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Methane input and evasion in a hardwood forest stream: Effects of subsurface flow from shallow and deep pathways

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Abstract

Streams are typically supersaturated and emit methane to the atmosphere. Much of this gas appears to be imported from groundwater and riparian zones, where anoxia and methane production are common. We investigated how methane evasion and the concentration in groundwater discharge varied between five stream sections with differing rates of groundwater discharge along the east fork of Walker Branch in eastern Tennessee. Evasion and groundwater concentration were determined from measurements of methane in surface water in conjunction with coinjection of conservative solute and volatile gas tracers. Methane in surface water was supersaturated, varying from 0.67 to 1.56 $\mu\text{g CH}_4 \text{ liter}^{-1}$, which translates to concentrations 17.6–41.4 times greater than those at atmospheric equilibrium. Methane evasion rates ranged from 0.4 to 13.2 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$. Differences in methane concentration and evasion were related to variation in subsurface discharge and concentration in groundwater. All study sections gained flow, although the rate of subsurface discharge into the second study section (section 2) was particularly low. Furthermore, the specific conductance of groundwater flowing into section 2 averaged only 82.3 $\mu\text{S cm}^{-1}$, compared with 110–125 $\mu\text{S cm}^{-1}$ in the other study sections, indicating that groundwater discharge was derived from riparian soils as opposed to deeper flow from fractured bedrock. The mean concentration of 549.2 $\mu\text{g CH}_4 \text{ liter}^{-1}$ in subsurface water flowing into section 2 was notably greater than in the other sections, where average groundwater concentration ranged from 158.9 to 376.2 $\mu\text{g CH}_4 \text{ liter}^{-1}$. Our results suggest that subsurface flow from riparian soils appears to be the major source of methane to streams, although deeper bedrock flow also supplies methane at a lower concentration to surface waters.

Streams and other aquatic ecosystems function as conduits for exchange of trace gases between terrestrial ecosystems and the atmosphere (Kling et al. 1991, 1992; Cole et al. 1994; Jones and Mulholland 1998). Methane is typically supersaturated in streams, and, as a result, most lotic ecosystems emit methane to the atmosphere. Methane is a metabolic end-product of obligate anaerobic bacteria. Whereas the sediments underlying streams can lack oxygen, anoxia is more common in riparian soils (Baker et al. 1994; Jones et al. 1994, 1995), indicating that riparian zones are a primary source of methane to streams.

Riparian zones are linked to streams via subsurface flow, which transports methane and other trace gases to surface waters. Subsurface flow into streams can be spatially, as well as temporally, variable because of heterogeneity in hydraulic

conductivity and hydraulic gradient (Genereux et al. 1993; Triska et al. 1993; Valett et al. 1996). The production of methane in riparian zones is also patchy because of variation in factors such as the availability of dissolved oxygen and other terminal electron acceptors and organic matter storage (Molongoski and Klug 1980; Kelly and Chynoweth 1981; Jones et al. 1995). Groundwater is also discharged to streams through deeper bedrock flow paths (Mulholland 1993), where biotic activity and methane production are likely lower (Pedersen and Ekendahl 1992*a,b*). The heterogeneity in methane production and in hydrologic flow paths between soils and streams undoubtedly results in high spatial variation in methane input into surface waters.

Using measurements of methane content of surface waters in conjunction with experimental injections of conservative solute and volatile gas tracers, we examined how methane input varied longitudinally along a stream with changes in the source of groundwater flow paths and rate of groundwater discharge. Our whole-stream approach allowed for the determination of methane evasion to the atmosphere from the stream surface, subsurface discharge rate into the stream, and concentration of methane in groundwater.

Site description

The study was conducted in the east fork of Walker Branch, a first-order stream (59.7-ha catchment) in the U.S.

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Department of Energy's Oak Ridge National Environmental Research Park (35°58'N, 84°17'W) in eastern Tennessee. The climate is typical of the humid southern Appalachians, with a mean annual temperature of 14.5°C and a mean annual rainfall of 140 cm distributed fairly evenly throughout the year.

Walker Branch drains a hardwood forest catchment underlain by the Knox Group, a 610-m-thick sequence of Cambrian and Ordovician siliceous dolomite that weathers rapidly to form deep soils with abundant chert (McMaster 1963). Soils are primarily Ultisols, with small areas of Inceptisols found in alluvial valleys adjacent to streams (Peters et al. 1970). Surface infiltration rates are very rapid, and rainfall infiltrates completely even during greatest intensity storms (Luxmoore 1983). Surface soils have high hydraulic conductivity because of their high macroporosity (Wilson and Luxmoore 1988). Hydraulic conductivity, however, declines rapidly with depth because of increasing clay content (Wilson et al. 1989), and zones of perched saturation develop in surface soil layers, producing rapid lateral flow during larger storms (Mulholland et al. 1990). Base flow is largely derived from deeper groundwater flow within bedrock fissures and cavities (Mulholland 1993).

Methods

Field procedures—The evasion of methane from the stream surface was determined from measurements of methane concentration in stream water and hydraulic and gas exchange rates determined using a coinjection of conservative solute and volatile gas tracers (Marzolf et al. 1994; Marzolf and Mulholland, in press). NaCl and propane were injected in the east fork of Walker Branch on three sampling dates (9 May, 19 June, and 24 July 1996) to determine flow rate, groundwater discharge and reach water travel time, and gaseous diffusion. Both tracers were injected upstream of a well-mixed riffle and sampled 11, 19, 37, 46, 61, and 69 m downstream, thus dividing the stream into five study sections (hereafter designated study sections 1–5). Sampling distances were selected on the basis of geomorphic and hydrologic features of the stream to sample study reaches with contrasting subsurface discharges and methane inputs. For example, section 2 was anticipated to receive considerable discharge from soils on the basis of data from a series of riparian wells (J. B. Jones unpubl. data), whereas section 5 was predominantly underlain by bedrock and was suspected to receive little groundwater discharge. Study reaches were relatively short to maximize variability between study sections to examine how methane input varies along the stream. The total study length was restricted to <70 m to ensure adequate detection of propane at all sampling stations. The concentration of NaCl in stream water was measured by specific conductance (Orion model 122).

Before an injection was initiated, specific conductance was measured, and samples were collected for dissolved methane analysis from each sampling station. Samples for methane were collected in 5-ml nylon syringes ($n = 3$ samples per station). NaCl was injected at a constant rate sufficient to elevate stream specific conductance at least 100 μS

cm^{-1} using a battery-powered peristaltic pump (Cole-Parmer model 7533-20). Propane was injected into the stream from a 20-lb tank of HD-5 (96% propane/4% ethane) through an air stone. Newly filled tanks deliver a greater proportion of ethane to propane because of the higher volatility of ethane. To compensate for the disproportionate discharge of ethane from the cylinder, the first pound of gas was outgassed from the tank before injections were started (Genereux and Hemond 1992). The gas was injected into the stream at a constant rate using a regulator set to 35 kPa. The proportion of propane dissolved into stream water was enhanced by placing a sheet of Plexiglas on the stream surface above the air stone to increase the contact time of gas and water. After the injection reached steady state (as determined by specific conductance; steady state was reached within 2 h on all three sampling dates), samples for propane analysis were collected at each sampling station in 5-ml nylon syringes ($n = 3$ samples per station) and placed on ice for transport to the laboratory. The concentration of propane in stream water is principally governed by advective mixing (as opposed to diffusion); thus, steady-state levels can be inferred from the concentration of the conservative solute tracer. After each injection, the mean width of the wetted channel was determined by measuring the channel width every 2 m along the 69-m study site.

Laboratory procedures—In the laboratory, 2 ml of helium was drawn into syringes containing samples for methane and propane analysis, and syringes were placed on a shaker table at low speed for 3 h to allow dissolved gases to equilibrate in the helium headspace. Methane and propane in headspace were analyzed by flame ionization detection on a Perkin-Elmer 3920 gas chromatograph with a 1-ml sample loop and a Porpak R column (precision $\text{CH}_4 = \pm 0.05 \mu\text{g CH}_4 \text{ liter}^{-1}$). The integrated area of propane was used for subsequent calculations instead of actual concentration (Marzolf et al. 1994), and methane standards were used for methane concentration determinations.

Calculations—Water travel times through each of the study sections (τ_i) was calculated by measuring the travel time from the injection point to the third sampling station (37 m from injection point) and extrapolating to the other study sections. Travel time to Sta. 3 was calculated as the time required to achieve 50% of the steady-state specific conductance (less background specific conductance). Lateral inflow into each study section was calculated from the proportional decline in steady-state specific conductance between consecutive sample stations (corrected for background levels; Stream Solute Workshop 1990).

The propane exchange coefficient (k_{propane}) was calculated as

$$k_{\text{propane}} (\text{min}^{-1}) = \tau^{-1} \times \ln \frac{G_i \times C_{i+1}}{G_{i+1} \times C_i}, \quad (1)$$

where C is the specific conductance ($\mu\text{S cm}^{-1}$) corrected for background concentration and G is the propane concentration expressed relative to the level at station one at upstream (i) or downstream ($i+1$) sampling stations, respectively (Genereux and Hemond 1990). k_{propane} was converted to k_{methane}

assuming a ratio of 0.93 (Jähne et al. 1987; Genereux and Hemond 1990, 1992).

The evasive flux of methane to the atmosphere from each study reach was determined as the product of discharge from the study section (Q_{i+1}) and the mass of methane lost per volume of stream water ($\Delta\text{CH}_{4\text{evasion}}$) as water flowed through the study reach:

$$\text{Evasive flux } (\mu\text{g CH}_4 \text{ reach}^{-1} \text{ s}^{-1}) = \Delta\text{CH}_{4\text{evasion}} Q_{i+1}. \quad (2)$$

The loss of methane per volume of stream water was calculated from k_{methane} and the difference between the average reach methane concentration and the equilibrium methane concentration,

$$\begin{aligned} \Delta\text{CH}_{4\text{evasion}} \text{ } (\mu\text{g CH}_4 \text{ liter}^{-1}) \\ = \left(\frac{\text{CH}_{4i} + \text{CH}_{4i+1}}{2} - \text{CH}_{4\text{equilib}} \right) \times k_{\text{methane}} \times \tau, \quad (3) \end{aligned}$$

where CH_{4i} , CH_{4i+1} , and $\text{CH}_{4\text{equilib}}$ are the upstream, downstream, and atmospheric equilibrium concentrations of methane, respectively ($\mu\text{g CH}_4 \text{ liter}^{-1}$; Marzolf et al. 1994). $\text{CH}_{4\text{equilib}}$ was calculated from the Bunsen solubility coefficient and a global average atmospheric concentration of 1.7 ppmv (Khalil and Rasmussen 1994).

From the loss of methane to the atmosphere and the difference in methane concentration between upstream and downstream stations, input of methane per volume of water ($\Delta\text{CH}_{4\text{input}}$) was estimated as

$$\begin{aligned} \Delta\text{CH}_{4\text{input}} \text{ } (\mu\text{g CH}_4 \text{ liter}^{-1}) \\ = \text{CH}_{4i+1} - \text{CH}_{4i} + \Delta\text{CH}_{4\text{evasion}} \quad (4) \end{aligned}$$

and converted to a methane input rate into a study reach as

$$\text{Input rate } (\mu\text{g CH}_4 \text{ reach}^{-1} \text{ s}^{-1}) = \Delta\text{CH}_{4\text{input}} Q_{i+1}. \quad (5)$$

Evasive flux and methane input rates were converted to area-specific rates by dividing by the surface area of the study reach. Input represents net methane production rate, where input = instream production + groundwater import - bacterial methane oxidation.

In addition to calculating methane evasion and input rates for each of the stream sections, the specific conductance and methane content of groundwater discharging into each section were estimated. The specific conductance of stream water at a given station is

$$C_{i+1} = \frac{C_i Q_i + C_{\text{GW}_i} Q_{\text{GW}}}{Q_{i+1}} \quad (6)$$

where Q is discharge (liter s^{-1}) at upstream (i) and downstream ($i + 1$) stations and by lateral inflow of groundwater into the study reach (Q_{GW_i}). C_{GW_i} , the specific conductance of groundwater, was determined by rearranging Eq. 6. The concentration of methane in groundwater discharging into a section (CH_{4GW_i}) was described by

$$\begin{aligned} \text{CH}_{4\text{GW}_i} = \frac{\text{CH}_{4i+1}}{1 - \frac{C_{i+1}}{C_i}} - \frac{\text{CH}_{4i}}{\frac{C_i}{C_{i+1}} - 1} \\ + \frac{(\text{CH}_{4i} + \text{CH}_{4i+1}) \left(\frac{C_{i+1}}{C_i} + 1 \right) F}{4 \left(1 - \frac{C_{i+1}}{C_i} \right)} \quad (7) \end{aligned}$$

where $F = \ln(G_i C_{i+1} / G_{i+1} C_i)$ and G_i and G_{i+1} are the upstream and downstream steady-state propane concentrations, respectively (derivation of equation given in Genereux and Hemond 1990). This calculation assumes all methane in stream water is derived from groundwater and that consumption by methane-oxidizing bacteria is negligible. The sediments of Walker Branch are well oxygenated and probably have little methane production. The assumptions, however, may not be appropriate for streams with more reduced sediments.

Using the specific conductance of groundwater (C_{GW_i}), we estimated the proportion of subsurface flow derived from soils and bedrock using data from Mulholland and Hill (1997). Data were collected weekly for 5 yr (1991–1995) from the west fork of Walker Branch, the watershed adjacent to the present study location, for a study that, in part, examined the sources of groundwater (soil vs. bedrock) feeding surface flow. Using an end-member mixing model in conjunction with Ca^{2+} and Mg^{2+} concentrations in surface, soil, and bedrock waters, Mulholland and Hill (1997) described the proportion of stream flow derived from the two subsurface environments (f_{soil} and f_{bedrock}). Soil water has low cation concentrations, resulting in reduced specific conductance relative to bedrock water. The specific conductance of surface water is closely correlated with the proportion of surface flow derived from soils ($R^2 = 0.89$), and, using linear regression analysis, we developed an equation describing f_{soil} as a function of surface-water specific conductance, C_{surface} ($f_{\text{soil}} = 1.056 - 3.724 \times 10^{-3} C_{\text{surface}}$).

Statistical analysis—The effects of stream reach and sampling date were assessed with two-way analysis of variance (ANOVA). The triplicate samples of methane provide an error term for methane concentration, but, because study reaches cannot be replicated, no error term can be assigned to evasion estimates. Given this lack of replication for evasion, groundwater discharge, and groundwater methane concentration, ANOVAs were run without an interaction term. Significant differences ($P < 0.05$) were further evaluated using Tukey's multiple-comparison test.

Results

Surface discharge in the east fork of Walker Branch varied nearly fourfold across the three sample dates, with flows of 6.71, 6.15, and 1.83 (liter s^{-1}) on 9 May, 19 June, and 24 July, respectively. All five study sections gained water, although the relative contribution of groundwater to surface flow varied (Fig. 1). The total groundwater discharge across all five study sections was 0.47, 0.46, and 0.70 liter s^{-1} in

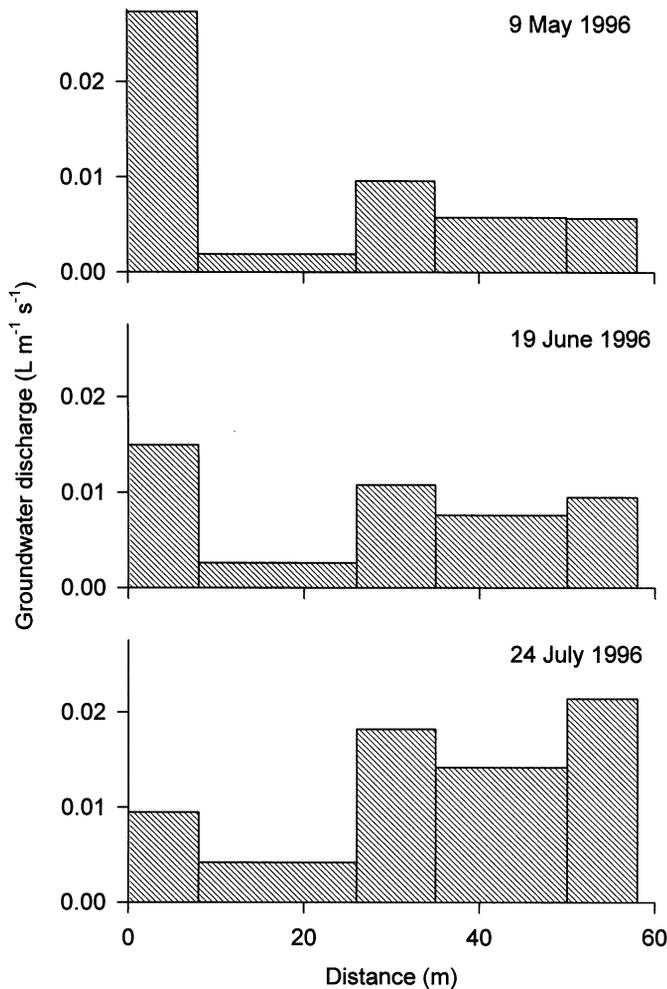


Fig. 1. Groundwater discharge per stream length into five study sections along the east fork of Walker Branch, Tennessee.

May, June, and July, corresponding to rates of 17, 20, and 32% of surface-water discharge, respectively. Groundwater discharge into the five sections ranged from 1.3 to 10.4% of surface flow, with rates per length of stream channel of 0.002–0.021 liter $m^{-1} s^{-1}$. The rate of groundwater discharge was always low in section 2, averaging 0.003 liter $m^{-1} s^{-1}$ across dates. Groundwater flow into the other study sections, in contrast, was temporally inconsistent. On the first two sampling dates (9 May and 19 June), groundwater flow was greatest into section 1 (0.015 and 0.027 liter $m^{-1} s^{-1}$), but on the third date (24 July), subsurface discharge was highest in section 5 (0.021 liter $m^{-1} s^{-1}$; Fig. 1).

Methane concentration, evasion, and input—The concentration of methane in Walker Branch did not differ significantly between sampling stations ($P = 0.176$) but varied temporally ($P = 0.003$; Fig. 2). Methane levels were not different between May and June, when the temperature was 15.0 and 16.0°C, respectively, averaging 0.77 $\mu g CH_4 liter^{-1}$, but increased 58% to a mean concentration of 1.22 $\mu g CH_4 liter^{-1}$ in July (17.9°C). Methane was always supersaturated, ranging from 17.6 to 41.4 times more than atmospheric equi-

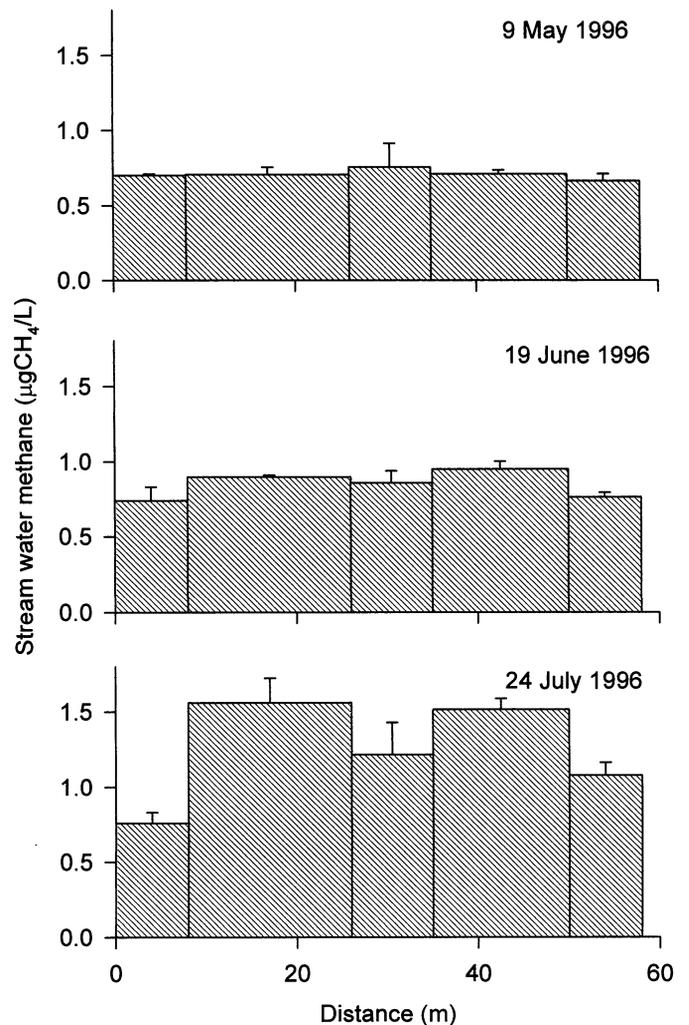


Fig. 2. Methane concentration (\pm SE) in surface water in five study sections along the east fork of Walker Branch, Tennessee.

librium (assuming an atmospheric concentration of 1.7 ppmv; Khalil and Rasmussen 1994).

Evasion of methane from the five study sections varied 33-fold from 0.4 to 13.2 $mg CH_4 m^{-2} d^{-1}$ (Fig. 3). The rate, however, did not differ significantly between sections ($P = 0.360$) or dates ($P = 0.058$). Input of methane into Walker Branch was equal to output via evasion, averaging 4.3 $mg CH_4 m^{-2} d^{-1}$ (Fig. 3). Similar to evasion, input did not differ between study sections ($P = 0.650$) or across dates ($P = 0.473$).

Groundwater methane concentration and specific conductance—The concentration of methane in groundwater discharging into the five study sections varied eightfold from 90.5 to 736 $\mu g CH_4 liter^{-1}$ ($P = 0.011$; Fig. 4), levels two to three orders of magnitude greater than in surface water and 2,400 to 19,500 times greater than atmospheric equilibrium. Methane concentration was particularly high in groundwater discharging in section 2 (mean = 546 $\mu g CH_4 liter^{-1}$), the section receiving the lowest groundwater flow (Fig. 1). Whereas groundwater entering section 2 was rich

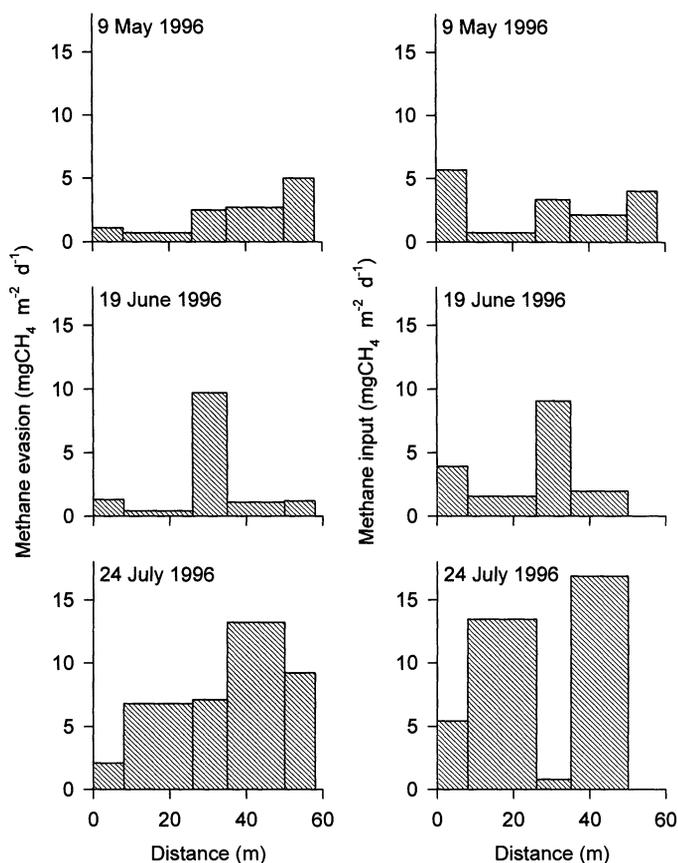


Fig. 3. Methane evasion and input into five study sections along the east fork of Walker Branch, Tennessee.

in methane, specific conductance was low compared with the other study reaches ($P = 0.003$; Fig. 4). The specific conductance of section 2 groundwater averaged $82.3 \mu\text{S cm}^{-1}$, compared with specific conductances of $110\text{--}125 \mu\text{S cm}^{-1}$ for groundwater in the other reaches. Groundwater methane did not significantly vary between dates, whereas specific conductance was greater in July than in May or June ($P < 0.001$).

Methane concentration in soil water—Groundwater specific conductance explained 48, 77, and 80% of the variance in groundwater methane concentration in May, June, and July, respectively (linear regression; $P < 0.05$). Based on the relationship between f_{soil} and specific conductance from Mulholland and Hill (1997), the contribution of soil water to groundwater discharge varied both between sections ($P = 0.003$) and dates ($P < 0.001$; Fig. 5). During the higher flows of May and June, most stream flow (82%) originated from soils. As surface flow dropped in July, however, f_{soil} declined to an average of 45% (Fig. 5). When sections were compared spatially, section 2 was distinct from the other sections because it always received the largest fraction of flow from soils (mean $f_{\text{soil}} = 0.81$).

The concentration of methane in groundwater was directly related to the proportion of subsurface discharge derived from soils ($P < 0.05$, $R^2 = 0.48\text{--}0.80$ across dates; Fig. 6).

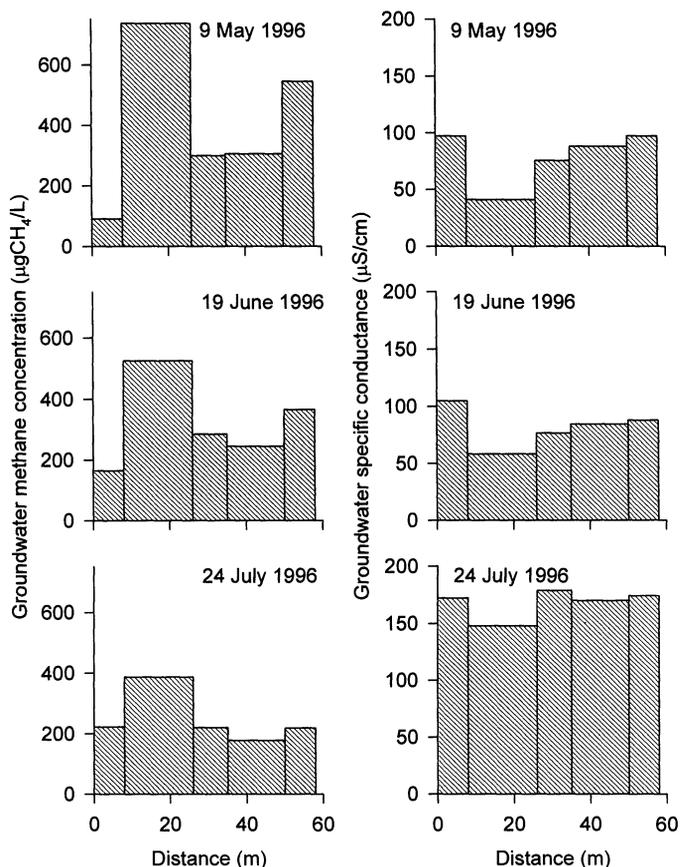


Fig. 4. Methane concentration and specific conductance of groundwater discharging into five study sections along the east fork of Walker Branch, Tennessee.

On all three sampling dates, the slopes of the linear regression equations did not differ significantly ($P > 0.05$), ranging from $1,450$ to $1,766 \mu\text{g CH}_4 \text{ liter}^{-1} f_{\text{soils}}^{-1}$ (mean = $1,638 \mu\text{g CH}_4 \text{ liter}^{-1} f_{\text{soils}}^{-1}$). In other words, for every 10% rise in the fraction of groundwater from soils, the concentration of methane in groundwater increased 145 to $177 \mu\text{g CH}_4 \text{ liter}^{-1}$.

Discussion

Methane evasion from the stream surface of Walker Branch was closely coupled to groundwater methane concentration and rate of subsurface flow into the stream. Groundwater concentration of methane, in turn, appeared to be governed by subsurface flow paths through riparian zones. Flow paths through soils generate groundwater rich in methane and are the principal source of methane to the stream surface.

Sources of methane—Methane is generated by obligate anaerobic bacteria; thus, production is restricted to regions of anoxia. The sediments underlying streams are typically oxygenated (Dahm et al. 1987, 1991; Triska et al. 1993; Baker et al. 1994; Jones et al. 1994, 1995). Anoxia is much more prevalent lateral to the channel; thus, riparian zone soils and/or deeper groundwater are likely the primary

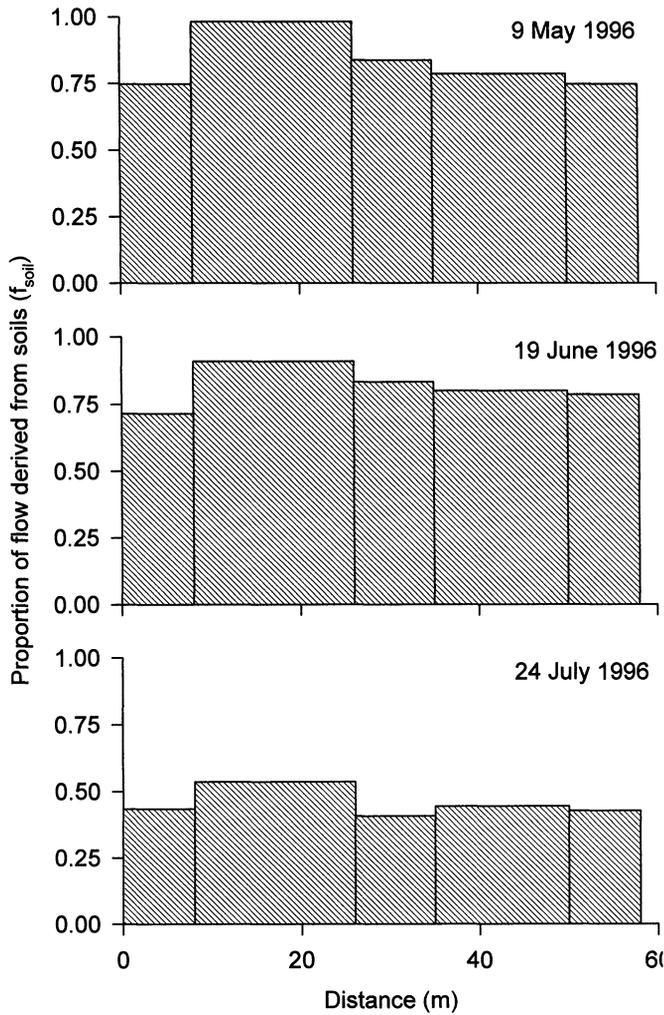


Fig. 5. Proportion of groundwater discharge flowing into five study sections along the east fork of Walker Branch, Tennessee, derived from soil.

sources of methane to lotic ecosystems. In the west fork of Walker Branch, deeper groundwater is usually rich in dissolved oxygen, with a mean concentration of $8.3 \text{ mg O}_2 \text{ liter}^{-1}$, whereas riparian groundwater commonly has $<2.3 \text{ mg O}_2 \text{ liter}^{-1}$ (Mulholland 1992), suggesting that riparian soils are the primary source of methane in Walker Branch. The concentration of methane in groundwater discharging into the east fork of Walker Branch varied as a function of water origin, with groundwater methane concentration being directly related to the proportion of flow derived from soils.

The linear regression of groundwater methane versus f_{soil} can potentially be used to estimate the concentration of methane in soils and bedrock by solving for $f_{\text{soil}} = 1$ and 0. Interestingly, however, the y intercepts from all three regressions were <0 , suggesting a theoretically impossible negative concentration. A negative intercept could result if a substantial quantity of methane is consumed by methane-oxidizing bacteria before groundwater discharges into the surface stream. Assuming the y intercepts = 0 (and hence bedrock water methane = $0 \text{ } \mu\text{g CH}_4 \text{ liter}^{-1}$) and solving for

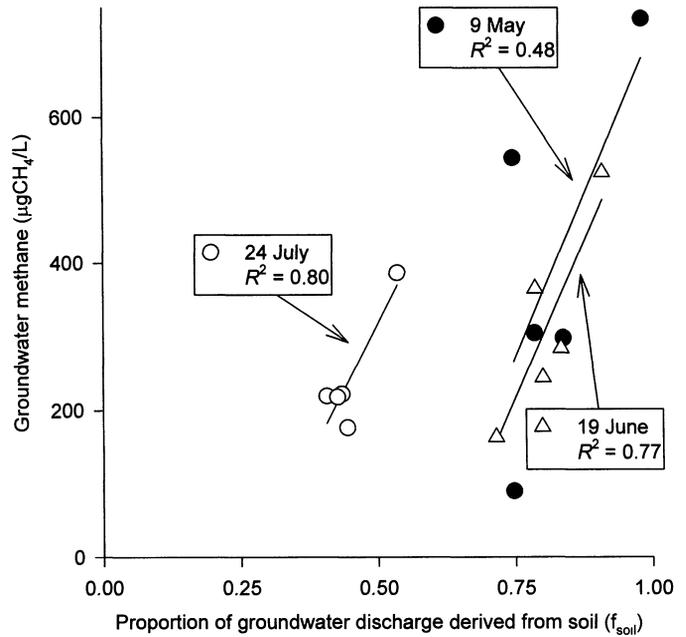


Fig. 6. Groundwater methane concentration versus the proportion of groundwater discharge derived from soil for three sampling dates in the east fork of Walker Branch, Tennessee.

$f_{\text{soil}} = 1$, soil water methane concentration was $1,770$, $1,700$, and $1,450 \text{ } \mu\text{g CH}_4 \text{ liter}^{-1}$ in May, June, and July, respectively. In support of the assumption that bedrock water methane = $0 \text{ } \mu\text{g CH}_4 \text{ liter}^{-1}$, the methane concentration in water discharging from springs along the east fork of Walker Branch that are fed by deeper groundwater was $\sim 4.0 \text{ } \mu\text{g CH}_4 \text{ liter}^{-1}$ (J. B. Jones unpubl. data). Furthermore, using the mean flux rate measured in the current study to back-calculate the concentration of methane in groundwater feeding the headwater springs located $\sim 100 \text{ m}$ upstream from our study reach yields a methane concentration estimate of only $16 \text{ } \mu\text{g CH}_4 \text{ liter}^{-1}$.

Our estimates of average groundwater and soil water methane concentrations are within the range of values reported from other studies and are similar to levels measured in groundwater wells located in the riparian zone adjacent to the study site. The concentration of methane in riparian zone groundwater is typically $<1,000 \text{ } \mu\text{g CH}_4 \text{ liter}^{-1}$, although small localized regions with levels upward of $3,200 \text{ } \mu\text{g CH}_4 \text{ liter}^{-1}$ are not uncommon (Dahm et al. 1987, 1991; Pulliam 1993; Baker et al. 1994; Jones et al. 1994, 1995). Methane measured from April through October 1995 in groundwater collected from 16 wells in the riparian zone adjacent to our study site on Walker Branch averaged $270 \text{ } \mu\text{g CH}_4 \text{ liter}^{-1}$ (J. B. Jones unpubl. data). During the summer sampling dates, the concentration of methane measured in riparian well water averaged $386 \text{ } \mu\text{g CH}_4 \text{ liter}^{-1}$, similar to the mean concentration in groundwater discharge of $319 \text{ } \mu\text{g CH}_4 \text{ liter}^{-1}$ estimated in the current study from stream-water chemistry. Furthermore, methane concentration in well water was as high as $1,830 \text{ } \mu\text{g CH}_4 \text{ liter}^{-1}$, in close agreement with the estimates of soil water methane ($1,450$ – $1,770 \text{ } \mu\text{g CH}_4 \text{ liter}^{-1}$) made from groundwater concentration versus f_{soil} .

Methane in surface water—From the riparian zone, methane is transported to the stream surface, where the concentration is considerably lower because of loss through evasion to the atmosphere and potentially from oxidation by methanotrophic bacteria. In Walker Branch, the mean concentration of $0.92 \mu\text{g CH}_4 \text{ liter}^{-1}$ in surface water was only 0.3% of the mean concentration in groundwater. Despite the dramatic reduction in methane, however, the concentration in surface water was 17.6–41.4 times greater than atmospheric equilibrium and resulted in a diffusive gradient from the stream to the atmosphere. Interestingly, whereas methane was highly supersaturated in Walker Branch, the concentration was low compared with that in other streams. Methane in streams is typically $5\text{--}10 \mu\text{g CH}_4 \text{ liter}^{-1}$ (Dahm et al. 1987, 1991; de Angelis and Lilley 1987; de Angelis and Scranton 1993; Pulliam 1993; Baker et al. 1994; Hamilton et al. 1995), and concentrations ranging from 25 to $50 \mu\text{g CH}_4 \text{ liter}^{-1}$ are not uncommon (Dahm et al. 1991; de Angelis and Lilley 1987; Jones and Mulholland 1998).

The concentration of methane in surface water is governed by smaller-scale inputs in groundwater, instream production and oxidation, and diffusion to the atmosphere, as well as larger-scale processes controlling the extent of anaerobic metabolism within a catchment. The longitudinal variation in methane concentration in Walker Branch is regulated by spatial heterogeneity in groundwater inputs. On a larger scale, however, characteristics of the catchments such as soil organic matter storage, hydrologic residence time, and subsurface flow paths regulate the extent of area where methane is produced and the rate at which it is generated (Jones and Mulholland 1998). For example, in another study, we examined the concentration of methane in streams in the Oak Ridge National Environmental Research Park that drain catchments underlain by either dolomite or shale (Jones and Mulholland 1998). The difference in concentration of methane in streams draining the two catchment types was striking; streams draining catchments underlain by dolomite had, on average, less than half the concentration of methane of streams draining catchments underlain by shale, with means of 1.92 and $4.37 \mu\text{g CH}_4 \text{ liter}^{-1}$, respectively. The more than twofold difference in methane concentration presumably results from differences in catchment geomorphology, valley floor width, soil development, and hydrologic residence times and flow paths, features regulated in part by geology (Jones and Mulholland 1998).

From the stream surface, methane is lost to the atmosphere via diffusion. The rate of evasion is principally regulated by gas concentration, temperature, and turbulence (Fortescue and Pearson 1967; Jähne et al. 1987; Wilcock 1988). As expected on the basis of the low concentration in surface water, the rate of evasion from Walker Branch was low compared with that from most small streams but similar to rates from several larger rivers in temperate North America. The mean evasion rate from Walker Branch across the three sampling dates of $4.3 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ was similar to evasion during August from the Hudson River, New York ($6.1 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$; de Angelis and Scranton 1993) and to the mean annual flux from the Moisie River and tributaries in Quebec, Canada ($0.3\text{--}1.8 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$; Naiman et al. 1987), and several rivers in western Oregon ($1.2\text{--}36 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$; de Angelis and Lilley 1987). Evasion

from Walker Branch, however, was considerably lower than from the surface water of the black-water Ogeechee River, Georgia, where the mean annual rate varied from 1.7 to $96.4 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ (Pulliam 1993). Moreover, evasion from Walker Branch was one to two orders of magnitude lower than evasion from the Pantamal and Amazon Rivers, Brazil, which ranged from 0 to $600 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ (Hamilton et al. 1995) and from 0 to $1,160 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ (Bartlett et al. 1990), respectively.

The oxidation of methane by methanotrophic bacteria can account for substantial loss from surface waters. In the Hudson River, the turnover of methane due to methanotrophic bacteria ranged from 0.005 to 0.033 d^{-1} during March to $0.11\text{--}0.70 \text{ d}^{-1}$ in August. The August oxidation rate translates to the pool of methane in the river turning over every 1.4–9.1 d. Similarly, in the Ogeechee River, methane oxidizers consume a sizable fraction of the methane, with a consumption rate of $1\text{--}12.5 \text{ d}^{-1}$ (Pulliam 1993). The upper rate of 12.5 d^{-1} corresponds to the pool of methane in surface water turning over in <2 h. Furthermore, the methane oxidation rate in the Ogeechee River was strongly correlated with temperature, increasing $0.92 \text{ d}^{-1} \text{ }^\circ\text{C}^{-1}$ (Pulliam 1993). Assuming the same relationship between oxidation and temperature in Walker Branch as in the Ogeechee River, methane oxidation consumes only $0.12\text{--}0.14 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ in May but increases to $0.61\text{--}1.26 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ in July. Expressed relative to methane import and export, methane oxidation potentially consumes 2.2–21.1% of methane inputs, rates equivalent to 2.6–36.4% of evasion.

Streams as conduits for methane evasion—Methane is a major greenhouse gas that is principally generated through biological processes. Streams function as pathways for methane evasion from groundwaters and riparian zones to the atmosphere, with the rate of evasion being dependent on the concentration of methane in groundwater and the rate of subsurface discharge. Our approach provides an effective means to measure evasion rates from stream and riparian ecosystems by focusing on hydrologic linkages. These hydrologic linkages, however, not only govern evasion from the stream surface but also impact stream functioning. As noted by Baker et al. (1994), methane is a labile organic carbon source for methanotrophic bacteria. The spatial heterogeneity of methane input likely results in regions with particularly high methanotrophic activity. Furthermore, subsurface flow paths rich in methane are also likely enriched in other reduced molecules, such as ammonium and ferrous iron, which has implications for nutrient cycling, photosynthesis, and chemoautotrophic production. Thus, methane can be used as a tracer to identify biogeochemically important pathways in stream ecosystems.

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