



Dissolved organic matter in Arizona reservoirs: assessment of carbonaceous sources

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Received 17 July 2003; accepted 2 March 2004
(returned to author for revision 14 October 2003)

Available online 27 April 2004

Abstract

Most studies of freshwater dissolved organic matter (DOM) have been conducted in temperate climates where allochthonous organic material is abundant. Because climatic conditions of the Southwestern USA are different than temperate environments, DOM from three freshwater reservoirs (Saguaro Lake, Bartlett Lake and Lake Pleasant) was investigated to determine the importance of allochthonous and autochthonous organic material. Results from the study show hydrophobic acids constitute a small percentage of the DOM, while the neutral and hydrophilic fractions are more prevalent. C/N ratios are comparatively low relative to other freshwater systems, ranging between 28 and 35 for the hydrophobic acid fractions, while DOC/DON ratios are seasonally influenced by epilimnetic algal growth. The isolated organic fractions were low in aromatic content measured by solid-state ¹³C NMR resulting in low aromatic to aliphatic carbon ratios. Organic material recovered from Saguaro Lake and Lake Pleasant display traits that suggest most allochthonous contributions are highly attenuated favoring organic material from autochthonous sources (low C/N and aromatic/aliphatic carbon ratios), whereas organic material from Bartlett Lake demonstrated a greater seasonal perturbation in source influence.

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1. Introduction

Freshwater dissolved organic matter (DOM) is a dynamic material that can be transported and transformed through natural biogeochemical processes (microbiological degradation, photolysis, hydrolysis, adsorption, precipitation, sedimentation) (Opsahl and Benner, 1998; Hertkorn et al., 2002; Barber et al., 2001). Most fresh-

water systems (rivers, lakes) in temperate climates are significantly influenced by terrestrial inputs, and allochthonous organic matter often dominates the organic carbon balance. Terrestrial material inputs derive from the decomposition of plant debris, the humification of soil organic matter. Allochthonous organic matter enters aquatic systems mainly from subsequent runoff from overland water flow during rainfall events (McKnight et al., 1994; Onstad et al., 2000). Temperate weather conditions prevailing throughout most of the United States and Western Europe are conducive for maintaining a constant source of terrestrially-derived organic

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material for surface waters and soils. These allochthonous carbon inputs contribute significantly to the dynamic global carbon cycle (Malcolm, 1990; Malcolm et al., 1994). When freshwater is impounded in lakes and reservoirs, the longer hydrologic residence times (typically on the order of months to a few years, compared to weeks in riverine systems) may be long enough to allow transformation of allochthonous carbon inputs. Additional DOM is formed by autochthonous production from algal and microbiological activity.

Chemical signatures of allochthonous and autochthonous DOM have been studied in end-member environments, from lowland rivers (e.g., Suwannee River, USA) dominated by allochthonous inputs, to lakes with extremely long residence times and little surrounding vegetative cover (e.g., Mono Lake in California, USA, Lake Fryxell, Antarctica). The signature of DOM in intermediate environments can be estimated as a blend of these end-member signatures (McKnight et al., 2001; Tenser et al., 1999). The relative contribution of autochthonous and allochthonous processes to aquatic DOM varies among environments. Terrestrial, or allochthonous material, tends to be higher in lignin content with high aromatic content and lower nutrient (N, P) inclusion. Freshwater riverine systems, including the Mississippi, Snake and Suwannee Rivers, are heavily influenced by organic materials originating from local watershed drainage areas (Onstad et al., 2000; McKnight et al., 1994; Malcolm et al., 1994). In contrast, autochthonous material derived from algal or microbiological productivity, tends to be more aliphatic with much higher nutrient inclusion. Phytoplankton, in particular, are major producers of autochthonous-DOM in lakes (Imai et al., 2002). Although autochthonous-derived DOM has been recognized to contribute to the DOM pool in the lower Great Lakes, terrestrially-derived DOC dominates the bulk DOM signature (Tenser et al., 1999). For example, higher C/N ratios (~40) were observed in St. Lawrence River sediments where the influx of anthropogenic organic material is significant, whereas more characteristic C/N ratios (~25) were observed near the river mouth/open ocean interface attributed to autogenic marine organic matter (Louchouart et al., 1997). The relative influence each end-member class determines the bulk chemical properties of the DOM, including hydrophobicity, metal binding, nutrient resources, drinking water treatability and biodegradation (Malcolm, 1990; Westerhoff et al., 1999).

Much of the understanding of autochthonous DOM has been obtained from studies involving several permanently ice-covered, dry-valley lakes and seasonal open water coastal lakes on the Antarctica mainland and in alpine regions dominated by snowmelt (McKnight et al., 1994; McKnight et al., 2001). Nearly all the DOM present in these systems is autochthonous formed by in situ production, modified by

subsequent transformations. There is little or no input of allochthonous DOM. Similarly, much of the DOM in the deep ocean results from in situ processes; this DOM is lost from the water column by degradation and sedimentation. Terrestrial contributions to the DOM balance appear to be most significant near riverine–ocean interfaces, but measurable contributions have been observed further offshore into the deeper continental margin regions (Mittra et al., 2000). Most allochthonous inputs are readily transformed, mineralized or deposited before substantial accumulation contributing to the seawater organic carbon pool.

Whereas DOM originating in temperate climates has been well studied, little is known about DOM in arid and semi-arid climates. In these regions, moderate to high air and water temperatures, greater seasonal hydrologic variations and widespread impoundment of rivers suggests that DOM could be different from that found in terrestrial systems. A typical annual hydrologic sequence for major rivers in arid and semi-arid regions includes a major hydrologic pulse associated with upland snowmelt, followed by a prolonged dry period with low stream flow. In the Southwestern USA, the dry period is interrupted by a brief monsoon season in the summer months. DOM loading in Southwest reservoirs reflects the hydrologic inputs, dominated by early season snowmelt, with low DOM loading during the dry season and a small but significant DOM pulse during the first monsoon events in the early summer months (Parks and Baker, 1997; Nguyen et al., 2002; Westerhoff and Anning, 2000). It is important to note that the prolonged period of warmth and abundant solar radiation (Marion and Wilcox, 1994) also influences DOM cycling, promoting algal and microbial productivity and possibly photo-oxidation. The implementation of a vast system of water storage reservoirs in arid and semi-arid regions have increased hydraulic residence times and most likely altered the DOM balance of these freshwater systems (Parks and Baker, 1997; Westerhoff and Anning, 2000; Nguyen et al., 2002).

In this study, we looked at DOM in three water storage reservoirs representative of the semi-arid Southwest USA. The main goal was to determine the importance of allochthonous and autochthonous production in these representative impounded waters.

2. Material and methods

2.1. Site descriptions

Water to the Phoenix metropolitan area is provided by the Salt River watershed, which originates in the White Mountains of eastern Arizona and New Mexico, and the Central Arizona Project (CAP), which delivers water from the Colorado River (below Lake Havasu). In

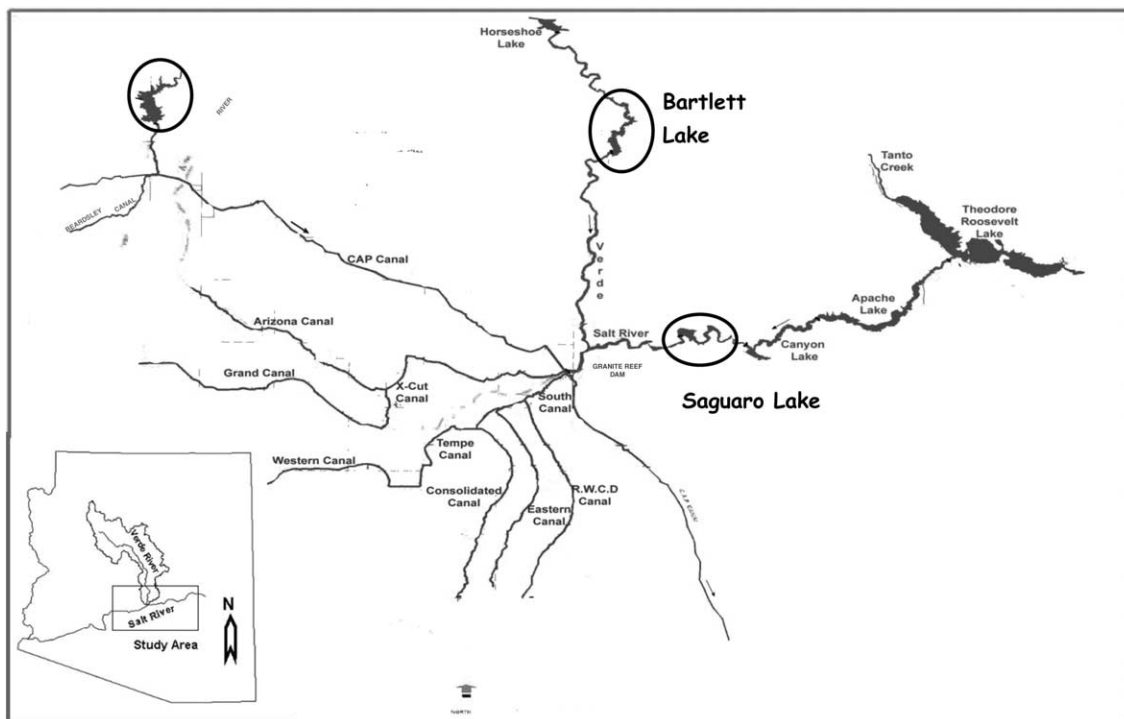


Fig. 1. Location of the reservoirs located around Phoenix, Arizona. Saguario Lake is located in the Salt River basin, Bartlett Lake is located on the Verde River and Lake Pleasant sits off-channel from the Central Arizona Project canal in the Aqua Fria River basin.

Table 1

Physical characteristics of the reservoirs used in this study (HRT, hydraulic retention time)

Reservoir	Average daily volume (m ³)	Average upstream storage (m ³)	Average annual runoff (cm yr ⁻¹)	Average HRT (days)	Inflow elevation ^a (m)	Elevation at impoundment (m)
Bartlett Lake	1.0×10^8	0.36×10^8	1.9	165	620	490
Saguario Lake	7.9×10^7	9.21×10^8	3.8	70	770	420
Lake Pleasant	7.1×10^8	^b	1.1	404	550	520

Each value is the daily average measured during the study period from August 1999 to July 2001.

^a Inflow elevation measured at the outflow of upstream catchments below upstream-most reservoir.

^b Excessive storage upstream on the Colorado River prior to CAP canal inlet.

the Salt River watershed, there are four reservoirs on the main stem of the Salt River and two on the Verde River, which joins the Salt River below the lowermost main-stream reservoir (Fig. 1). These reservoirs store water derived mainly from snowmelt at higher elevations. The CAP transports water from the Colorado River near Lake Havasu by way of a 200 km cement-lined canal with pump station. The inlet from the Colorado River is downstream of major on-stream reservoirs such as Lake Powell. Much of the Colorado River water delivered to the Phoenix area is stored in an off-stream reservoir (Lake Pleasant) near Phoenix.

We studied three reservoirs: Lake Pleasant, Bartlett Lake, the lowermost reservoir on the Verde River, used exclusively for water storage and flood control, and

Saguario Lake, the lowermost reservoir on the main stem of the Salt River, which is used for water storage, flood control and hydroelectric generation (Table 1). All three are located in the semi-arid Sonoran desert within 50 km of the Phoenix metropolitan area (Fig. 1). Over the period of the study snow pack in the adjoining watershed was less than the long-term average. Water levels fluctuate throughout the year, usually 10–20 m for Bartlett Lake, <4 m for Saguario Lake and >30 m for Lake Pleasant.

The volume of Bartlett Lake, which is located 1.2 km downstream of Horseshoe Reservoir, was less than 20% of maximum capacity during the study period. Bartlett Lake has a single outlet near the bottom of the containment dam (hypolimnetic withdrawal). Water is

stored throughout the summer, with minimal release to maintain channel flow in the Verde River, and released predominately during the winter months after October 1. The reservoir is monomictic, with a long summer stratification period. The temperature ranges from >25 °C (late summer epilimnion) to just below 10 °C in the winter. Further information on the limnology of Bartlett Reservoir is available (Parks and Baker, 1997). Samples were collected just downstream of the dam release area.

Saguaro Lake is primarily operated for hydropower generation considerations. Three of the upstream Salt River reservoirs have hydropower generation facilities, and pump-back piping from Saguaro to upstream reservoirs is used during summer months to increase hydropower revenue: water released from upstream reservoirs during peak demand periods (daytime) is pumped back to the upstream reservoirs upstream during off-peak periods (night-time). Saguaro Lake also has one channel outlet located near the bottom of the dam. Most substantial releases occur in the summer with minimal release between October and April.

Lake Pleasant is an off-stream water supply reservoir found near the Central Arizona Project (CAP) Canal. Between October and April, it is filled with water pumped from the Colorado River. Water is released from Lake Pleasant between April and October through one of two outlets, one near the bottom (485 m above MSL) and one at 519 m above MSL. Natural drainage from the Aqua Fria River supplies a small-added inflow (5% of the reservoir inflow during this study period) to Lake Pleasant. Water levels fluctuated considerably throughout the year.

2.2. Field sampling and preparation

Samples for DOM isolation were collected in April 2001. Sample collection occurred after a two-year drought. Water samples were collected in 50 L HDPE carboys and stored at 4 °C prior to isolation. Sample volumes were adjusted according to ambient DOC levels for adequate isolate recovery (each required roughly 150 L). Bulk water samples were passed through a Parker Filtration high-capacity filtration system fitted with pre-cleaned Balston 100-25-DH (25 μm nominal) and Balston 100-25-AH filters (0.9 μm nominal) arranged in series. The filtrate water was then softened using a pre-cleaned Thermodyne D8904 Na^+ saturated ion-exchange cartridge and concentrated to a final volume of 33 L using a reverse osmosis system fitted with a Koch TFC-HR 2540 reverse osmosis element (100 D molecular weight cut off). Total organic carbon mass balance recovery was greater than 92%. Concentrated samples were adjusted to pH 2 with concentrated HCl and stored for approximately 1 week at 4 °C prior to isolation.

Water quality parameters, such as Secchi disk transparency (observational error was approximately ± 0.3 m), DOC (dissolved organic carbon) and specific ultraviolet absorbance at 254 nm (SUVA), have been continuously measured monthly since July 1999. Chlorophyll-a was measured through July 2001 while dissolved organic nitrogen (DON) has been measured beginning in March 2002.

2.3. DOM isolation

DOM isolates were obtained by tandem XAD8/XAD4-resin adsorption chromatography fractionation (Aiken et al., 1992). All reagents were analytical grade or better, prepared in distilled/deionized water (nanopure). Briefly, the isolation procedure involved passing 33-L of filtered/acidified (pH 2.0) samples through a column containing XAD-8 resin, then through a column containing XAD-4 resin at a flow rate of 90 mL min^{-1} . Each column contained a resin volume of 540 mL. With this scheme, the hydrophobic acid fraction (HOA) is operationally defined as the fraction of DOM retained on XAD-8 resin at pH 2 that can be eluted with 0.1 M NaOH. The transphilic acid fraction is operationally defined as DOM that passes through the XAD-8 column but is retained on XAD-4 resin at pH 2 and can be eluted with 0.1 M NaOH. DOM that passes through both columns is defined as the hydrophilic fraction. Although this method is user-specific (many modifications are available), there are advantages of using a standard operational definition for its use, including: (1) quantification of hydrophobicity, (2) isolation and concentration of organic material for further analysis, and (3) comparison with many publications (Aiken et al., 1992). Each fraction was lyophilized and stored subsequently under desiccant for further analysis. Well-characterized fulvic acids from the Suwannee River obtained from the International Humic Substances Society (IHSS; Golden, CO) were used for comparison. Lyophilized NOM fractions were dissolved in Milli-Q water (Millipore Inc.) at least 24 h before use.

2.4. Spectroscopic methods

DOC (mg C L^{-1}) was measured by high temperature combustion analysis (Shimadzu TOC-5000) using non-purgable organic carbon analysis. Analytical variability was found to be $<5\%$. Ultraviolet absorption (UVA) of NOM isolates was measured at 254 nm using a Shimadzu UV160A single wavelength UV/Vis spectrometer. SUVA was calculated by normalizing UVA to the DOC concentration and is analogous to molar absorptivity ($\text{L cm}^{-1} \text{mg}^{-1}$). Chlorophyll-a was estimated using Method 10000H adopted from Standard Methods for Examination of Water & Wastewater (Clesceri et al., 1998),

with an analytical variability of <15%. DON (mg N L⁻¹) was measured (DON = N_{Total} - NO₃⁻ - NH₄⁺) using a high-speed continuous-flow wet chemistry analyzer (TRAACS 800 Autoanalyzer, Bran-Luebbe, Germany).

Solid-state ¹³C-nuclear magnetic resonance spectra were obtained on a Varian Inova 400 MHz spectrometer operating at 100.58 MHz. The sample was spun at 10 kHz using a 4 mm probe employing cross-polarization magic angle spinning. 27904 scans were accumulated for each analysis, each with a sweep width of 50 kHz, 3 s pulse delay and 3 ms contact time. Validation of the solid-state method used by the investigators is provided elsewhere (Drewes and Fox, 1999). ¹³C NMR results were analyzed by dividing the area beneath the spectrum into the following shift ranges (Aiken et al., 1996): Aliphatic-I (Al-I, 0–62 ppm) including unsubstituted saturated aliphatic carbons, Aliphatic-II (Al-II, 62–90 ppm) including carbon singly bonded with oxygen or nitrogen, Anomeric (90–110 ppm) including carbon singly bonded to two oxygen's such as acetal or ketal moieties, Aromatic (Ar-C, 110–160 ppm: unsaturated carbon) subdivided into Aromatic-I (110–140 ppm, protonated and alkyl-substituted aromatic carbon) and Aromatic-II (140–160 ppm, aromatic carbon substituted by oxygen and nitrogen) regions, Carboxyl (Carb-C, 160–190 ppm) mainly carboxyl groups and Ketonic (190–230 ppm) including carbonyl, amide, and ester groups.

2.5. Elemental analysis

Elemental analysis (used in the determination of C/N ratios) of the lyophilized samples was performed on a Perkin–Elmer 2400 Series II CHNS/O analyzer, operated for CHN analysis. A 1.2 mg sample of material, precisely weighted using a Perkin–Elmer AD-4 Microbalance, was encapsulated into a tin container. The sample was then flash combusted at 1760 °C. The resulting gaseous products were chemically scrubbed of halogens (and sulfur for CHN analysis), separated on a GC column and detected by a thermal conductivity detector (TCD). Statistical analyses of results were performed using the Wilcoxin rank sum test using a significance level of 0.05.

3. Results and discussion

3.1. Fractionalization analysis

The XAD 8/4-resin fractionation technique was used to isolate a representative quantity of organic material from these reservoirs. Recoverable acid fractions (hydrophobic plus transphilic acids) varied between 32% for Saguaro Lake, 36% for Lake Pleasant and 53% for Bartlett Lake (Fig. 2). The higher recoverable acid

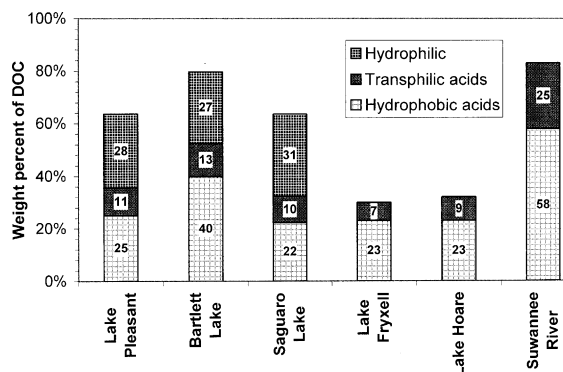


Fig. 2. Absolute weight percent of organic carbon hydrophobic and transphilic acid fractions isolated from the three reservoirs. Also included are organic fractions isolated from known autochthonous-dominated (Lake Fryxell and Lake Hoare) and allochthonous-dominated (Suwannee River) systems (Aiken et al., 1992). Base fractions were not included.

fraction for Bartlett Lake was due to a higher recovery (40%) of the hydrophobic fraction compared to Lake Pleasant (25%) and Saguaro Lake (22%). The fraction of transphilic acid was similar (10–13%) among reservoirs. The hydrophilic fraction was roughly 30% in all samples. The remainder of the unaccounted organic carbon material, most probably hydrophobic and hydrophilic neutral fractions (assuming a total mass recovery of 100%), ranges between 20% in the Bartlett Lake samples to 33% and 34% for Lake Pleasant and Saguaro Lake, respectively. Results were similar to samples isolated from the autochthonous end-member environment, including Lake Fryxell and Lake Hoare (Fig. 2), where recoverable organic acids were 30% and 32%, respectively (Aiken et al., 1992). Similar recoveries were obtained for the hydrophobic acid fractions (23% for both lakes) and transphilic acid fractions (7% and 9%, respectively). In contrast, a greater proportion of the DOM isolated from allochthonous end member environments can be recovered as hydrophobic and transphilic acid fractions. For example, Aiken et al. (1992) reported high recoverable acids from the Suwannee River (83%; Fig. 2). The low percentage of hydrophobic DOM in all three reservoirs is suggestive of a relatively high autochthonous source. Previous studies have associated increased algal activity, where enrichment in fatty acid content is augmented with increased amounts of nitrogen and hydrogen, in retention basins with increasing hydrophilic content (Barber et al., 2001).

The DOM from Bartlett Lake was more hydrophobic than DOM from the other two reservoirs based on the recoverable acid fractions. This can be explained by comparing the hydraulic residence times (HRTs) of the three systems. At the time of sampling, Bartlett Reservoir had a HRT of 165 days. Horseshoe Reservoir, located upstream, had a HRT of only 38 days, for a total

of 203 days. For comparison, Saguaro Lake had a HRT of 70 days; the HRT of upstream reservoirs was 816 days, for a total of 886 days, or 2.4 years. For the Colorado River, the combined HRT of Lake Mead and Lake Powell is ~4–5 years; total HRT for all reservoirs in the system above the Lake Havasu pumping station would be somewhat larger than this. We would thus expect in-lake processes (production, sedimentation and transformation) to have a greater influence on DOM in Lakes Pleasant and Saguaro than in Bartlett Lake.

C/N ratios of the hydrophobic acid fractions from the three study reservoirs were similar (Table 2). Values ranged between 28 and 30 for Saguaro Lake and Lake Pleasant, respectively, and 35 for Bartlett Lake. They are far lower ($p > 0.05$) than the C/N ratios for comparable fractions (Table 2) isolated from allochthonous-dominated temperate water systems such as the Suwannee River (values of 70 and 82) and Ogeechee River (58), but higher ($p > 0.05$) than values from the Antarctic autochthonous end-member lakes (11–19). They are also

Table 2

C/N ratio values from other published studies compared to the hydrophobic and transphilic acids isolated in this study (FA, fulvic acid)

Sample	C/N ratio (wt/wt)
Suwannee River FA – IHSS ^a	82
Ogeechee River ^b	58
Suwannee River ^c	
Hydrophobic acid ^c	70
Transphilic acid ^c	46
Hydrophilic acid ^c	34
Lake Hoare FA, Antarctica ^d	19
Pony Lake FA, Antarctica ^d	11
Lake Fryxell FA, Antarctica ^d	18
Algal material (<i>Scenedesmus quadricauda</i>) ^a	8.5
Algae culture ^c	12
Saguaro Lake ^f	
Hydrophobic acid	28
Transphilic acid	17
Bartlett Lake ^f	
Hydrophobic acid	35
Transphilic acid	18
Lake Pleasant ^f	
Hydrophobic acid	30
Transphilic acid	20

^a Nguyen (2002).

^b Westerhoff et al. (1999).

^c Benjamin et al. (2000).

^d McKnight et al. (1994).

^e Tuschall and Brezonik (1980).

^f This study.

somewhat higher than fulvic acids from pure algal cultures (9–12).

The transphilic acid fractions were more nitrogen enriched than the hydrophobic acid fraction for all three reservoirs. This is consistent with the expected increase in the electron-dense (polar) moiety content with decreasing hydrophobicity (Aiken et al., 1992; Westerhoff and Mash, 2002). Greater N enrichment in the transphilic fraction than the hydrophobic fraction has also been observed for Suwannee River isolates (Table 2; Benjamin et al., 2000). Our samples have lower C/N ratios in the transphilic and hydrophobic fractions than similar isolates from temperate freshwater systems (Table 2), a characteristic similar to aqueous environments with greater autochthonous production.

Similar solid-state ¹³C NMR spectra were obtained for all three reservoirs (Fig. 3 and Table 3). The Al-I range areas for the hydrophobic acid fractions were nearly identical among the three reservoirs (46–48%). The Al-I range for the transphilic acids was also nearly identical among reservoirs, comprising 39–41% of the area. The signal responses in the Al-II range were also nearly identical among the three reservoirs, comprising 16–18% of the total area for the hydrophobic fraction and 23–24% for the transphilic acids. The total aliphatic (Al-T, Al-I and Al-II) contribution was nearly identical among all three reservoirs and both fractions, 62–65%. The Ar-C content was also similar among reservoirs, but was more important in the hydrophobic acid fraction (12–14%) than in the transphilic fraction (7–9%). In summary, for each fraction, the ¹³C NMR spectra were nearly identical among reservoirs; the hydrophobic acid fraction had greater Al-I and Ar-C contribution and less Al-II contribution than the transphilic acid fraction.

The hydrophobic acid fractions (i.e., fulvic acids) derived from the Suwannee and Ogeechee Rivers have aromatic-to-aliphatic ratios (Ar-C/Al-T) consistent with large contributions from a terrestrial source with Ar-C/Al-T ratios approximately 0.5 (Table 3). In general, greater aromaticity can be directly correlated with increased hydrophobicity, with the highest aromatic content found in the hydrophobic acid fractions (Aiken et al., 1992; Traina et al., 1990). Previous studies have shown that aromatic DOM isolated from terrestrially dominated inputs reflects aromatic carbon derived from lignin and vegetative degradation by-products (Van Heemst et al., 2000; Louchouart et al., 1997). Conversely, the predominantly autochthonous-produced DOM isolated from the Antarctica freshwater lakes, Lake Fryxell and Lake Hoare are characterized by lower Ar:Al ratios, roughly 0.2 (McKnight et al., 1994). Ar-C/Ar-T ratios for the reservoir isolates were similar to those found for the Antarctic lake isolates ($p < 0.05$), while significantly less than ratio values observed in the allochthonous isolates. The Carboxyl-C signature in all reservoir samples was lower than in isolates taken from

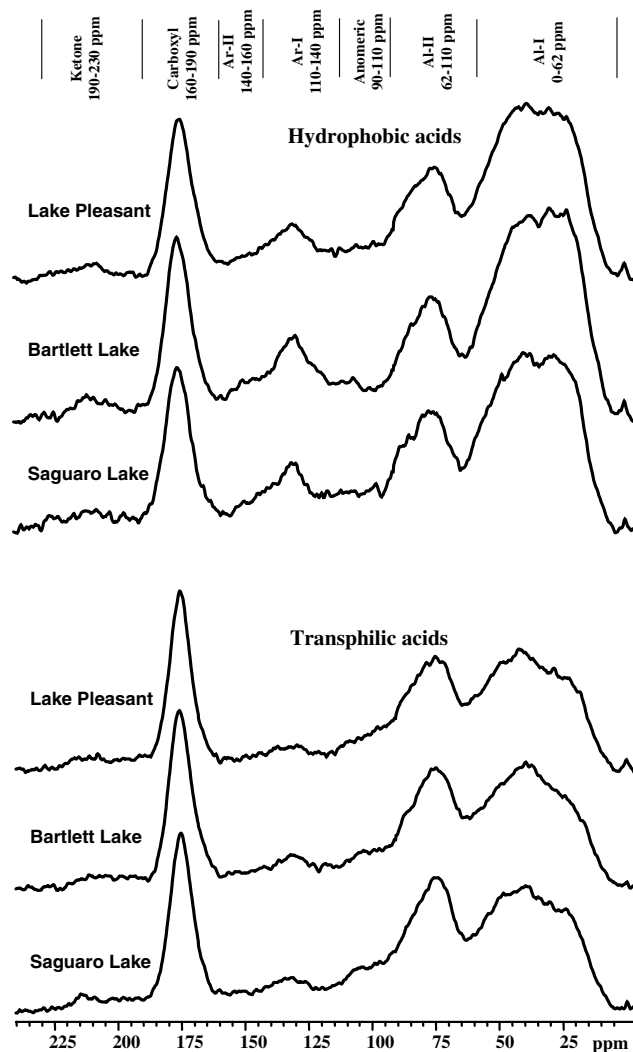


Fig. 3. Solid-state ^{13}C NMR spectra for the hydrophobic and transphilic acid isolates.

autochthonous sources. Since carboxyl moieties tend to be formed from microbial oxidation (McKnight et al., 1994), this result suggests that DOM in the reservoir hydrophobic acid fraction is diagenetically young.

For the DOM isolated in this study, more specifically for hydrophobic acids, C/N ratios increase with increasing ratios of aromatic to aliphatic carbon. Algal material (algal isolate and Antarctica Lake isolates) have lower Ar-C/Al-T and C/N ratio values, whereas terrestrial organic material (Ogeechee and Suwannee Rivers) have higher values. Previous XAD fractionation studies have correlated the increase in oxygen-containing and other heteronuclear moieties with decreasing hydrophobicity, lower Ar-C/Al-T ratios (Aiken et al., 1992; McKnight et al., 2001). These two end-member classes can be clearly distinguished in Fig. 4, with terrestrially-derived organic material residing at high C/N

(x -axis) and Ar-C/Al-T (y -axis) ratio values opposite algal-derived organic material. Points representing the reservoir fractions are shown in Fig. 4. Points along this continuum reflect varying mixtures of autochthonous and allochthonous DOM. The hydrophobic acids isolated from the study reservoirs plot on the lower left portion of this plot, close to points representing autochthonous DOM. The slight deviation of the Bartlett Lake sample from the other two reservoir samples in Fig. 4 suggests a slightly higher contribution from allochthonous-derived organic material, which may be a reflection of lower HRT.

Carbon loading in the three Arizona reservoirs studied is dominated by early spring snowmelt events (Nguyen et al., 2002). The influence of DOM entering Bartlett Lake during the early spring can be seen from a hydrophobic acid isolated from an upstream source. ^{13}C

Table 3

Relative peak areas from ^{13}C NMR spectra for measured carbon types for the isolates recovered from the Arizona reservoirs

	Relative peak areas (%)						Ar-C/Al-T ratio
	Al-I 0–62 ppm	Al-II 62–90 ppm	Al-T 0–90 ppm	Ar-C 110–160 ppm	Carb-C 160–190 ppm	Ketone 190–220 ppm	
Allochthonous end member							
Suwannee River – RO	32	19	51	20.9	16.0	3.9	0.41
Suwannee R. FA – IHSS ^a	34.9	15.5	50.4	21.9	16.1	4.4	0.43
Ogeechee River FA ^b	^c	^c	46.9	24.8	18.3	^b	0.53
Autochthonous end member							
Algal material (Scenedesmus quadricauda) ^c	43.3	20.7	64	12.4	15.0	2.8	0.19
Lake Fryxell FA ^c	48.4	12.2	60.6	11.9	20.7	4.4	0.20
Lake Hoare FA ^c	49.5	12.7	62.2	11.7	20.2	2.2	0.19
Hydrophobic acids ^d							
Bartlett Lake ^d	48.4	16.1	64.5	13.9	14.4	3	0.22
Lake Pleasant ^d	48.4	17.8	65.2	11.4	14.6	2.7	0.18
Saguaro Lake ^d	46.2	18.2	64.4	12.1	14.7	3.4	0.19
Verde River Above Bartlett ^a	^c	^c	55	17.3	15	^e	0.32
Transphilic acids ^d							
Bartlett Lake	39.8	23.5	63.3	9.0	18.6	2.6	0.14
Lake Pleasant	40.8	24.0	64.8	7.1	18.8	2.7	0.11
Saguaro Lake	38.6	24.2	62.8	8.5	17.7	2.9	0.14

Also included are results representing other studies consistent with alternately definitive end member DOM isolates. Suwannee River – RO is a reverse osmosis isolate.

^a Nguyen (2002).

^b Westerhoff et al. (1999).

^c McKnight et al. (1994).

^d This study.

^e Not reported.

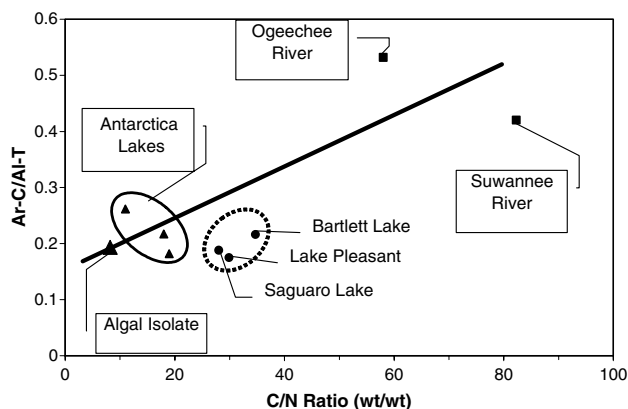


Fig. 4. Observed trend between C/N ratio and ^{13}C NMR aromatic carbon (110–160 ppm) to aliphatic carbon (0–90 ppm) ratio, Ar-C/Al-T, for different surrogate end member DOM classes and isolates from this study. Results represent hydrophobic acid fractions from known autochthonous dominated sites (\blacktriangle), identified allochthonous dominated sites (\blacksquare) and samples isolated in this study.

NMR analysis shows that the carbonaceous material derived from the local watershed is compositionally different ($p > 0.05$) from the reservoir DOM (Table 3). The sample isolated from the river upstream of Bartlett

Lake had a higher aromatic content and an ambiguity of distinguishing peaks, similar to hydrophobic acids isolated from waterways dominated by terrestrial DOM (Malcolm, 1990). This is in contrast to DOM isolated

from within the Bartlett Reservoir. Increased HRTs allow microbiological, algal and geochemical processes to change DOC resulting in less aromatic, less hydrophobic organic material. A more detailed description of the importance of each geochemical process on DOM genesis for Arizona reservoirs can be found in Nguyen et al. (2002). The extent and rate of change would be affected by retention times, thermal stratification and biological activity.

The decrease in the significance of the hydrophobic and transphilic acid fractions relative to isolates representing more temperate climates shows that the neutral fractions, that were not isolated as a part of this study, are much more important in defining the chemical character of the DOM material found in these reservoirs. Neutral fractions tend to have lower C/N ratios and SUVA values compared to acid fractions (Westerhoff and Mash, 2002). Neutral fraction isolates share similar characteristics with colloidal material originating from microbiological cell wall fragments (Westerhoff and Mash, 2002). The importance of carbonaceous material from non-terrestrial sources appears to significantly influence the composition of the DOM in the three reservoirs based on both the properties exhibited by the isolated acid fractions as well as the degree of hydrophobicity observed. Even moderate DOM inputs from upstream sources appear to be attenuated by in-reservoir processes.

3.2. Bulk chemical properties and algal abundance

Previous research has shown that SUVA values of DOM from water systems with greater autochthonous

production were lower in comparison with more terrestrially influenced water (Barber et al., 2001; Chin et al., 1994). For example, the Colorado River, which is heavily dependant on snowmelt and heavily influenced by large impoundments, had a lower SUVA value ($\sim 0.015 \text{ L cm}^{-1} \text{ mg}^{-1}$) than the Sacramento River ($> 0.030 \text{ L cm}^{-1} \text{ mg}^{-1}$), which is highly impacted from by agricultural drainage returns from peat-rich farmlands (Amy et al., 1990; Krasner et al., 1994). SUVA values are correlated with aromatic content, where lower SUVA values indicate autochthonous production or the depletion of allochthonous material (Traina et al., 1990; Weishaar et al., 2003). Low values of SUVA, coupled with low aromatic content, show the relatively low significance of primary terrestrial material, while more significantly related to autochthonous production or in situ transformations.

SUVA values for the Bartlett Lake epilimnion are lower in mid-to-late summer than at other times of the year (dotted-line circles; Fig. 5). Inlet SUVA values during runoff events (solid-line circles, Fig. 5) are $\geq 0.030 \text{ L cm}^{-1} \text{ mg}^{-1}$, reflecting terrestrially-derived DOM. During low flow periods, in-stream periphyton growth likely contributes significantly to the DOM pool, shown by low SUVA values (Figs. 5 and 6). SUVA values in the reservoir epilimnion decline to below $0.020 \text{ L cm}^{-1} \text{ mg}^{-1}$ during the spring and summer, reflecting autochthonous DOM production, but also may be indicative of in-lake physiochemical processes. Similarly measured median SUVA values at Bartlett Lake were elevated ($p > 0.05$) compared to Saguaro Lake and Lake Pleasant. There were no observable changes ($p < 0.05$) in SUVA values across either Saguaro Lake or Lake

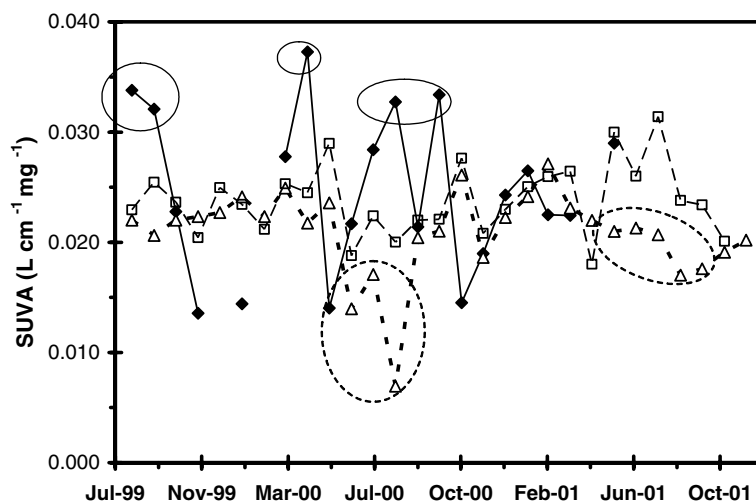


Fig. 5. SUVA values for DOM in and around Bartlett Lake: above reservoirs (\blacklozenge); within Bartlett Lake-epilimnion, (Δ); and below Bartlett Reservoir-Dam (\square). Data in circles (solid-line) represent the influence of surface runoff events; low SUVA values in the epilimnion of Bartlett Reservoir during the summer are also circled (dashed-line).

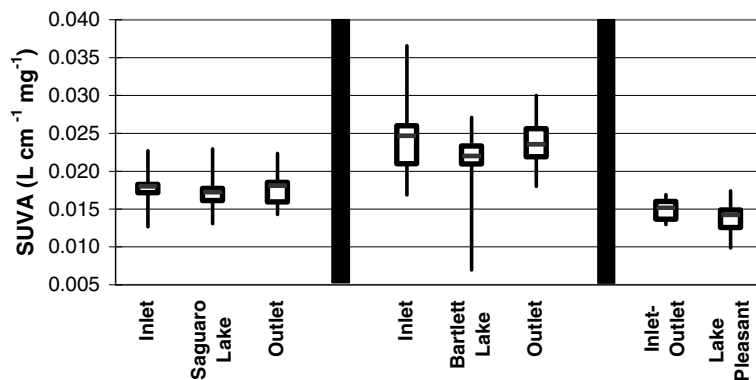


Fig. 6. SUVA values of DOM measured from the three reservoirs. The box represents 50% of the data: the upper quartile (UQ) and lower quartile (LQ) or 75th and 25th percentile, of the data, respectively. The middle bar is the median. The lines extending above and below the box represent the data spread.

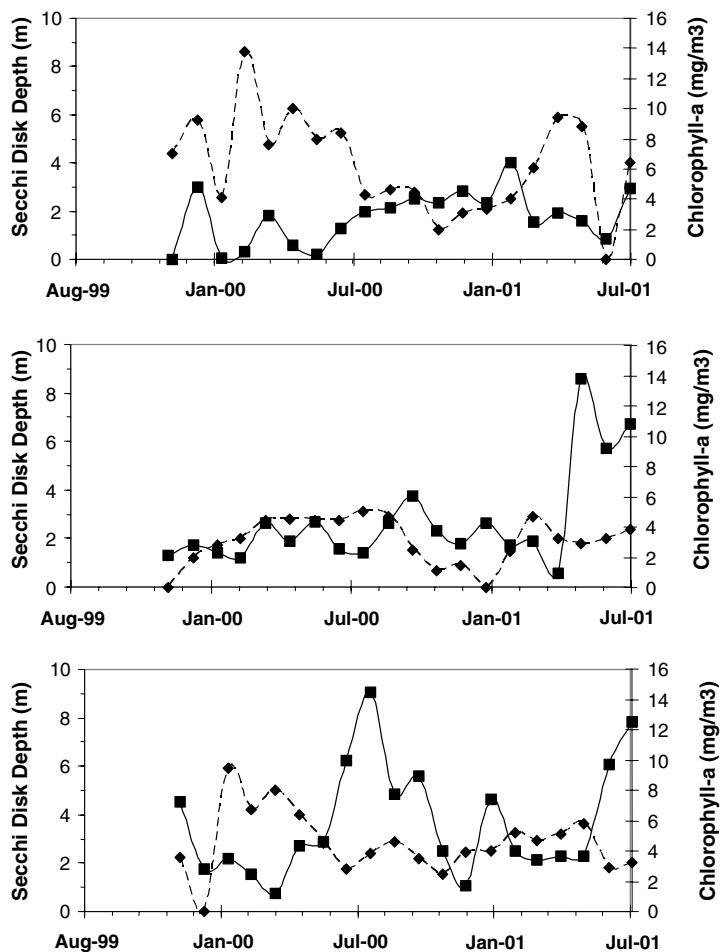


Fig. 7. Comparison between Secchi disk depth (\blacklozenge) and chlorophyll-A (\blacksquare) measurements taken between October 1999 and July 2001. Top, Lake Pleasant; middle, Bartlett Lake; bottom, Saguario Lake.

Pleasant (Fig. 6). However, SUVA values at the inlet to these lakes were below $0.020 \text{ L cm}^{-1} \text{ mg}^{-1}$ reflecting autochthonous DOM production in upstream reservoirs

on the Salt River (Saguario Lake) and the Colorado River (Lake Pleasant). Both higher median SUVA values and increased seasonal variability seen in Bartlett

Lake are a reflection of increased intermittent terrestrial carbon mass loading from upstream sources.

The Secchi disk is used for the in situ measurement of clarity of surface waters as defined by its depth of visibility. In Fig. 7, Secchi disk depths are compared to chlorophyll-a measurements within each of the three reservoirs. Increases in chlorophyll-a, indicating an increase in algal biomass, in general correspond to decreases in the Secchi disk depth in both Lake Pleasant and Saguaro Lake. Chlorophyll-a measurements in Bartlett Lake remain relatively stable through the summer of 2000, with an increase in activity associated with a gradual decrease in Secchi disk depth in the spring of 2001. For the period between March and October 2002, C/N (DOC/DON) was directly correlated ($R^2 = 0.4$) with Secchi disk depth measurements (Fig. 8). From both observed trends relative to Secchi disk depth, an inverse relationship between C/N ratio and chlorophyll-a results may be observed. This is consistent with the observation that autochthonous DOM has a lower C/N ratio than allochthonous DOM. During periods of high algae abundance, algae produce DOM contributing to lower C/N ratio in the reservoir. Bartlett Lake has the

greatest seasonal variability in C/N ratio values (35 to 7.4). This variability coincides favorably with seasonal variability in measured SUVA values. However, suppressed SUVA values and relatively steady chlorophyll-a measurements, during the summer of 2000 imply other in-reservoir processes (photobleaching and microbiological activity) may be important.

Allochthonous DOM production in arid region reservoirs has several management implications. Formation of autochthonous DOM will incorporate nutrients, resulting in a greater proportion of nutrients (nitrogen and phosphorus) in the organic form, and a lower proportion in the dissolved inorganic form (McKnight et al., 2001; Malcolm, 1990). This affects the availability of nutrients within the reservoir and in downstream rivers and canals and most likely has the effect of reducing the availability of nutrients to algae. Second, decreased hydrophobicity reduces the effectiveness of DOM removal in drinking water treatment plants, but also reduces the reactivity of DOM in forming disinfection byproducts (DBPs) (Amy et al., 1990; Weishaar et al., 2003).

Although beyond the scope of this current study, the effects of dissolved solids (i.e., calcium, magnesium, iron,

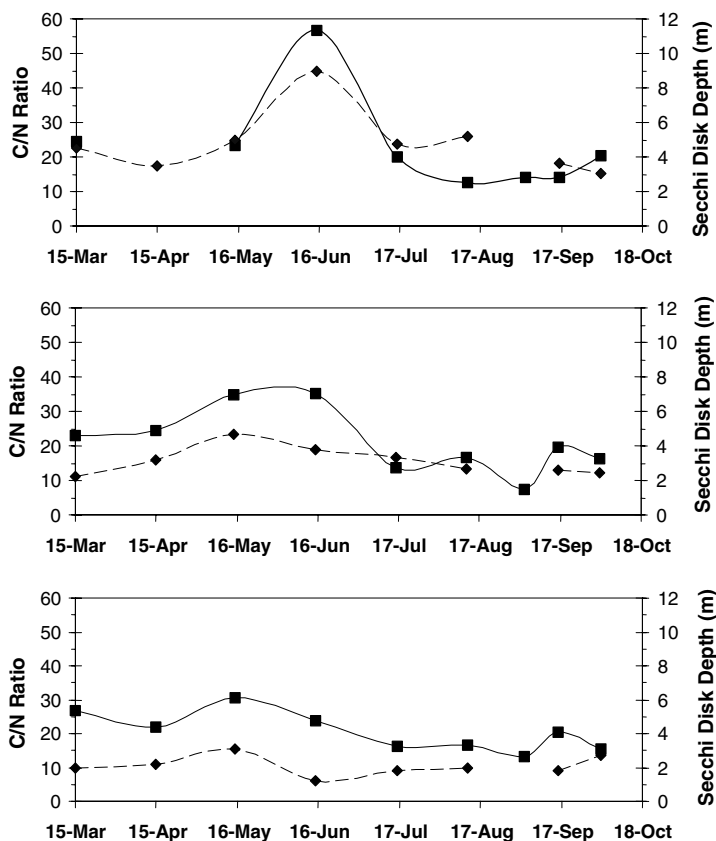


Fig. 8. Observed DOC/DON ratios (■) and Secchi disk depths (◆) measured between March and October 2002. Top, Lake Pleasant; middle, Bartlett Lake; bottom, Saguaro Lake.

aluminum) on DOM transformations in reservoirs may be as significant as microbial, algal or photolysis reactions (Stumm and Morgan, 1996). Geochemical processes, such as flocculation and sedimentation, could also be influential in these reservoirs because of the elevated salt concentrations observed in these reservoirs (563, 315 and 697 mg L⁻¹ total dissolved solids (TDS) below Lake Pleasant, Bartlett Lake and Saguaro Lake respectively) (Salt River Project, 1999). Many semi-arid regions of the world have elevated TDS waters, a factor also differentiating these surface waters from more temperate regions.

4. Conclusions

The goal of this research was to assess the importance of autochthonous and allochthonous sources in reservoirs found in arid climates where climatic conditions are less conducive for terrestrial runoff. Several lines of evidence suggest that a substantial fraction of the DOM in our study has a strong autochthonous component:

- Hydrophobic and transphilic acid fractions are low relative to the hydrophilic and neutral contributions.
- C/N ratios in both fractions are low.
- Aromatic contents are low.
- The observed C/N ratio and corresponding Ar–Al ratio for the hydrophobic acid fractions is similar to that of DOM from autochthonous water systems.
- Initially low SUVA values in Bartlett Lake increase during spring runoff, reflecting allochthonous inputs associated with snowmelt, then decline during summer, reflecting production of autochthonous DOM.
- The C/N ratio declines during the summer, as chlorophyll-A concentrations increase.

The autochthonous signature was strongest for DOM isolated from Saguaro Lake and Lake Pleasant, due to long total retention time for water in these reservoirs and in upstream reservoirs. The autochthonous signal is weaker (but still present) in Bartlett Reservoir, where shorter system-wide HRTs are observed. For all three reservoirs, low areal production rates of DOM in their watersheds and favorable conditions for algae production (an extended warm season and abundant sunlight) intensify the importance of autochthonous DOM production and the alteration and utilization of allochthonous organic material. Close scrutiny of the evidence shows that the DOM associated with these reservoirs represent autochthonous members within the autochthonous-allochthonous continuum for natural waters.

Acknowledgements

The authors acknowledge the City of Phoenix for their financial sponsorship of this research with

assistance from the Salt River Project and the Central Arizona Project for continued strategic and administrative support. Milton Sommerfeld contributed by leading parallel algae-studies along with the reported DOM work. Supporting research was provided by Mario Esparza, Kirsten Hintze, Tom Dempster, Mari Rodriguez, Michelle Cummings and Samanth Dawson. ¹³C NMR studies were performed at the ASU Nuclear Magnetic Facility (CHE-92-14799, CHE-9808678). The authors also acknowledge the valuable insight provided by the anonymous reviewers for this manuscript.

Associate Editor – E.A. Canuel

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