

Spatial and Temporal Patterns of THM Precursors in a Eutrophic Reservoir¹

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ABSTRACT

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Temporal and spatial patterns of trihalomethane (THM) precursors (measured as THM formation potential, THMFP) are described and analyzed for eutrophic Cannonsville Reservoir, NY, based on monitoring conducted weekly over the April to November interval of 1995 at three sites along the main axis of the reservoir. Ninety-eight percent of the precursors formed chloroform, and 94% were in a dissolved (0.45- μm filtrate) form. Distinct seasonal, vertical and longitudinal patterns were observed. Progressive increases in THMFP occurred from spring ($\sim 170 \mu\text{g} \cdot \text{L}^{-1}$) through mid-summer ($\sim 360 \mu\text{g} \cdot \text{L}^{-1}$) in the epilimnion of the lacustrine zone of the reservoir, followed by subsequent decreases through early fall. Progressive, but smaller, increases in THMFP occurred in the hypolimnion throughout the period of stratification. Vertical patterns in dissolved THMFP within the hypolimnion indicate the sediments were not an important source of precursors to the water column. Summer epilimnetic concentrations of THMFP were substantially higher than those reported for the inflows (Stepczuk et al. 1998a), establishing the operation of autochthonous sources. Features of the THMFP patterns, including epilimnetic enrichment, the seasonality, and higher concentrations in the more eutrophic riverine zone, and the results of a single laboratory experiment, indicate a linkage between primary production and autochthonous production of precursors. Dissolved organic carbon was not a good surrogate measure of THMFP.

Key Words: THM precursors, allochthonous sources, autochthonous sources, eutrophication, reservoir, primary productivity.

Identifying the origins and understanding the behavior of trihalomethane (THM) precursors should be considered fundamental to the development of an effective management strategy to minimize the

concentrations of THMs in water supplies. Lakes and reservoirs receive precursors, components of natural organic matter (NOM) from their watersheds (external, or allochthonous, sources; e.g., Stepczuk et al. 1998a), derived mostly from terrestrial vegetation (e.g., Aiken and Cotsaris 1995, Goel et al. 1995). Allochthonous

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inputs of NOM (Wetzel 1983, Thurman 1985), and apparently THM precursors (e.g., Stepczuk et al. 1998a), are mostly in a dissolved form. Internal (autochthonous) production of precursors is to be expected in lakes and reservoirs, as autochthonous formation of particulate and dissolved NOM, coupled directly or indirectly to primary production, is well known and has been widely documented (e.g., Wetzel 1983, 1992). Similarly, the operation of loss processes for precursors from the water column is to be expected, associated with decay, photolysis (e.g., Wetzel et al. 1995), and deposition of particulate forms.

The existence of autochthonous sources of THM precursors has been widely acknowledged (Briley et al. 1980; Hoehn et al. 1980, 1984; Karimi and Singer 1991; Martin et al. 1993; Oliver and Shindler 1980; Palmstrom et al. 1988). This position has been supported by both laboratory and field studies, however these inputs and related processes remain largely unresolved and unquantified. Uhler and Means (1985) reported the production of THMs from the chlorination of Potomac River sediments, and Martin et al. (1993) found lake sediments to be a source of THM precursors. Laboratory and field studies have established that algal biomass and their extracellular products (ECPs) can act as precursors (Briley et al. 1980; Hoehn et al. 1980, 1984; Oliver and Shindler 1980; Wachter and Andelman 1984). Hoehn et al. (1984) hypothesized an interplay between primary producers and heterotrophic bacteria in autochthonous production of THM precursors, based on observations from field investigations. This hypothesis is further supported by the documentation of seasonal trends for THM precursors (Edzwald et al. 1985, Hoehn et al. 1984, Palmstrom et al. 1988, Veenstra and Schnoor 1980) which are similar to those reported for algal, macrophyte, and bacterial production (Wetzel 1983). Autochthonous production of precursors has also been indicated by demonstrating that reservoir outputs have exceeded inputs (Karimi and Singer 1991, Palmstrom et al. 1988).

Resolution of temporal and spatial patterns in physical, chemical, and biological characteristics has been a fundamental component of limnological studies directed at identifying and describing phenomena, recurring trends, and interactions between processes and constituents (e.g., Hutchinson 1957, 1967; Wetzel 1983). Patterns for THM precursors in lakes and reservoirs have been incompletely resolved in time and/or space, and analyses of the interplay with ambient conditions have been limited. A detailed description and analysis of the temporal and spatial distributions of THM precursors in Cannonsville Reservoir, NY, over the April-November interval of 1995, are presented here to improve understanding of their origins, behavior and interplay with limnological processes, and provide

insights to support the development of a conceptual framework for a mechanistic model (e.g., Canale et al. 1997, Chapra and Reckhow 1983, Thomann and Mueller 1987) for precursors (see Stepczuk et al. 1998b).

Methods

Cannonsville Reservoir is a water supply and flow augmentation reservoir for New York City, located approximately 190 km northwest of the city. The setting, morphometry, and operation of the reservoir have been described in detail in preceding manuscripts of this issue (Effler and Bader 1998, Longabucco and Rafferty 1998, Owens et al. 1998). This study was conducted over the spring-fall interval of 1995; a major drawdown (to 23% capacity) was experienced during this period (Owens et al. 1998). The selection of Cannonsville Reservoir for this study and the timing of the investigation are supported by several considerations: (1) the reservoir is eutrophic (Effler and Bader 1998), thereby offering an opportunity to resolve a related autochthonous contribution to the THM precursor pool in the productive months (e.g., Palmstrom et al. 1988, Walker 1983); (2) a clear trophic state gradient is manifested along the longitudinal axis of the reservoir (Effler and Bader 1998), offering an additional opportunity to couple autochthonous precursor production to primary production; (3) limnological characteristics of the reservoir have been documented for the study period of 1995 (e.g., Effler and Bader 1998); and (4) comprehensive information on allochthonous inputs of THM precursors is available for the same interval (Stepczuk et al. 1998a).

Total and filtered (0.45- μ m) THM precursor concentrations were measured as THM formation potential (THMFP; APHA 1992). The filtered fraction is described here as dissolved THMFP (DTHMFP). The residual of the total THMFP (TTHMFP) and DTHMFP is specified as the particulate fraction (PTHMFP; e.g., Stepczuk et al. 1998a). Details of the sample handling and analytical protocol, and the quality assurance program (for the combined tributary and reservoir programs) were presented by Stepczuk et al. (1998a). The average coefficient of variation for triplicate analyses was ~2.5% (Stepczuk et al. 1998a). The average accuracy (laboratory standards, spikes, and external audit samples) was within 5% to 10% (Stepczuk et al. 1998a). Sampling for THMFP analyses was integrated into the overall larger (e.g., common limnological parameters) monitoring program for the reservoir of 1995, described by Effler and Bader (1998). Three reservoir locations were monitored, sites 1 (near dam), 4 (near intakes), and 6 (near mouth of West

Branch Delaware River (WBDR; Fig. 1). Sites 1 and 4 have been characterized as lacustrine, and site 6 as riverine (Effler and Bader 1998; Fig. 1), according to reservoir zones defined by Kimmel and Groeger (1984). Samples were collected weekly in 1995 from April to early November at depths of 0, 3 (i.e., epilimnion), and 18 m (hypolimnion, not existent at site 6 during severe drawdown). More detailed vertical resolution was based on 3-m interval profiles of THMFP collected for 16 of the samplings at site 4. The field and laboratory programs for other limnological parameters used to support this analysis were described by Effler and Bader (1998), Effler et al. (1998b), and Stepczuk et al. (1998a). One of those variables was *gelbstoff* (g_{440}), a measure of dissolved color, normally associated with humic substances (Davies-Colley and Vant 1987, Effler et al. 1998b). The concomitant sampling program for THMFP for WBDR (the major tributary) and Trout Creek (Fig. 1) was described by Stepczuk et al. (1998a).

A single laboratory experiment was conducted to evaluate the relationship between phytoplankton primary productivity and THMFP production. The experiment utilized the natural phytoplankton assemblage of the reservoir, collected on September 6, 1995, under controlled temperature (20 °C) and light intensities (I) ranging from 0 to 1000 $\mu E \cdot m^{-2} \cdot s^{-1}$, to assess the relationships between light, primary production (Auer 1998, Storey et al. 1993), and production of dissolved THMFP (DTHMFP). The light source generated light from the visible portion of the spectrum only. Details of the primary productivity experiments, conducted weekly, are described elsewhere in this issue (Auer 1998). Analyses of THMFP were conducted on the filtrates for the different light incubation experiments. Gross production of DTHMFP, normalized for chlorophyll (measure of phytoplankton biomass), was calculated by dividing the difference of the light and

dark ($I = 0 \mu E \cdot m^{-2} \cdot s^{-1}$) bottle concentrations by the incubation period and chlorophyll concentration.

Data were pooled for each site to support statistical analyses, and arithmetic means were calculated for spring, summer, and fall. Analysis of variance (ANOVA) and multiple comparisons (e.g., Tukey HSD method, SAS 1985) on log-transformed data were calculated to determine differences between sites and depths during turnover and stratified periods. Paired *t*-tests on transformed data (SAS 1985) were performed to determine the significance of differences between total and dissolved forms of THMFP and organic carbon. The relationships between TTHMFP, DTHMFP, and PTHMFP, the organic carbon pool [particulate (POC), dissolved (DOC) and total organic carbon (TOC)], limnological variables related to trophic state [total phosphorus (TP), total chlorophyll (C_T)], and selected abiotic factors (temperature and *gelbstoff*) were described spatially by Pearson product-moment correlation analysis for the upper stratified layer and site 4 vertical profiles. All data were transformed so that they were distributed according to the bivariate normal. For purposes of comparison, the correlation coefficients are characterized as strong ($r \geq 0.8$), weak ($r \leq 0.5$), or otherwise moderate (Devore and Peck 1986). Limnological analyses of the patterns of these parameters during the 1995 study period are presented elsewhere in this issue (e.g., Effler and Bader 1998, Effler et al. 1998b).

Results

Spatial and Temporal Patterns of THMFP

Ninety-eight percent of THMFP, on average, formed chloroform. Ninety-four percent of THMFP was as DTHMFP. Despite the dominant contribution of DTHMFP to the TTHMFP pool of the reservoir, the veracity of the estimates of the particulate fraction (PTHMFP), calculated as the difference between TTHMFP and DTHMFP, was supported by the significant ($p \leq 0.05$) differences observed between the measured fractions for all sites throughout the study period. The possibility that the imperfect partitioning of the phases of THMFP by filtration (0.45 μm) adopted here may have substantively influenced the apparent patterns in PTHMFP is acknowledged. The dominance of chloroform and the small contribution of PTHMFP to TTHMFP essentially matches the findings reported for WBDR and Trout Creek over the study period (Stepczuk et al. 1998a).

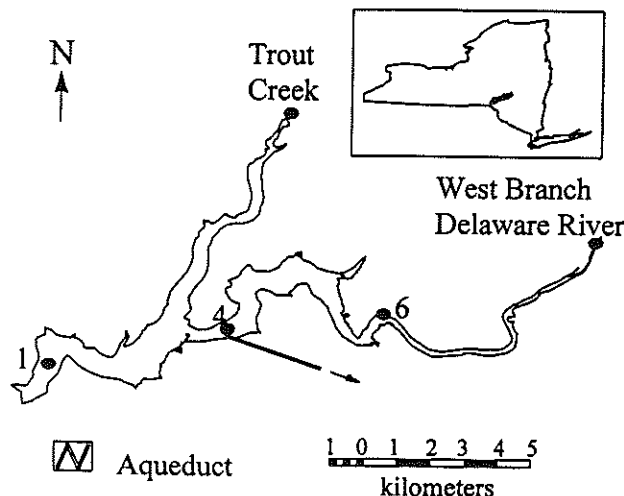


Figure 1.—Map of Cannonsville Reservoir, showing three sampling locations.

Distinct vertical patterns emerge from analyses of the DTHMFP and PTHMFP profiles from site 4, and are presented and discussed here within the context of the thermal stratification regime (Fig. 2a-u). ANOVA and multiple comparison analyses showed no significant differences between sites 1 and 4 at each corresponding depth; hence only site 4 data are presented here as representative of conditions for the lacustrine portions of the reservoir. Vertical patterns, particularly for DTHMFP, appear to be influenced greatly by stratification (Fig. 2o-u), as observed for many limnological parameters (e.g., Hutchinson 1957, Wetzel 1983); the highest DTHMFP values always, and PTHMFP values usually, occurred above the thermocline (Fig. 2b-f and i-m). The vertical structure of DTHMFP paralleled the thermal stratification structure; e.g., the depth of the

maximum gradient in DTHMFP approximately matched the position of the thermocline. DTHMFP concentrations within the epilimnion increased in a progressive manner through early August (Fig. 2a-e), and thereafter decreased to a level somewhat above the April observations (Fig. 2f-g). The DTHMFP values generally decreased with increasing depth from the thermocline toward the sediments (Fig. 2b-f), a vertical structure that suggests downward inputs from the enriched epilimnion. The very distinct seasonality of DTHMFP in the epilimnion is best viewed in a time-series format (Fig. 3a). Surface DTHMFP values at site 4 ranged from about $170 \mu\text{g} \cdot \text{L}^{-1}$ in April to a maximum of about $360 \mu\text{g} \cdot \text{L}^{-1}$ in mid-August. The progressive increase in DTHMFP in the reservoir's hypolimnion during the summer of 1995, which was much smaller

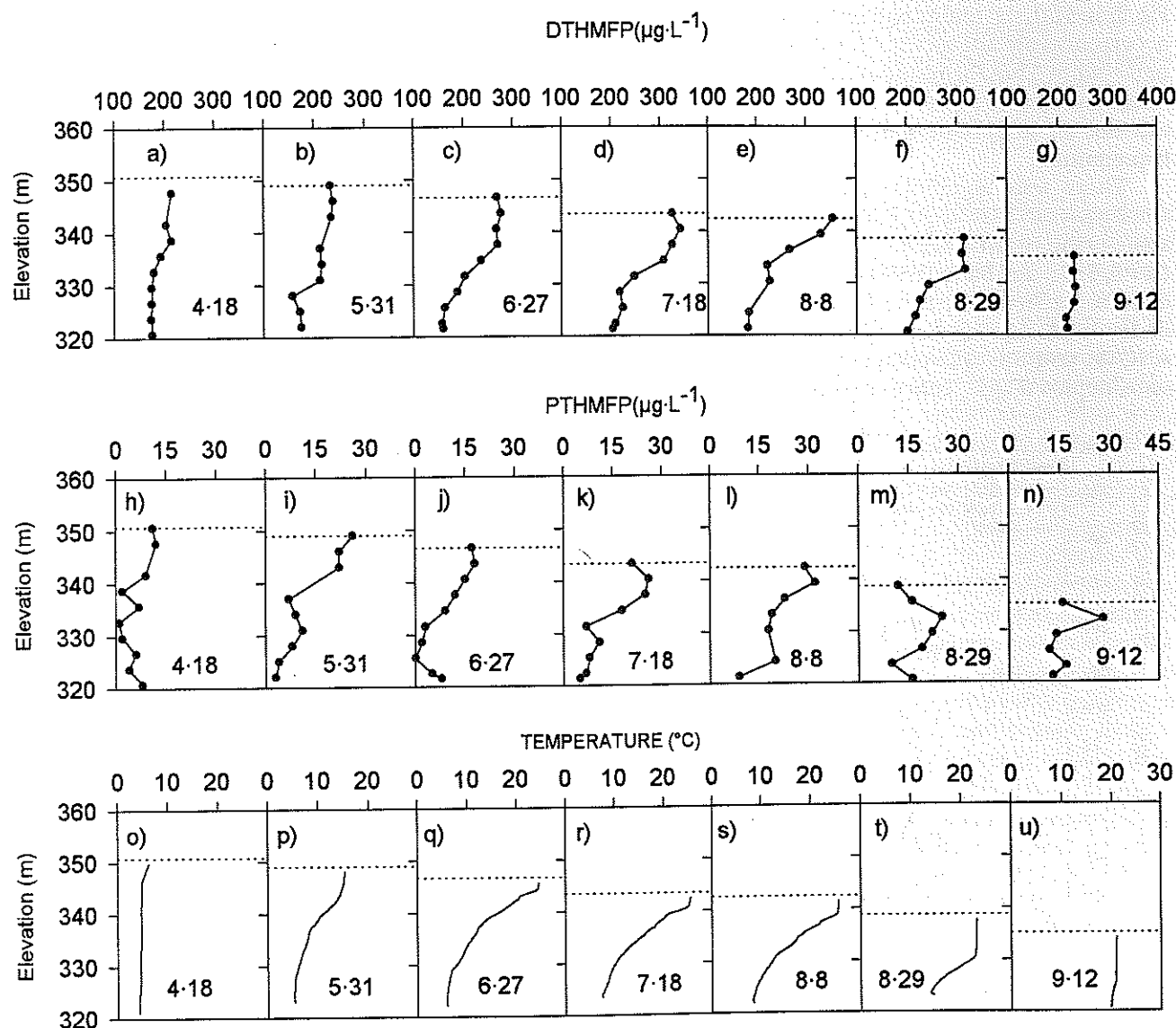


Figure 2.—Vertical profiles at site 4, Cannonsville Reservoir, 1995: a-g) DTHMFP, April 18, May 31, June 27, July 18, August 8, August 29, and September 12, respectively; h-n) PTHMFP, April 18, May 31, June 27, July 18, August 8, August 29, and September 12, respectively; o-u) temperature, April 18, May 31, June 27, July 18, August 8, August 29, and September 12, respectively.

than the increase observed in the epilimnion through early August, is again clearer in time-series format (Fig. 3a). This temporal pattern for the hypolimnion is consistent with vertical mixing-based inputs from the enriched epilimnion (e.g., Chapra and Reckhow 1983, Wodka et al. 1983).

The near-surface peaks in PTHMFP observed in the reservoir on several occasions (e.g., Fig. 2i-l) are similar in character to the vertical distributions reported for chlorophyll on several occasions (Doerr et al. 1998). However, the distributions of PTHMFP and C_T were poorly correlated for the epilimnion. Compared to DTHMFP, the uncoupling of the vertical structure of PTHMFP from the thermal structure in several instances (e.g., Fig. 2j and l) may reflect the time course of deposition of that fraction. Though near-bottom peaks in PTHMFP were observed on several occasions (e.g., Fig. 2j and m), the timing and vertical structure of these occurrences did not correspond to the patterns of TSS or turbidity. Thus the resuspension of bottom material documented over the study period (Effler et al. 1998a) was not an important source of precursors to the hypolimnion.

There were significant differences for THMFP among sites (ANOVA, $p \leq 0.05$). Multiple comparison analyses showed that THMFP levels in the riverine zone (site 6, Effler and Bader 1998) were significantly higher than in the lacustrine zone (sites 1 and 4, Effler and Bader 1998; Fig. 4a). A similar gradient (based upon ANOVA and multiple comparisons tests) in trophic state, depicted by C_T concentrations, was found along

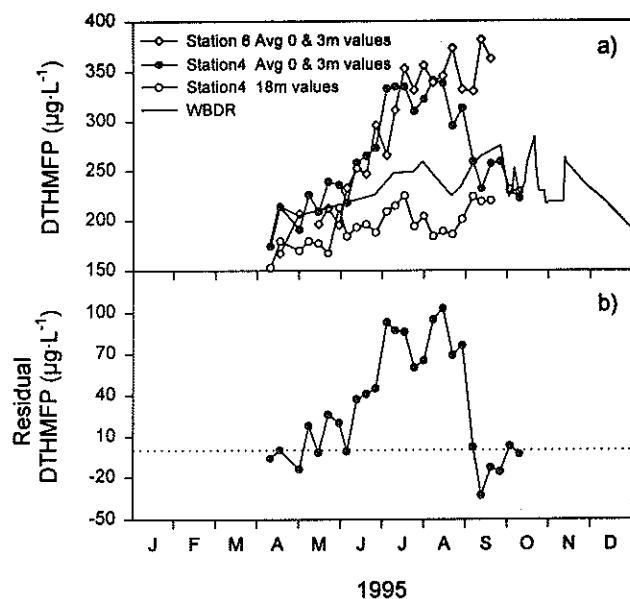


Figure 3.—Time series in Cannonsville Reservoir in 1995: a) DTHMFP, epilimnion (average of 0 and 3 m) at site 4, hypolimnion (18 m) at site 4, epilimnion at site 6, WBDR (from Stepiczuk et al. 1998a), and b) difference in DTHMFP values at site 4 epilimnion and WBDR, the major allochthonous source (from time interpolated values).

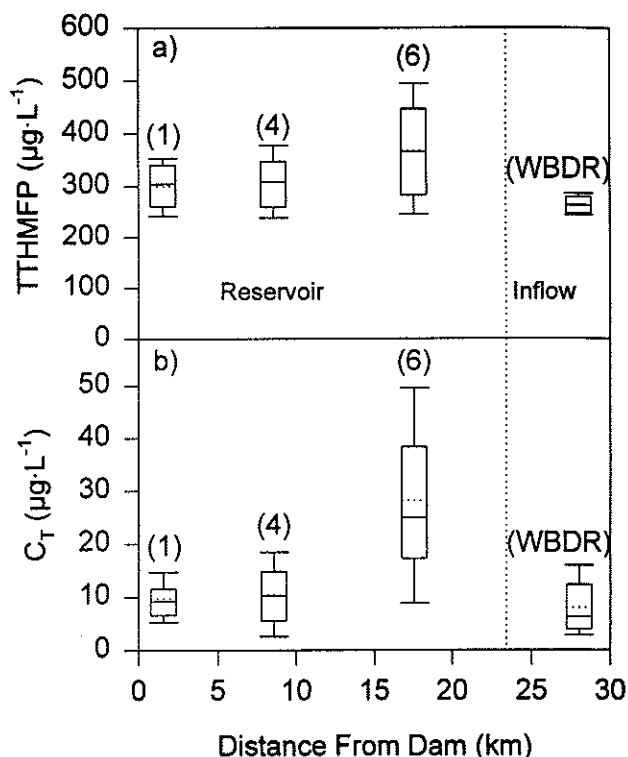


Figure 4.—Box plots for growing season epilimnetic longitudinal profiles, as depicted by sites 1, 4, and 6, for Cannonsville Reservoir, 1995, and corresponding inflow data: a) TTHMFP, and b) C_T (from Effler and Bader 1998).

the same axis (Fig. 4b). Corresponding concentrations for WBDR, the main inflow, were significantly ($p \leq 0.05$) lower than those of site 6 during the growing season, which suggests that THM precursor production was influenced by primary production. Values of DTHMFP (the main component of THMFP) at site 6 were similar to the concentrations measured at the lacustrine sites in April and May, but were generally greater thereafter (Fig. 3a). Concentrations of DTHMFP were higher at site 6 in August and September compared with the (Fig. 4a-b) lacustrine and inflow sites; a maximum concentration of $465 \mu\text{g}\cdot\text{L}^{-1}$ was observed at 0 m, about $100 \mu\text{g}\cdot\text{L}^{-1}$ greater than the maximum measured for site 4.

Phytoplankton/DTHMFP Production Experiment

Major differences were observed in the character of phytoplankton photosynthesis (oxygen production) as a function of I (often described as a P-I curve; Fig. 5a) versus gross DTHMFP production as a function of I (Fig. 5b). A saturating relationship was observed for photosynthesis: oxygen production increased sharply with relatively small increases in I and leveled off with

additional increases in I (Fig. 5a). These P-I curve characteristics are widely observed (e.g., Fahnenstiel et al. 1989, Field and Effler 1982, Jassby and Platt 1976). The results of P-I experiments conducted weekly for the reservoir during the 1995 study period are presented and evaluated in detail by Auer (1998), as part of a larger study of phytoplankton kinetics for the system. Gross production of DTHMFP increased (nearly linearly) over the low I range (e.g., $< 150 \mu\text{E} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$; Fig. 5b). Inhibition of DTHMFP production was observed at higher I values (Fig. 5b). Progressively lower rates of production of DTHMFP occurred as I was increased over the 150 to $400 \mu\text{E} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ range. The rate of production of DTHMFP remained approximately uniform for $I > 400 \mu\text{E} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ (Fig. 5b).

Discussion

Analysis of Temporal and Spatial Patterns

Correlation matrices for total dissolved, and particulate THMFP and organic carbon with the two trophic state (C_T and TP) and two abiotic (temperature and gelbstoff) variables were compared to determine possible interrelationships. Selected correlation coefficient results of that analysis are presented (Table 1). The first column presents an analysis of temporal correlations, limited to the thermal stratification period, for data collected throughout the upper layer of the reservoir. It is in this context that associations between THMFP, organic carbon, and trophic state indicators are best evaluated. The second column of correlation coefficients summarizes data from the site 4 vertical profiles (e.g., every 3 m), and introduces the effect of thermal stratification on these same associations. Separate correlation analyses were performed for each form of THMFP and organic carbon, but for the sake of simplicity, only correlations involving "total" forms are presented (note: associations with gelbstoff are an exception). In general, the dissolved species followed similar patterns while correlations for particulate species were lower.

Significant associations (Table 1) between THMFP and TOC, and TOC and chlorophyll were observed for both temporal and spatial distributions, as has been observed in previous studies (Amy et al. 1987, Edzwald et al. 1985, Singer et al. 1981, Symons et al. 1975, Walker 1983). Despite exhibiting similar patterns with respect to longitudinal differences (Fig. 4a, b) within the upper waters, as well as seasonality effects (Fig. 3), the association between THMFP and chlorophyll in

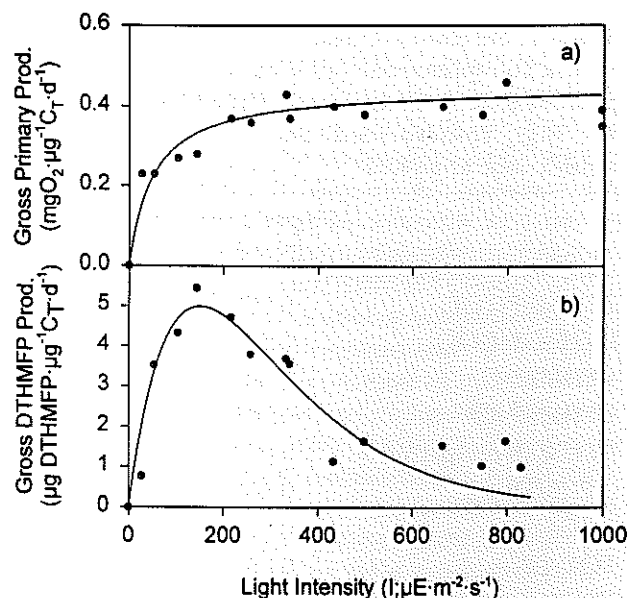


Figure 5.—Results of paired laboratory experiments with the natural phytoplankton assemblage of Cannonsville Reservoir: a) gross primary production as a function of light, and b) gross DTHMFP production, normalized for C_T , both as a function of light intensity, I .

the upper layer was weak (Table 1). This is probably reflective of the variability in the seasonal dynamics of the algae with respect to factors such as dominant type, physiological state, and predation. In order to evaluate possible common associations among THMFP, TOC, and chlorophyll, the strength of their respective correlations with TP and temperature was examined. The three variables exhibited correlations that were moderate to strong for TP and weak to moderate for temperature in the upper layer (Table 1). In contrast, the same associations in the vertical structure were reversed (e.g., correlations for temperature were strong, while those with TP were not). The associations with temperature observed in the vertical dimension may not be causal in nature, but may reflect the fundamental differences in the biology and chemistry of the epilimnion and hypolimnion. Additionally, factors other than nutrients may also influence the relationships between THM precursors, chlorophyll, and organic carbon, such as light availability and biological activity (e.g., bacteria, predation) within the epilimnion. It should be noted that associations with gelbstoff and DTHMFP and organic carbon were insignificant, or when significant, were only weakly correlated (Table 1). This is consistent with findings reported for inflows to Cannonsville Reservoir (Stepczuk et al. 1998a), where insignificant associations between THM precursors and gelbstoff were also observed.

Reservoir concentrations of TTHMFP were distinctly higher in the epilimnion throughout the reservoir during the summer of 1995 compared to

Table 1. Selected correlation coefficients (r) from a matrix for epilimnetic (all sites) and detailed vertical profiles (Site 4) during the stratification period. Data are \log_{10} transformed. An asterisk (*) denotes significance at $p \leq 0.05$.

| | Upper Layer (N=45) | Vertical Profile (N=97) |
|--------------------|-----------------------|----------------------------|
| TTHMFP-TOC | 0.76* | 0.78* |
| DTHMFP-DOC | 0.63* | 0.72* |
| TTHMFP- C_T | 0.49* | 0.77* |
| TTHMFP-TP | 0.74* | 0.12 |
| TTHMFP-temperature | 0.65* | 0.89* |
| DTHMFP- g_{440} | 0.46* | 0.08 |
| TOC- C_T | 0.75* | 0.81* |
| TOC-TP | 0.85* | 0.40* |
| TOC-temperature | 0.35* | 0.86* |
| DOC- g_{440} | 0.33* | 0.12 |
| C_T -TP | 0.69* | 0.24* |
| C_T -temperature | 0.08 | 0.73* |

concentrations in WBDR [Fig. 3; Trout Creek concentrations were even lower (Stepczuk et al. 1998a)], establishing a substantial contribution from autochthonous sources to the THMFP pool of the reservoir (e.g., Karimi and Singer 1991, Palmstrom et al. 1988). Several features of the reported distributions (Figs. 2-4) and the results of the single experiment (Fig. 5) indicate a link between primary production and internal THM precursor production in the reservoir. Macrophytes have been shown to be associated with the production of THM precursors, both during active growth and decomposition (Palmstrom et al. 1988). However, phytoplankton, identified by several investigators as a source of precursors (e.g., Briley et al. 1980; Hoehn et al. 1980, 1984; Wachter and Andelman 1984), is the more appropriate focus for evaluating the role of primary producers in mediating autochthonous contributions to the precursor pool of this eutrophic reservoir because of the relatively small macrophyte community supported in this system.

The general temporal structure of the autochthonous component of the DTHMFP pool (reflected by the residual of the epilimnetic and inflow concentrations, Fig. 3b), and the localization of the enrichment in the reservoir's epilimnion are consistent with the position that primary production plays an important role in internal production of precursors. The development of longitudinal differences in TTHMFP (Fig. 4a) along the trophic state gradient of the reservoir (Fig. 4b) further supports this position. Certain investigators (Hoehn et al. 1984, Oliver and

Shindler 1980, Wachter and Andelman 1984) have reported significant production of precursors by cyanobacteria during controlled laboratory experiments. It is noteworthy that cyanobacteria (particularly filamentous forms) were dominant in the phytoplankton community of the reservoir over the July - early October of 1995 (Siegfried 1998), and that particularly dense populations of these forms prevailed in the riverine section (e.g., site 6) when the highest concentrations of DTHMFP of the study period were documented (Fig. 3).

Hoehn et al. (1980) demonstrated a strong correlation between the dynamics of THM precursor levels and chlorophyll *a* in Occoquan Reservoir for a single year, but the relationship did not hold in other years. No consistent relationships were observed between algal population densities and THMFP concentrations in eutrophic Claytor Lake (Hoehn et al. 1984). Chlorophyll (Fig. 6b) was not a good estimator of the dynamics of precursors (Fig. 6a) in the epilimnion of Cannonsville Reservoir in 1995 nor was primary productivity [Fig. 6c; a short-term laboratory measurement that utilized the reservoir's phytoplankton assemblage (see Auer 1998)]. This should not be interpreted as inconsistent with the primary productivity hypothesis, as both of these indicators are dependent on the standing crop of phytoplankton which varied strongly throughout the study period (Fig. 6b). The dominance of DTHMFP in the TTHMFP pool of the reservoir and the gradual character of the seasonality of the precursors [e.g., Fig. 3 (site 4, epilimnion), again as Fig. 6a] instead imply continuing inputs to the pool from soluble species (e.g., ECPs; Briley et al. 1980; Hoehn et al. 1980, 1984; Oliver and Shindler 1980; Wachter and Andelman 1984) that are probably driven largely by phytoplankton production. Feuillade et al. (1990) reported the rate of ECP release from phytoplankton to be relatively uniform over a rather wide range of ambient and physiological conditions. The main products of release are low molecular weight amino acids and oligopeptides, and are thus more labile than refractory allochthonous DOC (e.g., Goel et al. 1995, Wetzel 1992).

Phytoplankton primary production, in general, can provide a large fraction of the food source for bacterial metabolism (as reviewed by Gajewski and Chrost 1995). The interplay between phytoplankton activity, production of ECPs, and bacterial activity has been described by a number of investigators (Cole et al. 1982, 1988; Lovell and Konopka 1985; Normann et al. 1995). Hoehn et al. (1984) speculated that heterotrophic bacteria interact with phytoplankton in mediating autochthonous production of THM precursors. For example, certain bacteria may convert ECPs to more reactive organic fractions with respect to

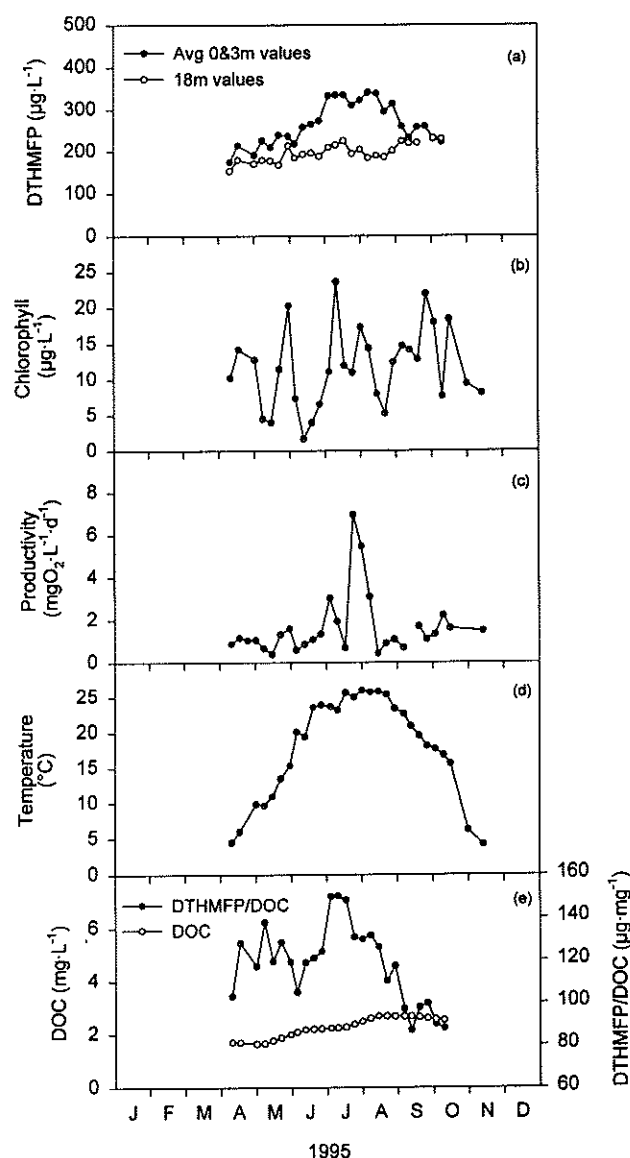


Figure 6.—Time series for the epilimnion (average of 0 and 3m) of Cannonsville Reservoir in 1995: a) DTHMFP, b) C_p , c) gross primary productivity (from Auer 1998), d) temperature, and e) DOC and the ratio (yield) DTHMFP:DOC.

THM formation. In diurnal studies, Hoehn et al. (1984) observed the maxima in THMFP and ECP release coincided. These investigators observed significant increases in THM precursor levels and CO_2 concentrations during the night and interpreted these results as indicating an important role of heterotrophic bacteria in precursor production.

The operation of sink processes on the epilimnetic THM precursor pool is indicated by the generally progressive decreases in THMFP observed after mid-August (Figs. 3, 6a). Potential contributing processes include export, increased vertical mixing-based losses to the lower layers, microbial decay, photolysis (e.g., Wetzel et al. 1995), and adsorption to

particles [particularly clays, present in rather high concentrations (Effler et al. 1998a)]. Sinks for THM precursors, particularly for the autochthonous component (e.g., greater lability), are likely continuously operative. Accordingly, the seasonality observed in the precursor pool (Figs. 3, 6a), would represent the temporal imbalance in sources and sinks; i.e., sources > sinks through July and sources < sinks after mid-August.

The ratio DTHMFP:DOC (also as TTHMFP:TOC), identified as yield, has been used by many investigators to represent the potency of various sources of organic carbon to form THMs (e.g., Canale et al. 1997). The temporal structure of yield in Cannonsville Reservoir (Fig. 6e) paralleled that of DTHMFP (Fig. 6a) because the concentration of DOC remained relatively uniform (Fig. 6e). This suggests a seasonality in the nature (also see Hoehn et al. 1984) and potency of the DOC pool of the reservoir with respect to THM production, and a fundamental limitation of the yield concept for comparing systems (particularly if eutrophic) and predicting precursor concentrations from measurements or predictions of organic carbon. This temporal variability in yield does not support a modeling approach for this system that would focus primarily on simulation of the organic carbon pool, with subsequent prediction of THMFP from a single yield value (e.g., Canale et al. 1997).

The absence of increases in DTHMFP with the approach to the sediment-water interface (Fig. 2a-g) indicates the sediments of Cannonsville Reservoir are not a significant source of dissolved precursors to the water column of the reservoir. Several investigators reported the release of precursors from sediments (Martin et al. 1993, Palmstrom et al. 1988, Uhler and Mean 1985). However, Martin et al. (1993) and Palmstrom et al. (1988) concluded, based on approximate material budget calculations, that the contribution of the sediments to the precursor content of the water column was quite small (e.g., < 1%). Thus, the results reported here for the lowermost waters of Cannonsville Reservoir (Fig. 2a-g) should not be considered inconsistent with the findings of these investigators. Further, according to the findings of Martin et al. (1993), the upward flux of precursors from the reservoir's sediments would be expected to decrease with the onset of anoxia that occurs in late summer in Cannonsville Reservoir (Effler and Bader 1998).

Light and Production of DTHMFP

The laboratory phytoplankton/DTHMFP production experiment (Fig. 5) indicates a direct relationship between primary production and formation of DTHMFP up to $1 \sim 150 \mu E \cdot m^{-2} \cdot s^{-1}$, and suggests the

operation of other factors influencing precursor production above this light intensity. These results are generally consistent with Hoehn's (1984) findings from diurnal studies, to the extent that peak precursor production was shifted from the time of maximum incident I . However, precursor production was greater in the light, throughout the experimental range of I , than in the dark (e.g., positive gross production values of Fig. 5b). A possible explanation for the observed decreased rate (inhibition) of precursor production at higher I values is inhibition of bacterial activity (Wetzel et al. 1995). Alternatively, or additionally, Hoehn et al. (1984) postulated that decreased levels of THMFP observed at high light intensities may be associated with a photorespiratory response by algae. In this case, either the net production or character of the photosynthate released to the external environment may change at high light intensities.

The light relationship of gross DTHMFP production (Fig. 5b) was evaluated within the context of light conditions that occurred in the water column of the reservoir in 1995. Time/depth contours of I values, critical to the structure of the indicated production relationship (Fig. 5b), are presented for two selected days of the study period of 1995 (Fig. 7) that largely bracket light penetration conditions observed (see Doerr et al. 1998) for incident light and light attenuation data (see Effler et al. 1998b). Even under maximum light penetration, production of precursors (i.e., above the dark rate) is essentially limited to depths above the thermocline (Fig. 7a; see Owens et al. 1998). Thus the character of the I response of DTHMFP production (Fig. 5b) is generally consistent with the observed localization of precursor enrichment within the lake's epilimnion (e.g., Fig. 2d, e). The irregular emergence of vertical structure within the epilimnion (e.g., Fig. 2d, e) is consistent with the light dependence indicated in the experiment (Figs. 5b, 2e), though such structure is expected only under low turbulence (e.g., calm) conditions. The lower the water clarity and incident light (e.g., extensive cloud cover) the more unlikely would be the development of vertical structure within the epilimnion (compare Fig. 7a, b). Further laboratory experiments need to be performed to assess the potential dynamics of THM precursor production as a function of I .

Management Perspectives

The findings of this study have both short-term and long-term implications for reservoir managers. For the short-term, deep water withdrawal options can be used during the summer, when possible, to avoid the higher

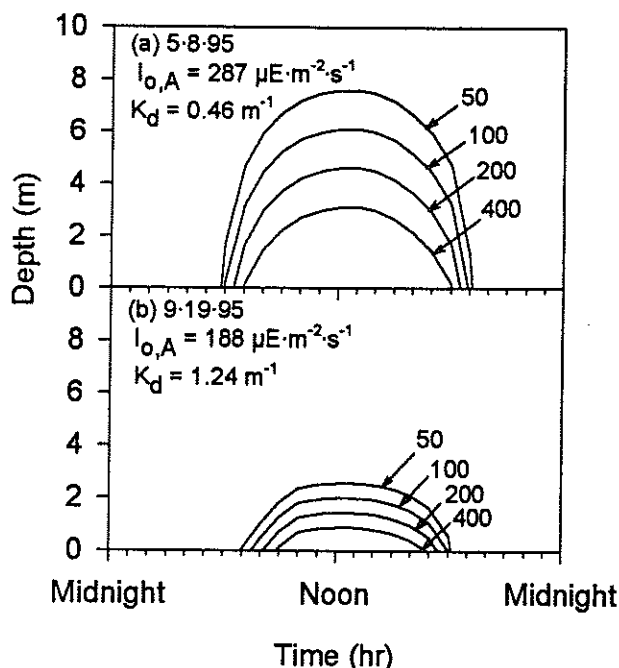


Figure 7.—Specified light intensities ($\mu\text{E} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) in Cannonsville Reservoir as a function of time and depth for 2 days representative of a wide range of light penetration conditions: a) May 8, and b) September 19. $I_{0,A}$ is the average incident light for the day, and K_d is the attenuation coefficient for downwelling irradiance (see Effler et al. 1998b).

THM precursor concentrations that develop in the reservoir's epilimnion. Additionally, filtration would do little to reduce the THMFP in this water supply, as the vast majority of the precursor pool is in a dissolved form. In the long-term, the character, origins and respective contributions of the internal versus external sources of NOM are important in the identification of alternative solutions aimed at its reduction in water supplies. Subsequently, in this issue, Stepczuk et al. (1998b) quantitatively evaluate the autochthonous versus allochthonous contributions to the precursor pool of Cannonsville Reservoir in 1995.

This study indicates, based on the analysis of temporal and spatial patterns of THMFP and the results of a single laboratory experiment, that the autochthonous contribution to the precursor pool of Cannonsville Reservoir is linked to primary productivity. Positive correlations between chlorophyll, organic carbon, and total phosphorus further support a linkage between THM precursor and primary production. Thus, the autochthonous inputs may be abated through a program of eutrophication control that would focus on reductions in phosphorus loading (see Walker 1983). Additional management options have been summarized in Cooke and Carlson (1989). However, the interrelationships between light, primary productivity, watershed nutrient loading, and THM precursor

production, and the lability of internally produced precursors need further resolution and quantification to support potentially expensive related management programs for water supplies. The development of a reliable predictive reservoir model that accommodates these interactions would be a valuable step in managing this water quality issue.

Results of this study indicate that a mechanistic model for THM precursors would need to accommodate the stratification/mixing regime of the reservoir, incident light and light penetration, and the simultaneous operation of precursor source and sink processes. The model analysis presented subsequently in this issue (Stepczuk et al. 1998b) makes contributions in this area by building on the findings of this study and parallel measurements (Stepczuk et al. 1998a) of precursor concentrations and estimation of loads in the reservoir's tributaries. The substantial temporal variability in yield (ratio DTHMFP:DOC) documented here for Cannonsville Reservoir does not support a modeling approach for precursors for this system that would focus on simulation of the overall organic carbon pool, with subsequent prediction of THMFP from a single yield value (Canale et al. 1997).

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References

- Aiken, G. R. and E. Cotsaris. 1995. Soil and hydrology: their effect on NOM. *J. AWWA* 87:36-45.
- Amy, G. L., P. A. Chadik and Z. K. Chowdhury. 1987. Developing models for predicting trihalomethane formation potential and kinetics. *J. AWWA* 79:89-97.
- APHA. 1992. Standard methods for the examination of water and wastewater. 18th edition, American Public Health Association, Washington, DC.
- Auer, M. T. and B. E. Forrer. 1998. Development and parameterization of a kinetic framework for modeling light- and phosphorus-limited phytoplankton growth in Cannonsville Reservoir. *Lake and Reserv. Manage.* 14(2-3):290-300.
- Briley, K. F., R. G. Williams, K. E. Longley and C. A. Sorber. 1980. Trihalomethane production from algal precursors. P. 117-129. *In:* R. L. Jolley, W. A. Brungs and R. B. Cumming (eds.). *Water chlorination: environmental impact and health effects*, Vol. 3. Ann Arbor Science Publishers, Inc., MI.
- Canale, R. P., S. C. Chapra, G. L. Amy and M. A. Edwards. 1997. Trihalomethane precursor model for Lake Youngs, Washington. *J. Wat. Resour. Plan. Manage.* ASCE 123:259-265.
- Chapra, S. C. and K. H. Reckhow. 1983. *Engineering approaches for lake management*, Vol. 2: Mechanistic modeling. Butterworth Publishers, Boston, MA. 492 p.
- Chrost, R. J., U. Munster, H. Rai, D. Albrecht, K. Witzel and J. Overbeck. 1989. Photosynthetic production and exoenzymatic degradation of organic matter in the euphotic zone of a eutrophic lake. *J. Plankton Res.* 11:223-242.
- Cole, J. J., G. E. Likens and D. L. Strayer. 1982. Photosynthetically produced dissolved organic carbon: an important carbon source for planktonic bacteria. *Limnol. Oceanogr.* 27:1080-1090.
- Cole, J. J., S. Findley and M. L. Pace. 1988. Bacterial production in fresh and saltwater ecosystems: a cross-system overview. *Mar. Ecol. Prog. Ser.* 43:1-10.
- Cooke, G. D. and R. E. Carlson. 1989. *Reservoir management for water quality and THM precursor control*. AWWA Research Foundation. 387 p.
- Davies-Colley, R. J. and W. N. Vant. 1987. Absorption of light by yellow substance in freshwater lakes. *Limnol. Oceanogr.* 32:416-425.
- Devore, J. and R. Peck. 1986. *Statistics: the exploration and analysis of data*. West Publishing Co., New York, NY. 699 p.
- Doerr, S. M., E. M. Owens, R. K. Gelda, M. T. Auer and S. W. Effler. 1998. Development and testing of a nutrient-phytoplankton model for Cannonsville Reservoir. *Lake and Reserv. Manage.* 14(2-3):301-321.
- Edzwald, J. K., W. C. Becker and K. L. Wattier. 1985. Surrogate parameters for monitoring organic matter and THM precursors. *J. AWWA* 77:122-132.
- Effler, S. W. and A. Bader. 1998. A limnological analysis of Cannonsville Reservoir, NY. *Lake and Reserv. Manage.* 14(2-3):125-139.
- Effler, S. W., R. K. Gelda, D. L. Johnson and E. M. Owens. 1998a. Sediment resuspension in Cannonsville Reservoir. *Lake and Reserv. Manage.* 14(2-3):225-237.
- Effler, S. W., M. G. Perkins and D. L. Johnson. 1998b. The optical water quality of Cannonsville Reservoir: spatial and temporal patterns, and the relative roles of phytoplankton and inorganic tripton. *Lake and Reserv. Manage.* 14(2-3):238-253.
- Fahnenstiel, G. L., J. F. Chandler, H. J. Carrick and D. Scavia. 1989. Photosynthetic characteristics of phytoplankton communities in Lakes Huron and Michigan: P-I parameters and end-products. *J. Great Lakes Res.* 15:394-407.
- Feuillade, M., J. Feuillade and V. Fiala. 1990. The effect of light on the release of organic compounds by the cyanobacterium *Oscillatoria rubescens*. *Can. J. Fish. Aquatic Sci.* 52:346-359.
- Field, S. D. and S. W. Effler. 1982. Photosynthesis-light mathematical formulations. *J. Envir. Engn. Div. ASCE* 108:199-203.
- Gajewski, A. J. and R. J. Chrost. 1995. Production and enzymatic decomposition of organic matter by microplankton in a eutrophic lake. *J. Plank. Res.* 17:709-728.
- Goel, S., R. M. Holzalski and E. J. Bouwer. 1995. Biodegradation of NOM: effect of NOM source and ozone dose. *J. AWWA* 87:90-105.
- Hoehn, R. C., D. B. Barnes, B. C. Thompson, C. W. Randall, T. J. Grizzard and P. T. Shaffer. 1980. Algae as sources of trihalomethane precursors. *J. AWWA* 72:344-350.
- Hoehn, R. C., K. L. Dixon, J. K. Malone, J. T. Novak and C. L. Randall. 1984. Biologically induced variations in the nature and removability of THM precursors by alum treatment. *J. AWWA* 76:134-141.
- Hutchinson, G. E. 1957. *A treatise of limnology*. Vol. I: geography physics and chemistry. John Wiley and Sons, NY.
- Hutchinson, G. E. 1967. *A treatise of limnology*. Vol. II: introduction to lake biology and the limnoplankton. John Wiley and Sons, NY.
- Jassby, A. D. and T. Platt. 1976. Mathematical formulation of the relationship between photosynthesis and light for phytoplankton. *Limnol. Oceanogr.* 21:540-547.
- Karimi, A. A. and P. C. Singer. 1991. Trihalomethane formation in open reservoirs. *J. AWWA* 83:84-88.
- Kimmel, B. C. and A. W. Groeger. 1984. Factors controlling primary production in lakes and reservoirs: a perspective. P. 277-281. *In:* *Lake and Reserv. Manage.* EPA 440/5-84-001.
- Longabucco, P. and M. Rafferty. 1998. Analysis of material loading to

- Cannonsville Reservoir: advantages of event-based sampling. *Lake and Reserv. Manage.* 14(2-3):197-212.
- Lovell, C. R. and A. Konopka. 1985. Excretion of photosynthetically fixed organic carbon by metalimnetic phytoplankton. *Microb. Ecol.* 11:1-9.
- Martin, A. B., G. D. Cooke and R. E. Carlson. 1993. Lake sediments as potential sources of trihalomethane precursors. *Water. Res.* 27:1725-1729.
- Normann, B., U. L. Zweifel, C. S. Hopkinson and B. Fry. 1995. Production and utilization of dissolved organic carbon during an experimental algal bloom. *Limnol. Oceanogr.* 40:898-907.
- Oliver, B. G. and D. B. Shindler. 1980. Trihalomethanes from the chlorination of aquatic algae. *Environ. Sci. Technol.* 14:1502-1505.
- Owens, E. M., R. K. Gelda, S. W. Effler and J. M. Hassett. 1998. Hydrologic analysis and model development for Cannonsville Reservoir. *Lake and Reserv. Manage.* 14(2-3):140-151.
- Palmstrom, N. S., R. E. Carlson and G. D. Cooke. 1988. Potential links between eutrophication and the formation of carcinogens in drinking water. *Lake and Reserv. Manage.* 4:1-15.
- SAS. 1985. SAS/STAT guide for personal computers, version 6 ed. SAS Institute, Inc. Cary, NC. 1028 p.
- Siegfried, C. A. 1998. An analysis of the plankton of Cannonsville Reservoir, NY. *Lake and Reserv. Manage.* (in review).
- Singer, P. C., J. J. Barry, F. M. Palen and A. E. Scrivner. 1981. Trihalomethane formation in North Carolina drinking waters. *J. AWWA* 73:392-401.
- Stepczuk, C., A. B. Martin, S. W. Effler, J. A. Bloomfield and P. Longabucco. 1998a. Allochthonous contributions of THM precursors in a eutrophic reservoir. *Lake and Reserv. Manage.* 14(2-3):344-355.
- Stepczuk, C. L., E. M. Owens, S. W. Effler, J. A. Bloomfield and M. T. Auer. 1998b. A modeling analysis of THM precursors for a eutrophic reservoir. *Lake and Reserv. Manage.* 14(2-3):367-378.
- Storey, M. L., M. T. Auer, A. K. Barth and J. M. Graham. 1993. Site-specific determination of kinetic coefficients for modeling algal growth. *Ecol. Model.* 66:181-196.
- Symons, J., T. A. Bellar, J. K. Carswell, J. DeMarco, K. L. Dropp, G. G. Robeck, D. R. Seeger, C. J. Slocum, B. L. Smith and A. A. Stevens. 1975. National organics reconnaissance survey for halogenated organics. *J. AWWA* 67:643-647.
- Thomann, R. V. and J. A. Mueller. 1987. Principles of surface water quality modeling and control. Harper and Row, NY. 644 p.
- Thurman, E. M. 1985. Organic geochemistry of natural waters. Nijhoff and Junk Publishers. Dordrecht, Netherlands. 497 p.
- Uhler, A. D. and J. C. Means. 1985. Reaction of dissolved chloride with surficial sediment: oxidant demand and production of trihalomethanes. *Environ. Sci. Technol.* 19:340-344.
- Veenstra, J. N., and J. L. Schnoor. 1980. Seasonal variations in trihalomethane levels in an Iowa river water supply. *J. AWWA* 9:583-590.
- Wachter, J. K. and J. B. Andelman. 1984. Organohalide formation on chlorination of algal extracellular products. *Environ. Sci. Technol.* 18:811-817.
- Walker, W. W. 1983. Significance of eutrophication in water supply reservoirs. *J. AWWA* 75:38-42.
- Wetzel, R. G. 1983. *Limnology* (2nd ed.). Saunders College Publ., NY.
- Wetzel, R. G. 1992. Gradient-dominated ecosystems: Sources and regulating functions of dissolved organic matter in freshwater ecosystems. *Hydrobiologia* 229:181-198.
- Wetzel, R. G., P. G. Hatcher and T. S. Bianchi. 1995. Natural photolysis by irradiance of recalcitrant dissolved organic matter to simple substrates for rapid bacterial metabolism. *Limnol. Oceanogr.* 1380.
- Wodka, M. C., S. W. Effler, C. T. Driscoll, S. D. Field and S. P. Devan. 1983. Diffusivity-based flux of phosphorus in Onondaga Lake. *J. Environ. Eng. ASCE* 105:1403-1415.