

# Summer Methane Fluxes and Fall Oxygen Resources of Onondaga Lake<sup>1</sup>

Jeffrey M. Address and Steven W. Effler

*Upstate Freshwater Institute*

*P.O. Box 506*

*Syracuse, NY 13214, U.S.A.*

## ABSTRACT

J. M. Address and S. W. Effler. 1996. Summer methane fluxes and fall oxygen resources of Onondaga Lake. *Lake and Reserv. Manage.* 12(1):91-101.

The sediment release and cycling of CH<sub>4</sub> in SO<sub>4</sub><sup>2-</sup>-rich hypereutrophic Onondaga Lake, New York, was assessed for the summer/fall interval of 1989 through a program of collection and analysis of ebullitive gas and monitoring of the lake's water column for dissolved CH<sub>4</sub>. Approximately 1x10<sup>7</sup> mol of CH<sub>4</sub> were released from the lake's sediments, at an average rate of 16 mmol/m<sup>2</sup>/d, from mid-June to mid-September; two-thirds was dissolved, one-third was in the gas phase. About 75% of the ebullitive release of CH<sub>4</sub>, or 25% of the total release, was lost from the lake to the atmosphere. Strong temporal variations in ebullitive flux were observed. Oxidation of entrained hypolimnetic accumulations of CH<sub>4</sub> contributed importantly to the major depletion of O<sub>2</sub> and highly undersaturated conditions observed for the lake's upper layers during the fall mixing period. This water quality problem is a manifestation of the cultural eutrophication of the lake.

Key Words: methane, ebullition, methane oxidation, trophic state, dissolved oxygen.

Methanogenesis is the dominant metabolic pathway in the anaerobic sediments of most lakes (e.g., Kelly and Chynoweth 1979, Kelly et al. 1988, Strayer and Tiedje 1978). Methane is an important end product of anaerobic decomposition and part of the carbon cycle of lakes (Rudd and Taylor 1980). Production of CH<sub>4</sub> in lakes has been related to organic deposition, and thereby trophic state (Kelly and Chynoweth 1981). Dissolved CH<sub>4</sub> accumulates in anoxic hypolimnia, and ebullitive releases from oversaturated pore waters can result in system losses of organic C (e.g., Fallon et al. 1980, Strayer and Tiedje 1978). Methane production can have negative implications for oxygen resources, as dissolved CH<sub>4</sub> reaching oxygenated waters is generally converted to CO<sub>2</sub> and cell material, thereby exerting an associated demand for O<sub>2</sub> (Rudd and Hamilton 1975, 1978, Rudd et al. 1974). Thus the progressive hypolimnetic accumulation of CH<sub>4</sub> observed in certain eutrophic lakes represents an oxygen debt that is met within the overlying oxygenated layers during the fall mixing period.

This study documents the sediment release and cycling of CH<sub>4</sub> in Onondaga Lake for the summer to fall turnover period of a single year (1989). A CH<sub>4</sub> budget for the lake's water column, that includes both

ebullitive and dissolved components, is developed for the summer stratification period. The impact of oxidation of hypolimnetic CH<sub>4</sub> on the lake's oxygen resources during fall mixing is delineated.

## Study System

Onondaga Lake is a hardwater alkaline system, enriched in SO<sub>4</sub><sup>2-</sup> (e.g., typical SO<sub>4</sub><sup>2-</sup> concentration at spring turnover is about 1.5 mmol/L (Driscoll et al. 1996, Effler et al. 1988)), and enriched in dissolved inorganic nitrogen (DIN) in the epilimnion (> 140 μmol N/L (Brooks and Effler 1990)) because of loads received from the Onondaga County Metropolitan Sewage Treatment Plant (METRO). Thus oxidation of CH<sub>4</sub> would not be limited in the epilimnion by low DIN levels, as observed in Canadian Shield lakes by Rudd et al. (1976).

Onondaga Lake is a culturally hypereutrophic lake (e.g., Effler et al. 1988, 1996). For example, the summer average particulate organic carbon (POC) deposition rate during the summer of 1989 (by sediment traps) was 54 mmol C/m<sup>2</sup>/d (Driscoll et al. 1994), among the highest downward fluxes reported in the literature (Effler 1996). Hydrogen sulfide accumulates in, and

<sup>1</sup>Contribution No. 136 of the Upstate Freshwater Institute.

$\text{SO}_4^{2-}$  is depleted from, the hypolimnion after the onset of anoxia, reflecting  $\text{SO}_4^{2-}$  reduction (Effler et al. 1988). Sulfate concentrations in the hypolimnion remain well above (e.g., 5x) the level described as limiting ( $\sim 0.2$  mmol/L (Ingvorsen et al. 1981)) to  $\text{SO}_4^{2-}$  reduction. Thus  $\text{SO}_4^{2-}$  reduction is a significant anaerobic pathway for the decomposition of organic material in this lake (e.g., Gelda et al. 1996).

## Methods

The water column of Onondaga Lake was monitored weekly over the June-October interval of 1989 at a buoyed, deep water ( $\sim 19$  m) station in the south basin used routinely in monitoring lake wide conditions (Hennigan and Effler 1996). Dissolved oxygen (DO) and temperature profiles (1 m intervals) were measured with a YSI (model 57) meter and a Montedoro-Whitney (model TC-5) thermistor, respectively. Water samples for  $\text{CH}_4$  analysis were collected with a submersible pump at a 1 m depth interval within the anoxic layers, extending at least 1 m above the oxic/anoxic boundary. Additionally, a near-surface sample was collected. All samples were collected in Wheaton BOD bottles, that were overflowed at least 3 times, carefully sealed, and put on ice until analysis to prevent degassing. Samples were analyzed the day of collection.

Ebullitive gas was collected with inverted LEXAN cones (0.75 m diameter). The cones were fitted with inverted 500 ml polypropylene separatory funnels. The stopcock end of the funnel was fitted with a rubber nipple so that aliquots of the collected gas could be drawn out without atmospheric contamination. Similar sampling devices have been used by a number of researchers (e.g., Chanton et al. 1989, Chau et al. 1977, Robertson 1979, Strayer and Tiedje 1978) to collect ebullitive gases and measure upward fluxes (e.g., through water displacement by the evolving gas). Aliquots (10 ml) of collected gases were brought back to the laboratory in 15 ml serum vials that had been filled with distilled water and fitted with teflon lined butyl rubber septa. The gas was put into the vials through water displacement, using a venting syringe. The primary cone deployment to assess seasonality in gas flux and composition was at the south basin station approximately 1 m above the sediment (i.e., depth  $\sim 18$  m). Cones were deployed in triplicate on sixteen occasions to assess variability. Paired deployments at the upper bound ( $\sim 10$  m) of the hypolimnion and at differing longitudinal locations were made to assess redissolution within the watercolumn and spatial heterogeneity, respectively. Flux measurements at the

south basin site were made on an average of once every three days. Hydrostatic pressure at the lake's maximum depth was calculated using continuous lake elevation measurements made by the United States Geologic Survey (Hennigan and Effler 1996).

All gas analyses were performed with a GOW-MAC 550 gas chromatograph equipped with a thermal conductivity detector, using ultra high purity helium as the carrier gas. Established operating conditions afforded a detection limit of approximately  $2 \times 10^{-3}$  mmol for the species analyzed. Dissolved  $\text{CH}_4$  was partitioned from the liquid phase to the gas phase using a syringe stripping technique (Rudd et al. 1974). This method has been shown to strip off  $\geq 97\%$  of dissolved  $\text{CH}_4$  (Fendinger and Adams 1986, Rudd et al. 1974). Aliquots of ebullitive gases were drawn out of the capped serum vials through water displacement. The analytical precision was generally high; the mean coefficient of variation for triplicate injections ( $n = 80$ ) of aliquots of collected gas was 0.45%, for triplicate sampling ( $n = 8$ ) of aliquots of collected gas it was 1.7%, and for triplicate analysis of dissolved  $\text{CH}_4$  samples it was 6.93%.

## Calculations

The diffusive loss of dissolved  $\text{CH}_4$  from the enriched hypolimnion to the epilimnion was estimated according to Chapra and Reckhow (1983)

$$(1) \quad W = v_t \cdot A_t \cdot (C_h - C_e)$$

where  $W$  is the upward flux (mol  $\text{CH}_4/\text{d}$ ),  $v_t$  is the vertical heat exchange coefficient (m/d),  $A_t$  is the surface area of the thermocline ( $\text{m}^2$ ), and  $C_h$  and  $C_e$  are the volume-weighted concentrations (mol/ $\text{m}^3$ ) of the hypolimnion and epilimnion ( $= 0$  mol/ $\text{m}^3$ ), respectively. The value of  $v_t$  was estimated from a heat budget calculation for the hypolimnion, from measured temperature profiles, according to Chapra and Reckhow (1983)

$$(2) \quad v_t = \frac{V_h}{A_t \cdot t_s} \cdot \ln \left[ \frac{T_{h,i} - T_e}{T_{h,f} - T_e} \right]$$

in which  $V_h$  = the volume of the hypolimnion ( $\text{m}^3$ ),  $t_s$  = the time interval over which the calculation is made (d),  $T_{h,i}$  and  $T_{h,f}$  = the initial and final hypolimnetic temperatures ( $^{\circ}\text{C}$ ) for the interval  $t_s$ , respectively, and  $T_e$  = the average epilimnetic temperature ( $^{\circ}\text{C}$ ) over the period of the calculation. Calculations of  $v_t$  and  $W$  were made at a time step of about one month, assuming a thermocline depth of 10 m (e.g., Owens and Effler 1989). Estimates of  $v_t$  for Onondaga Lake have been documented elsewhere (Owens and Effler 1996, Wodka et al. 1983).

## Results and Discussion

### *Dissolved CH<sub>4</sub>*

Vertical and temporal distributions of dissolved CH<sub>4</sub> and O<sub>2</sub> in Onondaga Lake for the summer/fall interval of 1989 are depicted by 20 paired profiles (Fig. 1). Temperature profiles are included for selected dates to establish the character of the thermal stratification regime, which was a major regulating factor. Dissolved CH<sub>4</sub> was not detected in oxygenated layers during the study period (Fig. 1a-t). Dissolved CH<sub>4</sub> was first detected on June 15, in the lowermost layers, approximately one week after the onset of anoxia. Concentrations of CH<sub>4</sub> increased progressively in the hypolimnion from mid-June until late September, and reached a maximum of 0.44 mmol/L just above the sediment. The vertical extent of detectable CH<sub>4</sub> often included the entire anoxic layer (up to a depth of 9 m on August 1; Fig. 1i). The depth interval of detectable CH<sub>4</sub> narrowed as the epilimnion deepened during the fall mixing period. Methane concentrations were always highest near the sediment and decreased progressively upward within the hypolimnion toward the oxic boundary. This vertical distribution is consistent with a sedimentary source of CH<sub>4</sub> and incomplete vertical mixing in the hypolimnion. Similar distributions have been documented for the hypolimnia of other eutrophic lakes (e.g., Kelly and Chynoweth 1979, Rudd and Hamilton 1978) and for other constituents in Onondaga Lake that are released from the sediments (Brooks and Effler 1990, Effler et al. 1988). An example is the H<sub>2</sub>S profile for September 19 (Fig. 1p, modified from Driscoll et al. 1996). Clearly, methanogenesis and SO<sub>4</sub><sup>2-</sup> reduction proceed in parallel in the sediments of Onondaga Lake, consistent with findings reported for other systems (e.g., Lovley et al. 1982, Lovley and Klug 1983).

The dissolved CH<sub>4</sub> concentrations reported here are not unusually high compared to values reported in the literature for eutrophic lakes. Ingvorsen and Brock (1982) reported a maximum concentration of 0.40 mmol/L for eutrophic Lake Mendota. Rudd and Hamilton (1975) reported a maximum concentration of 1.28 mmol/L in eutrophic Lake 227. Strayer and Tiedje (1978) reported maximum concentrations of 2.5 and 5.0 mmol/L for two consecutive years in hypereutrophic Wintergreen Lake.

Methane accumulates in the hypolimnion of Onondaga Lake through the summer and is lost during the fall mixing period (Fig. 2). The CH<sub>4</sub> pool calculations presented subsequently (see Table 1) were based on the vertical profiles (Fig. 1) and hypsographic

data for the lake (Owens 1987). Methane accumulated in a nearly linear manner ( $6.63 \times 10^4$  mol/d,  $r^2 = 0.98$ ) from mid-June through mid-September. The estimated maximum CH<sub>4</sub> pool was  $5.9 \times 10^6$  mol. Thereafter the CH<sub>4</sub> pool decreased rapidly ( $-2.11 \times 10^5$  mol/d,  $r^2 = 0.93$ ), associated with the entrainment into, and oxidation of CH<sub>4</sub> within, the deepening epilimnion with the approach to complete fall turnover. Methane was undetectable in the lake by mid-October (Fig. 1t) when mixing processes had distributed oxygen throughout the lower layers.

### *Ebullitive Gases*

Substantial variations in the composition of ebullitive gas, collected above (1 m) the sediments, occurred during the study (Fig. 3). The frequency distribution of % CH<sub>4</sub> in the gas could be described as bimodal, or perhaps skewed (Fig. 3). Within the context of a bimodal distribution, the dominant mode was centered around a composition of 86% CH<sub>4</sub>, and the secondary mode was centered around 67% CH<sub>4</sub> (Fig. 3). The balance of the gas was essentially N<sub>2</sub>; CO<sub>2</sub> was detected on several occasions. No temporal patterns or periodicity were manifested in gas composition. The driving forces for this variability remain unexplained.

This study gave more attention to the short-term dynamics and spatial heterogeneity of ebullition, and replication of measurements of ebullition, than other studies described in the literature (e.g., Fallon et al. 1980, Kelly and Chynoweth 1981, Rudd and Hamilton 1978). The magnitude of the ebullitive flux was highly dynamic during the study period; note that the variability in the results of analyses of replicate collections was relatively small (mean coefficient of variation = 16.1%, for 16 triplicate collections) compared to changes in flux over time (Fig. 4a). Variability at this time scale has not previously been documented for a stratifying lake. Total gas flux (essentially the summation of N<sub>2</sub> and CH<sub>4</sub>) for the study period averaged 7.3 mmol/m<sup>2</sup>/d; the maximum was 34.2 mmol/m<sup>2</sup>/d. Ebullitive CH<sub>4</sub> flux averaged 6.0 mmol/m<sup>2</sup>/d; the maximum was 30.9 mmol/m<sup>2</sup>/d.

Changes in hydrostatic pressure have been shown to exert a substantial effect on ebullitive rates in shallow systems (e.g., tidal freshwater estuaries < 1 m depth). Chanton et al. (1989) found that a reduction in the hydrostatic pressure of 5 to 7% brought about by tides was enough to cause distinct diurnal increases in ebullition. The phenomenon was also observed by Martens and Klump (1980). The changes in hydrostatic pressure experienced in Onondaga Lake during the study were much less abrupt; e.g., a 4% decrease in hydrostatic pressure occurred over the period of May

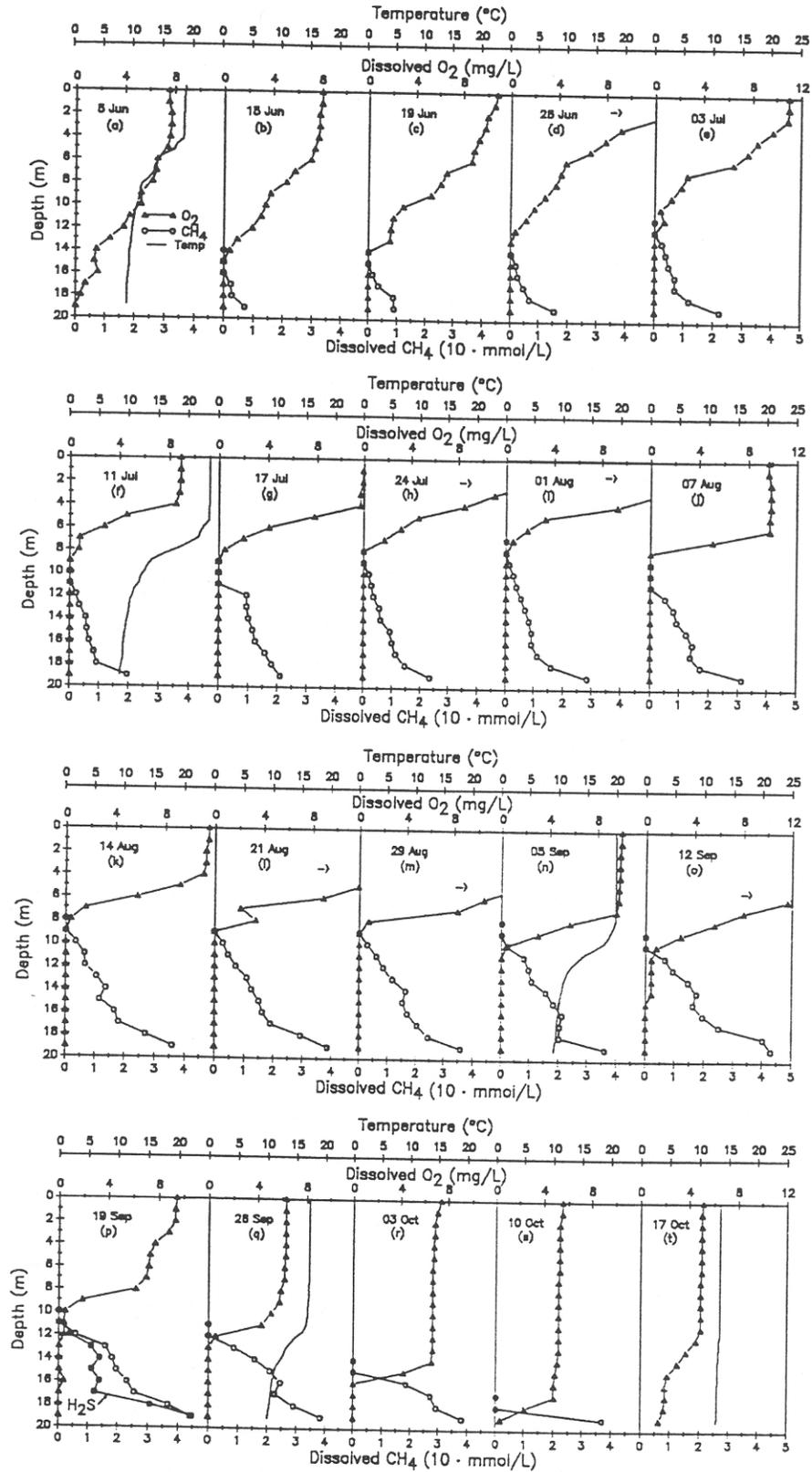


Figure 1.—Methane, oxygen, and temperature profiles for Onondaga Lake, 1989: a) 5 June, b) 15 June, c) 19 June, d) 26 June, e) 3 July, f) 11 July, g) 17 July, h) 24 July, i) 1 August, j) 7 August, k) 14 August, l) 21 August, m) 29 August, n) 5 September, o) 12 September, p) 19 September (hydrogen sulfide profile included), q) 26 September, r) 3 October, s) 10 October, and t) 17 October. Weekly methane and oxygen profiles depict the seasonality in the stratification regime. A single hydrogen sulfide profile typical of late summer is presented for 19 September.

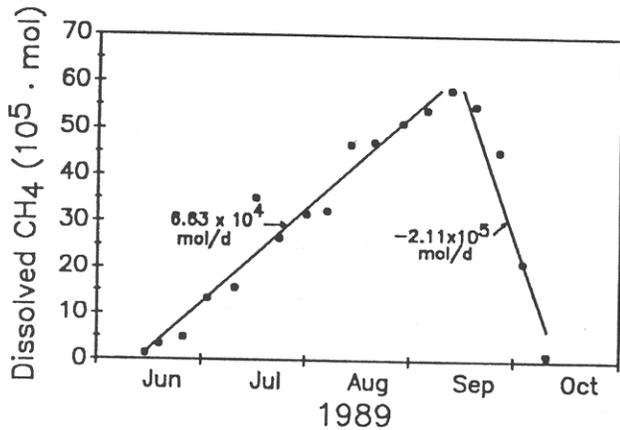


Figure 2.—Time series of estimated total lake content of methane in Onondaga Lake in 1989, determined from profiles (Figure 1) and hypsographic data, with estimates of net rates.

15-19, a 2% decrease occurred over the period June 20 - July 4, and 1% decrease occurred later in the study (Fig. 4b). The relationship in Onondaga Lake between ebullitive flux and hydrostatic pressure is either not simple or other factors contribute importantly to those dynamics, as changes in flux over the entire study period (Fig. 4a) were not strongly correlated to hydrostatic pressure (Fig. 4b). However, certain features of the dynamics of ebullitive flux were consistent with the effects of hydrostatic pressure; e.g., the events of greatest ebullitive flux (late May, early and late July, and mid-August) occurred over periods of substantial decrease in hydrostatic pressure, or when hydrostatic pressure was at a minimum. Lower fluxes were generally observed during periods when the lake level was increasing. The strong temporal variations observed in ebullitive flux (Fig. 4a) occur throughout the deep portions of the lake, e.g., the same temporal structure was observed at the south basin and north basin sites (Address 1990). Additional research is necessary to quantitatively resolve the factors responsible for the

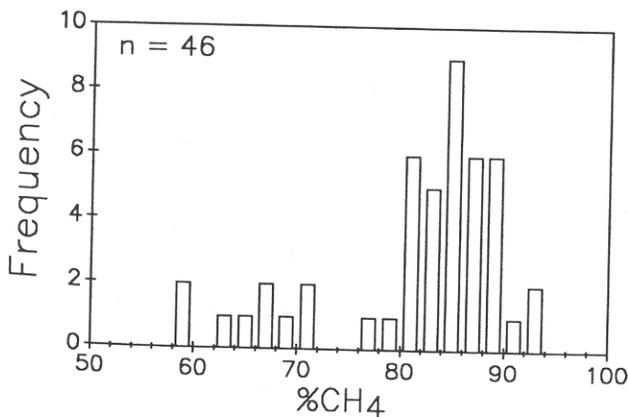


Figure 3.—Distribution of measurements of ebullitive gas composition (as % CH<sub>4</sub>) for collections 1 m above the sediments in the south basin of Onondaga Lake in 1989.

dynamics in ebullitive flux.

Based on the results of 9 paired deployments at the south basin site, at the upper boundary of the hypolimnion (depth = 10 m) and at the primary monitoring depth of about 18 m, ebullitive gas lost an average of 15% of its CH<sub>4</sub> as it rose through this 8 m interval of the hypolimnion. This corresponds to about 1.9% redissolution of CH<sub>4</sub> for each meter of bubble rise. The estimate is considered approximate because of the level of precision in gas collection (e.g., Fig. 4a), however, it is consistent with the estimate of redissolution presented by Robertson (1979).

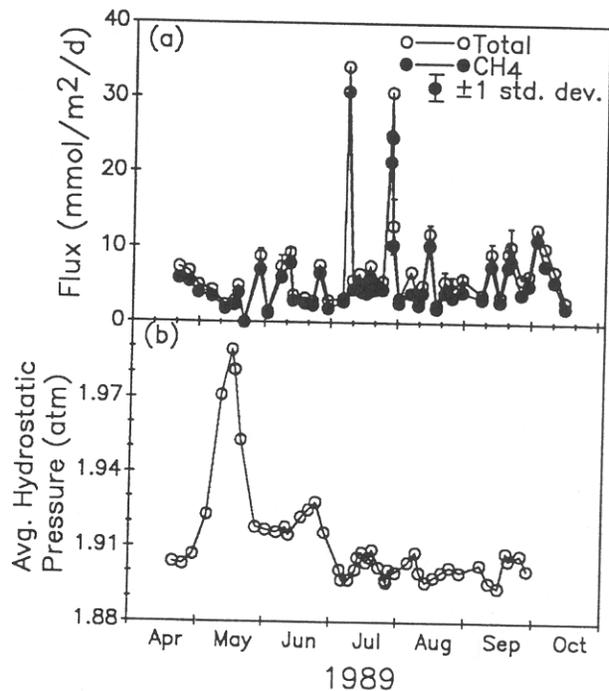


Figure 4.—Time series for Onondaga Lake, 1989: a) total ebullitive flux and methane gas flux, with standard deviation bars for measurements of triplicate collections, and b) average hydrostatic pressure for intervals of flux measurements at the maximum depth of the lake. Variations in hydrostatic pressure reflect changes in the elevation of the lake's surface.

### Summer Watercolumn CH<sub>4</sub> Budget

Based on watercolumn profiles (Fig. 1), measurements of ebullitive flux (Fig. 4a), and estimates of vertical mixing (Eq.'s (1) and (2)), a CH<sub>4</sub> budget was calculated (Table 1) for the water column of Onondaga Lake. Two lake layers (epilimnion and hypolimnion) are considered (Fig. 5), and demarcated at a depth of 10 m (e.g., Effler and Owens 1996). Methane is input from the sediments in two forms, dissolved (via diffusion from the sediments) and as a gas (ebullitive flux, Fig. 5). A portion of the rising gaseous CH<sub>4</sub> (re-)dissolves,

the remainder is lost to the atmosphere (Fig. 5). Methane "redissolved" in the hypolimnion augments diffusive inputs from the sediments (Fig. 5). Redissolution and vertical mixing-based inputs (from the enriched hypolimnion) into the epilimnion are oxidized (Fig. 5). The watercolumn budget is presented on a total mass basis, corresponding to the interval of hypolimnion accumulation of  $\text{CH}_4$  (rising limb of Fig. 2, mid-June to mid-September). Anaerobic oxidation (e.g.,  $\text{SO}_4^{2-}$  as the electron acceptor, Alperin and Reeburgh 1985, Iversen et al. 1987), a potential  $\text{CH}_4$  sink, has not been considered here. This is not expected to be a major pathway in dimictic lakes (Rudd and Taylor 1980).

The estimated total ebullitive  $\text{CH}_4$  release was about  $3.34 \times 10^6$  mol  $\text{CH}_4$ ; this corresponds to an average flux of  $5.3$  mmol/ $\text{m}^2$ /d. Redissolution of gaseous  $\text{CH}_4$  was estimated according to the observed

1.9%/m and average depths (of bubble rise) of the two lake layers (Table 1; hypsographic data of Owens (1987)). Accordingly, approximately 10% of the ebullitive release ( $3.34 \times 10^5$  mol  $\text{CH}_4$ ) entered the dissolved  $\text{CH}_4$  pool of the hypolimnion through redissolution, and about 16% redissolved in the epilimnion. The loss of  $\text{CH}_4$  across the water-air interface over the budget calculation interval, estimated by difference (Table 1), was about  $2.5 \times 10^6$  mol  $\text{CH}_4$  (Fig. 5, or about 75% of the ebullitive release from the sediments), corresponding to an average flux of about  $2.3$  mmol/ $\text{m}^2$ /d. This evasive flux falls well within the observations reported for lakes in the review of Aselmann and Crutzen (1989).

The total loss of  $\text{CH}_4$  from the hypolimnion to the epilimnion via diffusion over the mid-June to mid-September interval was estimated (Eqs. (1) and (2)) to be  $1.12 \times 10^6$  mol  $\text{CH}_4$ . The total diffusive release of

Table 1.—Features of a watercolumn  $\text{CH}_4$  budget for Onondaga Lake June 15 - September 12, 1989.

Component	Mass (mol x $10^6$ )	Comments
1. Ebullition		
a. release from sediments	3.34	fluxes from gas trap collections, 18 m
b. dissolved into hypolimnion	0.33	by flux differences (10%) measured <i>in situ</i> at 18 m and 10 m; loss of 1.9%/m bubble rise
c. dissolved/oxidized into epilimnion	0.53	assumes loss of 1.9%/m bubble rise, as in 1b.
d. released to atmosphere	2.48	calculated as 1a. minus the sum of 1b. and 1c.
2. Diffusive Inputs/ Dissolved $\text{CH}_4$		
a. diffused/oxidized into epilimnion	1.12	calculated from $v_t$ and $\text{CH}_4$ vertical gradients (Eqs. (1) and (2))
b. accumulation (net) in hypolimnion	5.86	calculated from depth profiles of $\text{CH}_4$
c. release from sediments	6.64	calculated as sum of 2a. and 2b., minus 1b.
3. Total Release from Sediments	9.98	calculated as sum of 1a. and 2c.

\*thermocline assumed to be at depth of 10 m.

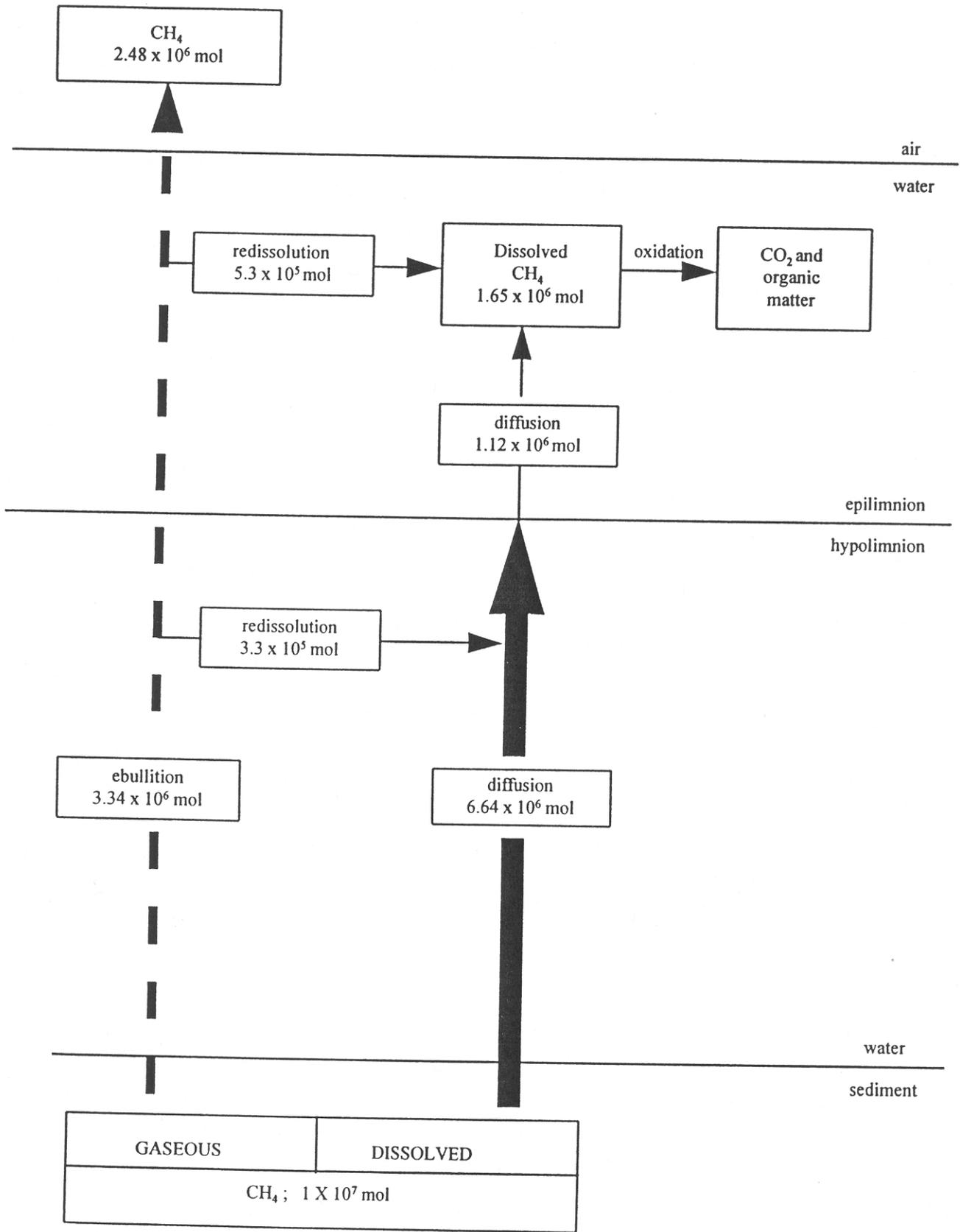


Figure 5.-Watercolumn  $\text{CH}_4$  budget for Onondaga Lake, 1989. See Table 1 for details of protocol for calculations.

dissolved  $\text{CH}_4$  from the sediments was estimated (as the sum of the net hypolimnion accumulation and the calculated upward loss to the epilimnion, minus the quantity redissolved into the hypolimnion from escaping ebullitive gas (Table 1)) to be  $6.64 \times 10^6$  mol. Thus the total release of  $\text{CH}_4$  from the hypolimnetic sediments was about  $1.0 \times 10^7$  mol  $\text{CH}_4$ ; two-thirds was dissolved, one-third was in the gas phase (Fig. 5). This corresponds to an average overall release rate over the three month period of  $16 \text{ mmol/m}^2/\text{d}$ . Nearly 90% of the released dissolved  $\text{CH}_4$  accumulated in the hypolimnion (Fig. 2), while 10% was transported to the epilimnion via vertical mixing. Similarly, Rudd and Hamilton (1978) estimated that only 10% of the diffusive release from the sediments of Lake 227 during summer stratification diffused across the thermocline. In contrast, Fallon et al. (1980) estimated approximately 45% of the  $\text{CH}_4$  release from the sediments of Lake Mendota diffused into the epilimnion. Approximately  $1.65 \times 10^6$  mol of dissolved  $\text{CH}_4$  reached the epilimnion of Onondaga Lake over the three month period from redissolution of gaseous  $\text{CH}_4$  and upward diffusion (Fig. 5). The loss of ebullitive  $\text{CH}_4$  to the atmosphere represented about 25% of the total sedimentary release (Fig. 5).

The relative role of methanogenesis in the carbon cycle of lakes has been evaluated by comparing  $\text{CH}_4$  fluxes and the deposition rates of organic carbon (Kelly and Chynoweth 1981). Kelly and Chynoweth's (1981) listing of these paired fluxes for eutrophic systems is expanded here to include Onondaga Lake (Table 2). These systems apparently represent a range of primary productivity, as differences in organic deposition of more than an order of magnitude are included (Table 2). The release percentage included in Table 2 should be considered a rough estimate of the fraction of deposited organic C recycled through methanogenesis, as both the methane and organic C fluxes are assumed to represent steady-state conditions (i.e., the water column and sediments are in equilibrium) for each of these lakes. The  $\text{CH}_4$  release from the sediments of Onondaga Lake during the June to September interval of 1989 was approximately 30% of the organic carbon deposited over the same period. This is somewhat lower than reported elsewhere (Table 2). While the reason for this discrepancy is not clear, the prevalence of elevated concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in Onondaga Lake may contribute. These species are important electron acceptors and oxidize a significant amount of organic matter deposited in the sediments of Onondaga Lake (Driscoll et al. 1996). The sulfate reduction and denitrification processes are probably not so prominent in the other lakes studied (Table 2). Accordingly, methanogenesis may be a somewhat less important pathway for organic matter

decomposition in Onondaga Lake, in comparison with these other lakes.

### *Fall Oxygen Resources: Management Implications*

The accumulation of  $\text{CH}_4$  and other reduced substances (e.g.,  $\text{H}_2\text{S}$  (Fig. 1p)), in the hypolimnion during summer represents an oxygen debt that must be satisfied by the oxygen resources of the overlying layers during the fall mixing period. As a result, abrupt lake-wide depletions of DO in the upper waters are observed annually during early fall with the approach to turnover (Effler et al. 1988, 1996), coincident with the abrupt loss (oxidation) of  $\text{CH}_4$  and  $\text{H}_2\text{S}$  (Figs. 1 and 2). In most years, the oxygen concentration throughout the upper waters drops below  $4 \text{ mg/L}$  (the minimum concentration standard in New York State, Effler et al. 1996). The exodus of most fish from the lake during this period has also been documented (Tango and Ringler 1996). This represents a severe degradation, and a clear loss of resources, for a lake that once supported a cold water fishery (Tango and Ringler 1996). Based on the detailed profile data presented in Fig. 1, and the stoichiometries of oxidation of  $\text{CH}_4$  and  $\text{H}_2\text{S}$  (e.g., DiToro et al. 1990, Jorgensen et al. 1979, Sweerts et al. 1991), we investigated here the extent to which the late-summer hypolimnetic pool of these oxygen-demanding reduced substances (particularly  $\text{CH}_4$ ) explains the observed lake-wide depletion of DO.

The principal oxygen-demanding constituents that accumulate in the lake's hypolimnion are  $\text{CH}_4$  (Fig. 1),  $\text{H}_2\text{S}$  (Effler et al. 1988) and ammonia (Brooks and Effler 1990). Ferrous iron concentrations remain very low by comparison, apparently as a result of very high concentrations of  $\text{H}_2\text{S}$ , which leads to  $\text{FeS}$  precipitation (Effler et al. 1988, Yin and Johnson 1984). The kinetics of nitrification (e.g., Bowie et al. 1985) are slow compared to the oxidation rates of  $\text{CH}_4$  (e.g., Jannasch 1975, Rudd et al. 1976) and  $\text{H}_2\text{S}$  (e.g., Jorgenson et al. 1979). Further, an alternate sink process for ammonia, phytoplankton uptake, appears to dominate ammonia dynamics during the fall mixing period of most years (Driscoll et al. 1996). Thus for this analysis of the lake's fall DO budget, we considered only the rapid oxidation of  $\text{CH}_4$  and  $\text{H}_2\text{S}$ . Because neither species has been detected within the oxygenated layers of the lake (Fig. 1, Effler et al. 1988), we assume that the respective oxygen demands of these two species are exerted rapidly and totally upon reaching the oxygenated layers. The stoichiometries of the oxidation reactions are (DiToro et al. 1990, Sweerts et al. 1991).

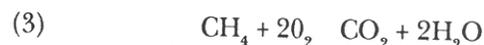
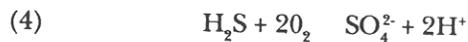


Table 2.—Comparison of CH<sub>4</sub> flux and percent of deposited organic carbon recycled via this flux.

Lake	Organic Deposition mmol C/m <sup>2</sup> /d	Methane Flux mmol C/m <sup>2</sup> /d	% Release	Reference
Onondaga Lake	54*	16	30	this study
Third Sister (1976)	15	5.4	36	Kelly & Chynoweth (1981)
Third Sister (1977)	9.2	3.5	38	Kelly & Chynoweth (1981)
227 (Ontario) (1974)	19	10.8	57	Rudd & Hamilton (1978)
Frain's (1977)	33	19	58	Kelly & Chynoweth (1981)
Frain's (1977)	25	12	48	Kelly & Chynoweth (1981)
Mendota (1977)	67.5	35.8	53	Fallon et al. (1980)
Wintergreen (1976)	127	49	39	Kelly & Chynoweth (1981)

\* from Driscoll et al. 1994a.

and (Jorgensen et al. 1979)



The oxygen demand exerted by the oxidation of CH<sub>4</sub> and H<sub>2</sub>S during the fall mixing period of 1989 has been estimated here from the water column content of these species on September 19 (Fig. 1p). The calculated oxygen demands for CH<sub>4</sub> and H<sub>2</sub>S, satisfied by October 17 (Fig. 1t) were 3.7 and 2.3 × 10<sup>8</sup> gO<sub>2</sub> equivalents, respectively. This oxygen sink greatly exceeds the net loss in O<sub>2</sub> documented over the same interval of 0.8 × 10<sup>8</sup> g (from oxygen profiles of Fig. 1p and t and hypsographic data). The oxygen deficit (difference between saturation and observed concentrations) of the water column on October 17 was about 7.3 × 10<sup>8</sup> g. Clearly the oxidation of the hypolimnetic accumulation of dissolved CH<sub>4</sub> (Figs. 1 and 2) played an important role in the lake-wide oxygen depletion observed within the upper waters of the lake in the fall of 1989, as this species represented about 60% of accumulated immediate O<sub>2</sub> demand. We are aware of only one other study where CH<sub>4</sub> accumulations were coupled to a lake-wide oxygen problem. In that study, Rudd and Hamilton (1978) found CH<sub>4</sub> oxidation was the most important contributor to the development of total lake anoxia under ice cover in an artificially eutrophic lake (Lake 227) of the Precambrian Shield.

There is compelling anecdotal evidence (e.g., Effler and Hennigan 1996, Tango and Ringer 1996) that the lake's hypolimnion was seldom, if ever, anoxic prior to the late 1800s. The loss of the lake's hypolimnion oxygen, the annual accumulation of large quantities of reduced species in the lower layers during summer, and the subsequent fall depletions of oxygen in the overlying waters (e.g., Fig. 1), are manifestations of cultural eutrophication (Effler 1996, Effler et al. 1988, 1996). The attendant increased deposition of organic

carbon (Rowell 1996) has driven increased anaerobic metabolism and production of the reduced oxygen-demanding by-products.

The watercolumn CH<sub>4</sub> budget developed in this work, together with attendant O<sub>2</sub> data (Fig. 1), have established the important role CH<sub>4</sub> plays in the fall oxygen depletion in Onondaga Lake. The partitioning of the gaseous and dissolved fluxes of CH<sub>4</sub> (Fig. 5) also yields some insight into the character of response to be expected from reductions in primary production. Beyond the delayed response expected from the lake sediments (e.g., DiToro et al. 1990), the existing significant ebullitive component of the CH<sub>4</sub> flux may result in an initial uncoupling of organic deposition and accumulation of oxygen debt during summer. Most of the ebullitive flux (approximately 75%, Fig. 5) exits the lake and therefore does not exert an oxygen demand. Initial reductions in organic deposition can reasonably be expected to first reduce the degree of oversaturation of CH<sub>4</sub> in the sediment pore water and thereby the ebullitive flux of CH<sub>4</sub>. These decreases would have a modest effect on the late summer hypolimnetic pool of CH<sub>4</sub> and the subsequent fall depletion of oxygen (e.g., Fig. 5). Greater reductions in organic deposition would result in a more directly coupled response by decreasing the diffusive flux of soluble CH<sub>4</sub> from the sediment, and thereby the late summer hypolimnetic pool of this oxygen-demanding species (e.g., Fig. 5).

Additionally, this analysis of CH<sub>4</sub> dynamics has served to support the development and testing of a mechanistic mathematical model for dissolved oxygen (Gelda and Auer 1996) which will guide related management action(s) for the lake. This validated model (Gelda and Auer 1996) accommodates the important source and sink processes for oxygen during the fall mixing period, and includes a submodel that

simulates the time course of hypolimnetic accumulation of  $\text{CH}_4$  and  $\text{H}_2\text{S}$  (in terms of  $\text{gO}_2$  equivalents, Gelda and Auer 1996).

**ACKNOWLEDGEMENTS:** This research was partially supported by grants from the New York State Department of Environmental Conservation, with funding provided by the U.S. Environmental Protection Agency under Sections 205(j), 106 and 604(b) of the Federal Water Pollution Control Act Amendments of 1987 (P.L. 100-4), administered by the Central New York Regional Planning and Development Board. B.A. Wagner assisted in field measurements and sampling. We thank an anonymous reviewer who provided comments on an earlier version of the manuscript. This is contribution No. 136 of the Upstate Freshwater Institute.

## References

- Address, J. M. 1990. Methane cycling in Onondaga Lake, New York. M.S. thesis, College of Environmental Science and Forestry, State University of New York, Syracuse, NY.
- Alperin, M. J. and W. S. Reeburgh. 1985. Inhibition experiments on anaerobic methane oxidation. *Appl. Environ. Microbiol.* 50: 940-945.
- Aselmann, J. and P. J. Crutzen. 1989. Global distribution of natural freshwater wetlands and rice paddies, their net primary productivity, seasonality and possible methane emissions. *J. Atmos. Chem.* 8: 307-358.
- Bowie, G. L., W. B. Mills, D. B. Porcella, C. L. Campbell, J. R. Pagenkopf, G. L. Rupp, K. M. Johnson, P. W. H. Chan, S. A. Gherini and C. Chamberlain. 1985. Rates, constants, and kinetic formulations in surface water quality modeling, 2nd edition, EPA/600/3-85/040. U.S. Environmental Protection Agency, Athens, GA. 455 p.
- Brooks, C. M. and S. W. Effler. 1990. The distribution of nitrogen species in polluted Onondaga Lake, NY, USA. *Wat., Air, Soil Pollut.* 52: 247-262.
- Chanton, J. P., C. S. Martens and C. A. Kelley. 1989. Gas transport from methane-saturated tidal freshwater and wetland sediments. *Limnol. Oceanogr.* 34:807-819.
- Chapra, S. C. and K. H. Reckhow. 1983. Engineering approaches for lake management. Volume 2. Mechanistic modeling. Butterworth Publishers, Boston, MA. 340 p.
- Chau, Y. K., W. J. Snodgrass and P. T. S. Wong. 1977. A sampler for collecting evolved gases from sediment. *Wat. Res.* 11:803-809.
- DiToro, D. M., R. P. Pagnin, K. Subburamu and D. A. Gruber. 1990. Sediment oxygen demand model: methane and ammonia oxidation. *J. Environ. Eng.* 116: 945-986.
- Driscoll, C. T., S. W. Effler and S. M. Doerr. 1995. Changes in inorganic carbon chemistry and deposition of Onondaga Lake, New York. *Environ. Sci. Tech.* 28: 1211-1218.
- Driscoll, C. T., S. W. Effler and S. M. Doerr. 1996. Anoxic organic carbon decomposition and the distribution of related chemical species (Chapter 5). *In* S. W. Effler (ed.). *Limnological and engineering analysis of a polluted urban lake. Prelude to environmental management of Onondaga Lake, New York.* Springer-Verlag, NY (in press).
- Effler, S. W. (ed.). 1996. *Limnological and engineering analysis of a polluted urban lake. Prelude to environmental management of Onondaga Lake, New York.* Springer-Verlag, NY (in press).
- Effler, S. W., C. M. Brooks and K. A. Whitehead. 1996. Domestic waste inputs of nitrogen and phosphorus to Onondaga Lake, and water quality implications. *Lake and Reserv. Manage.* 12(1):127-140.
- Effler, S. W., J. P. Hassett, M. T. Auer and N. Johnson. 1988. Depletion of epilimnetic oxygen and accumulation of hydrogen sulfide in the hypolimnion of Onondaga Lake, NY, USA. *Wat., Air, Soil Pollut.* 39: 59-74.
- Effler, S. W. and R. D. Hennigan. 1996. Onondaga Lake, New York: legacy of pollution. *Lake and Reserv. Manage.* 12(1):1-13.
- Effler, S. W. and E. M. Owens. 1996. Density stratification in Onondaga Lake: 1968-1994. *Lake and Reserv. Manage.* 12(1):25-33.
- Fallon, R. D., S. Harrets, R. S. Hanson and T. D. Brock. 1980. The role of methane in internal carbon cycling in Lake Mendota during summer stratification. *Limnol. Oceanogr.* 25:357-360.
- Fendinger, N. J. and D. D. Adams. 1986. A headspace equilibrium technique for measurement of dissolved gases in sediment pore water. *Intern. J. Anal. Chem.* 23: 253-265.
- Gelda, R. K. and M. T. Auer. 1996. Development and testing of a dissolved oxygen model for a hypereutrophic lake. *Lake and Reserv. Manage.* 12(1):165-179.
- Gelda, R. K., M. T. Auer and S. W. Effler. 1995. Determination of sediment oxygen demand by direct measurements and by inference from reduced species accumulation. *Mar. Freshwat. Res.* 46:81-88.
- Ingvorsen, K. and T. D. Brock. 1982. Electron flow via sulfate reduction and methanogenesis in the anaerobic hypolimnion of Lake Mendota. *Limnol. Oceanogr.* 27: 559-564.
- Ingvorsen, K., J. G. Zeikus and T. D. Brock. 1981. Dynamics of bacterial sulfate reduction in a eutrophic lake. *Appl. Environ. Microbiol.* 42:1029-1036.
- Iverson, N., R. S. Oremland and M. I. Klug. 1987. Big Soda Lake (Nevada). 3. pelagic methanogenesis and anaerobic methane oxidation. *Limnol. Oceanogr.* 32: 804-814.
- Jannasch, H. W. 1975. Methane oxidation in Lake Kivu (central Africa). *Limnol. Oceanogr.* 20: 860-864.
- Jorgensen, B. B., J. G. Kuenen and Y. Cohen. 1979. Microbial transformations of sulfur compounds in a stratified lake (Solar Lake, Sinai). *Limnol. Oceanogr.* 24: 799-822.
- Kelly, C. A. and D. P. Chynoweth. 1979. Methanogenesis: a measure of chemoorganotrophic (heterotrophic) activity in anaerobic lake sediments. *In*: J. W. Costerton and R. R. Colwell (eds.). *Native aquatic bacteria: enumeration, activity, and ecology*, American Society for Testing and Materials, ASTM STP 695:164-179.
- Kelly, C. A. and D. P. Chynoweth. 1981. The contributions of temperature and of the input of organic matter in controlling rates of sediment methanogenesis. *Limnol. Oceanogr.* 26: 891-897.
- Kelly, C. A., J. W. M. Rudd and D. W. Schindler. 1988. Carbon and electron flow via methanogenesis,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{4+}$  reduction in the anoxic hypolimnia of three lakes. *Arch. Hydrobiol. Beih. Ergebin. Limnol.* 31: 333-344.
- Lovley, D. R. and M. J. Klug. 1983. Sulfate reducers can outcompete methanogens at freshwater sulfate concentrations. *Appl. Environ. Microbiol.* 45: 187-192.
- Lovley, D. R., D. F. Dwyer and M. J. Klug. 1982. Kinetics analysis of competition between sulfate reducers and methanogens for hydrogen in sediments of a eutrophic lake. *Appl. Environ. Microbiol.* 43: 1373-1379.
- Martens, C. S. and J. V. Klump. 1980. Biochemical cycling in an organic-rich coastal marine basin: 1. Methane sediment-water exchange processes. *Geochimica Cosmochim. Acta* 44: 471-490.
- Owens, E. M. 1987. Bathymetric survey of Onondaga Lake. Onondaga County, Syracuse, NY. 16 p.
- Owens, E. M. and S. W. Effler. 1989. Changes in stratification in Onondaga Lake, New York. *Wat. Res. Bull.* 25: 587-597.
- Owens, E. M. and S. W. Effler. 1996. Hydrodynamics and transport (Chapter 4). *In* S. W. Effler (ed.). *Limnological and engineering analysis of a polluted urban lake. Prelude to environmental*

- management of Onondaga Lake, New York. Springer-Verlag, NY (in press).
- Robertson, C. K. 1979. Quantitative comparison of the significance of methane in the carbon cycles of two small lakes. *Arch. Hydrobiol. Bein. Ergebn. Limnol.* 12: 123-135.
- Rowell, H. C. 1995. Paleolimnology of Onondaga Lake: the history of anthropogenic impacts on water quality. *Lake and Reserv. Manage.* 12(1):35-45.
- Rudd, J. W. M., A. Furutani, R. J. Flett and R. D. Hamilton. 1976. Factors controlling methane oxidation in shield lakes: the role of nitrogen fixation and oxygen concentration. *Limnol. Oceanogr.* 21: 357-364.
- Rudd, J. W. M. and R. D. Hamilton. 1975. Methane oxidation in a eutrophic Canadian Shield lake. *Verh. Internat. Verein. Limnol.* 19: 2669-2673.
- Rudd, J. W. M. and R. D. Hamilton. 1978. Methane cycling in a eutrophic shield lake and its effects on whole lake metabolism. *Limnol. Oceanogr.* 23: 337-348.
- Rudd, J. W. M., R. D. Hamilton and N. E. R. Campbell. 1974. Measurement of microbial oxidation of methane in lake water. *Limnol. Oceanogr.* 19: 519-524.
- Rudd, J. W. M., and C. D. Taylor. 1980. Methane cycling in aquatic environments. *Adv. Aquat. Microbiol.* 2: 77-150.
- Strayer, R. F. and J. M. Tiedje. 1978. *In situ* methane production in a small, hypereutrophic, hard water lake: loss of methane from sediments by vertical diffusion and ebullition. *Limnol. Oceanogr.* 23: 1201-1206.
- Sweerts, J. P. A., M. J. Bar-Gilissen, A. A. Corneleuses and T. E. Cappenburg. 1991. Oxygen consuming processes at the profundal and littoral sediment-water interface of a small meso-eutrophic lake (Lake Vecht, The Netherlands). *Limnol. Oceanogr.* 36: 1124-1133.
- Tango, P. J. and N. H. Ringler. 1996. The role of pollution and external refugia in structuring the Onondaga Lake fish community. *Lake and Reserv. Manage.* 12(1):81-90.
- 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. Envir. Eng. Div. ASCE* 109: 830-844.
- Yin, C. and D. L. Johnson. 1984. An individual particle analysis and budget study of Onondaga Lake sediments. *Limnol. Oceanogr.* 29: 1193-1201.