The flux of CO₂ and CH₄ from lakes and rivers in arctic Alaska

George W. Kling, George W. Kipphut¹ & Michael C. Miller²

Department of Biology, University of Michigan, Ann Arbor, MI 48109, USA; ¹Institute of Marine Science, University of Alaska, Fairbanks, AK 99775, USA; present address: Center for Reservoir Research, Murray State University, Murray, KY 42071, USA; ²Department of Biological Sciences, University of Cincinnati, Cincinnati, OH 45221, USA

Key words: Alaska, arctic, carbon budgets, methane, limnology

Abstract

Partial pressures of CO₂ and CH₄ were measured directly or calculated from pH and alkalinity or DIC measurements for 25 lakes and 4 rivers on the North Slope of Alaska. Nearly all waters were supersaturated with respect to atmospheric pressures of CO₂ and CH₄. Gas fluxes to the atmosphere ranged from -6.5 to 59.8 mmol m⁻² d⁻¹ for CO₂ and from 0.08 to 1.02 mmol m⁻² d⁻¹ for CH₄, and were uncorrelated with latitude or lake morphology. Seasonal trends include a buildup of CO₂ and CH₄ under ice during winter, and often an increased CO₂ flux rate in August due to partial lake turnover. Nutrient fertilization experiments resulted in decreased CO₂ release from a lake due to photosynthetic uptake, but no change in CO₂ release from a river due to the much faster water renewal time. In lakes and rivers the groundwater input of dissolved CO₂ and CH₄ is supplemented by in-lake respiration of dissolved and particulate carbon washed in from land. The release of carbon from aquatic systems to the atmosphere averaged 24 g C m⁻² y⁻¹, and in coastal areas where up to 50% of the surface area is water, this loss equals 1/5 to 1/2 of the net carbon accumulation rates estimated for tundra.

Introduction

There are large stores of carbon in arctic environments (Bliss *et al.*, 1981). Arctic ecosystems are expected to be affected strongly by future climatic change (Lachenbruch & Marshall, 1986; Grotch, 1988; Abelson, 1989), and if these ecosystems either accumulate additional carbon or lose carbon to the atmosphere they will be important to the global carbon budget (Bolin *et al.*, 1986; Trans *et al.*, 1990; Post, 1990).

At present tundra ecosystems are considered to be small sinks for CO_2 . The amount of carbon extracted from the atmosphere during photosynthesis is slightly more than that respired by plants and soils and lost to the atmosphere (Chapin *et al.*, 1980; Billings, 1987). But these estimates of carbon balance in the arctic are only for terrestrial ecosystems; there is evidence that additional carbon loss to and from aquatic ecosystems may be important. Schell & Ziemann (1983) found that the rate of carbon loss by erosion of peat into coastal lakes, and through transport by rivers to the sea, was a substantial percentage of the long-term carbon accumulation rates on land. The input of terrestrial peat can dominate carbon cycling in more inland rivers as well (Peterson *et al.*, 1986). There is also some indication that terrestrial carbon washed into water bodies is respired and lost to the atmosphere as CO_2 . For example,

Coyne & Kelley (1974) found that one coastal pond and one coastal lake near Point Barrow were strongly heterotrophic, supersaturated with CO_2 , and continuously released CO_2 to the atmosphere. In contrast to the terrestrial CO_2 sink, tundra ecosystems are considered to be sources of CH_4 to the atmosphere (Whalen & Reeburgh, 1990a). Several taiga and arctic lakes have also been reported to release CH_4 to the atmosphere at rates similar to those observed for the tundra (Whalen & Reeburgh, 1990b).

The CO_2 flux data from this study were described in brief by Kling *et al.* (1991); in this paper we present the details of the processes controlling annual and seasonal variation in CO_2 flux from surface waters in the Arctic, and we present new data on CH_4 concentration and flux. We conclude that because some of the carbon respired in the terrestrial environment makes its way into lakes and rivers where it is released to the atmosphere, this loss of carbon from aquatic ecosystems must be included in regional carbon budgets for the Arctic.

Site description

All sites are located on the North Slope of arctic Alaska and cover an area from Mt. Roche stream (68.23° N) in the Brooks Range foothills to Lake Maxine (70.22° N) near Prudhoe Bay on the Arctic Ocean (Fig. 1, Table 1). All sites are within several kilometers of the Dalton Highway.

Fig. 1. Map showing the North Slope of Alaska and the location of the oil pipeline and Toolik Lake. Samples from the Kuparuk River were taken near the oil pipeline crossing. Exact locations and morphometric data for each site are given in Kling *et al.* (1992).

Sellmann *et al.* (1975) presented a contour map of water coverage for much of the North Slope. We have integrated their map contours by planimetry to arrive at the relative proportions of land (86%) and water (14%) for arctic Alaska north of latitude 69.5° and between Point Lay (162.5° W) and Brownlow Point (146° W) (Fig. 1).

Methods

 CO_2 partial pressures were measured directly or calculated given pH, temperature, and concentrations of alkalinity or dissolved inorganic carbon (DIC). Alkalinity was determined by potentiometric titration and the curves analyzed by the method of Gran (Stumm & Morgan, 1981). Once titration endpoints were known and found to be consistent over time for particular lakes, titrations were made to a specific endpoint. Water for DIC analysis was collected from just below the lake or stream surface without exposure to the atmosphere and preserved with HgCl₂. In the lab, samples were acidified with phosphoric acid and purged with nitrogen gas into a vacuum line. CO₂ was collected by cryogenic distillation and gas pressures measured by an electronic manometric gauge. The precision of this procedure was about $\pm 5 \,\mu$ mol CO₂ kg⁻¹. Dissociation constants from Plummer & Busenburg (1982) and carbonate species relations from Stumm & Morgan (1981) were used for conversion of alkalinity and DIC to dissolved $CO_2(aq)$ concentrations. In some waters, gas pressures were measured directly by equilibration of water samples with an air-filled (for CO_2) or nitrogen-filled (for CH_4) headspace. After equilibration, headspace gas was analyzed on a thermal conductivity (for CO_2) or a flame ionization (for CH_4) gas chromatograph. Atmospheric concentrations of CH₄ were taken as 1.7 μ atm; concentrations of CO₂ were taken as 350 µatm (Tans et al., 1990, Point Barrow Sta-



Lakes	DATE	N	Temp (°C)	$P_{CO_2}(\mu atm)$	CO_2 Flux (mmol m ⁻² d ⁻¹)
E1	Aug 83–Jul 86	3	_	2758 <u>+</u> 1215	59.8 ± 30.2
NE14	Aug 86–Jun 88	2	_	1954 <u>+</u> 904	39.7 <u>+</u> 21.3
Toolik	Jun 75-Aug 89	62	-	1847 ± 238	35.0 ± 5.3
N1	Aug 83–Jul 88	3	_	1170 ± 689	20.5 ± 16.4
Island	Jul 86–Jul 88	2	_	1040 ± 6	17.8 ± 0.3
N2	Aug 83-Aug 89	44	-	825 <u>+</u> 89	12.5 ± 2.2
S6	Jul 86–Jul 88	2	-	628 ± 303	7.8 <u>+</u> 7.6
18	22 July 86	1	14.0	2155	45.5
NE2	22 July 86	1	15.5	1972	41.5
Windy	8 July 88	1	14.0	1836	40.1
Dam	4 July 85	1	11.0	1591	30.9
Silhouette	8 July 88	1	13.0	1552	32.4
Galbraith	6 July 88	1	17.5	1477	29.1
Carolyn	9 July 88	1	11.0	1333	26.1
S3	22 July 86	1	17.0	1194	22.1
NE12	29 June 88	1	15.5	925	15.3
Africa	9 July 88	1	11.0	919	15.1
Charles	8 July 88	1	18.8	818	13.0
Coleen	10 July 88	1	11.0	761	11.0
Maxine	9 July 88	1	9.8	584	6.2
William	11 July 88	1	17.0	504	4.5
Bern	10 July 88	1	9.5	459	3.0
George	7 July 88	1	19.0	359	1.1
Anne	7 July 88	1	19.5	291	-0.7
Camp	13 July 88	1	20.5	93	- 5.5
Rivers					
Kuparuk	Aug 83–Aug 89	21	_	812 ± 177	11.9 ± 1.5
Hershey	Aug 85–Jul 88	3	-	845 ± 182	12.8 ± 4.3
Mt. Roche	6 July 88	1	10.5	369	1.4
Oksrukuyuk	7 July 88	1	13.9	418	2.3

Table 1. CO_2 flux data for North Slope lakes and rivers. Positive fluxes indicate evasion of CO_2 from water to atmosphere. Mean and grand mean values are given ± 1 SE. Site names and locations correspond to data in Klint *et al.* (this issue).

tion) and seasonal variations (up to 10 μ atm; Coyne & Kelley, 1974) were ignored. P_{CO2} and the concentration of CO₂ in equilibrium with the atmosphere (CO₂eq) was calculated using Henry's law and the CO₂ fugacity-pressure relationship presented in Weiss (1974). The concentration of CH₄ in equilibrium with the atmosphere was calculated using equations in Wilhelm *et al.* (1977). Corrections for vapor pressure were made using equations in Buck (1981).

 CO_2 and CH_4 flux was calculated using the equation

$$Flux = (D/z)*(Aq - Eq)$$

where D is the molecular diffusion of CO_2 or CH_4

 $(\text{cm}^2 \text{ s}^{-1})$ taken from Himmelblau (1964), z is the thickness of the surface boundary layer (μ m), Aq is the concentration of gas at the bottom of z, and Eq is the concentration of gas in water exposed to the atmosphere at the top of z (see Broecker & Peng, 1974). Because the pH of natural waters studied was typically much less than 9.0, chemically enhanced CO₂ gas exchange was assumed to be negligible (Emerson, 1975a).

From 1988 to 1990 wind speed was measured with an RM Young anemometer at 5 m height at two stations near Toolik Lake. The mean wind speed in the ice-free months (June–September) was 3.3 ± 0.2 m sec⁻¹ (± 1 SE; taken from a total of 7 monthly means of averaged daily wind speeds). This value was similar to the mean of 2.3 m sec⁻¹ at 0.5 m height reported by Miller *et al.* (1986). On the coastal plain at Barrow the average wind speed is somewhat higher (June–September mean = 6.3 ± 0.2 m sec⁻¹ at 10 m height, Hobbie, 1980), due in part to the greater height of measurement. Maximum wind speeds were seldom great enough to affect CO₂ saturation values due to bubble entrainment and 'wind pumping' (Smith & Jones, 1985; Merlivat & Memery, 1983).

The boundary layer z for all lakes was conservatively estimated as 200 μ m using an empirical relation with wind speed. The regression equation used was $\log_{10} (z, \mu m) = 2.56 - 0.133 * (wind)$ speed, m s⁻¹), SE_{intercept} = 0.04, SE_{slope} = 0.007, $r^2 = 0.71$, N = 147 (data not corrected to common reference height; values from Kanwisher, 1963; Hoover & Berkshire, 1969; Liss, 1973; Emerson, 1975b; Broecker et al., 1978; Broecker et al., 1980; Bower & McCorkle, 1980; Torgersen et al., 1982; Merlivat & Memery, 1983; Hartman & Hammond, 1984; Jähne et al., 1984; Wanninkhof et al., 1985, 1987). This value of 200 μ m, which translates to a CO₂ exchange coefficient at 10 °C of 2.11 cm hr⁻¹, may be somewhat too large. For example, using the CO₂ flux measurements of Coyne & Kelly (1975) for an arctic coastal lake, which were made directly in chambers and are therefore independent of the assumptions required to estimate z, we back calculated a boundary layer z equal to only 44 μ m. This value is similar to recent measurements made in other lakes (Wanninkhof et al., 1985). Boundary layer thickness in rivers is difficult to estimate because surface turbulence is generated by advection in addition to wind sheer. Wanninkhof et al. (1990) estimated a gas exchange coefficient of 21 cm hr⁻¹ (boundary layer of about 25 μ m) for a river; we assumed a thickness of $200 \,\mu m$ for both the rivers and lakes in our study. Therefore, our value of 200 μ m may be conservative in some lakes and is most likely too conservative in the rivers, and thus our calculated CO₂ fluxes may underestimate actual fluxes.

We tested this flux equation in one lake by measuring wind speed and the flux of CO_2 into a

floating plexiglass chamber (surface area $= 0.2 \text{ m}^2$). The calculated flux of 8.6 mmol m⁻² d⁻¹ (estimated boundary layer of 400 μ m at ambient conditions) compared very well to a measured chamber flux of 6.7 mmol m⁻² d⁻¹.

Annual and seasonal variations in CO₂ flux as well as the effects of nutrient fertilization were estimated from weekly data taken from Lake N2. From 1985 to 1990 this lake has been divided by a plastic curtain and one half fertilized with phosphoric acid and NH₄NO₃. Each year nutrients were added continuously starting on 1 July and ending on 15 August at loading rates of about 3 mmol N m⁻² d⁻¹ and 0.25 mmol P m⁻² d⁻¹. Chlorophyll a (CHLa) was extracted in 90% acetone and concentrations were calculated using equations in Wetzel & Likens (1979). Primary production was measured using 24 hr incubations with ¹⁴C labeled bicarbonate (method details in Miller et al., 1986). Numeric variables used for statistical analyses were log transformed to normalize distributions and to reduce heteroscedasticity.

Results and discussion

Although the 25 lakes and 4 rivers studied lie in varied terrain, there were no systematic patterns of gas flux with site location. Nor were there statistically significant linear or non-linear trends of gas flux with lake area or maximum depth.

The mean surface water P_{CO2} for all lakes was 1162 ± 134 µatm (± 1 SE), which is supersaturated by more than 3 times with respect to the atmosphere (Table 1). The flux of CO₂ from water to the atmosphere ranged from -5.5 to 59.8 mmol m⁻² d⁻¹, and averaged 20.9 ± 3.3 (N = 25) in the lakes and 7.1 ± 3.0 mmol m⁻² d⁻¹ in the rivers (N = 4). Only two lakes showed invasion of CO₂ from the atmosphere to water (negative fluxes). These CO₂ evasion rates are similar to rates reported previously for North Slope waters: 44.3 and 12.7 mmol m⁻² d⁻¹ for a pond and a lake, respectively, located near Point Barrow (Coyne & Kelley, 1974). Hesslein *et al.* (1980) reported smaller fluxes for an oligotrophic lake in northwestern Ontario.

The mean surface water P_{CH4} for the 9 sites examined was $272 \pm 50 \mu \text{atm} (\pm 1 \text{ SE}, \text{N} = 10)$, or more than 150 times the pressure at atmospheric saturation (Table 2). The calculated CH_4 flux to the atmosphere averaged 0.43 ± 0.08 mmol $m^{-2} d^{-1}$ (N = 10). We also measured directly a CH_4 flux of 0.13 mmol m⁻² d⁻¹ using a floating plexiglass chamber in Dam Pond. CH₄ supersaturation in unmanipulated arctic and taiga surface waters was also reported by Whalen and Reeburgh (1990b), who measured fluxes ranging from 0.29 to 8.17 mmol m⁻² d⁻¹ (N = 6, median = 0.52). There was a substantial buildup of CH_4 over winter at the bottom of the fertilized side of Lake N2 and in Lake N3 (Table 2). Lake N3 lies just downstream of N2 and has been affected by fertilizer addition to Lake N2. Some of the CH₄ that accumulated in these lakes was oxidized or lost to the atmosphere during ice-out and spring turnover; in Lake N2 bottom water, P_{CH4} decreased from 70590 μ atm in May to 4100 μ atm in July after ice-out. The origin of this CH₄ is due to microbial decomposition in anaerobic sediments or bottom waters; it is unlikely that large amounts of CH₄ are transported into the lake during winter when the ground is frozen. Similar CH₄ concentrations have been reported for a

eutrophic lake on the Canadian shield (Rudd & Hamilton, 1978) and for oligotrophic lakes in the Canadian arctic (Welch *et al.*, 1980).

Variations in CO_2 flux

Year to year variations in CO_2 flux for Lake N2 are shown in Table 3. The results are based on weekly data taken from late June through August

Table 2. Methane pressure, concentration, and flux in lakes and in the Kuparuk River; P_{CH_4} was measured directly and the concentration of CH₄ was calculated using solubility data. Pond386 is located next to the Dalton Highway at a latitude of 69°50' N. The values for Lake William are duplicates, and the values for Lakes N3 and N2-fert on 12 May 90 were taken under ice.

Site	Date	Depth (m)	Temp (°C)	CH_4 (µmol 1 ⁻¹)	Ρ _{CH4} (µatm)	$CH_4 Flux (mmol m-2 d-1)$
Toolik	14 Jul 90	0	15	1.10	642	1.02
		23	4	0.46	203	
N2-cont	14 Jul 90	0	15	0.57	333	0.53
		6	8	0.25	123	
N2-fert	14 Jul 90	0	15	0.25	146	0.23
		6	8	0.28	138	
		10	6	8.80	4097	
	12 May 90	3	1.6	0.15	62	
		5	2.5	0.26	110	
		6	2.8	0.17	72	
		7	3.0	0.13	56	
		8	3.0	0.55	235	
		9	3.0	165	70590	
N1	14 Jul 90	0	15	0.09	53	0.08
		12	6	0.08	37	
Dam	14 Jul 90	0	15	0.46	269	0.43
	15 Jul 90	0	15	0.55	321	0.51
William	5 Aug 90	0	12	0.34	185	0.29
		0	12	0.37	201	0.32
Coleen	5 Aug 90	0	8	0.41	201	0.31
Windy	5 Aug 90	0	9	0.29	146	0.23
Pond386	5 Aug 90	0	10	0.62	321	0.50
N3	12 May 90	3.5	2.5	16.7	7042	
Kuparuk R.	5 Aug 90	0	8	0.48	236	0.36

Table 3. Year to year variations in CO_2 flux (FCO₂), DIC, CHLa, and temperature in Lake N2. Samples were taken weekly and mean values are reported ± 1 SE. Temp (°C) is reported as the average value from 0 to 3 m depth to reduce variability introduced by short term fluctuations in surface temperatures. ANOVA statistics are given for the null hypothesis that the response of these variables is the same across years. Scheffe's multiple comparison of means is reported only when the overall F value is significant; different letters indicate statistically significant differences between years (P < 0.05).

Year	Lake N2–Control						
	$FCO_2 \text{ (mmol m}^{-2} \text{ d}^{-1}\text{)}$	DIC (μ mol 1 ⁻¹)	CHLa (µg l ⁻¹)	Temp (°C)			
1985	0.9 ± 1.6A	792 ± 50A	0.65 ± 0.12	13.4 ± 0.6			
1986	$8.9 \pm 1.3 AB$	$849 \pm 47A$	0.90 ± 0.14	14.7 ± 0.9			
1987	15.5 + 6.1B	1105 + 42B	1.38 ± 0.33	14.9 ± 0.7			
1988	12.5 + 4.6B	1268 + 52B	1.82 + 0.53	13.4 + 1.0			
1989	$15.5 \pm 3.4B$	$1317 \pm 38B$	-	13.7 ± 0.4			
ANOVA F	5.94	31.3	1.87	0.86			
df	42	42	26	40			
P > F	0.0008	0.0001	0.16	0.49			
Year	Lake N2–Fertilized						
	$FCO_2 \text{ (mmol m}^{-2} d^{-1}\text{)}$	DIC (μ mol l ⁻¹)	CHLa (µg 1 ⁻¹)	Temp (°C)			
1985	- 4.4 + 1.0	782 + 50A	5.41 + 1.78	138 + 0.6			
1986	$\frac{-}{1.0+2.1}$	1334 + 43BC	4.63 + 0.88	14.1 + 0.6			
1987	5.4 + 4.5	1231 + 29B	7.40 + 1.80	14.7 + 0.7			
1988	2.0 + 1.6	1515 + 33D	7.28 + 1.75	12.8 + 0.8			
1989	1.4 ± 2.0	$1457 \pm 24 DC$	_	13.2 ± 0.5			
ANOVA F	1.91	72.7	0.27	1.38			
df	51	51	32	43			
P > F	0.12	0.0001	0.85	0.26			

for the period 1985–1989. An analysis of variance (ANOVA) shows that the variation in CO_2 flux over time is significant (F = 5.94, df = 42,P<0.0008), and an *a posteriori* multiple comparison of means indicates that the average CO_2 flux was significantly lower in 1985 than in subsequent years (Table 3). The reasons for this difference in 1985 are unclear, although DIC concentrations were also significantly lower in 1985 and 1986 than in other years. DIC concentrations may have been altered because installation of the curtain restricted flow between the two sides of the lake and confined the major stream inflow to the control side. Insufficient data exist over these years to determine the effect of variable rain and snowfall on CO₂ flux.

Year to year variations in CO_2 flux for Toolik Lake were also small. Although the overall F-test for the hypothesis that CO_2 flux is the same among years was significant (P > F = 0.009), Scheffe's test was unable to discriminate between any two specific years (Table 4). There were also no significant differences in DIC concentrations among all years (Table 4). The absence of a strong trend over the last 14 years suggests that such CO₂ flux is not a recent phenomenon; it is probable, but not demonstrable, that CO₂ evasion has been a characteristic of these arctic ecosystems for a minimum of several tens to several hundreds of years.

Inter-annual variability in CO_2 flux of other lakes ranged from low in Island Lake (17.6 and 18.1 mmol m⁻² d⁻¹ in July 1986 and July 1988, respectively) to high in Lake E1 (58, 8.4, and 113 mmol m⁻² d⁻¹ in August 1983, June 1985, and July 1986). Part of this high annual variation in Lake E1 may be due to the fact that sampling was done in different seasons each year.

Year	TOOLIK LAKE				
	N	CO_2 Flux (mmol m ⁻² d ⁻¹)	DIC (μ mol l ⁻¹)		
1975	4	20.5 ± 6.7	396 ± 53		
1976	7	34.6 ± 19.8	501 ± 46		
1977	11	66.7 ± 20.0	568 <u>+</u> 56		
1978	5	58.3 ± 19.7	495 ± 45		
1979	10	27.9 ± 5.5	516 ± 22		
1980	10	37.0 ± 10.1	557 ± 49		
1983	5	12.2 ± 1.4	478 ± 34		
1984	2	10.6 ± 0.6	633 <u>+</u> 64		
1989	8	10.7 ± 1.8	517 ± 23		
ANOVA F		2.92	1.83		
df		61	73		
P > F		0.009	0.092		

Table 4. Year to year variations in CO₂ flux and DIC concentrations in Toolik Lake. Means $(\pm 1 \text{ SE})$ are reported for N surface water samples taken weekly during eacht ice-free season (see Fig. 3). ANOVA statistics are given for the null hypothesis that the response of these variables is the same across years.

Seasonal variations in CO₂ flux were studied intensively in Lake N2 and Toolik Lake. Figure 2 illustrates the general trends in CO₂ flux, pH, and concentrations of DIC and CHLa during the summer growing season in Lake N2 over 5 years. In the control side of the lake there were no strong seasonal trends in any variable for each year or when all five years were grouped together; for example, none of the slopes of the regression of CO₂ flux on sampling date were significantly different (P < 0.05) from zero for each year. With few exceptions, the CO₂ flux was always from the lake to the atmosphere. In the fertilized side of the lake, however, there were distinct seasonal trends as well as statistically significant differences in the response of these variables relative to the control side (Fig. 2, Table 5). Just after ice-out in mid to late June the CO_2 flux was positive and roughly equal in both sides of the lake. With the onset of nutrient enrichment the CHLa concentrations increased in the fertilized side. As the phytoplankton reduced the pool of $CO_2(aq)$ in the fertilized side, surface water pH rose and CO₂ flux fell. After mid July the flux of CO₂ from water to atmosphere reversed and there was net invasion of CO_2 into the fertilized side of the lake (Fig. 2). This invasion of CO₂ may be somewhat underestimated due to chemically enhanced CO₂ exchange at high pH, although the relatively thin boundary layer and high DIC concentrations in Lake N2 would moderate the enhancement (see Emerson, 1975a). Maximum invasion rates during this time were similar to invasion rates in



Fig. 2. Seasonal variation in CO_2 flux, DIC, CHLa, and pH for years 1985–1989 in Lake N2. All values are for surface water.

Table 5. Statistical comparison between control and fertilized sides of Lake N2 and reaches of Kuparuk River for CO₂ flux (mmol m⁻² d⁻¹), DIC (μ mol l⁻¹), P_{CO2} (μ atm), CHLa (μ g l⁻¹), pH and temperature (°C). Temperature is reported as the average value from 0 to 3 m depth to reduce variability introduced by short term fluctuations in surface temperatures. All years with data are lumped together for each analysis. ANOVA statistics are given for the null hypothesis that the response of the variables is the same between control and fertilized sides.

Lake N2-Control vs. Fertilized						
	CO ₂ flux	DIC	CHLa	Temp	pH	
Mean + SE						
Control	12.6 ± 2.2	1120 ± 38	1.2 ± 0.2	14.0 ± 0.32	7.93 <u>+</u> 0.03	
Fert	1.4 ± 1.0	1351 <u>+</u> 35	6.5 ± 0.9	13.6 ± 0.30	8.36 <u>+</u> 0.05	
ANOVA F	35.8	17.9	47.7	0.87	60.2	
df	94	94	59	84	94	
P > F	0.0001	0.0001	0.0001	0.35	0.0001	
Kuparuk River-C	Control vs. Fertilized					
		СС	2 flux		P _{CO2}	
Mean <u>+</u> SE						
Control		12.	846 <u>+</u> 102			
Fert		11.0 ± 1.8			775 <u>+</u> 76	
ANOVA F		0.21			0.16	
df		11			11	
P > F		0.66			0.69	

other softwater lakes (Herczeg, 1987). As summer progressed into August, the highest CO_2 evasion rates and DIC concentrations tended to occur for both sides of Lake N2. Hypolimnetic water had higher $CO_2(aq)$ concentrations than did surface water, and therefore this tendency may be in response to partial breakdown of thermal structure as the lake cooled and hypolimnetic water was mixed to the surface.

In Toolik Lake the highest CO_2 evasion rates occurred very early in the season in most of the 9 years studied (Fig. 3). These high rates were associated with DIC concentrations and primary production rates that were also highest at this time of year (Fig. 3). It is apparent that uptake of CO_2 during photosynthesis is an unimportant control on CO_2 flux in this oligotrophic lake. These early season fluxes suggest that CO_2 builds-up under ice during winter. Evasion of this CO_2 during ice-out may be missed if sampling begins in late June or early July as it did in Lake N2. For example, P_{CO_2} values calculated under ice on 10 May 1990 were higher than maximum values recorded during the open water season in Lakes N1, N2, S6, and Toolik (Table 6). Similar increases in P_{CO2} under ice were found in arctic coastal plain lakes (Coyne & Kelley, 1974). Some of this CO₂ may be depleted by photosynthetic

Table 6. Calculated P_{CO_2} values for under-ice versus openwater samples. Under-ice samples were taken on 10 and 11 May 1990. Open-water samples are presented as a mean with the maximum value in parentheses (see Table 1).

Lake	P_{CO_2} (µatm)			
	Open-water	Under-ice		
N1	1170(2548)	3913,4894		
S6	628 (930)	6348		
N2 control	825(2916)	8866		
(all years)				
N2 fert	373(1581)	5547		
(all years)				
Toolik	758(1125)	3701		
(1989)				



Fig. 3. Seasonal variation in CO_2 flux, DIC, and primary production in Toolik Lake during 1975–1980, 1983, 1984, and 1989. All values are for surface water. Production data for 1975–1980 are from Miller *et al.* (1986).

uptake before ice-out, because net primary production can be substantial under ice if there is little snow cover (Hobbie, 1980; Miller et al., 1986). Such depletion appears to be small in these lakes; for example in Lake N2, a net production rate of 2.5 mmol C m⁻³ d⁻¹ from 10 May to 10 June (rate taken from June 1988) would decrease the concentration of $CO_2(aq)$ in surface waters from a measured 600 μ mol 1⁻¹ to 525 μ mol 1⁻¹. This value of 525 μ mol 1⁻¹ is still more than an order of magnitude higher than CO₂(aq) concentrations measured at the end of June following ice-out. Thus there must be a large evasion of CO₂ from these lakes during ice-out and lake turnover in early June. While CO₂ evasion most likely continues until freeze-up, episodes of CO₂ invasion from the atmosphere are probably rare because of deteriorating conditions for photosynthesis in late August and September (Miller et al., 1986).

The seasonal response of decreased CO_2 flux' with increased phytoplankton growth following fertilization in Lake N2 contrasts with a similar fertilization experiment done in the Kuparuk

River. Since 1983 the Kuparuk has been fertilized with P and N and a control reach was maintained upstream (Peterson *et al.*, 1985). In 1985, 1988, and 1989 we sampled both fertilized and control reaches, and found no significant differences in CO_2 flux (Table 5). This contrast between lake and river most likely exists because the renewal time of water in the river is much faster than in the lake, and thus the amount of DIC moving through the fertilized reach during summer is too great to be changed by algal uptake.

We have no measurements of diurnal variations in CO_2 flux. Miller *et al.* (1986) reported that diurnal variations in photosynthesis in Toolik Lake were related positively to light and temperature. If the negative relationship between algal uptake of CO_2 and the flux of CO_2 from lake to atmosphere seen in lake N2 is typical during midsummer, our measurements made during the middle of the day will slightly underestimate the total daily CO_2 flux. This assumes that wind conditions remain constant or are higher at night.

Sources of CO₂

We believe that much of the CO_2 released from these lakes and rivers originates in the terrestrial environment. In most lakes of low to moderate alkalinity the invasion of CO₂ from the atmosphere supports net primary production, and the lakes are considered autotrophic (Schindler et al., 1972). If CO_2 is continually released to the atmosphere, however, the lakes are heterotrophic or they are acting as conduits for terrestrially produced CO₂. In either case, there must be a net influx of carbon or a critical change in sediment conditions such that old organic carbon accumulated in the sediment is respired. It is unlikely that bottom mud is being depleted to provide the CO_2 lost from these systems, judging from sediment accumulation rates in arctic lakes (Livingstone et al., 1958; Cornwell, 1985). In addition, rates of net benthic respiration, which include respiration of terrestrial detritus washed into the lake, are much less than the flux of CO_2 to the atmosphere in Lake N2 and Toolik Lake. In the control side

of Lake N2 net benthic respiration is on the order of 5 mmol C m⁻² d⁻¹ (Kipphut, unpubl. data). In Toolik Lake, net consumption of O₂ by the sediments averages 7.6 mmol m⁻² d⁻¹ (N=5; Cornwell & Kipphut, this issue), which is almost 5 times less than the CO₂ flux to the atmosphere (respiration quotient of 1; Table 1). Welch & Bergmann (1985) report an average respiration rate in ten arctic lakes of about 6 mmol O₂ m⁻² d⁻¹.

On the other hand, there are several lines of evidence indicating an important influx of dissolved and particulate carbon of terrestrial origin to arctic lakes and rivers. Thermokarst and fluvial processes cause great erosion of peat into lakes, especially along the coast (Sellmann *et al.*, 1975; Schell & Ziemann, 1983), and some of this terrestrial carbon is transferred to the aquatic food chain (Schell, 1983). In the Kuparuk River, Peterson *et al.* (1986) showed that the carbon cycle was dominated by inputs of peat from the streambank and dissolved organic carbon leached from tundra.

There is also direct evidence that DIC in groundwater is moving from land to surface waters. For example, from 1985 to 1990, P_{CO2} values from 11 soil lysimeters near the Kuparuk River averaged $8315 \pm 2191 \mu$ atm (N = 16; range 2240 to 26650 μ atm). These are minimum values because CO₂ in the large headspace of the lysimeter was not measured. High groundwater P_{CO2} values were also measured in the Toolik Lake watershed in summer 1990 (up to $46500 \,\mu atm$). Such high P_{CO2} values are due in part to permafrost conditions; groundwaters are confined by permafrost to shallow (50 cm) organic rich soil layers, where they can accumulate CO_2 produced by plant and microbial respiration. Movement of these CO₂-charged groundwaters into the Kuparuk River can explain the high P_{CO2} observed in the river (mean = $812 \pm 177 \ \mu atm$).

Our proposed mechanism of gas transport in groundwater is supported by CH_4 measurements. P_{CH4} values in two water samples from soil lysimeters near Toolik Lake were 36 500 and 12 600 μ atm (collected 14 July 1990). These values are much higher than the values we measured in lakes and rivers, suggesting that terrestrially produced CH_4 in groundwater moves into surface waters where it is released to the atmosphere.

An independent estimate of the importance of CO₂ transport from land to water comes from balancing the inputs and outputs of $CO_2(aq)$ in the Kuparuk River basin. On the basis of $CO_2(aq)$ concentrations in rainwater (air-saturated water) and an average groundwater P_{CO2} of 8315 μ atm in the upper Kuparuk basin, we calculate that 295×10^5 mol CO₂(aq) are input to the basin each year. Losses include a river output of 182 $\times 10^5$ mol C y⁻¹, a CO₂ flux to the atmosphere of 1.4×10^5 mol y⁻¹ (areal flux from Table 1 and a river surface area of 0.12 km²), and consumption by net primary production of 1.3×10^5 mol $CO_2(aq) y^{-1}$ (Peterson *et al.*, 1986), leaving an excess input from the terrestrial system of 110×10^5 mol C yr⁻¹. The river output assumes an average DIC concentration of 308 μ mol 1⁻¹ and that respiration of peat in the river is negligible (Peterson et al., 1986). This output includes CO₂(aq) plus bicarbonate and therefore is conservative with respect to the contribution of CO_2 from the terrestrial landscape. Thus in this river it appears that the excess CO₂ originates mainly from soil respiration and transport by groundwater. By comparison, in lakes the groundwater input of dissolved CO₂ is supplemented by inlake respiration of particulate and dissolved organic carbon washed in from the land, especially in sites on the coastal plain.

Tundra carbon budgets

The North Slope of Alaska is considered to be a net sink for carbon both today and in the past (Billings, 1987). This results from an excess of CO_2 uptake by plants over release of CO_2 during soil and root respiration. Chapin *et al.* (1980) assembled data from several sources and estimated this accumulation to be from 59 to 120 g C m⁻² y⁻¹ on the basis of a one year budget at Point Barrow. Billings (1987) estimated the arctic tundra accumulation to be about 41 g C m⁻² y⁻¹. On the basis of an eddy correlation

method involving profiles of CO₂ concentration above tundra at Barrow, Coyne & Kelley (1975) estimated a net accumulation of 40 g C m⁻² y⁻¹. If one assumes that the lower atmosphere is wellmixed on a spatial scale of one to two km², this eddy correlation method would include CO2 efflux from lakes and ponds. The additional efflux of CH₄ is less than 4 g C m⁻² y⁻¹ (39 mg C $m^{-2} d^{-1}$, from Whalen & Reeburgh, 1990b; 100 active days per year). Even so, the above estimates imply that the inventory of soil carbon stored above permafrost could have accumulated in the unreasonable time of only several hundred years (Billings, 1987). In comparison to these budget estimates, Schell & Ziemann (1983) used ¹⁴C dating of peat cores and reported a smaller long-term carbon accumulation rate of 13.3 g C $m^{-2} y^{-1}$ on the coastal plain.

Estimates of the importance of carbon transport from terrestrial to aquatic systems vary in these published budgets. Chapin et al. (1980) considered this pathway of carbon to play a 'relatively minor role in the annual budgets' of tundra near Barrow, and Billings (1987) assumed (but questioned) a loss of only $2 \text{ g C m}^{-2} \text{ y}^{-1}$ to aquatic systems. In their study of peat erosion and accumulation on the coastal plain, Schell & Ziemann (1983) found instead that loss of carbon to aquatic environments was a 'major factor'. The method of ¹⁴C-dating of peat cores measures a long-term net accumulation and would account for carbon losses from land to aquatic systems that the experimental measures would miss. We found that roughly 24 g C m⁻² are lost to the atmosphere from lakes and ponds on the North Slope each year (100 active days per year; includes 0.5 g C m⁻² lost as CH₄). The true value may be slightly higher considering that under-ice respiration in lakes is not included. In tundra rivers, some of the DOC and POC exported to the sea will be respired and lost to the atmosphere. Assuming that 50% of the surface area near the coast is water or marsh (Sellmann et al., 1975), this loss through aquatic systems is up to half of the terrestrial carbon accumulation rate. Subtracting 24 g C m⁻² y⁻¹ from the terrestrial budget estimates of carbon accumulation results

in a net accumulation closer to radiocarbon based estimates of long-term storage. Accounting for this loss of carbon to aquatic systems also gives more reasonable accumulation rates when considering the inventory of carbon currently in soils (Billings, 1987). Although lake density decreases away from the coast, water coverage on the entire North Slope above 69.5° latitude is still about 14% of the total surface area. The total loss of carbon from tundra lakes and rivers is about 0.02 Pg C y^{-1} , which is 7-20% of the current estimated carbon sink of 0.1-0.3 Pg C y⁻¹ for arctic tundra (14% water coverage, tundra area of 5×10^6 km²; see Post, 1990). These results support the idea that transport and eventual loss of dissolved and particulate carbon from land to water is an important process in Alaskan and probably other arctic environments.

CO_2 flux and changing climate

According to global climate models, northern latitudes will experience the largest temperature changes (4-12 °C) under a scenario of future global warming with a doubling of greenhouse gases (Grotch, 1988; Abelson, 1989; Lachenbruch & Marshall, 1986). Accumulation or loss of arctic carbon stocks depends on the balance between primary production and decomposition, although at present the effect of climate warming and the associated buildup of greenhouse gases on carbon cycling in the Arctic is unresolved. It is known, however, that in general primary production in aquatic and terrestrial arctic ecosystems is limited by nutrients rather than by temperature (Kalff & Welch, 1974; Hobbie, 1980; Miller et al., 1986; Chapin et al., 1980; Billings et al., 1984; Shaver & Chapin, 1986). On the other hand, temperature is most limiting to decomposition or respiration and thus to the generation and release of CO₂ (Heal et al., 1981; Billings et al., 1982). Because of these relationships between production, respiration, and temperature, recent projections hold that large releases of CO_2 to the atmosphere will occur given a 5 °C increase in average annual temperature (Post, 1990). The release of CH_4 to

the atmosphere is also expected to increase (Post, 1990; Livingston & Morrissey, 1990), although the importance of methane consumption in soils and its response to changing temperature and moisture regimes is somewhat in question (Whalen & Reeburgh, 1990a).

These increased carbon releases were predicted for terrestrial systems. our results indicate that they would be substantially augmented by CO₂ evasion from lakes and rivers. It is preliminary to assign values to future aquatic gas fluxes, because the response of land plants and the role of hydrology and nutrients remain ill-defined. The generation and transport of carbon through the landscape may be altered by changing water availability (Lachenbruch & Marshall, 1986; Post, 1990), and nutrient loss from the soil as a result of warmer temperatures (Nadelhoffer et al., 1991) may stimulate primary production in receiving water bodies. Our experiments indicate that given substantial nutrient enrichment and a slow water renewal time, photosynthesis could reduce the loss of CO₂ from naturally heterotrophic Arctic waters.

Acknowledgements

S. Whalen provided the CH_4 data for Lakes N2 and N3 on 12 May 90, and pH and alkalinity data for some sites. B. Moller, S. Sugai, B. Wang, M. Cheek, M. Castro, and A. Giblin assisted in the lab and field. We thank J. Hobbie, G. Shaver, B. Peterson, D. Schell, and one anonymous reviewer for discussion and comments. Research was supported by the National Science Foundation grants BSR8702328, DPP8722015, and DPP8320544, and by the A. W. Mellon Foundation. This is The Ecosystems Center, Marine Biological Center, University of Alaska Institute of Marine Science Contribution 901.

References

- Abelson, P. H., 1989. The Arctic: A key to world climate. Science 243: 873.
- Billings, W. D., 1987. Carbon balance of Alaskan tundra and

taiga ecosystems: past, present and future. Quat. Sci. Rev. 6: 165–177.

- Billings, W. D., J. O. Luken, D. A. Mortensen & K. M. Peterson, 1982. Arctic tundra: A source or sink for atmospheric carbon dioxide in a changing environment? Oecologia 53: 7–11.
- Billings, W. D., K. M. Peterson, J. O. Luken & D. A. Mortensen, 1984. Interaction of increasing atmospheric carbon dioxide and soil nitrogen on the carbon balance of tundra microcosms. Oecologia 65: 26–29.
- Bliss, L. C., O. W. Heal & J. J. Moore, 1981. Tundra ecosystems: A comparative analysis. IBP Handbook 25. Cambridge University Press, Cambridge, 715 pp.
- Bolin, B., B. R. Doos, J. Jager & R. A. Warrick, 1986. The greenhouse effect, climate change, and ecosystems. SCOPE 29. John Wiley & Sons, New York, 541 pp.
- Bower, P. & D. McCorkle, 1980. Gas exchange, photosynthetic uptake, and carbon budget for a radiocarbon addition to a small enclosure in a stratified lake. Can. J. Fish. aquat. Sci. 37: 464–471.
- Broecker, H. C., J. Peterman & W. Siems, 1978. The influence of wind on CO₂-exchange in a wind-wave tunnel, including the effects of monolayers. J. Mar. Res. 36: 595–610.
- Broecker, W. S. & T.-H. Peng, 1974. Gas exchange rates between air and sea. Tellus 16: 21-35.
- Broecker, W. S., T.-H. Peng, G. Mathieu, R. Heslein & T. Torgersen, 1980. Gas exchange rate measurements in natural systems. Radiocarbon 22: 676–683.
- Buck, A. L., 1981. New equations for computing vapor pressure and enhancement factor. J. appl. Meteorol. 20: 1527– 1532.
- Chapin, F. S., III, P. C. Miller, W. D. Billings & P. I. Coyne, 1980. Carbon and nutrient budgets and their control in coastal tundra. In J. Brown, P. C. Miller, L. L. Tieszen & F. K. Bunnell (eds), An Arctic Ecosystem, the Coastal Tundra at Barrow, Alaska. IBP Handbook 12. Dowden, Hutchinson & Ross, Inc., Stroudsburg: 458-482.
- Cornwell, J. C., 1985. Sediment accumulation rates in an Alaskan arctic lake using a modified ²¹⁰Pb technique. Can. J. Fish. aquat. Sci. 42: 809–814.
- Cornwell, J. C. & G. W. Kipphut, 1992. Biogeochemistry of manganese- and iron-rich sediments in Toolik Lake, Alaska. Hydrobiologia 240: 45–59.
- Coyne, P. I. & J. J. Kelley, 1974. Carbon dioxide partial pressures in arctic surface waters. Limnol. Oceanogr. 19: 928– 938.
- Coyne, P. I. & J. J. Kelley, 1975. CO₂ exchange over the Alaskan arctic tundra: meteorological assessment by an aerodynamic method. J. appl. Ecol. 12: 587–611.
- Emerson, S., 1975a. Chemically enhanced CO₂ gas exchange in a eutrophic lake: A general model. Limnol. Oceanogr. 20: 743–753.
- Emerson, S., 1975b. Gas exchange rates in small Canadian shield lakes. Limnol. Oceanogr. 20: 754–761.
- Grotch, S. L., 1988. Regional intercomparison of general circulation model predictions and historical climate data.

DOE/NBB-0084 TR041. U.S. Department of Energy. Washington. 291 pp.

- Hartman, B. & D. E. Hammond, 1984. Gas exchange rates across the sediment-water and air-water interfaces in south San Francisco Bay. J. Geophys. Res. 89: 3593– 3603.
- Heal, O. W., P. W. Flanagan, D. D. French & S. F. MacLean, Jr., 1981. Decomposition and accumulation of organic matter in tundra. In L. C. Bliss, O. W. Heal & J. J. Moore (eds), Tundra Ecosystems: A Comparative Analysis. IBP Handbook 25. Cambridge University Press, Cambridge: 587-633.
- Herczeg, A. L., 1987. A stable carbon isotope study of dissolved inorganic carbon cycling in a softwater lake. Biogeochemistry 4: 231–263.
- Hesslein, R. H., W. S. Broecker, P. D. Quay & D. W. Schindler, 1980. Whole-lake radiocarbon experiment in an oligotrophic lake at the Experimental Lakes Area, Northwestern Ontario. Can. J. Fish. aquat. Sci. 37: 454–463.
- Hobbie, J. E., 1980. Limnology of tundra ponds. IBP Handbook 13. Dowden, Hutchinson & Ross, Inc., Stroudsburg, 514 pp.
- Hoover, T. E. & P. C. Berkshire, 1969. Effects of hydration on carbon dioxide exchange across air-water interface. J. Geophys. Res. 74: 456–474.
- Himmelblau, D. M., 1964. Diffusion of dissolved gases in liquids. Chem. Rev. 64: 527-550.
- Jähne, B., K. H. Fischer, J. Imberger, P. Libner, W. Weiss, D. Imboden, U. Lemnin & J. M. Jaquet, 1984. Parametrization of air/lake gas exchange. In W. Brutsaert and G. H. Jirka (eds), Gas Transfer at Water Surfaces. D. Reidel, Dordrecht: 459-466.
- Kalff, J. & H. E. Welch, 1974. Phytoplankton production in Char Lake, a natural polar lake, and in Meretta Lake, a polluted polar lake, Cornwallis Island, Northwest Territories. J. Fish. Res. Bd Can. 31: 621–636.
- Kanwisher, J., 1963. On the exchange of gases between the atmosphere and the sea. Deep-Sea Res. 10: 195–207.
- Kling, G. W., G. W. Kipphut & M. C. Miller, 1991. Arctic lakes and streams as gas conduits to the atmosphere: implications for tundra carbon budgets. Science 251: 298– 301.
- Kling, G. W., W. J. O'Brien, M. C. Miller & A. E. Hershey, 1992. The biogeochemistry and zoogeography of lakes and rivers in arctic Alaska. Hydrobiologia 240: 1–14.
- Lachenbruch, A. H. & B. V. Marshall, 1986. Changing climate: Geothermal evidence from permafrost in the Alaskan arctic. Science 234: 689–696.
- Liss, P. S., 1973. Process of gas exchange across an air-water interface. Deep-Sea Res. 20: 221–238.
- Livingston, G. P. & L. A. Morrissey, 1990. An interannual comparison of arctic methane emissions: a climatic warming scenario. p. 105 In International Conference on the Role of the Polar Regions in Global Change, June 11–15, 1990, University of Alaska, Fairbanks. 230 pp.
- Livingstone, D. A., K. Bryan, Jr. & R. C. Leahy, 1958. Effects

of an arctic environment on the origin and development of freshwater lakes. Limnol. Oceanogr. 3: 192-214.

- Merlivat, L. & L. Memery, 1983. Gas exchange across an air-water interface: Experimental results and modeling of bubble contribution to transfer. J. Geophys. Res. 88: 707– 724.
- Miller, M. C., G. R. Hater, P. Spatt, P. Westlake & D. Yeakel, 1986. Primary production and its control in Toolik Lake, Alaska. Arch. Hydrobiol. Suppl. 74: 97–131.
- Nadelhoffer, K. J., A. E. Giblin, G. R. Shaver & J. A. Laundre, 1991. Effects of temperature and substrate quality on element mineralization in six arctic soils. Ecology 72: 242– 253.
- Peterson, B. J., J. E. Hobbie, A. E. Hershey, M. A. Lock, T. E. Ford, J. Robie Vestal, V. L. McKinley, M. A. J. Hullar, R. M. Ventullo & G. S. Volk, 1985. Transformation of a tundra river from heterotrophy to autotrophy by addition of phosphorus. Science 229: 1383–1386.
- Peterson, B. J., J. E. Hobbie & T. L. Corliss, 1986. Carbon flow in a tundra stream ecosystem. Can. J. Fish. aquat. Sci. 43: 1259-1270.
- Plummer, L. N. & E. Busenberg, 1982. The solubilities of calcite, aragonite and vaterite in CO_2 -H₂O solutions between 0 and 90 °C, and an evaluation of the aqueous model for the system CaCO₂-CO₂-H₂O. Geochim. Cosmochim. Acta 46: 1011–1040.
- Post, W. M., 1990. Report of a workshop on climate feedbacks and the role of peatlands, tundra, and boreal ecosystems in the global carbon cycle. Publ. No. 3289. Oak Ridge National Laboratory, Environmental Sciences Division, Oak Ridge, 32 pp.
- Rudd, J. W. M. & R. D. Hamilton, 1978. Methane cycling in a eutrophic shield lake and its effects on whole lake metabolism. Limnol. Oceanogr. 23: 337–348.
- Schell, D. M., 1983. Carbon-13 and carbon-14 abundances in Alaskan aquatic organisms: delayed production from peat in Arctic food webs. Science 219: 1068–1071.
- Schell, D. M. & P. J. Ziemann, 1983. Accumulation of peat carbon in the Alaska arctic coastal plain and its role in biological productivity. pp. 1105–1110. In Permafrost, Fourth International Conference, National Academy Press, Washington. 1524 pp.
- Schindler, D. W., G. J. Brunskill, S. Emerson, W. S. Broecker & T.-H. Peng, 1972. Atmospheric carbon dioxide: its role in maintaining phytoplankton standing crops. Science 177: 1192–1194.
- Sellmann, P. V., J. Brown, R. I. Lewellen, H. McKim & C. Merry, 1975. The classification and geomorphic implications of thaw lakes of the arctic coastal plain, Alaska. Report 344. U.S. Army Cold Regions Research and Engineering Lab, Hanover, 24 pp.
- Shaver, G. R. & F. S. Chapin, III, 1986. Effect of NPK fertilization on production and biomass of Alaskan tussock tundra. Arct. Alp. Res. 18: 261–268.
- Shaver, G. R., K. J. Nadelhoffer & A. E. Giblin, 1992. Biogeochemical diversity and element transport in a heteroge-

neous landscape, the North Slope of Alaska. In M. Turner & R. Gardner (eds), Quantitative Methods in Landscape Ecology. Springer-Verlag. In press.

- Smith, S. D. & E. P. Jones, 1985. Evidence for wind-pumping of air-sea gas exchange based on direct measurements of CO₂ fluxes. J. Geophys. Res. 90: 869–875.
- Stumm, W. & J. J. Morgan, 1981. Aquatic chemistry, 2nd edition. John Wiley & Sons, New York, 780 pp.
- Tans, P. P., I. Y. Fung & T. Takahashi, 1990. Observational constraints on the global atmospheric CO₂ budget. Science 247: 1431–1438.
- Torgersen, T., G. Mathieu, R. H. Hesslein & W. S. Broecker, 1982. Gas exchange dependency on diffusion coefficient: direct ²²²Rn and ³He comparisons in a small lake. J. Geophys. Res. 87: 546-556.
- Wanninkhof, R., J. R. Ledwell & W. S. Broecker, 1985. Gas exchange-wind speed relation measured with sulfur hexafluoride on a lake. Science 227: 1224–1226.
- Wanninkhof, R., J. R. Ledwell & W. S. Broecker, 1987. Gas exchange on Mono Lake and Crowley Lake, California. J. Geophys. Res. 92: 14567–14580.
- Wanninkhof, R., P. J. Mulholland & J. W. Elwood, 1990.

Gas exchange rates for a first-order stream determined with deliberate and natural tracers. Water Resour. Res. 26: 1621–1630.

- Weiss, R. F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Mar. Chem. 2: 203–215.
- Welch, H. E. & M. A. Bergmann, 1985. Winter respiration of lakes at Saqvaqjuac, N.W.T. Can. J. Fish. aquat. Sci. 42: 521-528.
- Welch, H. E., J. W. M. Rudd & D. W. Schindler, 1980. Methane addition to an Arctic lake in winter. Limnol. Oceanogr. 25: 100-113.
- Wetzel, R. G. & G. E. Likens, 1979. Limnological analyses. W. B. Saunders, Philadelphia, 357 pp.
- Whalen, S. C. & W. S. Reeburgh, 1990a. Consumption of atmospheric methane by tundra soils. Nature 346: 160– 162.
- Whalen, S. C. & W. S. Reeburgh, 1990b. A methane flux transect along the Trans-Alaska pipeline Haul Road. Tellus B42: 237–245.
- Wilhelm, E., R. Battino & R. J. Wilcock, 1977. Low-pressure solubility of gases in liquid water. Chem. Rev. 77: 219–262.