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Allochthonous Contributions of THM Precursors to a Eutrophic Reservoir[1]

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ABSTRACT

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Temporal patterns in trihalomethane (THM) precursor concentrations (measured as THM formation potential, THMFP) and loads are documented for West Branch Delaware River (WBDR), the primary tributary for Cannonsville Reservoir, NY, and a secondary tributary, for a 12-month period. The analysis was supported by routine and runoff event-based (11 events) sampling at the mouth of WBDR, and 3 synoptic surveys along its length. Ninety-eight percent of the precursors from WBDR formed chloroform, and 94% were in a dissolved form (DTHMFP). Temporal variations on a seasonal scale, as well as during runoff events, are reported. The range in DTHMFP was 151 to 325 $\mu g \cdot L^{-1}$. Increases in precursor concentration observed (from 140 to 240 $\mu g \cdot L^{-1}$) moving from upstream toward the mouth of WBDR may reflect anthropogenic contributions. A time series of daily loads of DTHMFP from WBDR to the reservoir is presented for the April-December interval of 1995. The volume-weighted concentration for this period was 228 $\mu g \cdot L^{-1}$. Dissolved organic carbon had only limited value as a surrogate measure of THM precursor concentration.

Key Words: THM precursors, allochthonous sources, load, runoff event, organic carbon.

Organic carbon plays an important role in the geochemical and ecological processes of aquatic systems (Aiken and Cotsaris 1995, Thurman 1985). Natural organic matter (NOM) has become increasingly important for water supplies because it has been associated with the formation of certain disinfectant by-products during drinking water treatment, which represents a health risk. Trihalomethanes (THMs) are among this group of compounds; their formation is of concern since they are considered carcinogenic (Krasner et al. 1994). Chloroform is usually the most abundant THM, but brominated species tend to increase in regions which have high ambient concentrations of bromide (Owen et al. 1995). The U.S. Environmental Protection Agency (USEPA) will soon promulgate a Disinfectant/Disinfection By-Products (DDBP) Rule, under the Safe Drinking Water Act, which will specify more restrictive standards for THMs. Stage 1 is scheduled for promulgation in December 1996; it will reduce the current standard of 0.1 $mg \cdot L^{-1}$ to 0.08 $mg \cdot L^{-1}$. Stage 2,

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expected to be promulgated in the year 2002, will reduce the standard further to 0.04 mg · L^{-1}. THM analyses are routinely performed after disinfection in many water supplies. Additionally, a standardized procedure has been developed (APHA 1992) to quantify the potential of source waters to form THMs, described as THM formation potential. This analysis serves managers in assessing the potential of the NOM pool for THM formation prior to water treatment. Various organic molecules common in the NOM of surface waters act as precursor material which forms THMs during chlorination (Rook 1976). Aquatic humic substances (humic and fulvic acids) make up about 50% of NOM (Thurman 1985), and have been reported to be potent precursors (Rook 1976). Recent studies (Owen et al. 1995), however, have found non-humic substances also can be important contributors to the THM precursor pool. Organic matter from municipal wastewater treatment facilities can also be a source of THM precursors (Randtke et al. 1987).

Organic carbon in lakes and reservoirs originates from two sources: the watershed, where allochthonous material is leached from soils or decaying vegetation, and from within the reservoir itself as a result of autochthonous production of algae, macrophytes, and bacteria (Wetzel 1983). Most of the stream contributions (80-90%) to a lacustrine organic carbon pool are in the dissolved form (Wetzel 1992). Wetzel (1992) reports that a selective removal of organic compounds by activities such as microbial decay and adsorption occurs as they move downstream from upland to lacustrine regions. This tends to shift the composition of dissolved organic carbon (DOC) to more refractory forms as water flows to the mouths of streams and rivers (Wetzel 1992). The magnitude and composition of allochthonous contributions of NOM from soils and plants depend on such factors as soil layer depth, soil type, and state of decomposition (Aiken and Cotsaros 1995). Differences in THM precursor production among leaf litter types have been observed (Martin 1995). The magnitude and composition of NOM are also influenced by hydrologic factors (e.g., flow, antecedent conditions) within the watershed (Aiken and Cotsaris 1995). It is generally observed that DOC concentrations are relatively low during baseflow conditions, and increase during the rising stage of a runoff event (Thurman 1985). Increases of more than a factor of two are not unusual during such events. Similarly, Smith et al. (1997) found substantial increases in gelbstoff [g_{440}, an index of the color imparted to the dissolved phase by humic substances (Davies-Colley and Vant 1987)] over a range of flows. Mulholland (1992) has attributed increases in DOC to canopy washout and leaching of organic soil horizons and stream channel debris, while Smith et al. (1997) have suggested soil water displacement as the cause of increased dissolved color during high runoff periods. Thurman (1985) describes the changes in DOC (and particulate organic carbon, POC) concentration in a stream as characterized by two distinct seasons, wet and dry. The inclusion of a wide range of flow conditions in related sampling programs is considered important in evaluating the distribution and loading of NOM (Aiken and Cotsaris 1995, Cooke and Carlson 1989, Jacangelo et al. 1995). Given the nature of the sources of organic carbon and the biogeochemical influences on these sources, stream THM precursor concentrations should be expected to vary temporally as well as spatially along its length.

The identification, characterization, and quantification of watershed sources of THM precursors have received only limited research attention. For example, Veenstra and Schnoor (1980) observed that increased precursor concentrations were associated with fall wet periods and spring snowmelt from sampling of the Iowa River for a 1-year period. Similarly, Palmstrom et al. (1988) observed fall and winter peaks of precursors near the upstream boundary of an Ohio reservoir during periods of rainfall. Veenstra and Schnoor (1980) observed a distinct seasonality in THM precursors, where concentrations in the Iowa River were lowest during the winter and reached maximum levels during the summer. Seasonal changes in TOC concentrations, however, remained small, suggesting a dependence of precursor production on the nature, rather than simply the quantity, of NOM. Jacangelo et al. (1995) reported only modest variations in inter-annual mean precursor concentrations (CV = 12%, n = 14) for the Ohio River. However, large variations were observed within years, in the absence of recurring seasonal trends (Jacangelo et al. 1995). Based on a single synoptic survey (34 sites), Randtke et al. (1987) identified both point and nonpoint discharges as THM precursor sources. They reported that agricultural runoff, particularly from cattle feedlots, produced higher concentrations than those found for urban runoff. The importance of agricultural activities as sources of THM precursors has also been reported by others (Amy et al. 1990, Morris and Johnson 1976).

Resolution of the relative contributions of allochthonous and autochthonous sources to the THM precursor pool of water supply lakes and reservoirs is fundamental to the development of effective system-specific management strategies for this water quality issue. Currently there are no reliable chemical methods to distinguish the allochthonous versus the autochthonous components of the precursor pool of these water supplies. Thus, it is essential to accurately quantify external loading of precursors if the contributions of allochthonous versus autochthonous sources are to be

resolved. Allochthonous loads of DOC have been estimated as part of the development of organic carbon budgets for lakes (Wetzel 1983), and to support the testing of related mechanistic models (Bowie et al. 1985, Canale et al. 1997, Thomann and Mueller 1987). However, the coupling between stream NOM (e.g., DOC) and THM precursor concentrations in streams and rivers remains uncertain (e.g., Jacangelo et al. 1995, Veenstra and Schnoor 1980). Loads for precursors, based on stream precursor concentrations, have only rarely been estimated (e.g., Palmstrom et al. 1988, Veenstra and Schnoor 1980). Neither of these efforts were supported by runoff event-based sampling, that has been found necessary to develop accurate loads for many other constituents. (e.g., Canale et al. 1993, Effler and Whitehead 1996, Heidtke and Auer 1992, Longabucco and Rafferty 1998). Differences observed in the patterns of NOM based on flow regime (Aiken and Cotsaris 1995, Thurman 1985, Wetzel 1992) support the need to elucidate patterns for THM precursors over a wide range of runoff conditions.

This study investigates several features of the allochthonous contributions of THM precursors to Cannonsville Reservoir, NY, including: (1) documentation of the temporal patterns of precursor concentration, and selected potential surrogate measures in the two largest tributaries; (2) evaluation of the relationship between precursor concentration and flow; (3) evaluation of the efficacy of the selected surrogate parameters as estimators of precursor concentrations and loads; and (4) determination of external precursor loads to the reservoir. This paper, and the parallel study of the distributions of precursors in this reservoir (Stepczuk et al. 1998a), are fundamental building blocks supporting the development and application of mass-balance modeling techniques to resolve the contributions of allochthonous and autochthonous sources to the reservoir's precursor pool, and the simulation of features of the precursor behavior within this reservoir (Stepczuk et al. 1998b).

Site Description

Cannonsville Reservoir, NY, (1160-km² watershed) is a Y-shaped eutrophic (Effler and Bader 1998) impoundment (Fig. 1), operated by New York City as a water supply, and to augment downstream flows. The West Branch Delaware River (WBDR) sub-basin comprises 916 km², or 79% of the total. The upstream boundary of the principal (WBDR) arm of the reservoir is at Beerston (Fig. 1, site 1). Discharge in the WBDR is monitored continuously at Walton, NY (site 3, 8 km upstream of Beerston,) by the U.S. Geologic Survey (USGS). The drainage basins of ten smaller streams make up the remaining watershed, with Trout Creek draining the largest area (55 km², 5% of the total).

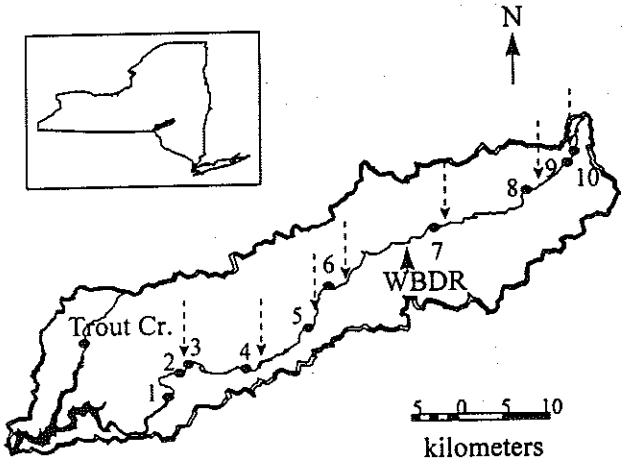

Figure 1.–Cannonsville Reservoir watershed, with two routine monitoring sites [WBDR (1), and Trout Creek]. The 10 synoptic survey sites, including site (1) for WBDR, are also shown. Dashed lines indicate point source locations (see Fig. 3a for point source identification).

The reservoir's watershed, located in the northwestern Catskill section of the Appalachian plateau, has a variable topography, ranging in elevation from 350 m above sea level at the dam, to 1010 m, with an average slope of 20%. The underlying bedrock is comprised of consolidated sandstone, siltstone and shales covered by surficial deposits of glacial till and stratified drift composed of gravel, sand, silt, and clay. Soil infiltration rates are slow in the upland areas, while the soils along the stream corridors possess superior drainage capability, and are associated with prime farmland within the watershed (Brown et al. 1983).

The vegetative cover for the watershed is approximately 70% forest (NYCDEP 1995), while approximately 24% and 3% of the vegetative cover is classified as grass (pasture and hay) and corn/alfalfa, respectively. Wetlands comprise <1% of the total drainage basin. Agriculture is most prevalent along the watershed's stream corridors, while the urban areas are localized primarily along WBDR, with five municipal wastewater treatment plants (WWTPs), a spray irrigation treatment operation for dairy waste dispersal, a dairy manufacturing plant, a landfill, and a meat processing facility along the main stem. The largest point source input is the effluent from the Walton WWTP (more than triple the discharge of all the other treatment plants combined; mean daily discharge <1% of the mean daily WBDR flow), located approximately 7 km upstream on the WBDR (between sites 2 and 3) from the inflow to the reservoir.

Methods

Laboratory Analyses

An operationally defined procedure has been established to measure THM precursors (APHA 1992). THM precursors from all types of organic carbon are measured under controlled laboratory conditions and reported as THM formation potential (THMFP). Samples for THMFP analyses were collected in 250-ml glass bottles according to Method 5710B (APHA 1992), kept in the dark on ice, and shipped for analysis within 7 days of collection (Hoehn et al. 1994). Each batch of field samples contained a distilled water blank and a field duplicate. Subsamples from each sample were filtered, using Gelman 0.45-μm-membrane filters. The filtrate has been operationally defined here as the dissolved fraction of THMFP (DTHMFP). Chlorine demand and dose for filtered and unfiltered samples were determined according to Standard Methods (APHA 1992). Free chlorine residual was determined according to Method 4500-Cl B, (APHA 1992). All of the samples were buffered at pH 7.0, chlorinated with an excess of free chlorine, and stored at 25°C for 7 days to allow for the reaction to approach completion (APHA 1992). After the 7-day reaction period, the samples were quenched with sodium thiosulfate; those with a chlorine residual of less than 1 gm · m^{-3} were discarded. Reagent blanks and field blanks were included in each batch of samples for quality control. Triplicate analyses, and subsequent precision analysis on the triplicates, were performed on all samples for THMFP analyses. The average coefficient of variation (CV) for the triplicate analyses was ~ 2.5%; for field duplicates it was ~ 4%. The average accuracy was within 5% to 10%, based on results from laboratory standards, spikes, and external audit samples.

The THM analytical method (Liquid-Liquid Extraction Gas Chromatographic Method) used is described in section 6232 B of Standard Methods (APHA 1992). The results for the individual THMs (bromoform, bromodichloromethane, dibromochloromethane, and chloroform) were reported for total and dissolved forms. Total THMFP (TTHMFP) and DTHMFP were obtained by summation of the four precursor species; particulate THMFP (PTHMFP) was calculated as the difference.

Organic carbon (DOC and POC) was measured with a Carlo Erba Model EA1108 Elemental Analyzer. Gelbstoff was measured according to the method of Davies-Colley and Vant (1987). The method of Parsons et al. (1984) was used to measure total chlorophyll. Associations between THMFP and other variables were characterized by Pearson product-moment correlation and least squares linear regression analysis.

Monitoring Program and Calculation of Loads

Fifty samples were collected for THMFP and the other selected analytes close to the mouth of the two major inflows, WBDR and Trout Creek (Fig. 1), from April through December 1995, during low flow and minor runoff periods. An additional 85 THMFP samples were collected at the WBDR site during 11 different runoff events over the October 1995-May 1996 interval, as part of a longer term (1991 to date) runoff event-oriented monitoring program aimed at determining loads for a number of constituents for this tributary (Longabucco and Rafferty 1998). Event sampling commenced before a substantial rise in the hydrograph occurred. Samples were collected based on changes in stage, as measured by the USGS gauge in Walton, with the aim of adequately characterizing changes in water chemistry over the entire rise, peak, and fall of the hydrograph. A subset of the samples was selected for analysis of THMFP and DOC. Further details of the event-based monitoring protocols are described elsewhere in this issue (Longabucco and Rafferty 1998).

Daily loads of THMFP and DOC (evaluated as a surrogate measure of precursor concentration) were calculated for WBDR for the April-December interval of 1995, as described for other parameters by Longabucco and Rafferty (1998). Daily loads during events were calculated as the summation of the hourly loads (see Longabucco and Rafferty 1998). Concentrations (hourly) between sampling times were estimated by linear interpolation. During non-event periods, average daily loads were determined for WBDR by the product of the mean daily flow and the concentration from the most recently collected sample. Daily flow-weighted concentrations were calculated for events for comparison with non-event periods.

Three synoptic surveys were conducted along WBDR (two in fall 1995, and one in spring 1996) to explore possible origins of precursors within the watershed. Ten sites (Fig. 1), extending from the headwaters to the mouth, were selected with consideration for proximity to point sources. Sampling was completed within 2 hours for all of the surveys. The first survey was conducted during low flow conditions (October 4). The second survey captured high flow conditions during the largest fall (October 21) storm, and the third survey represented spring runoff (April 30) conditions. Analytes measured on the survey samples included TTHMFP, DTHMFP, DOC, and g_{440}.

Results and Discussion

Temporal Patterns in Precursors and Surrogate Measures

There were no substantial runoff events in the watershed over the mid-April to mid-October interval of 1995. Flows in WBDR (Fig. 2a) and Trout Creek (highly correlated to WBDR; Owens et al. 1998) remained relatively low throughout that interval. Runoff events were common over the fall 1995 to spring 1996 period; the 11 runoff events captured in the THMFP monitoring program are identified in the hydrographs (Fig. 2a; see inset).

The vast majority of the tributary THMFP formed chloroform, and occurred in the dissolved form. For example, the dissolved and chloroform percentages were 94 (Fig. 2b) and 98, respectively, in WBDR, and 90 (Fig. 2b) and 95 for Trout Creek. The predominance of DTHMFP has been reported by others (Oliver and Lawrence 1979, Palmstrom et al. 1988) and essentially matches the findings reported for the water column of Cannonsville Reservoir over the same period (Stepczuk et al. 1998a). The gross temporal patterns for DTHMFP in Trout Creek and WBDR (flow-weighted fall runoff event concentrations are included for WBDR, Fig. 2b) could be interpreted as reflecting seasonality, e.g., concentrations were slightly lower in the winter and spring months. The extent to which these patterns are recurring can only be assessed through a program of multiple-year monitoring. The ranges of the precursor concentrations in these two tributaries (Table 1) were narrow by comparison with the limited observations reported for other systems (Jacangelo et al. 1995, Palmstrom et al. 1988, Veenstra and Schnoor 1980).

The DTHMFP concentrations of the WBDR were about twice those measured for Trout Creek (Fig. 2b, Table 1). However, the concentrations of DOC for these tributaries were quite similar (Fig. 2c, Table 1). Precursor yield, the quotient of precursor and organic carbon concentration, has been used (Amy et al. 1990, Hoehn et al. 1980, Rook 1976) to represent the potency of NOM as a source for THM precursors. The yield concept has recently been adopted in a mechanistic model for THM precursors (Canale et al. 1998). It is expressed here as the quotient of DTHMFP and DOC. A greater potency of the organic carbon pool of WBDR for precursor formation, compared to Trout Creek, is indicated by the generally higher yield values in WBDR (Fig. 2d, Table 1). The yield values reported for these tributaries are both substantially higher (Table 1) than the value adopted by Canale et al. (1997; 25 $\mu g \cdot mg^{-1}$) for Lake Youngs, WA, and its primary tributary. Unlike the observations for THMFP, a conspicuous increase in DOC concentrations in WBDR (Fig. 2c) occurred during the fall runoff events (Fig. 2a) that resulted in a substantial decrease in yield (Fig.2d) during that

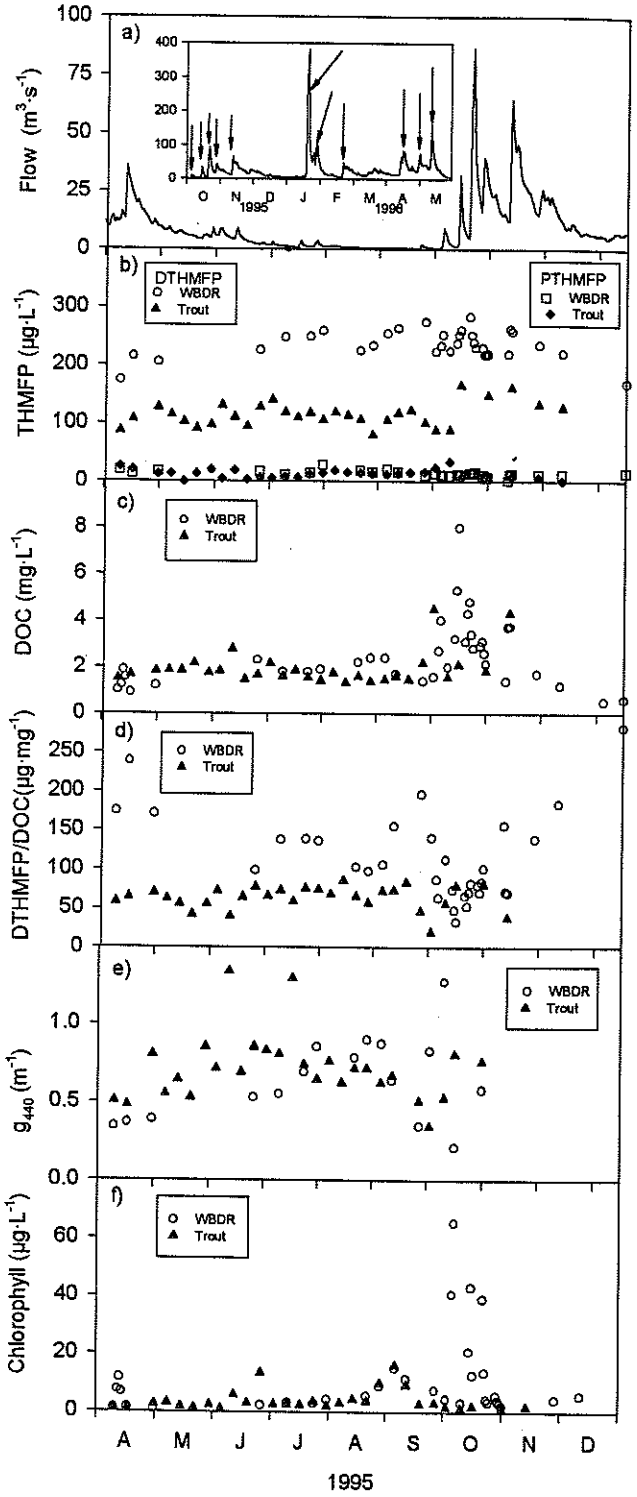

Figure 2.–Time series of data for WBDR and Trout Creek for the April-December interval of 1995: a) discharge for WBDR at Beerston (inset identifies eleven runoff events for the fall 1995-spring 1996 interval), b) DTHMFP and PTHMFP, c) DOC, d) DTHMFP/DOC (yield), e) g_{440}, and f) chlorophyll.

Table 1.–Comparison of selected variables for Trout Creek and WBDR from the routine monitoring program* April-December 1995.

Variables	Units	Trout Cr.			WBDR		
		Avg.	Range	N	Avg.	Range	N
DTHMFP	$\mu g \cdot L^{-1}$	114	79-165	31	235	174-275	19
PTHMFP	$\mu g \cdot L^{-1}$	13	0-34	31	15	7-28	19
DOC	$mg \cdot L^{-1}$	1.9	1.0-4.5	29	2.0	0.9-4.4	19
POC	$mg \cdot L^{-1}$	0.5	0.1-1.2	24	0.8	0.2-3.7	19
Yield**	$\mu g \cdot mg^{-1}$	60	20-86	29	119	48-239	19
g_{440}	m^{-1}	0.7	0.4-1.3	27	0.6	0.2-1.3	16

* Monitoring that was part of the routine program, and not specifically associated with high runoff periods.
**μg DTHMFP / mg DOC.

period. Detailed treatment of the dynamics of precursor and DOC concentrations for individual runoff events are presented subsequently. The dynamics of DTHMFP and DOC concentrations were uncorrelated for both tributaries.

Rather strong temporal changes in g_{440} were observed in both tributaries (Fig. 2e). Differences between the two tributaries for g_{440} were modest (no runoff event data available, see Fig. 2e), and no seasonal correlations were found between g_{440} and DTHMFP (or DOC), indicating that g_{440} is not a viable surrogate measure of precursors for those tributaries. This is perhaps surprising in that g_{440} is attributed to dissolved humic substances (Davies-Colley and Vant 1987). Precursor and color potencies of the various components of this group of substances apparently differ greatly. Autochthonous production of precursors has been linked to phytoplankton activity (e.g., Hoehn et al. 1980, 1984; Stepczuk et al. 1998a). However, there is no clear indication that this was a significant source of precursors in WBDR, as no noteworthy increases in DTHMFP (Fig. 2b) occurred during peaks of chlorophyll concentration in the WBDR observed in late September and early October (Fig. 2f).

Longitudinal (Synoptic) Surveys

Concentrations of THM precursors generally increased from the headwaters to the mouth of WBDR in the synoptic surveys (Fig. 3a), with the largest increase observed during the fall (October 21) high flow survey. The highest concentration at the mouth was also observed for that survey (Table 2), while the lowest concentration was observed during the spring (April 30) survey (Table 2). The two fall surveys showed similar patterns along the length of the river (Fig. 3a). DOC patterns were quite variable for the three surveys (Fig. 3b), with the greatest longitudinal variability found for the fall high flow survey. The higher DOC concentrations for the fall high flow survey (Fig. 3b, Table 2) were not coupled to similar increases in DTHMFP (Fig. 3a), thus the yields (Fig. 3c) were correspondingly lower, indicating a reduced potency of the NOM as a source for precursors. DOC and g_{440} (Fig. 3b and d) were well correlated ($r = 0.92$, $n = 30$) spatially for all three surveys, but not with DTHMFP. The uncoupling of THM precursor concentrations from these parameters was most pronounced in the fall surveys. The general reduction in DOC with stream length observed in fall (Fig. 3b) is somewhat atypical for lotic systems (e.g., Leff and Meyer 1991, Vannote et al. 1980, Wetzel 1992). The increase in THM precursor concentrations (Fig. 3a), and therefore yield (Fig.3c), with the approach to the reservoir indicate an increase in potency of DOC (e.g., by a shift in composition) as a THM precursor source.

The relative role of point versus nonpoint sources in this spatial structure cannot be resolved from these data. Some of the inflections are consistent with inputs from the point sources, but no conspicuous impact of the Walton WWTP was observed in the three surveys (Fig. 3a). Land use data for WBDR do not indicate any significant regionalization of land use types along WBDR. The largest incremental increase in drainage area was associated with the stream reach between sites 8 and 6 (Fig. 1), and included 47% of the watershed (Fig. 3e). No recurring spatial pattern in precursor concentration (Fig. 3a) or yield (Fig. 3c) emerged for this reach from these surveys. The fall leaf-off, which has been documented as a THM precursor source (Martin 1995), may explain the elevated THMFP (and DOC) observed during the fall high flow survey (Table 2).

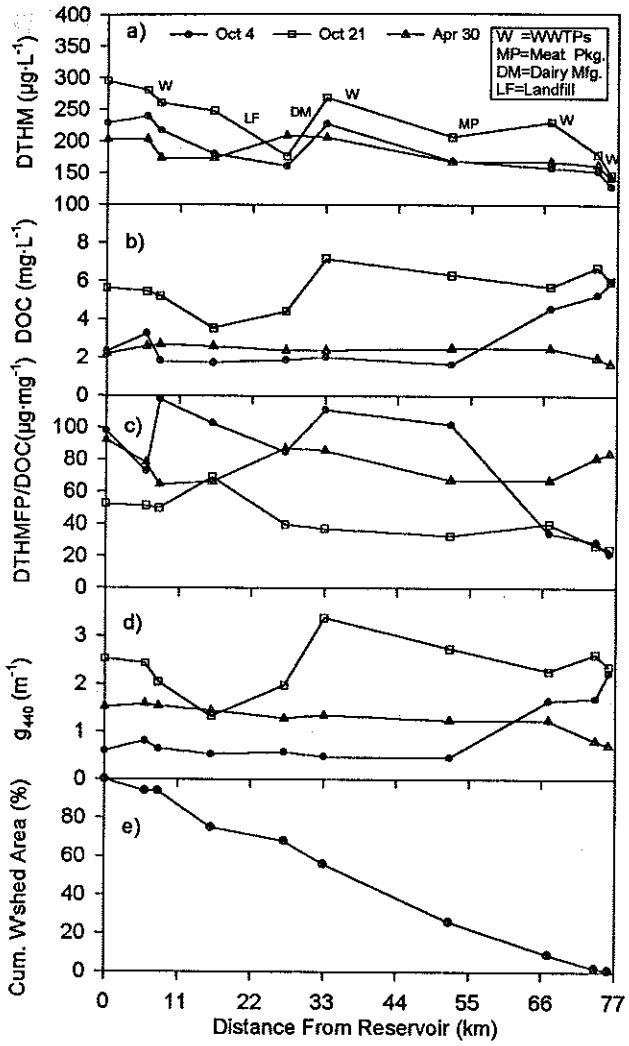

Figure 3.–Profiles for WBDR for three synoptic surveys: a) DTHMFP, b) DOC, c) yield, d) g_{440}, and e) cumulative watershed area. Point source identification/locations are included (Figure 3a).

Runoff Events

The behavior of DTHMFP and DOC during runoff events is characterized and contrasted for the 11 monitored runoff events through selected summary statistics (Table 3, all events) and presentation of paired hydrographs and concentration time series for 3 of the events (Figs. 4-6). A wide range of hydrologic cases was captured, as depicted by the percentiles for both peak flow and total volume (Table 3); these events bracket the total population of 61 events monitored on WBDR since the fall of 1991 (see Longabucco and Rafferty 1998). The first two storms did not cause much of a perturbation with respect to DTHMFP concentrations, despite substantial changes in DOC (Table 3). The third storm, which was the largest of the fall events, produced a larger response in DTHMFP and DOC concentrations (Table 3, Fig. 4). The concentration of DOC increased (Fig. 4b) over the period of the rising limb of the hydrograph (Fig. 4a) and then decreased more slowly as flow decreased. The relative increase in precursor concentration was smaller, and the concentration returned to pre-event conditions more rapidly (Fig. 4b). This storm coincided with fall leaf-off, and produced the highest THM precursor concentrations of all the runoff events (Table 3). This probably reflects a partial flushing of the leaf-off NOM from the watershed. The next major runoff event occurred in mid-January 1996 (Table 3, Fig. 5), after a 1-month period of cold air temperatures (e.g., mostly < 0°C) and snow cover throughout the watershed. This was a record high flow event (~100 year flood, Fig. 5a). Relatively wide variations in DTHMFP and DOC concentrations were observed (Table 3), but DOC was again much more responsive to the dynamics of runoff

Table 2.–Selected data for three synoptic surveys of WBDR. Conditions at the mouth (0-km station at Beerston) and over the stream length are presented.

Date	10/4/95	10/21/95	4/30/96
Mean Daily Flow ($m^3 \cdot s^{-1}$)	1	57	55
DTHMFP ($\mu g \cdot L^{-1}$)			
@Beerston *	229	295	203
Stream Average	186	229	181
Range	129-239	148-295	142-209
DOC ($mg \cdot L^{-1}$)			
@Beerston *	2.3	5.6	2.2
Stream Average	3.1	5.6	2.4
Range	1.8-5.9	3.6-7.2	1.7-2.7
g_{440} (m^{-1})			
@Beerston *	0.6	2.5	1.5
Stream Average	1.0	2.4	1.3
Range	0.5-2.2	1.3-3.4	0.7-1.6

* Mouth of WBDR.

Table 3. Selected hydrologic and water quality data for eleven runoff events for WBDR, October 1995-April 1996.

Runoff Events (1995-1996) Date	Starting Flow* ($m^3 \cdot s^{-1}$)	Peak Flow ($m^3 \cdot s^{-1}$)	%-ile** Peak Flow %	%-ile** Volume %	DTHMFP Flow-wtd. Conc. ($\mu g \cdot L^{-1}$)	DTHMFP Range ($\mu g \cdot L^{-1}$)	DOC Flow-wtd. Conc. ($mg \cdot L^{-1}$)	DOC Range ($mg \cdot L^{-1}$)	Flow-wtd. Avg. Yield ($\mu g \cdot mg^{-1}$ C)‡
10/5	1	11	0	0	243	231-268	3.6	2.0-4.3	68
10/14	2	41	23	10	254	240-275	5.0	3.7-5.8	51
10/21	5	132	85	75	255	249-325	4.2	2.0-5.3	61
10/27	16	55	38	35	223	215-246	2.9	2.0-3.3	76
11/11	12	81	60	55	259	237-279	3.6	1.8-4.1	72
1/18	12	555	100	100	214	169-249	3.7	1.1-4.8	58
1/27	41	166	92	92	163	151-229	2.1	1.5-2.7	78
2/20	6	60	40	37	180	161-233	2.9	1.0-3.6	62
4/12	13	74	47	48	175	161-209	1.9	1.3-2.3	92
4/29	20	88	65	78	225	220-254	2.1	1.2-2.6	107
5/11	32	172	93	97	223	218-258	2.3	1.6-3.3	97
Event Avg.	131	219	3.1	70					

Routine Monitoring Date	Avg. Flow ($m^3 \cdot s^{-1}$)	Avg. Conc. ($\mu g \cdot L^{-1}$)	Range ($\mu g \cdot L^{-1}$)	Avg. Conc. ($mg \cdot L^{-1}$)	Range ($mg \cdot L^{-1}$)	Avg. Yield ($\mu g \cdot mg^{-1}$ C)‡
4/95-12/95	3	235	174-275	2.0	1.0-4.4	119

* Base flow = ~ 16 ($m^3 \cdot s^{-1}$).

** Percent storms exceeded (out of 61 total).

‡ Yield is the quotient of DTHMFP and DOC.

(Fig. 5b). Concentrations in DOC exhibited changes of a greater magnitude (by a factor of 5, see Table 3) and remained elevated for a longer time interval than was noted for DTHMFP. The relatively high DOC and DTHMFP concentrations observed for this event (Table 3) are most likely due to a more complete washout of accumulated organic matter from leaf decay. While increases in DTHMFP were found during each storm, this pattern was generally short-lived compared to those of DOC, that is, there was an uncoupling of

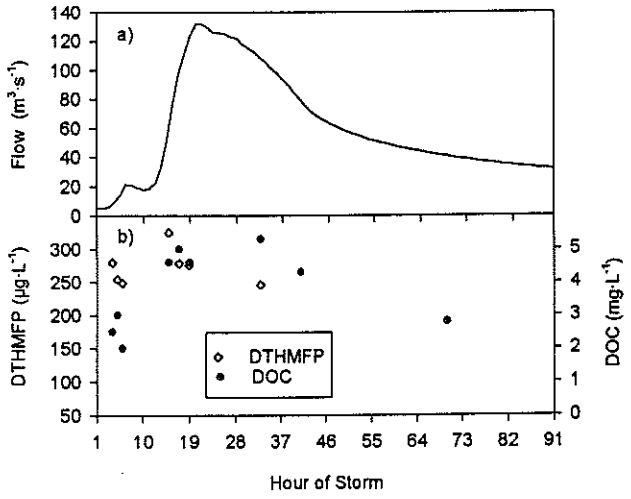

Figure 4.–Time series for runoff event for WBDR starting on October 21, 1995: a) hydrograph, and b) concentrations of DTHMFP and DOC.

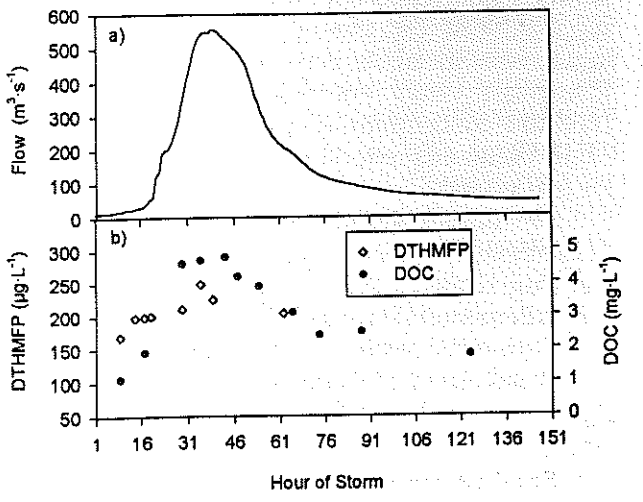

Figure 5.–Time series for runoff event for WBDR starting on January 18, 1996: a) hydrograph, and b) concentrations of DTHMFP and DOC.

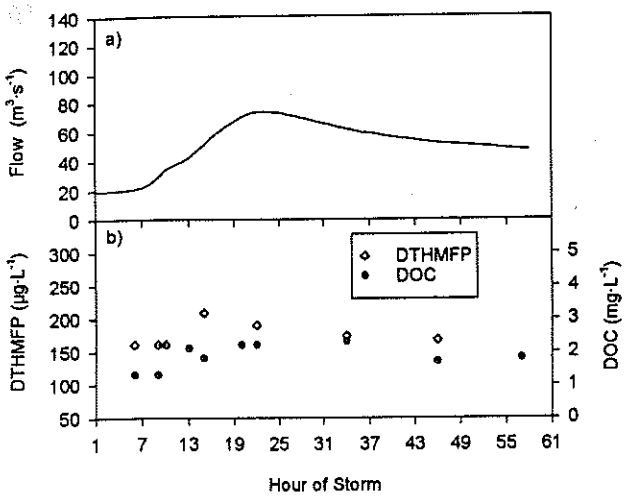

Figure 6.–Time series for runoff event for WBDR starting on April 12, 1996: a) hydrograph, and b) concentrations of DTHMFP and DOC.

DTHMFP and DOC after the rising limb of the hydrograph.

The runoff event of mid-April (Fig. 6a) was moderate in magnitude (Table 3); it began before base flow conditions were restored from previous runoff events. The modest response in DOC and DTHMFP concentrations (Fig. 6b) to this event is consistent with other studies which found that antecedent events flushed much of the available NOM from the watershed (Aiken and Cotsaris 1995). The flow-weighted event average DTHMFP values of the spring high runoff events were similar to those reported for discrete observations the previous spring (Fig. 2a and b). In general, the fall runoff events exhibited higher concentrations of NOM and THM precursor than were found during the spring (Table 3). This apparent seasonality is probably influenced not only by the dynamics of the supply of NOM (e.g., leaf-off), but also by the seasonality in microbial metabolic activity driven by temperature (Thurman 1985). For example, the increase in DTHMFP concentrations (and yields) for the last two runoff events may reflect increases in soil temperatures for that period.

The flow-weighted yields determined for the 11 events were rather variable (Table 3, range = 51-107), and uncorrelated with flow. However, the yields during runoff events were shifted distinctly lower than those of the routine (i.e., non-event) observations (Table 3). This is associated primarily with the generally higher DOC concentrations observed for the runoff events, combined with the lack of a similar systematic shift in the distribution of DTHMFP values for the runoff versus the routine observations. Thus, the DOC washed from the watershed during runoff events has a lower THM precursor potential. It is noteworthy that the extent of variation in organic carbon concentrations for WBDR contrasts with that reported for the Iowa River (Veenstra and Schnoor 1980), where precursor concentrations were observed to be more variable than those of TOC. However, temporal changes in the potency of the NOM pool were evident for both systems.

Loading Estimates

Flow-concentration relationships are routinely evaluated as part of the process of developing estimates of loading (e.g., Effler and Whitehead 1996). Where strong relationships exist, concentrations can be predicted from flow for periods when samples were not collected. The relationships between flow and concentration of DTHMFP and DOC are evaluated here (Fig. 7) for WBDR based on the observations of 1995. The concentration populations include instantaneous non-event (e.g., routine sampling program) and daily flow-weighted event concentrations. No relationship with flow emerges for this tributary for low or high flow subsets (Fig. 7) for DTHMFP (Fig. 7a). A moderately strong ($r = 0.7$) relationship was found for DOC only for the high flow range (Fig. 7b). The absence of a strong flow-concentration relationship for DTHMFP supports the use of the sampling/loading calculation protocol adopted here. The similarity of the frequency distributions for all the daily flows for the

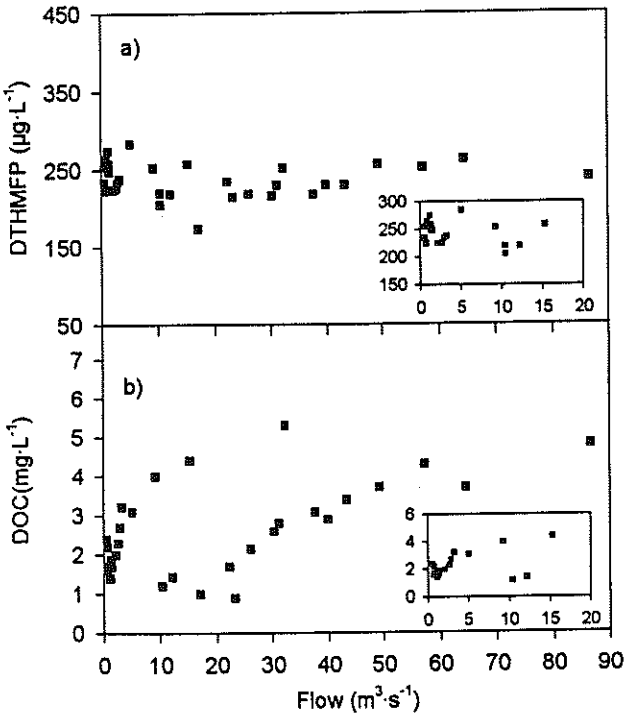

Figure 7.–Evaluation of the relationship between concentration and daily average flow in WBDR: a) DTHMFP (inset for non-event data only), and b) DOC (inset for non-event data only).

April-December interval (n = 275, Fig. 8a) and the subset of daily flows for which sampling was conducted (n = 33, Fig. 8b) supports the sampling program as representative of the flow regime of WBDR for that period. The emphasis on wet weather events is desirable within the context of material loading calculations (e.g., Effler and Whitehead 1996, Heidtke and Auer 1992).

The dynamics of the calculated DTHMFP load for the April-December 1995 period (Fig. 9a) approximately track the hydrograph (Fig. 2a). The volume-weighted concentration for this period was 228 $\mu g \cdot L^{-1}$. Loads were somewhat elevated in mid-April but became progressively lower throughout the low flow period (through mid-October). Increased loads were associated with the runoff events of the fall and early winter. Approximately 65% of the total load received over the April-December interval occurred during the events of the fall and early winter. Assuming the other minor tributaries have precursor concentrations similar to Trout Creek, the WBDR load represented approximately 90% of the allochthonous DTHMFP source to Cannonsville Reservoir between April and December 1995. The time series of daily loads from WBDR to Cannonsville Reservoir is used subsequently in this issue of the journal by Stepczuk et al. (1998b) to specify

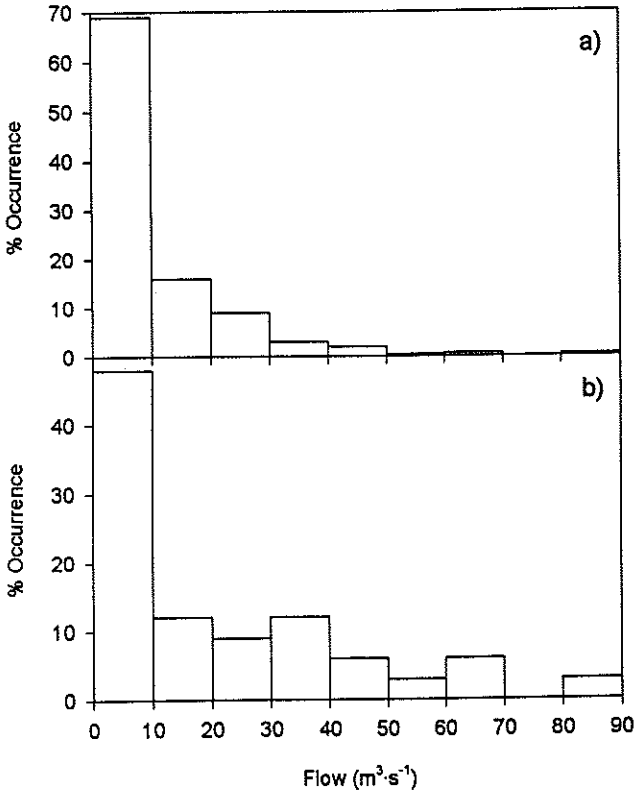

Figure 8.–Comparison of distributions of daily average flow in WBDR for the April-December interval of 1995: a) all days, and b) days on which DTHMFP and DOC samples were collected.

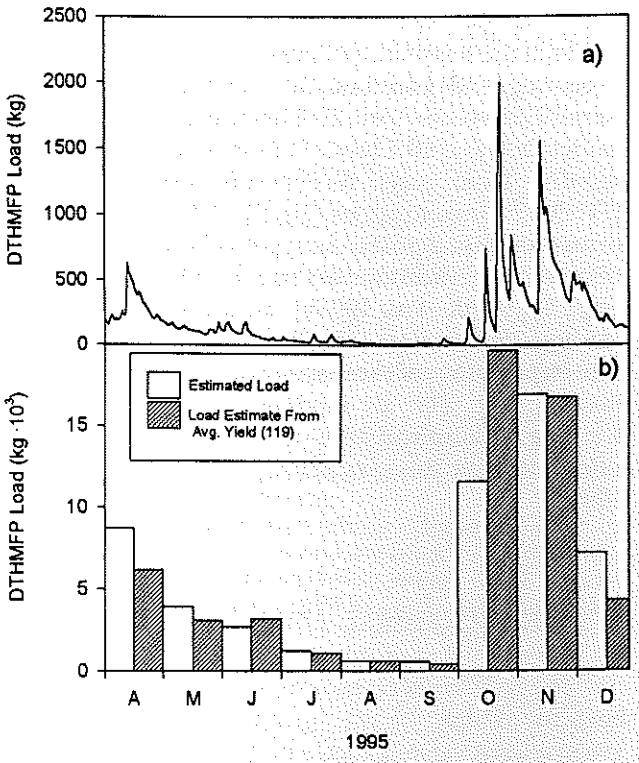

Figure 9. Estimates of DTHMFP loads from WBDR to Cannonsville Reservoir, April-December 1995: a) daily, and b) comparison of monthly, from DTHMFP (as in a), and DOC (from a yield of 119 $\mu g \cdot mg^{-1}$ C) concentrations.

allochthonous contributions to the reservoir in related mass balance modeling analyses.

The yield concept is attractive because precursor loads could be generated from DOC loads that are more widely available and less expensive (analytically) to develop (Canale et al. 1997). However, great caution needs to be exercised in adopting such an approach. First, results presented here (e.g., WBDR versus Trout Creek; Table 1) and in the literature (e.g., Jacangelo et al. 1995, Veenstra and Schnoor 1980) do not support a single yield value for all systems. Further, yield varies temporally in lotic systems (Fig. 2d, Table 3, also see Jacangelo et al. 1995, Veenstra and Schnoor 1980). We have pursued alternate THM precursor loading estimates based on the average yield (119 μg DTHMFP $\cdot$ mg^{-1} DOC) determined from the routine (non-event) monitoring program (Table 3). The total precursor load for WBDR for the April-December interval determined from the DOC concentration time series and the average yield closely matched (within 5%) the total load based on the DTHMFP time series. However, we have little confidence that this same yield value would perform similarly for different years with widely different hydrology, based on the variations in yield reported here for different hydrologic conditions (e.g., Table 3). Further,

adoption of a constant yield value produces systematic errors in the seasonality of precursor loading (Fig. 9b). Precursor loads based on DOC and the average yield were 30% lower in April, 20% lower in May, 65% higher in October, and 40% lower in December, compared to monthly loads based directly on measurements of DTHMFP concentrations (Fig. 9b). Within the context of an established goal to support seasonal simulations of precursor concentrations in a water supply reservoir (e.g., Stepczuk et al. 1998b), such errors in external loading of precursors (Fig. 9b) may not be acceptable. The implications of these systematic errors in external loading (Fig. 9b) for modeling precursor concentrations in Cannonsville Reservoir are evaluated subsequently in this issue of the journal (Stepczuk et al. 1998b).

Management Implications

The time series of daily DTHMFP loads developed here for WBDR for the April-December interval of 1995 (see Fig. 9a) represents the dominant (e.g., 94%) portion of the allochthonous contribution to the THM precursor pool of Cannonsville Reservoir for that period (Stepczuk et al. 1998a), and is a major forcing function for related mass balance model simulations of that pool (Stepczuk et al. 1998b). Increases in precursor concentrations observed along the length of WBDR indicate anthropogenic effects may contribute to these loads. Quantification of precursor loads relied on a runoff event-oriented sampling program for DTHMFP over the period of loading calculations. Strong and/or recurring relationships between precursor concentration and tributary flow, or seasonality in concentration, did not emerge. Thus, we cannot recommend reductions in the sampling program conducted here that would not compromise the accuracy of seasonal loading estimates to this reservoir. A sampling program similar to that adopted here for WBDR is recommended for other systems where external loading of precursors to a water supply lake or reservoir is an important issue.

Dissolved organic carbon (DOC) or gelbstoff (g_{440}) were not found to be reliable surrogate measures of THM precursor concentrations. Particular attention was given to evaluating DOC as a surrogate of DTHMFP, represented as yield (the ratio of DTHMFP/DOC) to support estimates of precursor loads. The yield concept should be attractive to managers concerned with the water supply precursor issue, as there is a large data base for DOC available describing many lentic and lotic systems, and this parameter is more routinely measured. However, results presented here are not supportive of the yield concept as a basis to estimate seasonal tributary precursor concentrations and loads. For example, values of yield were nearly twice as great on average in WBDR compared to Trout Creek. Yield varied substantially in WBDR over the period of monitoring, within runoff events, from one event to the next, and along the length of WBDR. The yield concept may have value for supporting "screening level" analyses (e.g., first approximations), but only after making system-specific paired measurements of precursor (e.g., DTHMFP) and organic carbon (e.g., DOC) concentrations.

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