Biogeochemistry **40:** 57–72, 1998.

Influence of drainage basin topography and elevation on carbon dioxide and methane supersaturation of stream water

JEREMY B. JONES, JR[1] & PATRICK J. MULHOLLAND[2]
[1]*Department of Biological Sciences, University of Nevada, Las Vegas, 4505 Maryland Parkway, Las Vegas, Nevada 89154-4004, U.S.A.;* [2]*Environmental Sciences Division, Oak Ridge National Laboratory, PO Box 2008, Bldg 1506, Oak Ridge, Tennessee 37831-6036, U.S.A.*

Accepted 9 September 1997

Key words: carbon dioxide, eastern Tennessee, ecosystem metabolism, methane, streams, Smoky Mountains

Abstract. The partial pressures of CO_2 (pCO_2) and CH_4 (pCH_4) in streams are not only governed by instream processes, but also by transformations occurring in soil and groundwater ecosystems. As such, stream water pCO_2 and pCH_4 can provide a tool to assess ecosystem respiration and anaerobic metabolism throughout drainage basins. We conducted three surveys sampling the gas content of streams in eastern Tennessee and western North Carolina to assess factors regulating ecosystem metabolism in catchments with contrasting geomorphologies, elevations and soil organic matter storage. In our first survey, the influence of drainage basin geomorphology on ecosystem respiration was examined by sampling streams draining catchments underlain by either shale or dolomite. Geomorphology is influenced by geology with shale catchments having shallower soils, broader, unconstrained valley floors compared with dolomite catchments. pCO_2 varied little between catchment types but increased from an average of 3340 ppmv in spring to 9927 ppmv in summer or 9.3 and 28 times atmospheric equilibrium ($pCO_{2(equilib)}$), respectively. In contrast, pCH_4 was over twice as high in streams draining shale catchments (306 ppmv; $pCH_{4(equilib)}$ = 116) compared with more steeply incised dolomite basins (130 ppmv; $pCH_{4(equilib)}$ = 51). Using the ratio of pCH_4:pCO_2 as an index of anaerobic metabolism, shale catchments had nearly twice as much anaerobiosis (pCH_4:pCO_2 = 0.046) than dolomite drainages (pCH_4:pCO_2 = 0.024). In our second survey, streams were sampled along an elevational gradient (525 to 1700 m) in the Great Smoky Mountains National Park, USA where soil organic matter storage increases with elevation. pCO_2 did not vary between streams but increased from 5340 ppmv ($pCO_{2(equilib)}$ = 15) to 8565 ppmv ($pCO_{2(equilib)}$ = 24) from spring to summer, respectively. During spring pCH_4 was low and constant across streams, but during summer increased with elevation ranging from 17 to 2068 ppmv ($pCH_{4(equilib)}$ = 10 to 1216). The contribution of anaerobiosis to total respiration was constant during spring (pCH_4:pCO_2 = 0.017) but during summer increased with elevation from 0.002 at 524 m to 0.289 at 1286 m. In our last survey, we examined how pCO_2 and pCH_4 changed with catchment size along two rivers (ca. 60 km stretches in both rivers corresponding to increases in basin size from 1.7–477 km^2 and 2.5–275 km^2). pCO_2 and pCH_4 showed opposite trends, with pCO_2 decreasing ca. 50% along the rivers, whereas pCH_4 roughly doubled in concentration downstream. These opposing shifts resulted in a nearly five-fold increase of pCH_4:pCO_2 along the rivers from a low of 0.012 in headwaters to a high of 0.266 65-km downstream. pCO_2 likely declines moving downstream as groundwater influences on stream chemistry decreases, whereas pCH_4 may increase as the prevalence of anoxia in rivers expands due to finer-grained sediments and reduced hydrologic exchange with oxygenated surface water.

Introduction

The partial pressure of CO_2 (pCO_2) in streams is nearly always supersaturated with respect to the atmosphere (e.g., Hope et al. 1994). Surface water CO_2 is governed not only by instream metabolism but also by import in groundwater. Carbon dioxide attributable to instream biotic processes is typically low indicating that the major source is groundwater (Kling et al. 1992). In groundwater, carbon dioxide primarily originates in soils where levels are elevated due to root and heterotrophic respiration (Castelle & Galloway 1990; Piñol & Avila 1992). Further, the generation of CO_2 in soil and stream ecosystems is regulated by factors such as nutrient availability, temperature, organic matter quantity and quality, and oxygen (e.g., Yavitt et al. 1987, 1995; Hedin 1990; Howard & Howard 1993; Jones 1995; Raich & Potter 1995). Variability in pCO_2 between streams should reflect differences in soil respiration in different catchments and potentially can be used to characterize variation in soil metabolic activity and to test hypotheses about soil CO_2 production.

Methane, like CO_2, is typically supersaturated in streams and is almost entirely derived from biotic processes (e.g., de Angelis & Scranton 1993; Pulliam 1993; Baker et al. 1994; Jones et al. 1995). Methane is generated by obligate anaerobic bacteria. The sediments underlying streams are commonly oxygenated and as a consequence probably do not have much methane production. Anoxia is more common in riparian and other terrestrial zones indicating that soils are the primary source of methane (Dahm et al. 1987, 1991). Stream water methane content should reflect the extent of methanogenesis in soils and, as with CO_2, stream water CH_4 levels can potentially be used to characterize patterns of soil anaerobiosis. Moreover, using pCO_2 and pCH_4 in conjunction allows for assessing the proportion of organic matter decomposed anaerobically in stream and soil ecosystems.

Using gas content of stream water, we assessed factors regulating ecosystem metabolism and anaerobiosis in different catchments. Specifically we conducted three surveys examining how ecosystem respiration and anaerobic metabolism were affected by 1) catchment geomorphology and groundwater flowpaths, 2) soil organic matter storage, and 3) drainage basin area and stream size. In our first survey examining catchment geomorphology, we hypothesized that drainage basins with lower geomorphic relief and shallower subsurface flowpaths will have greater anaerobiosis due to longer contact time of groundwater with soils. We also hypothesized that geomorphology and subsurface pathways of flow would have little effect on the total rate of ecosystem respiration (aerobic and anaerobic) assuming that all other variables are constant. In our second survey we reasoned that soil organic matter storage would stimulate the total rate of respiration which

in turn would lead to greater oxygen consumption and enhanced anaerobic metabolism. Finally, in our last survey, we examined the relative contributions of soil and instream processes to CO_2 and CH_4 partial pressures with increasing stream size. Whereas the first two surveys addressed factors regulating pCO_2 and pCH_4 in small headwater streams, our third study examined how these interactions change with drainage basin and stream size.

Methods

Study sites

The effects of geomorphology and subsurface flowpaths were evaluated by sampling headwater streams draining catchments underlain by two distinct geologic formations on the U.S. Department of Energy's Oak Ridge National Environmental Research Park in eastern Tennessee, USA. Bedrock of this area is composed predominantly of either shale or dolomite, oriented in parallel bands that form northeast-southwest trending ridges (Hatcher et al. 1992). Geomorphology and hydrology of drainage basins are influenced by geology with shale catchments having shallower soils, broader, unconstrained valley floors, and more rapid hydrologic response times compared with dolomite catchments (Clapp et al. 1992; Solomon et al. 1992). A total of ten headwater streams (n = 5 on each ridge type; catchment areas <1.2 km^2) located within a 40 km^2 area were sampled.

Climate of the Research Park is typical of the humid southern Appalachian region with mean annual temperatures of 14.5 °C and mean annual precipitation of 140 cm. Vegetation is second-growth deciduous forest dominated by oak and hickory, with scattered pines on some ridges and mesophytic hardwoods such as tulip poplar and beech in valleys. The Research Park has been largely undisturbed since 1940. Land use before that was a mixture of row-crop agriculture, pasture and woodlots.

Effects of soil organic matter were explored by sampling 24 streams along an elevational gradient in the Great Smoky Mountains National Park (GSMNP), USA where soil organic matter storage increases with elevation (McGinnis 1958; Shanks & Olson 1961). The elevation of sampling sites ranged from 525 to 1700 m and catchment areas varied from 0.07 to 7.81 km^2. Climate in the GSMNP is humid with mean annual precipitation of ca. 220 cm (Shanks 1954). The area consists of Precambrian to Cambrian metasedimentary rock, mostly quartzite and phyllite, which is relatively resistant to weathering and provides little neutralization capacity (King et al. 1968). Outcroppings of a pyritic carbonaceous phyllite, the Anakeesta Formation, occur at higher elevations (King et al. 1968). Soils are poorly developed, rich in

organic matter, and acidic (Herrman & Baron 1980). Vegetation is dominated by mature stands of red spruce and fraser fir at high elevation, with beech and hemlock becoming important at lower elevations and in riparian zones. Rhododendron is abundant, forming a dense subcanopy at high elevations and near stream channels at all elevations. The topography is steep with streams flowing in deeply incised valleys.

We examined the effects of drainage basin area and stream size on ecosystem metabolism by sampling along 46 and 65 km reaches of the Little Pigeon River and Little River in eastern Tennessee, USA, respectively. Catchment area increased from 1.7 to 477 km^2 in the Little Pigeon River and 2.5 to 275 km^2 in the Little River from headwater to downstream sampling stations. The headwaters of both rivers are in the GSMNP and the study reaches extend into the Tennessee River Valley where environmental conditions are similar to those of the Oak Ridge National Environmental Research Park. Headwater reaches were <2 m wide, whereas downstream channels were 30–50 m wide.

Analytical methods

The Oak Ridge National Environmental Research Park streams were sampled on 30 March 1995 and 7 September 1995, the GSMNP streams were sampled on 25 April 1995 and 15 September 1995, and the Little Pigeon River and Little River were sampled on 21 June 1995. Unfiltered samples were collected for alkalinity and pH determination by sealing bottles underwater to prevent exposure to atmosphere, placed on ice, returned to the laboratory, and refrigerated until analysis. Water temperature and specific conductance were measured in the field (Orion model 122). On the first sampling dates from each of the three surveys (30 March 1995, 25 April 1995 and 21 June 1995), water samples were collected for analysis of solute concentrations. Samples for solute analysis were filtered in the field (Gelman type A/E glass-fiber filter), placed on ice, returned to the laboratory, and refrigerated until analysis. Samples were analyzed for N and P within 4 d of collection. Samples for cation analysis were preserved with 0.5% high purity HNO_3, and cation and anion samples were analyzed within 4 months of collection.

pH and alkalinity were measured with a Fisher autotitrator model 380/381 equipped with an Orion Ross pH electrode (precision of pH = $\pm$0.01 units). Alkalinity was determined by potentiometric titration to fixed end-points of 4.5 and 4.2 using 0.01 N HCl (precision = ± 10 μEq/L). Concentrations of Al, B, Ba, Ca, Fe, Mg, Na, Si, and Sr were measured by inductively coupled plasma emission spectroscopy and K by atomic adsorption spectrometry. Concentrations of SO_4^{2-} and Cl^- were measured by ion chromatography. Soluble reactive phosphorus (SRP) was measured by the ascorbic acid method (American Public Health Association 1989). Samples were analyzed manu-

ally with a 10-cm spectrophotometer cuvette to achieve low analytical detection limit (0.5 μgP/L) and high precision ($\pm$0.4 μgP/L). NH_4^+ was measured by automated phenate colorimetry (detection limit = 2 μgN/L, precision = $\pm$1 μgN/L) and NO_2^- + NO_3^- was measured by automated Cu-Cd reduction followed by azo dye colorimetry (detection limit = 1 μgN/L, precision = $\pm$0.5 μgN/L; American Public Health Association 1989). The proportion of total alkalinity (as determined by potentiometric titration) derived from carbonate alkalinity was assessed from solute chemistry and alkalinity using PHREEQC (Parkhurst 1995).

pCO_2 was calculated from alkalinity (measured by titration) and pH and was corrected for ionic strength (estimated from conductivity; Snoeyink & Jenkins 1980). The dissociation constants K_H, K_1 and K_2 were corrected for temperature using equations given in Stumm & Morgan (1981). The precision of pCO_2 estimates varied primarily as a function of alkalinity ranging from $\pm$10, 6, 3 and 2% at alkalinities of 50, 100, 500 and 6000 μEq/L, respectively.

Water for pCH_4 determination was collected with a syringe (3 ml) then injected and stored in evacuated vials (vacutainers). The headspace gas in vials was analyzed within 48 h with a flame ionization detector on a Perkin Elmer 3920 gas chromatograph with a Porpak R column (Jones et al. 1995). Background level of CH_4 in vacutainers averaged 1.02 ppmv (0.3–2.2% of stream concentration) and precision of measurement was $\pm$10 ppmv.

Statistical analysis

The effects of geology and season on pH, alkalinity and gas partial pressures were assessed with two-way analysis of variance. Following an initial test for homogeneity of slopes, analysis of covariance was used to evaluate seasonal difference in data from the GSMNP survey and differences between the Little Pigeon River and Little River (elevation and longitudinal location used as covariates). Elevational and longitudinal effects were analyzed with linear regression. Data for linear regressions were pooled if results from analysis of covariance results were non-significant ($p \geq 0.05$).

Results

Geomorphic patterns

pH in streams of the Oak Ridge National Environmental Research Park ranged from 7.32 to 8.95 but was not significantly related with catchment geology (p = 0.751) or sampling date (p = 0.191; Figure 1a). Alkalinity also did not differ between shale and dolomite catchments (p = 0.120) but was significantly greater in summer than spring averaging 5155 and 2663 μEq/L, respectively

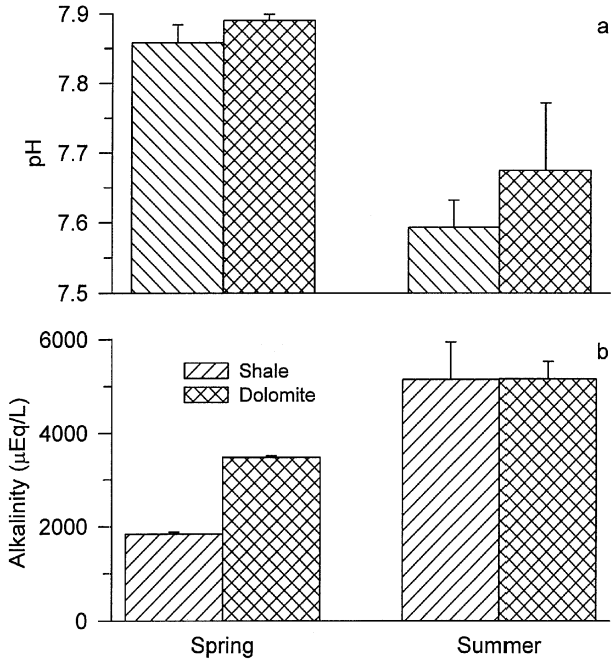

Figure 1. Mean (± SE) pH (a) and alkalinity (b) of surface waters in dolomite and shale drainage basins on the Oak Ridge National Environmental Research Park, Tennessee, USA.

($p < 0.001$; Figure 1b). Based upon the ion concentrations measured on the first sampling date, carbonate alkalinity was strongly correlated with total alkalinity (linear regression, $r^2 = 1.000$, $p < 0.001$). The equation for the line describing the relationship between carbonate and total alkalinity had a slope of 0.976 indicating that most acid neutralizing capacity was from carbonates and pCO_2 concentrations were overestimated by only 2.4%.

pCO_2 in stream water did not differ significantly with catchment geology ($p = 0.602$; Figure 2a). However, mean pCO_2 increased three-fold from 3340 to 9927 ppmv as stream temperatures increased from 12.3 °C in the spring to 16.1 °C during summer ($p = 0.004$; Figure 2b). These partial pressures translate to saturations relative to atmospheric equilibrium ($pCO_{2(equilib)}$; assuming atmospheric pCO_2 of 360 ppmv; Keeling et al. 1994) of 9.3 and 28 in spring and summer, respectively. In contrast, pCH_4 did not vary seasonally ($p = 0.076$), but was significantly greater in shale than dolomite catchments ($p = 0.042$; Figure 2b). Mean pCH_4 was over twice as high in shale (306 ppmv) than dolomite catchments (130 ppmv; $pCH_{4(equilib)}$ of 116 and 51, respectively, assuming an atmospheric pCH_4 of 1.7 ppmv; Khalil & Rasmussen 1994). Using the ratio of pCH_4 to pCO_2 as an index of anaerobic metabolism, shale

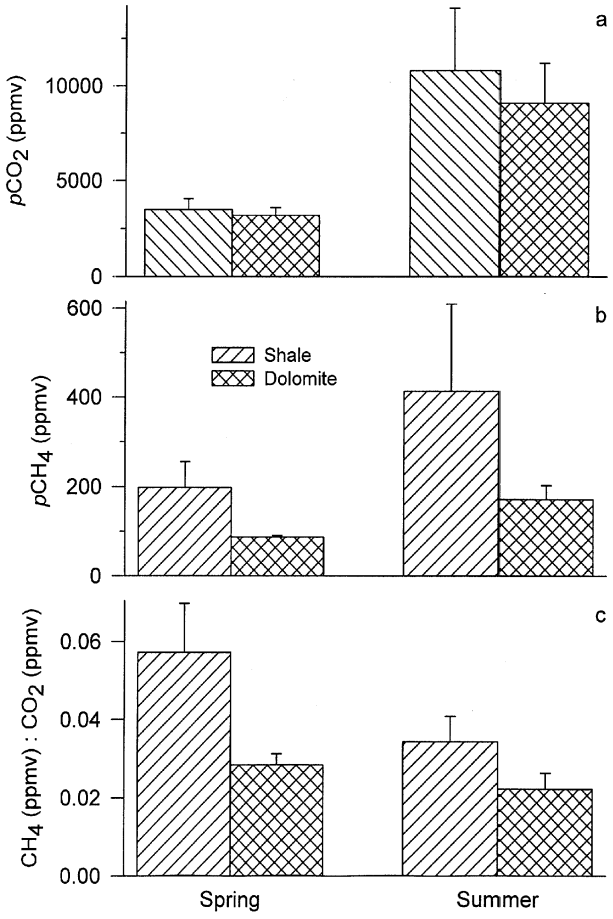

Figure 2. Mean (± SE) partial pressures of carbon dioxide (a) and methane (b) in surface waters, and index of ecosystem anaerobiosis (pCH_4:pCO_2; c) in dolomite and shale drainage basins on the Oak Ridge National Environmental Research Park, Tennessee, USA.

catchments had nearly twice as much anaerobiosis than dolomite drainages with pCH_4:pCO_2 of 0.046 and 0.024, respectively (p = 0.006; Figure 2c). Interestingly, pCH_4:pCO_2 declined significantly from an average of 0.043 during spring to 0.028 during summer (p = 0.036).

Elevational patterns

In the GSMNP, pH did not vary between samples dates (p = 0.557) but declined with elevation ($p < 0.001$; Figure 3a). pH in streams below 800 m averaged 6.45 but declined to a mean of 5.72 above 1200 m. Similarly, alkalinity exhibited an elevation gradient ($p < 0.001$) declining from as much

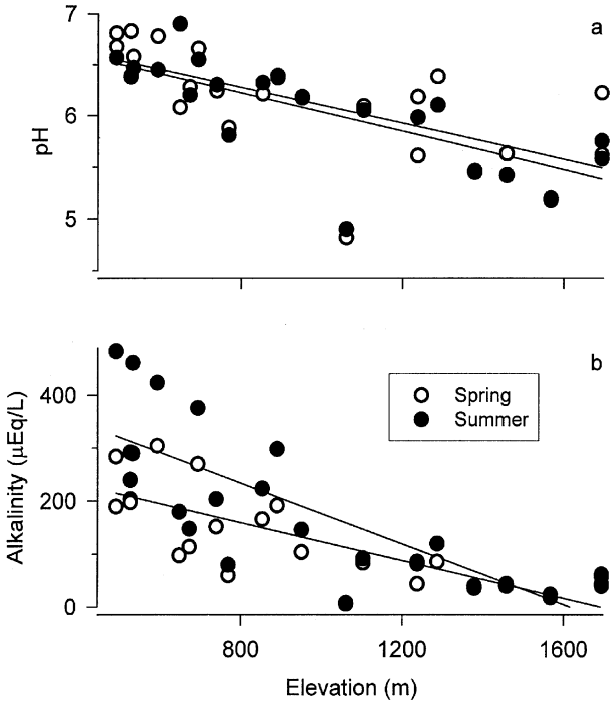

Figure 3. Stream water pH (a) and alkalinity (b) along an elevational gradient in the Great Smoky Mountains National Park, USA.

as 484 μEq/L at 488 m to only 6 μEq/L at 1061 m (Figure 3b). Alkalinity also differed between sampling dates ($p = 0.023$) averaging 130 μEq/L in spring compared with 185 μEq/L in summer. The correlation between carbonate and total alkalinity was much reduced compared to that observed in the Oak Ridge survey ($r^2 = 0.443$, $p < 0.001$) with a slope of 0.610 indicating greater uncertainty and overestimates of pCO_2 by as much as 39%.

As in the Oak Ridge stream survey, pCO_2 in streams of the GSMNP did not vary with elevation ($p = 0.368$; Figure 4a). pCO_2, however, did increase seasonally from a mean of 5340 ppmv ($pCO_{2(equilib)} = 15$) in spring (mean stream temperature = 8.4 °C) to 8565 ppmv ($pCO_{2(equilib)} = 24$, mean stream temperature = 14.3 °C) in summer ($p < 0.001$; Figure 4a). During the spring, methane was also constant with elevation (71 ppmv, $pCH_{4(equilib)} = 42$; $p = 0.075$), but during the summer significantly increased with altitude ($p < 0.001$), ranging from 17 to 2068 ppmv and 10 to 1216 $pCH_{4(equilib)}$ (Figure 4b). Furthermore, the contribution of anaerobiosis to total respiration was constant during the spring (pCH_4:$pCO_2 = 0.017$; $p = 0.070$) but ranged from 0.002 to 0.289 in summer ($p = 0.005$; Figure 4c).

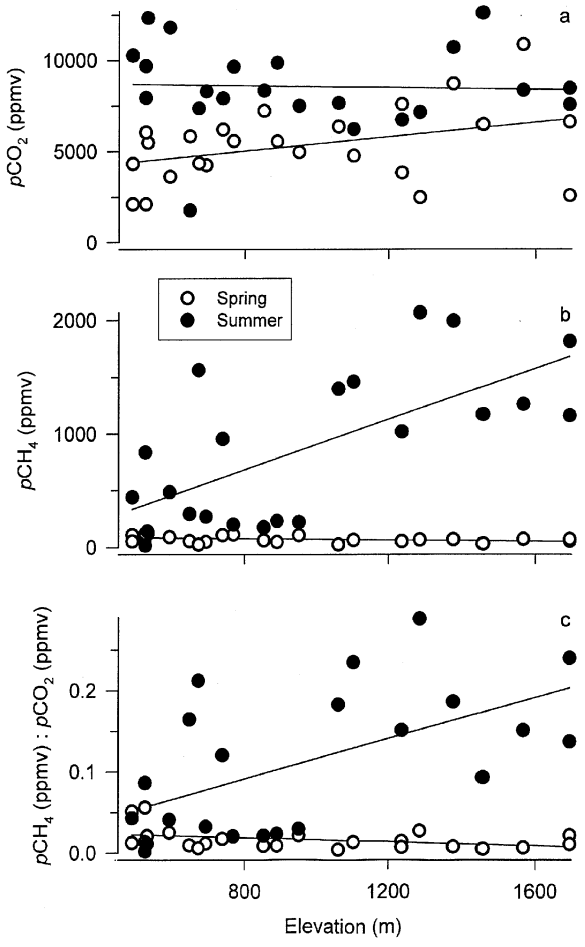

Figure 4. Stream water pCO_2 (a), pCH_4 (b) and index of ecosystem anaerobiosis (pCH_4:pCO_2; c) along an elevational gradient in the Great Smoky Mountains National Park, USA.

Longitudinal trends

In the longitudinal survey, pH rose with distance from headwaters ($r^2 = 0.88$, $p < 0.001$) increasing from ca. 6.40 in headwater streams to 7.96 65-km downstream (Figure 5a). Similarly, alkalinity increased from as low as 68 μEq/L in headwaters to as high as 2022 μEq/L at downstream sites ($p < 0.001$; Figure 5b). As in the Oak Ridge survey, nearly all alkalinity was attributable to carbonates (slope = 0.989, $r^2 = 1.000$, $p < 0.001$) producing overestimates of pCO_2 by only 1.1%.

In contrast to a lack of spatial variation in pCO_2 in the previous two surveys, pCO_2 declined along the Little Pigeon River and the Little River

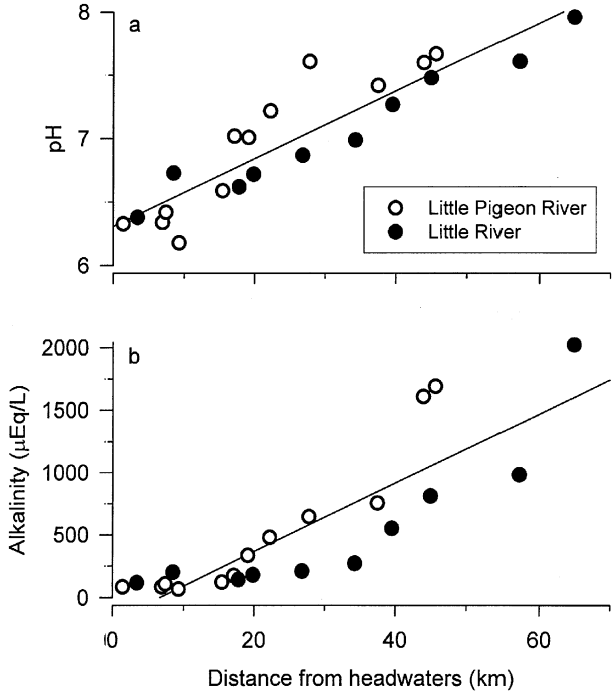

Figure 5. Longitudinal changes in stream water pH (a) and alkalinity (b) in the Little Pigeon River and Little River in eastern Tennessee.

(p = 0.031) although pCO_2 did not differ between rivers (p = 0.806). In headwaters, pCO_2 ranged from 2905 to 3454 ppmv ($pCO_{2(equilib)}$ = 8.1 to 9.6), but declined ca. 50% to <2000 ppmv ($pCO_{2(equilib)} < 5.6$) 63-km downstream (Figure 6a). Whereas pCO_2 declined, pCH_4 increased longitudinally ($p <$ 0.001) and like pCO_2, concentration did not vary between drainages (p = 0.536). pCH_4 content doubled from <200 ppmv ($pCH_{4(equilib)} < 118$) in headwater streams to >400 ppmv ($pCH_{4(equilib)} > 235$) at downstream sites (Figure 6b). These opposing longitudinal shifts in gases resulted in a five-fold increase of pCH_4:pCO_2 along the ca. 60 km lengths of river ($p <$ 0.001; Figure 6c).

Discussion

As initially hypothesized, pCH_4 was related to catchment geomorphology, whereas pCO_2 was not. Geomorphology presumably influences subsurface hydrologic flowpaths through drainage basins, contact time between groundwaters and soil organisms, the consumption of oxygen, and the extent of

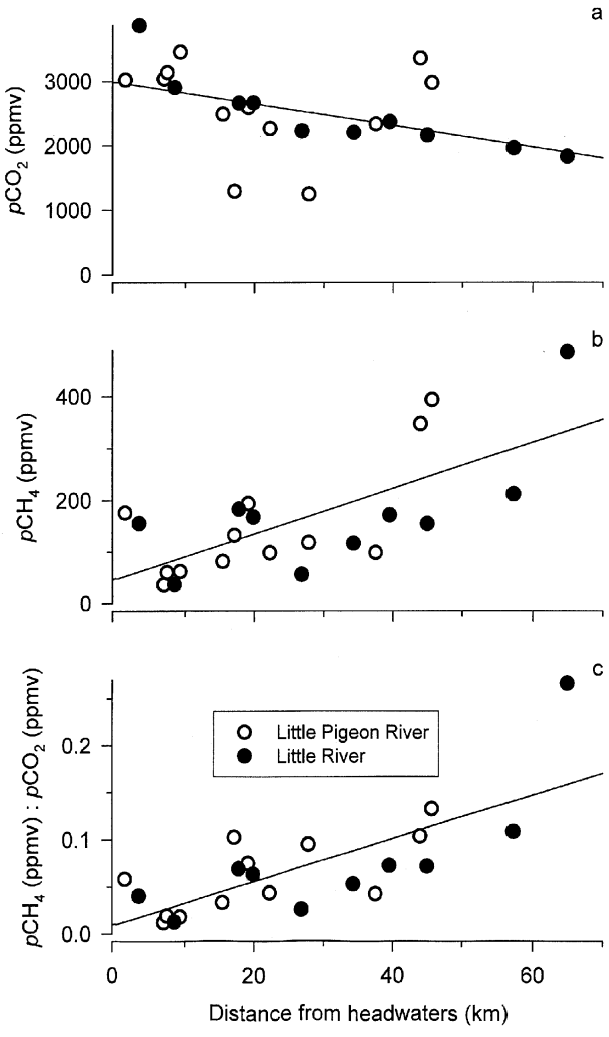

Figure 6. Longitudinal changes in stream water pCO_2 (a), pCH_4 (b) and index of ecosystem anaerobiosis (pCH_4:pCO_2; c) in the Little Pigeon River and Little River in eastern Tennessee.

anoxia and anaerobiosis. In contrast, however, the overall rate of ecosystem respiration may be more closely coupled to climate. Similarly, as hypothesized, stream water pCH_4 was related to elevation, and presumably soil organic matter storage. In contrast to our initial expectations, however, elevation had no effect on pCO_2, although estimates of pCO_2 in the GSMNP survey had considerable uncertainty given the low correlation between carbonate and total alkalinity observed on the first sampling date. As with geomorphology, soil organic matter may regulate rate of oxygen consumption and thus the

prevalence of methanogenesis. The lack of relationship between elevation and pCO_2 suggests that other factors such as climate are controlling the overall rate of decomposition.

Carbon dioxide in streams

Streams are typically supersaturated with CO_2 relative to the atmosphere with $pCO_{2(equilib)}$ commonly ranging from 2 to 10 (e.g., Kling et al. 1991; Piñol & Avila 1992; Neal & Hill 1994; Dawson et al. 1995) and in some streams as high as 50 to 100 $pCO_{2(equilib)}$ (Lorah & Herman 1988; Hoffer-French & Herman 1989). Stream water pCO_2 is governed by instream decomposition of organic matter, diffusive exchange with the atmosphere, and groundwater inputs. In one of the streams sampled in the Oak Ridge survey, the West Fork of Walker Branch, a sizable proportion of CO_2 in surface water appears to come from groundwater inputs. In a previous study, the pCO_2 concentration in groundwater discharging into Walker Branch averaged 3160 ppmv, over two-fold greater than the mean pCO_2 concentration of 1560 ppmv in the stream (Wanninkhof et al. 1990).

Groundwater CO_2 originates from soils where the concentration is elevated due to root respiration and heterotrophic oxidation of detritus (e.g., Raich & Potter 1995). Soil respiration, in turn, is potentially governed by organic matter quantity and quality, and oxygen (Magnusson 1993; Yavitt et al. 1995), although temperature and soil moisture appear to be the dominant controls (Yavitt et al. 1987, 1995; Castelle & Galloway 1990; Crill 1991; Howard & Howard 1993; Raich & Potter 1995). The coupling between temperature and respiration results in distinct seasonal pattern of soil CO_2 with a summer high and a winter low. These seasonal patterns of soil CO_2 have been shown to influence stream water chemistry. In White Oak Run, located in the Shenandoah National Park, Virginia, a region with climate similar to the sites herein, bicarbonate in stream water closely tracked soil CO_2 probably due to weathering of parent material by dissolved CO_2 produced by respiration in soils (Castelle & Galloway 1990). Similarly, in the present study temperature appears to be an important factor regulating stream water pCO_2. Geomorphology and soil organic matter storage had no effect on stream pCO_2, but gas levels increased from spring to summer.

Methane in streams

Methane, like carbon dioxide, is usually supersaturated in streams with levels ranging from 1 to 598-fold greater than atmospheric equilibrium (Brooks & Sackett 1973; Wilkniss et al. 1978; de Angelis & Lilley 1987; de Angelis & Scranton 1993; Jones et al. 1995). Unlike the production of CO_2, which

is generated both aerobically and anaerobically, methanogenic bacteria are obligate anaerobes and thus restricted to regions of anoxia. The input of CH_4 into stream water results from an interplay between the extent of anoxia and the rate of methanogenic activity. In our studies examining geomorphology and soil organic matter storage, pCO_2 was not affected by these factors and indicated a lack of variation in the rate of ecosystem respiration between catchments. Assuming methanogenic rate is also unaffected by geomorphology and soil organic matter storage, differences observed in stream water methane levels must result from greater anoxia.

Oxygen levels in stream sediments and terrestrial soils are controlled by respiration, diffusive exchange with the atmosphere, and hydrologic transport in groundwater. The shallower subsurface flowpaths in shale catchments presumably result in greater contact of groundwater with organic-rich surface soils and reduced dissolved oxygen in pore spaces compared with dolomite catchments. Consequently, anoxia is likely more prevalent resulting in greater methane production. Similarly, in the GSMNP, soils with deep organic horizons probably result in greater contact between groundwater and soil organic matter. This increased contact time does not appear to raise respiration rate, but enhances the amount of oxygen stripped from groundwater as it flows through the catchment. Thus, the total rate of subsurface respiration may be largely governed by temperature, whereas the extent of anaerobic metabolism is regulated by geomorphology, subsurface hydrology, and soil organic matter.

Longitudinal controls of carbon dioxide and methane

In contrast to the lack of variation in pCO_2 between headwater streams, pCO_2 levels decline with increasing river size likely due to reduced influence of groundwater inputs (Lorah & Herman 1988; Dawson et al. 1995). Groundwater discharge into headwater streams accounts for a substantial fraction of stream flow and has a large impact on stream chemistry. In larger streams with greater flow, recent groundwater discharge contributes much less to flow and the quantity of solutes and gases supplied by groundwater discharge are small relative to levels in streamflow. The large contribution of groundwater discharge to headwater streams results in high pCO_2 in headwaters. As water flows downstream CO_2 is lost to the atmosphere and pCO_2 declines towards equilibrium with the atmosphere. In larger streams, surface water has been exposed to the atmosphere for a greater length of time resulting in lower pCO_2. However, larger streams and rivers remain supersaturated, never achieving equilibrium, in part due to some discharge of groundwater enriched in CO_2.

Whereas pCO_2 levels decline downstream, pCH_4 levels appear to increase, based upon the data of this study and that of de Angelis & Lilley (1987). This downstream increase in pCH_4 may be a function of greater zones of anoxia

with increasing river size. de Angelis & Lilley (1987) suggested that the major source of CH_4 to river water is from lateral seeps and that the prevalence of seeps increases down-river. Headwater streams are commonly higher gradient and as a consequence have larger sized substrates than downstream reaches. Hydraulic conductivity and the potential for hydrologic exchange between surface and subsurface waters is directly related to particle size. In headwaters subsurface flow is probably relatively rapid minimizing the extent of anoxia and methane production. As channel gradient declines and particle size of the river bed decreases the potential for anaerobiosis is enhanced. Further, the longitudinal increase in pCH_4 in conjunction with a decline in pCO_2 indicates that the proportion of organic matter decomposed anaerobically increases along rivers.

Freshwater ecosystems as conduits for gas exchange

Lakes are commonly supersaturated with CO_2 relative to the atmosphere (Cole et al. 1994) and, as suggested by Kling et al. (1991), function as conduits for CO_2 transport from terrestrial ecosystems to the atmosphere. The streams we studied were also supersaturated, both in carbon dioxide and methane, with $pCO_{2(equilib)}$ 3.5 to 48 (median = 13) and $pCH_{4(equilib)}$ 10 to 1217 (median = 78), respectively. Thus, like lakes, streams function as conduits for gas exchange to the atmosphere. In headwater streams where groundwater discharge is relatively high, much of this gas likely comes from the catchment. With increasing river size, however, riparian or instream gas generation, particularly methane, becomes more important. Although all catchments primarily emitted carbon dioxide, large basins, or those dominated by shallow hydrologic flowpaths or high soil organic matter content, emitted a greater proportion of respiratory end-products as methane.

Acknowledgements

We thank R. Wilkerson, T. Carey and S. Roimando for help in the laboratory and field, and R. Cooke, N. Grimm, W. Hill and two anonymous reviewers for their comments. J.B. Jones was supported by a Global Change Distinguished Postdoctoral Fellowship from the U.S. Department of Energy. The research was performed in part on the U.S. Department of Energy's Oak Ridge National Environmental Park. The work was a contribution of the Walker Branch Project supported by the Environmental Sciences Division, Office of Health and Environmental Research, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

References

American Public Health Association (1989) Standard methods for the examination of water and waste water, 17th ed. APHA

Baker MA, Dahm DN, Valett HM, Morrice JA, Henry KS, Campana ME & Wroblicky GJ (1994) Spatial and temporal variation in methane distribution at the ground water/surface water interface in headwater catchments. In: Stanford JA & Valett HM (Eds) Proceedings of the Second International Conference on Ground Water Ecology (pp 29–37). American Water Resources Association, Herndon, Virginia

Brooks JM & Sackett WM (1973) Sources, sinks and concentrations of light hydrocarbons in the Gulf of Mexico. J Geophys Res 78: 5248–5258

Castelle AJ & Galloway JN (1990) Carbon dioxide dynamics in acid forest soils in Shenandoah National Park, Virginia. Soil Sci Soc Am J 54: 252–257

Clapp RB, Timmins SP & Huston MA (1992) Visualizing the surface hydrodynamics of a forested watershed. In: Russell TF, Ewing RE, Brebbia CA, Gray WG & Pinder GF (Eds) Computational Methods in Water Resources IX, Vol. 2: Mathematical Modeling in Water Resources (pp 765–772). Elsevier Applied Science, London

Cole JJ, Caraco NF, Kling GW & Kratz TK (1994) Carbon dioxide supersaturation in the surface waters of lakes. Science 265: 1568–1570

Crill PM (1991) Seasonal patterns of methane uptake and carbon dioxide release by a temperate woodland soil. Global Biogeochem Cycles 5: 319–334

Dahm CN, Trotter EH & Sedell JR (1987) Role of anaerobic zones and processes in stream ecosystem productivity. In: Averett RC & McKnight DM (Eds) Chemical Quality of Water and The Hydrologic Cycle (pp 157–178). Lewis Publishers, Chelsea

Dahm CN, Carr DL & Coleman RL (1991) Anaerobic carbon cycling in stream ecosystem. Verh. Internat. Verein. Limnol. 24: 1600–1604

Dawson JJC, Hope D, Cresser MS & Billett MF (1995) Downstream changes in free carbon dioxide in an upland catchment from northeastern Scotland. J Environ Qual 24: 699–706

de Angelis MA & Lilley MD (1987) Methane in surface waters of Oregon estuaries and rivers. Limnol Oceanogr 32: 716–722

de Angelis MA & Scranton MI (1993) Fate of methane in the Hudson River and estuary. Global Biogeochem Cycles 7: 509–523

Hatcher RD, Lemiszki PJ, Dreier RB, Ketelle RH, Lee RR, Leitzke DA, McMaster WM, Foreman JL & Lee SY (1992) Status Report on the Geology of the Oak Ridge Reservation 1. Department of Energy, Oak Ridge National Laboratory, Oak Ridge

Hedin LO (1990) Factors controlling sediment community respiration in woodland stream ecosystems. Oikos 57: 94–105

Hermann R & Baron J (1980) Aluminum mobilization in acid stream environments. GSMNP, USA. In: Drablos D & Tollan A (Eds) Proceedings of the International Conference on the Ecological Impact of Acid Precipitation, SNSF Project (pp 218–219). Oslo

Hoffer-French KJ & Herman JS (1989) Evaluation of hydrological and biological influences of CO_2 fluxes from a karst stream. J Hydrol 104: 189–212

Hope D, Billett MF & Cresser MS (1994) A review of the export of carbon in river water: Fluxes and processes. Environ Pollut 84: 301–324

Howard DM & Howard PJA (1993) Relationships between CO_2 evolution, moisture content and temperature for a range of soil types. Soil Biol Biochem 25: 1537–1546

Jones JB (1995) Factors controlling hyporheic respiration in a desert stream. Freshwat Biol 34: 101–109

Jones JB, Holmes RM, Fisher SG, Grimm NB & Greene DM (1995) Methanogenesis in Arizona, USA dryland streams. Biogeochemistry 31: 155–173

Keeling CD & Whorf TP (1994) Atmospheric CO_2 records from sites in the SIO air sampling network. In: Boden TA, Kaiser DP, Sepanski RJ & Stoss FW (Eds) Trends '93: A Compendium of Data on Global Change (pp 16–26). Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge

Khalil MAK & Rasmussen RA (1994) Global CH_4 record derived from six globally distributed locations. In: Boden TA, Kaiser DP, Sepanski RJ & Stoss FW (Eds) Trends '93: A Compendium of Data on Global Change (pp 268–272). Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge

King PB, Neuman RB & Hadley JB (1968) Geology of the Great Smoky Mountains National Park, Tennessee and North Carolina. US Geological Survey Profession Paper 587. US Government Printing Office, Washington

Kling GW, Kipphut GW & Miller MC (1991) Arctic lakes and streams as conduits to the atmosphere: Implications for tundra carbon budgets. Science 251: 298–301

Kling GW, Kipphut GW & Miller MC (1992) The flux of CO_2 and CH_4 from lakes and rivers in arctic Alaska. Hydrobiologia 240: 23–36

Lorah MM & Herman JS (1988) The chemical evolution of a travertine-depositing stream: Geochemical processes and mass transfer reactions. Water Resour Res 24: 1541–1552

Magnusson T (1993) Carbon dioxide and methane formation in forest mineral and peat soils during aerobic and anaerobic incubations. Soil Biol Biochem 25: 877–883

McGinnis JT (1958) Forest Litter and Humus Types of East Tennessee. Thesis, University of Tennessee

Neal C & Hill S (1994) Dissolved inorganic and organic carbon in moorland and forest streams: Plynlimon, Mid-Wales. J Hydrol 153: 231–243

Parkhurst DL (1995) User's guide to PHREEQC – a computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations. Water-resources investigation report 95-4227, US Geological Survey, Lakewood

Piñol J & Avila A (1992) Streamwater pH, alkalinity, pCO_2 and discharge relationships in some forested Mediteranean catchments. J Hydrol 131: 205–225

Pulliam WM (1993) Carbon dioxide and methane exports from a southeastern floodplain swamp. Ecol Monogr 63: 29–53

Raich JW & Potter CS (1995) Global patterns of carbon dioxide emissions from soils. Global Biogeochem Cycles 9: 23–36

Shanks RE (1954) Climate of the Great Smoky Mountains. Ecology 35: 354–360

Shanks RE & Olson JS (1961) First-year breakdown of leaf litter in southern Appalachian forests. Science 134: 194–195

Snoeyink VL & Jenkins D (1980) Water Chemistry. Wiley, New York

Solomon DK, Moore GK, Toran LE, Dreier RB & McMaster WM (1992) Status Report, Hydrologic Framework for the Oak Ridge Reservation. Department of Energy, Oak Ridge National Laboratory, Oak Ridge

Stumm W & Morgan JJ (1981) Aquatic Chemistry: an Introduction Emphasizing Chemical Equilibria in Natural Waters. Wiley, New York

Wanninkhof R, Mulholland PJ & Elwood JW (1990) Gas exchange rates for a first-order stream determined with deliberate and natural tracers. Water Resour Res 26: 1621–1630

Wilkniss PE, Lamontagne RE, Larson RE & Swinnerton JW (1978) Atmospheric trace gases and land and sea breezes at the Sepik River coast of Papua, New Guinea. J Geophys Res 83: 3672–3674

Yavitt JB, Lang GE & Wieder RK (1987) Control of carbon mineralization to CH_4 and CO_2 in anaerobic, *Sphagnum*-derived peat from Big Run Bog, West Virginia. Biogeochemistry 4: 141–157

Yavitt JB, Fahey TJ & Simmons JA (1995) Methane and carbon dioxide dynamics in a northern hardwood ecosystem. Soil Sci Soc Am J 59: 796–804