. Supply - Res. Technol. Aqua* **54**(8), 475–507.
- Chow, A. T., Guo, F., Gao, S. D. & Breuer, R. 2005b Size and XAD fractionation of trihalomethane precursors from soils. *Chemosphere* (in press).
- Chow, A. T., Tanji, K. K. & Gao, S. D. 2003 Production of dissolved organic carbon (DOC) and trihalomethane (THM) precursor from peat soils. *Wat. Res.* **37**(18), 4475–4485.
- Croue, J. P., Korshin, G. V. & Benjamin, M. M. 2000 *Characterization of Natural Organic Matter in Drinking Water*. AWWA Research Foundation and American Water Works Association, Denver, CO.
- Franworth, J. J. 1995 Comparisons of the sorption from solution of a humic acid by Supelite DAX-8 and by XAD-8 resins. *Int. Humic Substances Soc. Newsletter* **13**, 8–9.

- Fujii, R., Ranalli, A. J., Aiken, G. R. & Bergamaschi, B. A. 1998 Dissolved organic carbon concentrations and compositions, and trihalomethane formation potentials in waters from agricultural peat soils, Sacramento-San Joaquin Delta, California; implications for drinking-water quality. *Water Resources Investigations Report WRI 98-4147*. Geological Survey, Reston, pp. 1–75.
- Korshin, G. V., Li, C. W. & Benjamin, M. M. 1997 Monitoring the properties of natural organic matter through UV spectroscopy: a consistent theory. *Wat. Res.* **31**(7), 1787–1795.
- Krasner, S. W. 1999 Chemistry of disinfection by-product formation. In: Singer, P. C. (ed.) *Formation and Control of Disinfection By-Products in Drinking Water*. American Water Works Association, Denver, CO, pp. 27–52.
- Leenheer, J. A. & Croue, J. P. 2005 Characterizing aquatic dissolved organic matter. *Environ. Sci. Technol.* **37**(1), 18a–26a.
- Li, C. W., Benjamin, M. M. & Korshin, G. V. 2000 Use of UV spectroscopy to characterize the reaction between NOM and free chlorine. *Environ. Sci. Technol.* **34**(12), 2570–2575.
- Li, C. W., Korshin, G. V. & Benjamin, M. M. 1998 Monitoring DBP formation with differential UV spectroscopy. *J. AWWA* **90**(8), 88–100.
- Li, S. Y., Yang, X. H., Qiu, R. L. & Wang, P. 2003 Contents and leaching of trihalomethane precursors in soils. *Wat. Air Soil Pollut.* **145**(1), 35–52.
- Malcolm, R. L. 1990 Variations between humic substances isolated from soils, stream waters, and groundwaters as revealed by ¹³C-NMR spectroscopy. In: MacCarthy, P., Clapp, C. E., Malcolm, R. L. & Bloom, P. R. (eds) *Humic Substances in Soil and Crop Sciences*. American Society of Agronomy, Soil Science Society of America, Madison, WI, pp. 13–35.
- Nawrocki, J. & Kalkowska, I. 1999 Humic and fulvic acids as precursors of aldehydes - ozonation byproducts. *Toxicol. Environ. Chem.* **68**, 297–306.
- Novak, J. M., Mills, G. L. & Bertsch, P. M. 1992 Estimating the percent aromatic carbon in soil and aquatic humic substances using ultraviolet absorbency spectrometry. *J. Environ. Qual.* **21**(1), 144–147.
- Ogura, N. & Hanya, T. 1966 Nature of ultraviolet absorbance in seawater. *Nature* **212**, 758–759.
- Owen, D. M., Amy, G. L. & Chowdhury, Z. K. 1993 *Characterization of Natural Organic Matter and Its Relationship to Treatability*. AWWA Research Foundation and American Water Works Association, Denver, CO.
- Peuravuori, J., Ingman, P., Pihlaja, K. & Koivikko, R. 2001 Comparisons of sorption of aquatic humic matter by DAX-8 and XAD-8 resins from solid-state C-13 NMR spectroscopy's point of view. *Talanta* **55**(4), 733–742.
- Peuravuori, J., Koivikko, R. & Pihlaja, K. 2002a Characterization, differentiation and classification of aquatic humic matter separated with different sorbents: synchronous scanning fluorescence spectroscopy. *Wat. Res.* **36**(18), 4552–4562.
- Peuravuori, J., Lehtonen, T. & Pihlaja, K. 2002b Sorption of aquatic humic matter by DAX-8 and XAD-8 resins – comparative study using pyrolysis gas chromatography. *Anal. Chim. Acta* **471**(2), 219–226.
- Rook, J. J. 1976 Haloforms in drinking-water. *J. AWWA* **68**(3), 168–172.
- Saleh, D. K., Domagalski, J. L., Kratzer, C. R. & Knifong, D. L. 2003 *Organic Carbon Trends, Loads, and Yields to the Sacramento-San Joaquin Delta, California, Water Years 1980–2000, Water Resources Investigation Report 03-4070*. US Geological Survey, Sacramento, CA.
- Senesi, N., Miano, T. M., Provenzano, M. R. & Brunetti, G. 1989 Spectroscopic and compositional comparative characterization of IHSS reference and standard fulvic and humic acids of various origins. *Sci. Total Environ.* **81-2**, 143–156.
- Stevenson, F. J. 1994 *Humus Chemistry: Genesis, Composition, Reactions*, 2nd edn. John Wiley & Sons, New York.
- Stevenson, F. J. & Cole, M. A. 1999 *Cycles of Soil: Carbon, Nitrogen, Phosphorus, Sulfur, Micronutrients*, 2nd edn. John Wiley & Sons, New York.
- Summers, R. S., Hooper, S. M., Shukairy, H. M., Solarik, G. & Owen, D. 1996 Assessing the DBP yield: Uniform formation conditions. *J. AWWA* **88**(6), 80–93.
- Swietlik, J., Dabrowska, A., Raczky-Stanislawiak, U. & Nawrocki, J. 2004 Reactivity of natural organic matter fractions with chlorine dioxide and ozone. *Wat. Res.* **38**(3), 547–558.
- Swift, R. S. 1985 Fractionation of soil humic substances. In: Aiken, G. R., McKnight, D. M., Wershaw, R. L. & MacCarthy, P. (eds) *Humic Substances in Soil, Sediment, and Water*. John Wiley & Sons, New York, pp. 387–408.
- Symons, J. M., Fu, P. L. K., Dressman, R. C. & Stevens, A. A. 1987 The influence of bromide ion on organic chlorine and organic bromine formation during free chlorination. *J. AWWA* **79**(9), 114–118.
- Traina, S. J., Novak, J. & Smeck, N. E. 1990 An ultraviolet absorbance method of estimating the percent aromatic carbon content of humic acids. *J. Environ. Qual.* **19**(1), 151–153.
- USDA 1977 *Soil Survey of Contra Costa County, California*. US Department of Agriculture, California.
- USDA 1993 *Soil Survey of Sacramento County, California*. US Department of Agriculture, California.
- Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R. & Mopper, K. 2003 Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* **37**(20), 4702–4708.
- Xie, Y. 2004 *Disinfection Byproducts in Drinking Water: Formation, Analysis, and Control*. Lewis Publishers, Boca Raton, FL.
- Xie, Y. & Reckhow, D. A. 1996 Hydrolysis and dehalogenation of trihaloacetaldehydes. In: Minear, R. A. & Amy, G. L. (eds) *Disinfection By-products in Water Treatment: The Chemistry of their Formation and Control*. CRC Press, Boca Raton, FL, pp. 283–291.
- Zhang, X. R. & Minear, R. A. 2002 Decomposition of trihaloacetic acids and formation of the corresponding trihalomethanes in drinking water. *Wat. Res.* **36**(14), 3665–3673.