

Source Characterization of Disinfection Byproduct Precursors in Two Arkansas Water-Supply Reservoirs

Introduction

In the mid-1970s, a new water-quality problem was recognized. Johannes J. Rook of the Rotterdam (The Netherlands) Waterworks found that chlorine, commonly used to disinfect drinking water, reacted with natural organic compounds in the water to form volatile trihalomethane (THM) compounds. Other workers found that chlorination of water containing these natural organic compounds also yielded halogenated acetic acids (HAA), and the chlorination of resorcinol, or more technically, meta-dihydroxybenzene structures, yielded both THM and HAA (fig. 1). Together, THM and HAA compose part of a growing list of compounds recognized as disinfection byproducts (DBP). Potentially carcinogenic and toxic to digestive and urinary organs, THM and HAA in finished drinking water are recognized as a public health risk. The U.S. Environmental Protection Agency (USEPA) is currently reviewing health standards for THM and HAA in finished drinking water in an effort to reduce the exposure for people whose drinking water is chlorinated.

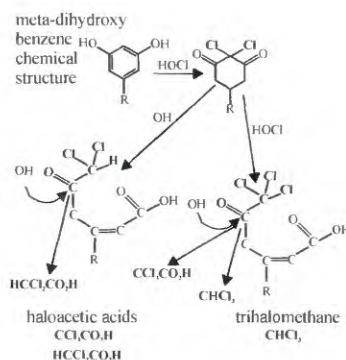
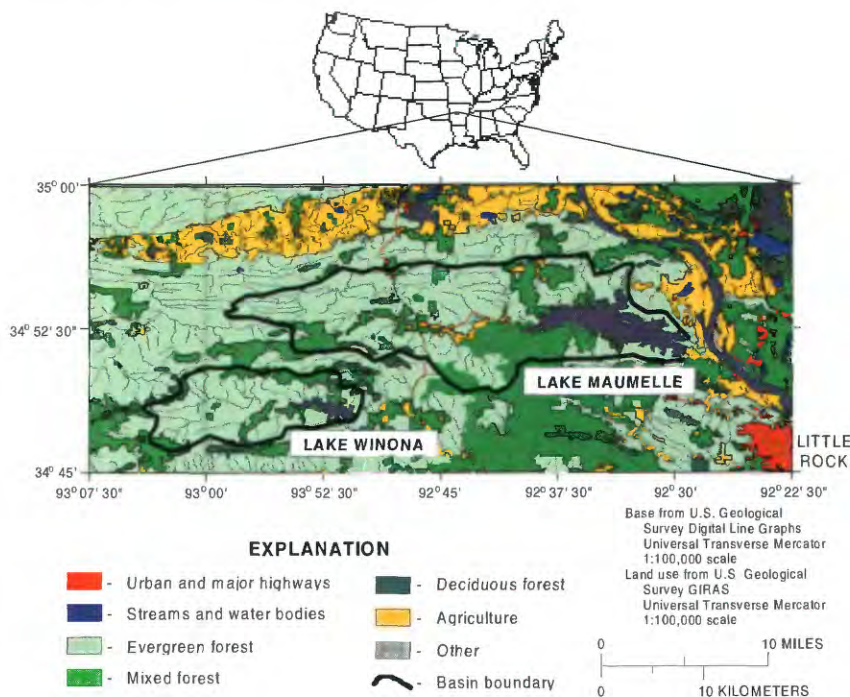


Figure 1. Hypochlorous acid (HOCl) attacks the carbon atom between the two hydroxyl groups (-OH) on the benzene ring to yield THM (CHCl₃-chloroform) and HAA (HCCl₂CO₂H--dichloroacetic acid, CCl₂CO₂H--trichloroacetic acid) during chlorination. Brominated THM and HAA form when bromide is in source water.

The natural organic compounds, known as dissolved organic carbon (DOC), result from the decay of plant

Figure 2. Location map and land uses surrounding Lakes Maumelle and Winona, two water-supply reservoirs operated by the Little Rock Municipal Water Works.



material. Plant material and its decay products can be brought into the stream or lake from the terrestrial environment or can be produced by plants in the water. DOC is operationally defined as the organic carbon remaining in the water sample after it has been filtered through a 0.45-micron filter. A variety of properties and chemical structures that characterize the DOC can be used to identify the original vegetative source. The ability to identify and characterize source and origin of DOC is extremely important to the study of DBP's and other water-quality problems.

Study of Lakes Maumelle and Winona

Concern over risks to public health and changing regulations prompted the Little Rock Municipal Water Works to work with the U.S. Geological Survey in an attempt to find the cause of THM and HAA production in water from two Arkansas water-supply reservoirs, Lakes Maumelle and Winona. The USEPA has

proposed a maximum contaminant level (MCL) of 60 micrograms per liter (µg/L) for HAA and a decrease in the MCL for THM (currently 100 µg/L) to 80 µg/L because of greater perceived health risk (U.S. Environmental Protection Agency, 1994). In general, water from Lake Winona has greater DOC concentrations, about 4 milligrams per liter (mg/L), than Lake Maumelle, about 3 mg/L. Water from Lake Winona yields more THM and HAA than Lake Maumelle following chlorination, often approaching the proposed MCL.

Lake Maumelle (completed in 1956) is 13.9 square miles (mi²) in size, located about 10 miles (mi) northwest of Little Rock, and is in the 137 mi² basin of the Maumelle River. Lake Winona (completed in 1938) is 1.9 mi² in size, located about 30 mi west of Little Rock, in the 44 mi² basin of the Alum Fork of the Saline River (fig. 2). Evergreen and mixed forests are the predominant land cover in both reservoir basins.

In September 1994, water samples were collected in Lakes Maumelle and Winona to determine the source of DOC and the chemical structures responsible for THM and HAA. Specific objectives of the investigation included: (1) determination of concentrations of aquatic humic substances (AHS), subcomponents of DOC; (2) identification of the source of the AHS in Lakes Maumelle and Winona; (3) identification of meta-dihydroxybenzene chemical structures in AHS; and (4) assessment of how much THM and HAA would be produced given the concentrations of AHS that occur in Lakes Maumelle and Winona. This Fact Sheet summarizes the results, which contribute to improved understanding of DBP's in our nation's water supplies. The evaluation is based on analyses of two 300-liter (L) samples of source water collected in September 1994 at the intake structures of Lakes Maumelle and Winona.

CHARACTERIZATION OF AHS

Aquatic humic substances are yellow colored, large molecular weight, organic acids. AHS are composed of humic and fulvic acids that account for nearly 50 percent of DOC in water (Thurman, 1985). Humic acids differ from fulvic acids because humic acids precipitate from acidic solutions (pH < 2.0), whereas fulvic acids remain soluble. Together, humic and fulvic acids commonly contain characteristics that can be traced back to the vegetative source.

Source characterization of disinfection byproduct precursors is the process of identifying the chemical structure and vegetative source of AHS. Common characterization techniques include: elemental analysis, titrations, $\delta^{13}\text{C}$ determination, and copper-oxide (CuO) oxidation.

Elemental analysis data give the percentages of carbon, hydrogen, oxygen, and nitrogen in AHS. Titration tests quantify the carboxylic acid and phenol groups in AHS (fig. 3) by adding base in measured increments. $\delta^{13}\text{C}$ determinations relate differences in the ratio of two carbon isotopes, ^{12}C and ^{13}C . Plants can either incorporate or exclude ^{13}C during photosynthesis. Plants like corn and warm season grasses incorporate and become isotopically enriched in ^{13}C , commonly

resulting in $\delta^{13}\text{C}$ values between -10 to -18 per mil (‰) (Lawlor, 1993). Plants like most trees, shrubs, and cool season grasses will exclude ^{13}C during photosynthesis and become isotopically depleted, resulting in $\delta^{13}\text{C}$ values between -22 to -34‰. CuO oxidation is a destructive chemical technique by which AHS are broken down to lignin degradation products. All terrestrial land plants contain lignin, and ratios of lignin degradation products can be used to identify the type of plant that was the source of AHS.

RESULTS OF ANALYSES

DOC and AHS. Smaller concentrations of DOC were found in water collected from Lake Maumelle (2.8 mg/L, as C) than Lake Winona (3.7 mg/L, as C) (table 1). In addition, AHS composed a smaller proportion of DOC in Lake Maumelle (45 percent) than in Lake Winona (51 percent). The humic acid concentration in Lake Winona was 3.2 times greater than that in Lake Maumelle, and the fulvic acid concentration was 1.4 times greater.

Table 1. Concentrations and values of DOC, AHS, and humic and fulvic acids in water from Lakes Maumelle and Winona

	Lake Maumelle	Lake Winona
DOC, in mg/L, as C	2.8	3.7
AHS, in mg/L, as C	1.26	1.89
Percent DOC as AHS	45	51
Humic acid, in mg/L, as C	0.085	0.27
Fulvic acid, in mg/L, as C	1.18	1.62

Elemental Analysis. AHS from Lakes Maumelle and Winona are characterized by low nitrogen (N) contents (table 2). Low N contents (< 1 percent) indicate that phytoplankton and other algae in the reservoir contribute very little DOC to the water in the reservoirs (Leenheer, 1994). Furthermore, low elemental N contents are found in AHS obtained by soaking terrestrial plants in water (Pomes, 1995).

Table 2. Elemental analysis of fulvic acids, as percent ash free

	Lake Maumelle	Lake Winona
Carbon	53.49	52.96
Hydrogen	5.78	5.21
Oxygen	40.01	41.20
Nitrogen	0.72	0.62

Titration. Humic acids from Lakes Maumelle and Winona generally had smaller carboxylic acid and greater phenol contents than fulvic acids (table 3). In general, the lower carboxylic acid content for humic acids causes them to precipitate under acidic conditions. The greater phenol content indicates that lignin from land plants is included in the AHS (Thurman, 1985). Generally, phenol concentrations > 0.5 microequivalents per milligram ($\mu\text{eq}/\text{mg}$) indicate that terrestrial plants are a source of AHS.

Table 3. Carboxylic acid and phenol groups

	Lake Maumelle	Lake Winona
AHS		
Carboxylic acid, in $\mu\text{eq}/\text{mg}$	5.0	5.0
Phenol, in $\mu\text{eq}/\text{mg}$	1.4	1.4
Humic acid		
Carboxylic acid, in $\mu\text{eq}/\text{mg}$	2.0	2.6
Phenol, in $\mu\text{eq}/\text{mg}$	2.3	2.9
Fulvic acid		
Carboxylic acid, in $\mu\text{eq}/\text{mg}$	5.2	5.2
Phenol, in $\mu\text{eq}/\text{mg}$	1.2	1.4

Fulvic acids and AHS from Lakes Maumelle and Winona had carboxylic acid contents of about 5.0 $\mu\text{eq}/\text{mg}$ (table 3). Such carboxylic acid contents indicate that terrestrial plants are a source of AHS. If phytoplankton and algae in the reservoirs were the major source, carboxylic acid contents generally would exceed 6.0 $\mu\text{eq}/\text{mg}$ (Thurman, 1985).

$\delta^{13}\text{C}$ Determinations. AHS from Lakes Maumelle and Winona yielded $\delta^{13}\text{C}$ values of about -27‰ (table 4). This is within the -22 to -34‰ range that is typical for most woody vegetation (Lawlor, 1993), and indicates AHS in

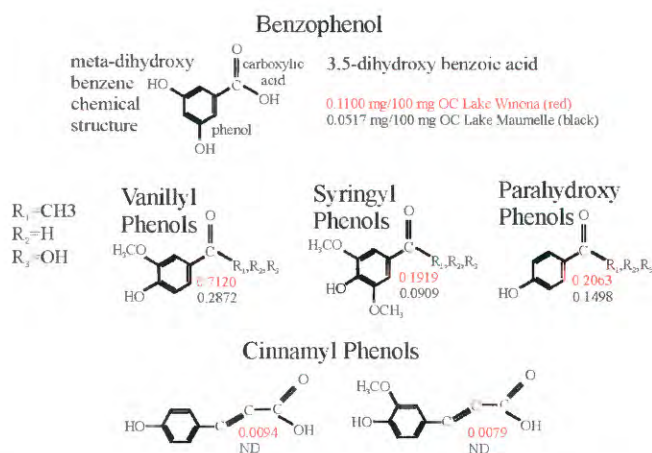


Figure 3. Benzophenol and lignin phenols generated from CuO oxidation of AHS from Lakes Maumelle and Winona. AHS from Lake Winona yielded 0.110 mg/100 mg OC of 3,5-dihydroxybenzoic acid which shows the meta-dihydroxybenzene chemical structure thought to be responsible for the production of THM and HAA during chlorination.

Lakes Maumelle and Winona originate from the forests that surround both reservoirs.

Table 4. $\delta^{13}\text{C}$ determination of AHS from Lakes Maumelle and Winona

	Lake Maumelle	Lake Winona
AHS	-27.16 ‰	--
Humic acid	--	-27.46 ‰
Fulvic acid	--	-27.34 ‰

CuO Oxidation. Reasonably high yields of degradation products known as benzophenols and lignin phenols (fig. 3) were obtained from the CuO oxidation of AHS from Lakes Maumelle and Winona. Ratios of lignin degradation products can be used to interpret the origin of the organic material (Ertel and others, 1984; 1993). Low cinnamyl/vanillyl (C/V) and para-hydroxy/vanillyl (P/V) ratios (table 5) indicate that wood is a major source of the AHS in Lakes Maumelle and Winona. Low syringyl/vanillyl (S/V) ratios of about 0.3 suggest that gymnosperms (pine trees) may be the principal source of lignin that occurs in the AHS.

Lake Winona AHS yielded greater quantities of the benzophenol, 3,5-dihydroxybenzoic acid (3,5-DHBA), which contains meta-dihydroxybenzene chemical structures capable of producing THM and HAA following chlorination. The concentration of 3,5-DHBA from Lake Winona (0.1100 mg/100 mg of organic carbon) was about twice as great as the

concentration from Lake Maumelle (0.0517 mg/100 mg of organic carbon). Also, water from Lake Winona contained about twice the amount of the lignin phenols (vanillyl, syringyl, parahydroxy, and cinnamyl) than water from Lake Maumelle. From these results, it would be expected that water from Lake Winona has the potential to form greater quantities of DBP's than water from Lake Maumelle.

Table 5. Lignin degradation product ratios from CuO oxidation of AHS from Lakes Maumelle and Winona

	Lake Maumelle	Lake Winona
Syringyl/vanillyl	0.32	0.27
Parahydroxy/vanillyl	0.52	0.29
Cinnamyl/vanillyl	Not detected	0.02

DBP Formation Potentials. DBP formation potentials predict the THM and HAA concentrations that could be attained in water during chlorination. DBP formation potential tests were conducted by inoculating solutions of Lakes Maumelle and Winona AAS, humic, and fulvic acid with chlorine. After incubation, THM and HAA concentrations were measured. Fulvic acids, accounted for most of the predicted formation potentials for THM and HAA (table 6).

Table 6. Predicted THM and HAA formation potential of AHS from Lakes Maumelle and Winona [$\mu\text{g/L}$, micrograms per liter]

	Lake Maumelle	Lake Winona
AHS		
Predicted THM formation potential, in $\mu\text{g/L}$	77.9	147
Predicted HAA formation potential, in $\mu\text{g/L}$	21	55.1
Humic acid		
Predicted THM formation potential, in $\mu\text{g/L}$	2.33	15.8
Predicted HAA formation potential, in $\mu\text{g/L}$	0.70	2.6
Fulvic acid		
Predicted THM formation potential, in $\mu\text{g/L}$	75.8	126
Predicted HAA formation potential, in $\mu\text{g/L}$	23.6	42.0

In a comparison between the two reservoirs, AHS from Lake Winona yielded greater predicted formation potentials for THM and HAA than AHS from Lake Maumelle. Lake Winona AHS and fulvic acids yielded predicted formation potentials for THM that exceeded the 100 $\mu\text{g/L}$ MCL established by the USEPA (U.S. Environmental Protection Agency, 1994). HAA formation potential for Winona AHS and fulvic acids approached the proposed MCL of 60 $\mu\text{g/L}$.

AHS and fulvic acids from Lake Winona yielded greater predicted THM and HAA formation potentials because of the greater abundance of chemical structures that yield THM and HAA during chlorination. As mentioned above, greater quantities of 3,5-dihydroxybenzoic acid, itself a meta-dihydroxybenzene chemical structure, were found during CuO oxidation of AHS from Lake Winona than Lake Maumelle (fig. 3). Thus, results from Lake Maumelle and Winona show that increased quantities of meta-dihydroxybenzene structures in AHS correspond with greater THM and HAA formation potentials during chlorination.

Conclusions

AHS composed 45 percent of the DOC (2.8 mg/L) in water collected from Lake Maumelle and 51 percent of the DOC (3.7 mg/L) in water collected from Lake Winona. Results suggestive of ter-

restrial plants as the source of AHS in Lakes Maumelle and Winona include: elemental N contents < 1 percent, phenol content > 0.5 µeq/mg, and $\delta^{13}\text{C}$ values of about -27‰ . Low ratios of syringyl to vanillyl phenols indicate that pine trees may be the predominant source of the lignin in the AHS.

Lignin degradation products with meta-dihydroxybenzene chemical structures (3,5-dihydroxybenzoic acid) were found during the CuO oxidation of AHS from Lakes Maumelle and Winona. AHS from Lake Winona yielded greater quantities of 3,5-dihydroxybenzoic acid during CuO oxidation and yielded greater formation potentials for THM and HAA. Thus, the positive association between 3,5-dihydroxybenzoic acid and increased THM and HAA formation potential reflects a relation between a lignin degradation product and DBP production.

Implications and Future Work

CuO oxidation was performed on AHS derived from different vegetation sources (Pomes, 1995), and the 3,5-dihydroxybenzoic acid content of Lake Winona AHS was similar to that of samples derived from deciduous leaves, twigs, and prairie grass (table 7). Various source materials produce different $\delta^{13}\text{C}$ results (table 7), and the presence of 3,5-dihydroxybenzoic acid in AHS may not be dependent on specific vegetative type. Prairie grass $\delta^{13}\text{C}$, at -15‰ , is characteristic of warm season grasses, whereas deciduous leaf litter, twigs, and Lake Winona AHS have $\delta^{13}\text{C}$ values indicative of woody vegetation (-22 to -34‰), and both contain 3,5-dihydroxybenzoic acid. Thus, DBP production from reservoirs receiving AHS from a variety of terrestrial plant sources is to be expected because most plants (deciduous trees, pine trees, and grass) contain lignin with meta-dihydroxybenzene chemical structures.

Despite sharing pine tree sources for AHS, Lakes Maumelle and Winona differ in two important respects. Greater DOC and AHS concentrations occurred in Lake Winona and AHS from Lake Winona yielded greater quantities of 3,5-dihydroxybenzoic acid during CuO oxidation. Basin characteristics like size and topography, channel slope and sinuosity need to

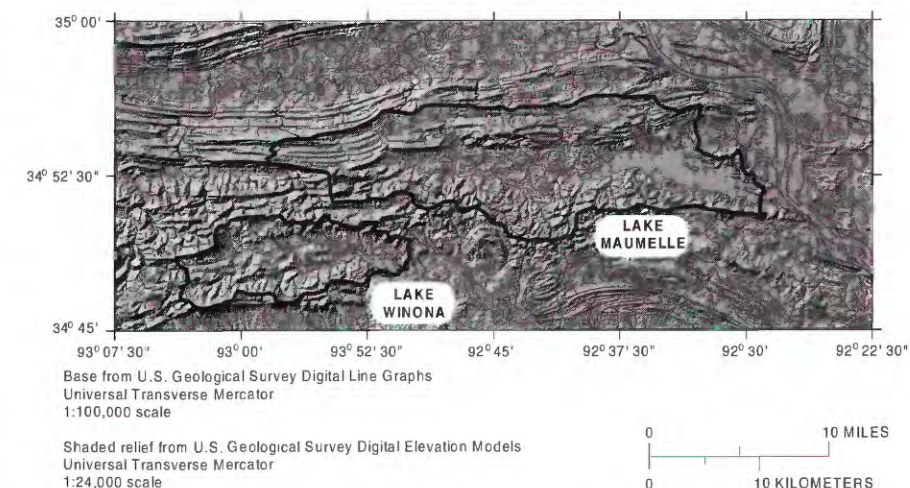


Figure 4. Shaded relief map showing topography surrounding Lakes Maumelle and Winona.

be considered. Lake Winona's smaller basin size and steeper topography (fig. 4) may allow greater mass loading of particulate organic matter relative to reservoir volume than Lake Maumelle. The lower slope and more sinuous channel characteristics in the basin of Lake Maumelle, may allow the capture of organic matter prior to reservoir entry. Also, water residence time in Lake Winona (0.71 years) is much shorter than Lake Maumelle (1.78 years) allowing less time for microbial degradation.

Table 7. Yields of 3,5-dihydroxybenzoic acid from AHS derived from different vegetation sources (from Pomes, 1995) [DHBA, dihydroxybenzoic acid; PDB, Peedee Belemnite standard for carbonate]

Vegetation source	3,5-DHBA yield, in mg/100 mg OC	$\delta^{13}\text{C}$ relative to PDB
Deciduous leaf litter	0.490	-28‰
Twigs	0.288	-27‰
Prairie grass	0.194	-15‰

Further investigation at these and other reservoirs could be used to assess the relation between topography, basin size, channel slope and sinuosity, water residence time, and DBP-producing chemical structures in AHS. Additionally, more work could determine if AHS with DBP-producing chemical structures vary seasonally. Particularly, autumn leaf fall could increase the amount of DOC- and AHS-containing DBP-producing structures in reservoirs, ultimately leading to

greater concentrations of THM and HAA in water after chlorination.

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