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A Modeling Analysis of THM Precursors for a Eutrophic Reservoir[1]

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ABSTRACT

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Mass balance modeling analyses were conducted for trihalomethane (THM) precursors in eutrophic Cannonsville Reservoir to resolve the contributions of allochthonous and autochthonous inputs to the reservoir's precursor pool, and to move toward a predictive tool that would support related management actions. The analyses focus on the April-November interval of 1995, and are supported by detailed external loading (Stepczuk et al. 1998a) and reservoir water column (Stepczuk et al. 1998b) data for precursors. Net autochthonous production of precursors in the epilimnion, apparently driven by primary productivity, was a major source of precursors for the reservoir, representing about two-thirds of the cumulative mass input over the April-mid-summer interval. An undefined loss process(es) operated simultaneously during the study period. Major differences in behavior of the dissolved organic carbon (DOC) and THM precursor pools of the reservoir, depicted by the modeling analysis, are not supportive of the use of DOC as a surrogate estimator of precursor concentration. A preliminary mechanistic precursor model, developed by adding a primary production-based source term and a first order loss/decay term to a eutrophication model for the reservoir (Doerr et al. 1998), performed reasonably well in matching the precursor patterns observed for the lacustrine zone of the reservoir in 1995. An analysis conducted with this model indicates the need to resolve differences in the lability of allochthonous and autochthonous inputs within the model framework.

Key Words: THMFP, THM precursors, NOM, water quality, model, mass balance, mass balance model, mechanistic model, reservoir, eutrophication.

Trihalomethanes (THMs) are an important public health issue for water supply lakes and reservoirs because they have been found to have carcinogenic properties (Krasner et al. 1994). They are presently regulated under Safe Drinking Water Act standards; tightening of this standard, based on the Disinfectants/Disinfection/By-Products Rule, is expected. THMs are a subset of a group of compounds known as disinfection-by-products (DBPs), all of which are formed from the

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reaction of chlorine with naturally occurring organic matter (NOM). The fraction of NOM known as THM precursors (measured as THM formation potential, or THMFP), which reacts with chlorine during the disinfection process in water supplies to form THMs, originates from two sources: 1) the watershed (allochthonous), primarily in the form of humic and fulvic acids (Rook 1974, 1976), and 2) within the reservoir itself (internal, or autochthonous, production). Autochthonous formation of precursors has been associated with primary production (Hoehn et al. 1980, 1984, Palmstrom et al. 1988, Stepczuk et al. 1998b). Thus, reduction in phosphorus loading represents a potential option to reduce autochthonous THM precursor production (Cooke and Carlson 1989, Walker 1983). Resolution of the relative contributions of allochthonous and autochthonous sources of THM precursors in water supply lakes and reservoirs would be valuable in guiding managers in the evaluation of the effectiveness and cost/benefit characteristics of various strategies for reducing precursor concentrations prior to disinfection (Aiken and Cotsaris 1995, Cooke and Carlson 1989, Krasner et al. 1994) in order to meet regulatory requirements.

Credible mechanistic mass balance quality models have been developed to simulate the behavior of a wide variety of constituents in surface waters (Chapra 1997, Chapra and Reckhow 1983, Thomann and Mueller 1987). Models support basic research by providing a quantitative framework for the synthesis of scientific data and the development and testing of hypotheses. Once the credibility of a model has been established through rigorous testing, the model becomes an invaluable quantitative predictive tool to support management deliberations (Chapra 1997, Thomann and Mueller 1987).

Mass balance modeling analyses are presented here for eutrophic Cannonsville Reservoir for the April-November interval of 1995 to: 1) resolve the contributions of autochthonous and allochthonous inputs to the reservoir's THMFP pool, 2) gain insights concerning the in-reservoir behavior of precursors, 3) identify desirable features of a mechanistic model for precursors, 4) provide preliminary mechanistic model simulations of the precursor pool, and 5) identify study needs that may lead to a credible predictive management model for precursors. This analysis takes advantage of unusually comprehensive loading (Stepczuk et al. 1998a) and in-reservoir (Stepczuk et al. 1998b) data sets for THMFP. Three different analytical frameworks have been adopted that represent a wide range of complexity. First, a relatively simple overall mass balance analysis for THMFP was conducted for the reservoir to estimate the seasonal variation of net autochthonous production. Second, a two-layer mass balance model for precursors that accommodates the fundamental transport processes of the system (Owens 1998a), was used to assess the seasonality of internal production of precursors in the epilimnion and hypolimnion. The last, and most complex, approach used was a one-dimensional multi-layer eutrophication model of the reservoir (Doerr et al. 1998) that was modified to accommodate primary production-based production of precursors and decay/loss processes to simulate the distribution of THMFP. Recommendations are made to extend this work toward the development of a general mechanistic model that would serve as a reliable management tool for precursors in lakes and reservoirs.

System Description and Related Studies

Cannonsville Reservoir is a eutrophic (Effler and Bader 1998), flow augmentation and water supply impoundment located in Delaware County, New York (Fig. 1). It is the third largest (373×10^6 m^3) reservoir in the New York City water supply. Details of the reservoir's morphometry, watershed characteristics, hydrology and water quality characteristics have been described (Effler and Bader 1998, Owens et al. 1998, Stepczuk et al. 1998b). Longabucco and Rafferty (1998) have quantified material loading for a number of water quality constituents of concern in this system and have described their sources. The reservoir's main tributary, West Branch Delaware River (WBDR), drains ~ 80% of the 1160 km^2 watershed (Fig. 1), while the remaining drainage consists of 10 smaller streams, of which Trout Creek is the largest (5%). Water outflows are of three types: spill and hypolimnetic release at the dam, and a water supply intake at the mid-reservoir sampling location (site 4, Fig. 1). The intake has openings at three depths (10, 20 and 37 m for a full reservoir), but water is almost always withdrawn from the 20-m intake.

Detailed tributary (2 sites; Stepczuk et al. 1998a) and in-reservoir (3 sites; Stepczuk et al. 1998b) monitoring (Fig. 1) was conducted from April to November 1995 to define and characterize loads and the dynamics of the reservoir THM precursor pool. External loads (Stepczuk et al. 1998a) were calculated according to methods described by Longabucco and Rafferty (1998). The detailed vertical profiles of THMFP from site 4 (Fig. 1; Stepczuk et al. 1998b) were used to calculate the mass of precursors in the reservoir. Nearly all (94%) of the THMFP found in the external load and the in-reservoir pool was in the dissolved form (Stepczuk et al. 1998a, b). Here, total THMFP is used to be

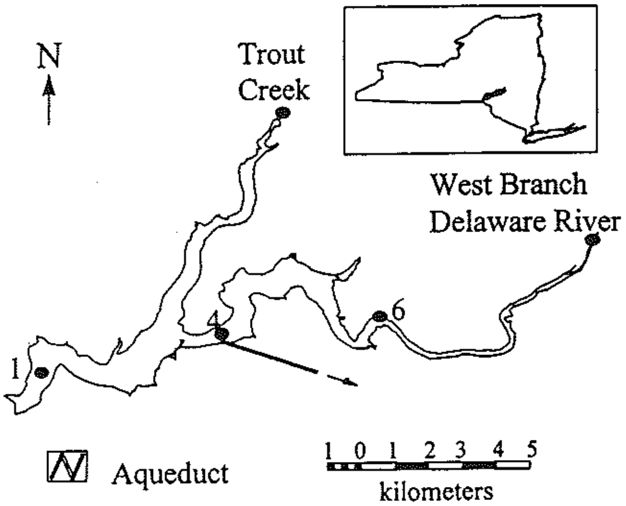

Figure 1.–Map of Cannonsville Reservoir, showing reservoir (3) and tributary (2) sampling stations.

consistent with prevailing management and regulatory perspectives. Dissolved organic carbon (DOC) was included in portions of this analysis to continue to evaluate its use as a potential surrogate for THMFP (Canale et al. 1997, Stepczuk et al. 1998a, b).

Inflow to the reservoir was relatively low throughout the April-September interval (Fig. 2a). As a result, a major drawdown occurred in the reservoir (Fig. 2b) to augment downstream flows. Reservoir volumes increased during the fall in response to several runoff events (Fig. 2a). Longitudinal differences in a number of water quality parameters, including THM precursors, have occurred between the riverine and lacustrine zones (e.g., Effler and Bader 1998), but uniform distributions of THM precursors prevailed within the lacustrine zone (Stepczuk et al. 1998b). Concentrations of precursors in the epilimnion were higher than those observed for the hypolimnion or inflows for most of the study period (Fig. 2c), representing clear evidence of autochthonous THM precursor production. The lacustrine epilimnetic THMFP maximum of mid-July was 360 $\mu g \cdot L^{-1}$; substantially greater than concentrations in the hypolimnion and WBDR inflow (270 and 230 $\mu g \cdot L^{-1}$, respectively). Thereafter, concentrations in the upper layer declined, possibly due to flushing by the more dilute inflows, an imbalance between export and loading in late summer, and/or the operation of a loss process which exceeded production. There is strong circumstantial evidence that autochthonous production of THM precursors in Cannonsville Reservoir in 1995 was linked to primary productivity, including: 1) the occurrence of the highest THMFPs in the upper layer, 2) a longitudinal distribution of THMFP concentrations that tracked trophic state indicators (Effler and Bader 1998), 3) a distinct seasonal pattern which was generally consistent with the seasonality of primary production in north temperate lakes, and 4) the results of a laboratory experiment which determined chlorophyll-specific THMFP production as a function of light (Stepczuk et al. 1998b). Further, Stepczuk et al. (1998b) presented evidence that the sediments were not an important source of precursors to the reservoir's water column (also see Martin et al. 1993).

Modeling Analyses

Overall Reservoir Mass Balance

The equation which underlies the general mass balance analysis for the entire reservoir may be expressed as

$$\Delta M = W - E + S \tag{1}$$

where ΔM is the change in mass stored in the water column of the reservoir over a time interval, W is the

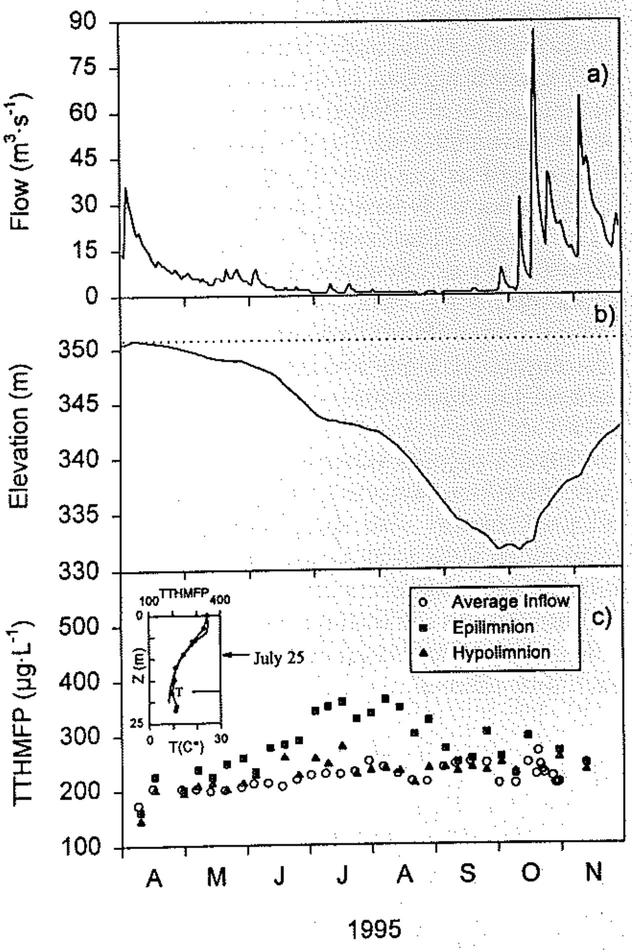

Figure 2.–April-November 1995 data in Cannonsville Reservoir: a) daily hydrograph for the mouth of WBDR, b) water surface elevation, and c) THMFP in the epilimnion, hypolimnion (Stepczuk et al. 1997b) and inflows (Stepczuk et al. 1997a).

allochthonous mass loading from tributaries over the interval, E is mass export over the interval associated with water flowing out of the reservoir, and S is the net autochthonous production/loss of mass within the reservoir. The value of S incorporates gross production processes and decay (loss) processes. The decay processes may operate on allochthonous as well as autochthonous inputs. However, allochthonous inputs are often comparatively recalcitrant (e.g., Wetzel 1992). Rearranging Eq. (1) yields an expression for S as

$$S = \Delta M - W + E \tag{2}$$

The terms on the right side of Eq. (2) were calculated from tributary and reservoir monitoring data, allowing estimation of net autochthonous production, S. The magnitude of S, relative to allochthonous loading, is represented by the ratio S/W.

Values of M were computed on days when reservoir monitoring was conducted according to

$$M = \Sigma C_i \Delta V_i \tag{3}$$

where C_i is the measured concentration in layer i, (V_i is the water volume of layer i, and the summation is performed over the entire volume of the reservoir for each monitoring day. Daily loading rates determined by Stepczuk et al. (1998a) were summed to determine W for a given interval. The daily average export, E, was determined as the sum of rates associated with the three forms of reservoir outflow: spill, release, and water supply withdrawal (Owens et al. 1998). Each export rate was calculated as the product of a water export rate, as incorporated in the hydrologic model of Owens et al. (1998), and an associated precursor concentration. Daily average water export rates for each of the three outflows were obtained from New York City Department of Environmental Protection (NYCDEP) records (Owens et al. 1998). Epilimnetic concentrations (Stepczuk et al. 1998b) were used to calculate export with spill, and hypolimnetic concentrations were used to calculate export associated with release. Export associated with water supply withdrawals was calculated using the appropriate layer concentration for the operative withdrawal depth for each time interval.

Two-Layer Model Analysis

A two-layer model divided the reservoir volume into two completely mixed layers, the epilimnion (volume V_E) and the hypolimnion (volume V_H) that are separated by the thermocline. This simple structure accommodates the vertical distribution of precursors observed in the reservoir (e.g., see inset of Fig. 2c, also Stepczuk et al. 1998b). The two-layer framework has been adopted widely for models of other water quality constituents with vertical distributions sensitive to thermal stratification (Chapra 1997). The hydrologic model of Owens et al. (1998) specified all inflows and outflows. Thermocline depth was determined from observed temperature profiles, and hypsographic data (Owens et al. 1998) for the reservoir basin were used to calculate V_E and V_H over time. Volume-weighted concentrations of THMFP were calculated for each layer from profiles reported for site 4 (Stepczuk et al. 1998b).

The equations for constituent mass balance for the epilimnion (E) and hypolimnion (H), respectively, are

$$\frac{d}{dt}(V_E C_E) = W_E - Q_{OE} C_E - v_T A_T (C_E - C_H) + Q_V C^* + V_E S_E \tag{4a}$$

$$\frac{d}{dt}(V_H C_H) = W_H - Q_{OH} C_H - v_T A_T (C_E - C_H) + Q_V C^* + V_H S_H \tag{4b}$$

where C_E and C_H are THMFP concentrations, W_E and W_H are tributary loading rates, Q_{OE} and Q_{OH} are layer outflows, v_T is a mass transfer coefficient which quantifies mixing between the two layers, A_T is the area of the thermocline, Q_v is the water flow across the thermocline, C^* is the concentration of THMFP associated with the water flow Q_v, and s_E and s_H are the rates of net internal production/loss per unit volume in each layer. This model is operated by specifying initial conditions for C_E and C_H at the start of the simulation (observed conditions on April 11) and integrating Eq. (4) to yield a predicted variation of C_E and C_H over time.

Since all watershed tributaries enter at the shoreline, it was assumed that all tributary water and constituent loading is to the epilimnion. Thus, W_E is set to equal the total loading rate, and $W_H = 0$. The outflow rates Q_{OE} and Q_{OH} consider the vertical location of the three outflows, with spillway flow contributing to Q_{OE}, dam release contributing to Q_{OH}, and drinking water withdrawal occurring from either the upper or lower layer depending on the depth of the active withdrawal relative to the thermocline. The mass transfer coefficient, v_T, is determined through the application of an analogous two-layer temperature model for the reservoir, and is based on measured temperature profiles (Owens 1998a).

Linkage To Eutrophication Model

A eutrophication model that utilizes an independently tested, one-dimensional, multi-layer transport model (Owens 1998b) has been developed and tested for the lacustrine zone of Cannonsville Reservoir (Doerr et al. 1998). The transport model routes inflows to a layer according to their density, as mediated by mixing processes (Owens 1998b). The underflow phenomenon prevailed for certain intervals in the 1995 study period (Owens 1998a), but accommodation of this in the transport submodel (Owens 1998b) does not substantively influence simulations of precursor concentrations. The eutrophication model simulated phosphorus and nitrogen cycling, phytoplankton growth, and loss processes in the reservoir (see Doerr et al. 1998). Phytoplankton biomass [as indicated by the concentration of chlorophyll (chl)] was simulated as a function of nutrients, light and temperature. THMFP has been added here to this model as a state variable and is partitioned between two pools, precursors supplied from allochthonous inputs ($THMFP_{al}$) and precursors produced autochthonously ($THMFP_{au}$). Internal precursor production was simulated as a function of depth and time based on simulated chl concentrations and light intensity according to the following expression, which was developed from the results of an experiment reported by Stepczuk et al. (1998b; see Fig. 6 of that manuscript)

$$\text{autochthonous production} = \left(R_{max} * \left[\frac{I}{I_{sat}} * e^{\left(\frac{-I}{Isat} + 1 \right)} \right] * chl \right) \tag{5}$$

where R_{max} = maximum rate ($5\ \mu g\ THMFP \cdot \mu g\ chl^{-1} \cdot d^{-1}$) of $THMFP_{au}$ production, I = irradiance, and I_{sat} = light saturation ($150\ \mu E \cdot m^{-2} \cdot s^{-1}$). The form of the expression is that used by Steele (1962) to accommodate the effects of photoinhibition on phytoplankton growth. Accordingly, autochthonous production was greatest in sub-surface layers (within the epilimnion), but very limited below the thermocline (Effler et al. 1998).

The following first order loss terms for $THMFP_{au}$ and $THMFP_{al}$ were included to represent loss processes:

$$\text{decomposition of autochthonous component} = k_{L(au)} * THMFP_{au} \tag{6a}$$

$$\text{decomposition of allochthonous component} = k_{L(al)} * THMFP_{al} \tag{6b}$$

where $k_{L(au)}$ and $k_{L(al)}$ are first order loss coefficients (d^{-1}) for autochthonous and allochthonous portions of the THMFP pool. Temperature adjustments for the coefficients $k_{L(au)}$ and $k_{L(al)}$ were made according to the widely used (Bowie et al. 1985) Arrhenius format

$$k_{L,T} = k_{L,20} * \theta^{(T-20)} \tag{7}$$

where $k_{L,T}$ and $k_{L,20}$ are values of k_L at temperature T and 20/C, respectively, and θ (= 1.03) is a dimensionless temperature coefficient (e.g., Bowie et al. 1985, Thomann and Mueller 1987). Initial conditions were based on observations for April 11. Volume-weighted concentrations of THMFP were calculated for the epilimnion and hypolimnion from observations (Stepczuk et al. 1998b) and from output of the multi-layer model to support evaluation of model performance. Thermocline depths were specified from the simulations of the calibrated and verified one-dimensional hydrothermal transport submodel (Owens 1998b).

Results and Discussion

Overall Reservoir Mass Balance

Widely different temporal patterns emerged for the various components of the THMFP mass balance over the analysis interval of 1995 (cumulative masses of each presented in Fig. 3a). The cumulative external load (W) increased relatively slowly during the dry weather period, but increased more rapidly when inflows increased in fall (Fig. 3a, also see Fig. 2a). Export (E) was decidedly greater than W over this interval (Fig. 3a) because outflows exceeded inflows (i.e., water surface elevation decreased, Fig. 2b) and concentrations in the reservoir, particularly in the epilimnion, exceeded those in the tributaries (Fig. 2c). The storage term, ΔM (or change in reservoir mass), increased initially in response to early increases in THMFP within the reservoir (Fig. 2c), which more than compensated for the early loss of volume from drawdown (Fig. 2b), but decreased progressively from early September through early October (Fig. 3a) as a result of the continued drawdown of the reservoir. A net loss of in-reservoir THMFP mass, relative to that observed initially on April 11, occurred by about mid-August (Fig. 3a), when the reservoir had been reduced to 55% of its full capacity (see Fig. 2b).

Net autochthonous production of precursors was evident in the reservoir over the study period (S>0, Fig. 3a). The cumulative mass, represented by S, increased in a progressive manner through mid-July, and subsequently decreased through most of the remainder of the study period (Fig. 3a). It is instructive to consider these findings over selected time segments of the study period, and within the context of relative magnitudes of the net autochthonous (S) and

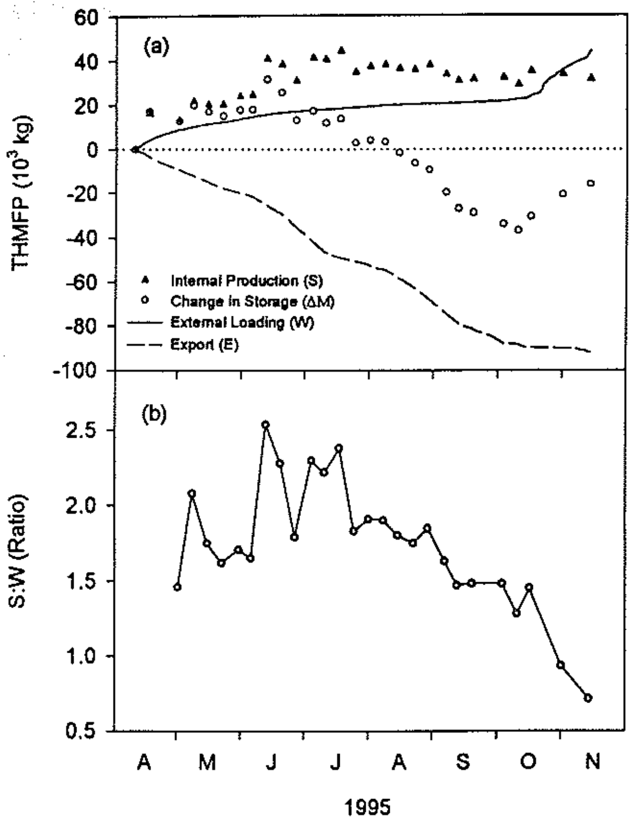

Figure 3.–Mass balance analysis of observed THMFP in Cannonsville Reservoir, based on April-November 1995 in-reservoir and inflow data: a) cumulative mass of mass balance components, internal (net autochthonous) production (S) determined by difference [Eq. (2)], and b) ratio of net autochthonous: allochthonous (S:W) THMFP mass during the study period.

allochthonous (W) sources (Fig. 3b; Table 1). Three time segments are considered here: 1) from the start of the study to July 18 (the day of maximum S), 2) July 18 to the end of the study, and 3) the entire study period (Table 1). The estimated net internal production of precursors by mid-July was about 44 x 10^3 kg (Table 1). This is about 40% greater than the value of S (~31 x 10^3 kg) for the entire interval, establishing there was a net loss of THMFP (~13 x 10^3 kg, Table 1) from the water column of the reservoir over the later time segment. These findings support the position that there were both source and sink processes for THMFP in the water column; i.e., sources > sinks (S increasing) for the first segment, and sources < sinks (S decreasing) for the later segment.

The autochthonous sources of precursors were relatively more important than allochthonous inputs in this eutrophic reservoir; i.e., the ratio S:W was ≥ 1.0 (1.0 corresponds to equal net autochthonous and allochthonous contributions) from late April until late October (Fig. 3b). Cumulatively, net inputs from internal production were estimated to have contributed more than two-thirds of the total input (i.e., S:W > 2.0) to the reservoir in portions of June and July of 1995 (Fig. 3b). Subsequent decreases in the contribution of net autochthonous inputs (Fig. 3b) reflect first the operation of the sink process(es), and later the abrupt, runoff-event-based increase in external loading (W, Fig. 3a).

The results of the mass balance analysis for DOC were superficially similar (compare Fig. 4a to Fig. 3a); i.e., there was a clear net autochthonous contribution (S>0) to the reservoir's DOC pool. However, closer inspection reveals distinct differences in the relative magnitude and timing of internal production of DOC relative to THMFP (compare Fig. 4b to Fig. 3b). Internal production of THMFP was distinctly greater relative to external loads (S:W); the average ratio for precursors was 1.7 for the study period, compared to 0.7 for DOC. Further, a conspicuous mid-summer minimum occurred in the DOC ratio (Fig. 4b) that was not observed for THMFP (Fig. 3b). The seasonal patterns of net production/loss, determined at monthly intervals for THMFP and DOC were uncorrelated (r<0.3, Fig. 5). These differences in behavior continue to underscore (see Stepczuk et al. 1998a,b) the limitations of using DOC as a surrogate estimator for THMFP. The results presented here (Figs. 3 to 5) indicate that the in-reservoir dynamics of THMFP (a component of DOC) differ substantially from those of the larger DOC pool. Primary production appears to drive (at least in

Table 1.–Example mass balance calculations (values in 10^3 kg).

Model Parameter	April 11-Jul. 18*	July 18-Nov. 13**	April 11-Nov. 13
M	14.0	-30.1	-16.1
W	18.6	25.7	44.3
E	48.7	43.1	91.8
S	44.1	-12.7	31.4

* Include the results for the period of increasing S (net production).
** Include the results for the period of decreasing S (net loss).

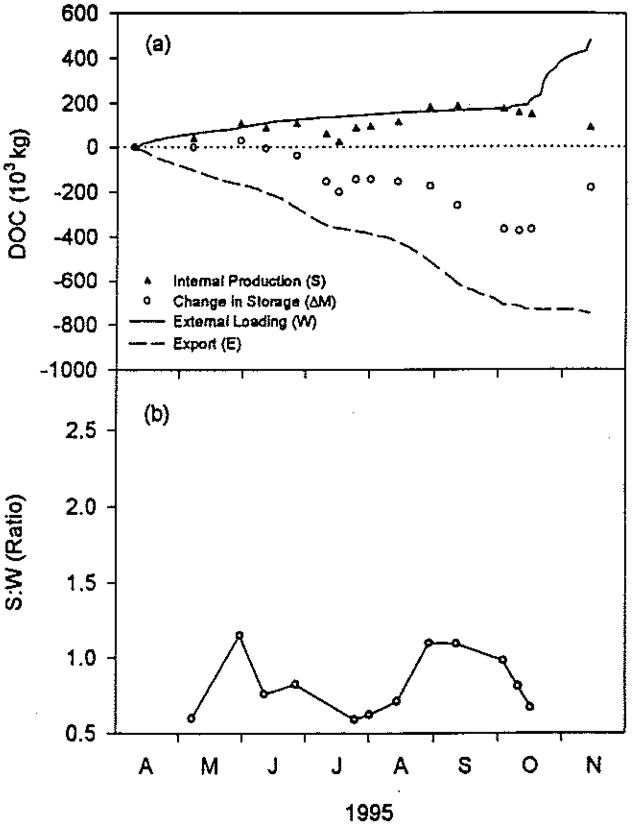

Figure 4.–Mass balance analysis of observed DOC in Cannonsville Reservoir, based on April-November 1995 in-reservoir and inflow data: a) components, internal (net autochthonous) production (S) determined by difference [Eq. (2)], and b) ratio of net autochthonous: allochthonous (S:W) THMFP mass during the study period.

part) the autochthonous production of both THMFP and DOC, but perhaps the precursor component is preferentially influenced. Further, different loss rates may be operating for the larger DOC pool versus the THM precursor pool. For example, photolytic or bacterial degradation rates may differ for THM precursors and the other components of the DOC pool. The photolytic effects of light on organic matter, particularly within the UV range, have been described (Wetzel 1995). Li et al. (1996) reported decreases in TOC concentrations upon exposure to UV light, yet increases in THMFP concentrations were observed, depicting an uncoupled behavior for these pools. Bacterial degradation rates would also be expected to vary among different forms of DOC (Wetzel 1992).

This analysis provides an estimate of net autochthonous production within the entire reservoir and depicts its temporal pattern in 1995. Differing hydrologic conditions almost certainly would result in different relative contributions of autochthonous and allochthonous sources to the reservoir's precursor pool. However, anticipating the effect of different hydrologic conditions on the overall THMFP pool, and the relative contributions of internal and external inputs, would be difficult without the benefit of a predictive model. For example, increased allochthonous loading of THM precursors, that may occur in a high runoff year (see Stepczuk et al. 1998a), may be accompanied by increased nutrient loading, and subsequent higher net autochthonous production in the reservoir, resulting in increases in both components of the precursor pool.

Two-layer Mass Balance Model

The first simulation with the two-layer mass balance model treated THMFP as a conservative substance; i.e., the in-reservoir reaction terms for the two layers, s_E and s_H [Eqs. (4a and b)], were set to zero. The absence of decay of allochthonous inputs is implicit in this scenario. Little temporal structure emerged for this simulation (Fig. 6a) because of the low stream flows, until the higher runoff period of October and November (Fig. 2b). More importantly, this simulation greatly underpredicts the observed reservoir concentrations of THMFP (particularly for the epilimnion, Fig. 6a), confirming the position (Fig. 3a) that autochthonous sources contributed substantially to the precursor pool in the reservoir during this period.

Next, the reaction terms were adjusted in both layers so that predictions matched observed data (Fig. 6a). The intent of this curve-fitting exercise is to

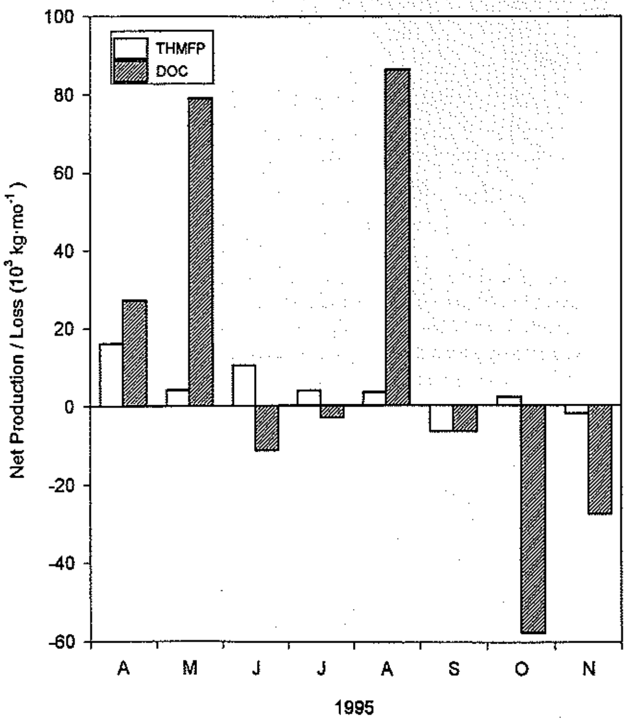

Figure 5.–Estimated net monthly production of THMFP and DOC over the April-November 1995 study period.

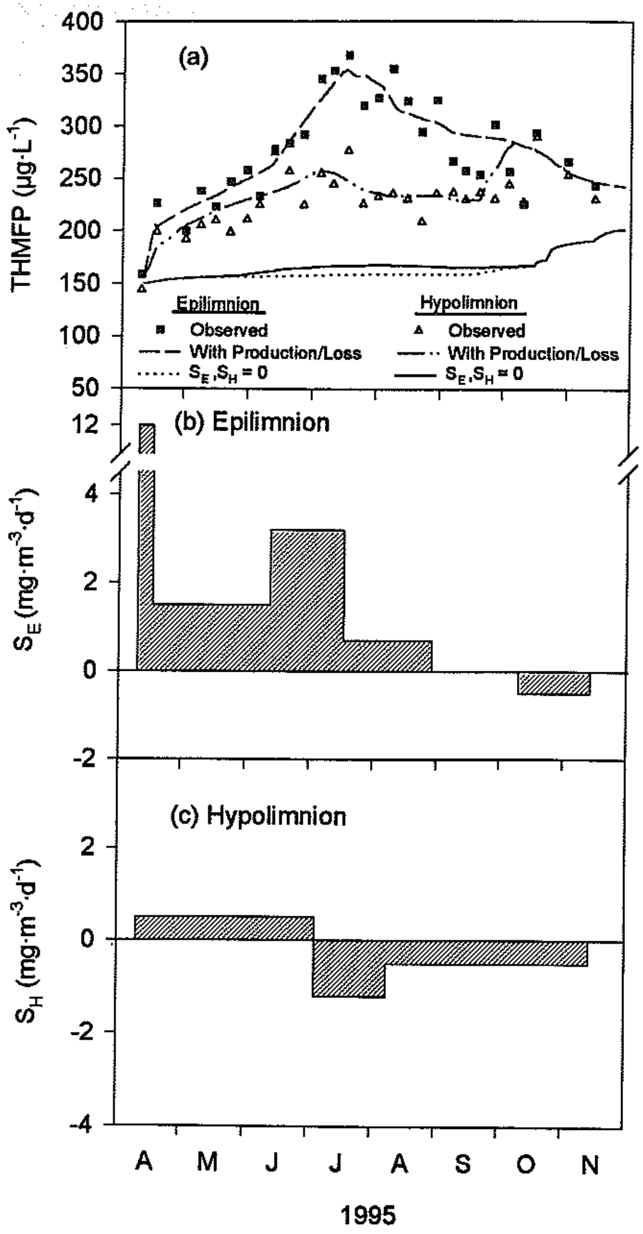

Figure 6.–Two-layer mass balance model simulations of THMFP in Cannonsville Reservoir: a) simulations for the epilimnion and hypolimnion for the two scenarios, conservative behavior, and adjustments in s_E and s_H to match observations (curve-fitting), b) time distribution of s_E from curve fit, and c) time distribution of s_H from curve fit.

assess the magnitude, seasonality, vertical differences, and source/sink character of the reaction terms, s_E and s_H, and to gain insights into the process/kinetic needs of a predictive mechanistic model for precursors. The values of s_E and s_H, determined in this way, differed substantially (Fig. 6b and c). The net production term for the epilimnion (s_E) varied over time (Fig. 6b), with the highest production rate (12 mg · m^{-3} · d^{-1}) in April. Excluding this high initial rate, an average rate of ~ 2 mg · m^{-3} · d^{-1} characterized the epilimnion between April and mid-July (Fig. 6b). Source and sink terms were balanced in this layer during September, followed by a net loss of 0.5 mg · m^{-3} · d^{-1} during October. A relatively small net source was determined for the hypolimnion (s_H) for the April- to mid-July interval (~ 0.1 mg · m^{-3} · d^{-1}), followed by a loss (avg. = -0.9 mg · m^{-3} · d^{-1}) thereafter (Fig. 6c). This vertical structure, and the limited light penetration in the reservoir (Effler et al. 1998), are consistent with other observations (Stepczuk et al. 1998b) that indicate autochthonous production of precursors in the reservoir in 1995 was linked to primary production. The particularly high production determined for the first week of the study in April (Fig. 6b), associated with the abrupt increase in THMFP (Fig. 6a), tends to draw into question the validity of the earliest measurements. However, we have no sound basis to reject these data.

Stepczuk et al. (1998b) suggested that the modest increases in hypolimnetic THMFP in 1995 were conceptually consistent with vertical mixing-based inputs (e.g., Wodka et al. 1983) from the enriched epilimnion. This two-layer model represents an appropriate framework to test that hypothesis. To evaluate this hypothesis a simulation was made that invoked no reactions in the hypolimnion (i.e., $s_H = 0$), but retained the curve fit distribution determined for s_E (Fig. 6b). The predicted changes for the epilimnion (feedback from changes in hypolimnion predictions mediated by vertical mixing) were insignificant (Fig. 7). This simulation captured the overall seasonal structure of THMFP in the hypolimnion, but underpredicted the spring to early summer interval and overpredicted in the fall. The root mean square error (RMSE) of the predicted THMFP for the lower layer for the conservative case was 58 µg · L^{-1} (see Fig. 7) compared to 39 µg · L^{-1} for the curve fit case (Fig. 6a). The favorable performance of the simulation in which $s_H = 0$ supports the position that vertical mixing was important in mediating the observed temporal pattern in THMFP in the reservoir's hypolimnion in 1995. Further, the somewhat conservative behavior of the hypolimnetic pool (Fig. 7) indicates a recalcitrant character for the precursors that comprised this pool at the onset of stratification. The THMFP pool of the reservoir in spring probably reflects allochthonous sources, which are known (e.g., Wetzel 1992) to be in rather recalcitrant forms relative to the larger DOC pool of most lotic systems.

Eutrophication Model Analysis

As a first step, the precursor production expression [Eq. (5)] that is linked to primary production (Stepczuk et al. 1998b) was incorporated into the calibrated

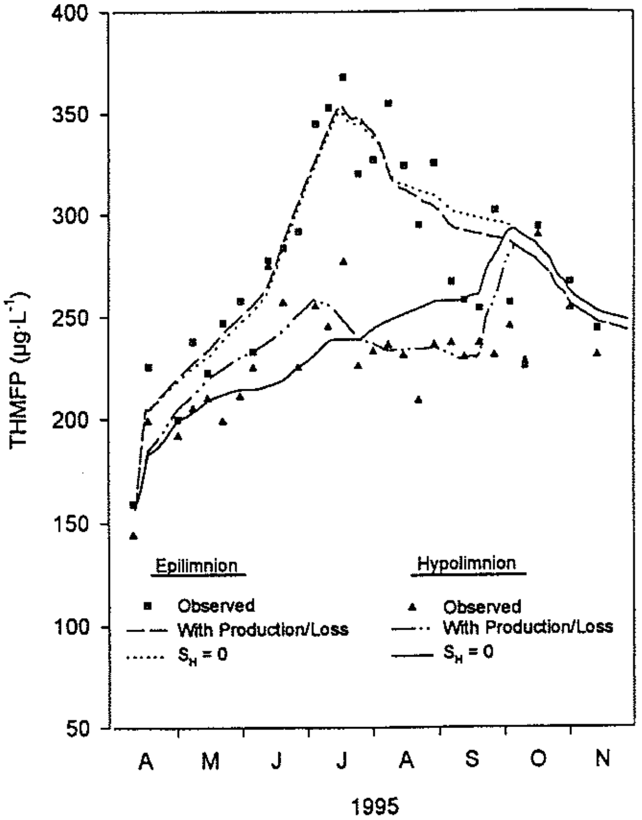

Figure 7.–Two-layer model simulation of THMFP with $S_H = 0$, and S_E as shown in Fig. 6b.

eutrophication model for the reservoir (Doerr et al. 1998) without the addition of a precursor loss process [e.g., Eq. (6)]. This simulation greatly overpredicted the THMFP concentrations measured in the reservoir's epilimnion. Next, the first order loss process was added [Eq. (6)] without differentiating decay of allochthonous versus autochthonous portions of the precursor pool (i.e., $k_{L(au)} = k_{L(al)}$). A value of k_L that produced adequate simulation of the epilimnetic pattern resulted in gross underpredictions of hypolimnetic concentrations of THMFP, which progressively worsened through the stratified period. The decay was then limited to the epilimnion, with equal decay rates for autochthonous and allochthonous contributions to the precursor pool of that layer. Only the value of k_L was adjusted during the calibration effort for this modeling approach. The fit obtained with $k_L = 0.08$ d^{-1} showed some promising performance features (Fig. 8a), particularly for the epilimnion. However, hypolimnetic concentrations were underpredicted, and predictions of major decreases in THMFP throughout the water column during fall turnover were not observed (Fig. 8a). This framework is consistent with the largely allochthonous origins of the hypolimnetic precursor pool at the onset of stratification and the known recalcitrant character of external DOC inputs for many streams (e.g., Wetzel 1992). However, this framework does not accommodate differences in the lability of the autochthonous and allochthonous components of the precursor pool in the reservoir's epilimnion where internally produced precursors are the major contributors (e.g., Fig. 6b).

Partitioning decay of the autochthonous and allochthonous components of the precursor pool resulted in further improvements in model performance (Fig. 8b). The allochthonous component was assumed to be conservative (i.e., $k_{L(al)} = 0$). The best performance was obtained with $k_{L(au)} = 0.15$ d^{-1}. The fit of the epilimnetic pattern (e.g., RMSE = 33) was better (Fig. 8b) than obtained with the preceding unpartitioned decay approach (e.g., RMSE = 50; Fig. 8a). The much better fit during fall turnover (Fig. 8b) was the most striking improvement of the partitioned decay model framework. This framework is further supported by its consistency with the widely accepted comparative lability of autochthonously produced DOC versus that supplied as allochthonous inputs (e.g., Goel et al. 1995, Wetzel 1992). We are unaware of any experimental determinations of decay

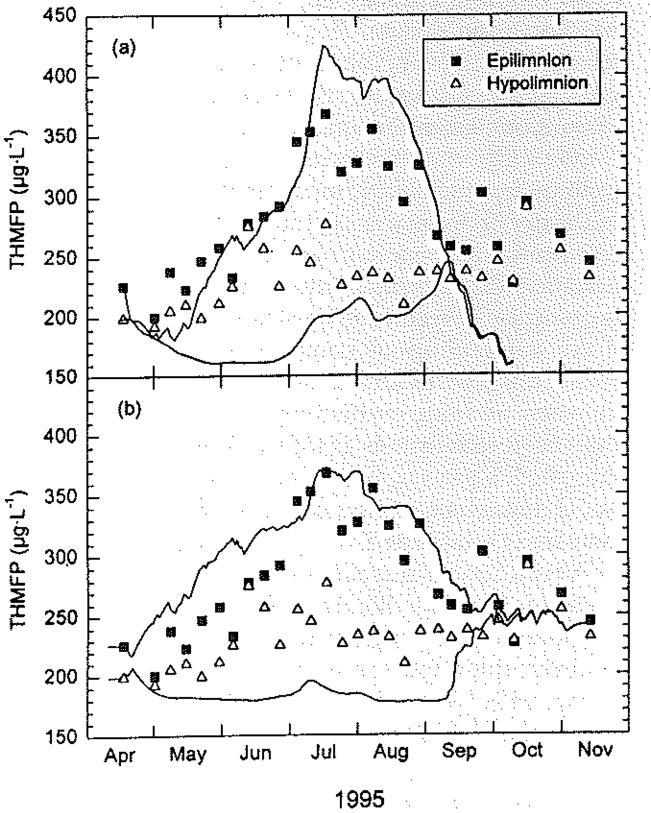

Figure 8.–Preliminary testing of a mechanistic THMFP model for Cannonsville Reservoir: a) with $k_{L(al)} = k_{L(au)} = 0.08$ d^{-1} in the epilimnion, and $k_{L(al)} = k_{L(au)} = 0.00$ d^{-1} in the hypolimnion, and b) with $k_{L(al)} = 0.00$ d^{-1} and $k_{L(au)} = 0.15$ d^{-1} throughout the water column. Lines are model simulations, symbols are volume-weighted concentrations.

rates for allochthonous and autochthonous THM precursors that could guide independent specification of these kinetic coefficients. Further, the apparently uncoupled distributions and behavior of THM precursors versus the larger DOC pools is not supportive of the selection of decay rates determined previously for DOC for other systems.

The partitioned decay model continued to underpredict THMFP in the reservoir's hypolimnion (Fig. 8b), particularly through the first half of the stratification period. Various factors may contribute to this shortcoming, including limitations in the model framework (e.g., source and sink processes accommodated and kinetic expressions). For example, the chl-specific THM precursor source term, as a function of light [Eq. (5)], is the result of a single experiment conducted with the natural phytoplankton assemblage (collected on September 6, 1995; Stepczuk et al. 1998b). Interestingly, increases observed in the hypolimnetic precursor pool in May and June that were not matched by the model, coincided with short-term increases in light penetration (Effler et al. 1998), suggesting the short-comings in performance (Fig. 8b) may be related to the light-based production process. This production process may be sensitive to phytoplankton composition, which changes substantially through the spring-fall interval (unpubl. data, Siegfried 1995). Additionally, decomposition of depositing phytoplankton may represent a source process for this layer that is not presently accommodated in the model.

Overall, the performance of the calibrated preliminary mechanistic model for THM precursors in Cannonsville Reservoir is considered good (Fig. 8b). This preliminary model has the attributes of accommodating allochthonous inputs of precursors as well as the interplay between nutrient loadings and production of the autochthonous component of the precursor pool. Thus, the model is attractive for management purposes, allowing evaluation of scenarios of loading reductions of nutrients as well as precursors from the watershed. However, simulations of scenarios with this model remain speculative until credibility can be more completely established.

Verification of this eutrophication-based precursor model for Cannonsville Reservoir would be a valuable component in a program to establish its credibility. However, the opportunity for a rigorous verification testing, with widely different environmental forcing and in-reservoir conditions, may not present itself. Alternatively, testing this framework for other well-defined systems of substantially different trophic state may be as valuable. Regardless, additional research is needed to identify other important source and sink processes for precursors, and develop kinetic relationships that quantify these processes as a function of regulating ambient conditions (e.g., Bowie et al. 1985). There are several potentially important pathways for precursors that deserve investigation, including: 1) biodegradation (Palmstrom et al. 1988), 2) photochemical decay (Wetzel et al. 1995), 3) hydrolysis, and 4) adsorption to particles (Aiken and Cotsaris 1995). Photolysis is largely associated with UV wavelengths, thus this effect was not included in the THMFP production experiment [see Eq. (5); also Stepczuk et al. 1998b]. The extent to which other loss processes were embedded in this experiment is uncertain. In sharp contrast to THM precursors, there is extensive literature that independently supports the various components of mechanistic mass balance modeling for other constituents that have been of concern for many years, such as phytoplankton and dissolved oxygen (Bowie et al. 1985).

A mechanistic model for THM precursors for oligotrophic (e.g., average total phosphorus concentration (6 $\mu g \cdot L^{-1}$) Lake Youngs, Washington, has recently been published (Canale et al. 1997). It is valuable to compare the mechanistic model developed here to that work. Both models accommodate allochthonous inputs as well as an autochthonous contribution that is driven by a eutrophication/primary production (sub-model). These eutrophication models (see Doerr et al. 1998) share many features that are common to this type of model (see review of Bowie et al. 1985). There are minor differences, such as the partitioning of dissolved phosphorus into inorganic and organic forms in the Cannonsville model (Doerr et al. 1998), versus the non-partitioned approach of Canale et al. (1997). An important feature of the Lake Youngs model is the inclusion of organic carbon (as total organic carbon, TOC) in the eutrophication model, because simulations of TOC support predictions of THMFP through application of a constant "THMFP yield" (ratio THMFP:TOC = 2.5%, Canale et al. 1997). This approach is attractive from the perspectives of data availability (TOC data more readily available than THMFP data) and the cost and difficulty of THMFP analyses. However, a modeling approach that incorporates a constant THMFP yield is not supported for Cannonsville Reservoir, because of the strong variations in yield documented for allochthonous inputs (Stepczuk et al. 1998a) and within the reservoir (Stepczuk et al. 1998b). This is further supported by the differences in the behavior of the reservoir pools of precursors and DOC demonstrated in this manuscript (Fig. 5). It seems likely that these shortcomings would be common to other eutrophic systems. The Cannonsville Reservoir model, in contrast, simulates THMFP directly (included as a state variable) and is forced by external precursor loads. Both models accommodate a recalcitrant component of the precursor pool. In the Lake Youngs model this component is a constant concentration. The recalcitrant component is accommodated by the partitioning of the precursor pool according to allochthonous and autochthonous components in the Cannonsville Reservoir model [see Eq. (6) and Fig. 8b]. This feature of the models should be re-evaluated following the completion of related process studies, as suggested above.

Management Perspectives

Analyses conducted here have demonstrated that internal production, localized within the epilimnion, was the most important source of THM precursors throughout the summer of 1995 in this eutrophic reservoir. Further, precursor production was coupled, at least in part, to primary production. This analysis represents strong support for nutrient loading to be considered in the management control of THM precursors in this reservoir (see also Cooke and Carlson 1989, Walker 1983). Managers are faced with the need to continue to meet standards for THMs that are becoming more restrictive, despite increasing costs of treatment. It is therefore important that source (e.g., watershed) management be evaluated as a means to supplement or prevent the need for other options. However reduction of nutrient and NOM loads from watersheds is costly and requires careful consideration.

A reliable quantitative model that integrates external loads and internal source and sink processes is needed to guide management actions related to THM precursors. This analysis has contributed to that goal. In particular, a mechanistic model for precursors, that builds on an existing eutrophication model (Doerr et al. 1998) and comprehensive paired loading (Stepczuk et al 1998a) and in-reservoir (Stepczuk et al. 1998b) THMFP data sets, has demonstrated encouraging results in the preliminary application presented here. This tool accommodates the linkage of phosphorus loading to internal precursor production, as mediated through primary production, as well as the contrasting lability of the external and internal components. However, an integrated program of field studies, kinetic studies of precursor source and sink processes, and model development and testing that covers a range of test systems is recommended before this, or any other, mechanistic precursor model is applied to guide expensive management programs intended to control THM precursors.

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