Biogeochemistry **31:** 155–173, 1995.

Methanogenesis in Arizona, USA dryland streams

JEREMY B. JONES, JR.[1], ROBERT M. HOLMES, STUART G. FISHER, NANCY B. GRIMM & DENA M. GREENE
Department of Zoology, Arizona State University, Tempe, Arizona 85287-1501 USA;
[1] *Present address: Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Bldg. 1506, Oak Ridge, Tennessee 37831-6034 USA*

Received 29 July 1994; accepted 17 August 1995

Abstract. Methanogenesis was studied in five streams of central and southern Arizona by examining the distribution of methane in interstitial water and evasion of methane in three subsystems (hyporheic, parafluvial and bank sediments). In Sycamore Creek, the primary study site (studied during summer and early autumn), methane content of interstitial water exhibited a distinct spatial pattern. In hyporheic (sediments beneath the wetted channel) and parfluvial zones (active channel sediments lateral to the wetted channel), which were well oxygenated due to high hydrologic exchange with the surface stream and had little particulate organic matter (POM), interstitial methane concentration averaged only 0.03 mgCH_4-C/L. Bank sediments (interface between the active channel and riparian zone), in contrast, which were typically vegetated, had high POM, low hydrologic exchange and concomitantly low dissolved oxygen levels, had interstitial concentration averaging 1.5 mgCH_4-C/L. Methane emission from Sycamore Creek, similar to methane concentration, averaged only 3.7 mgCH_4-C$\cdot$m$^{-2}\cdot$d^{-1} from hyporheic and parafluvial zones as opposed to 170 mgCH_4-C$\cdot$m$^{-2}\cdot$d^{-1} from anoxic bank sediments. Methane in four additional streams sampled (one sampling date during late winter) was low and exhibited little spatial variation most likely due to cooler stream temperatures. Interstitial methane in parafluvial and bank sediments of all four streams ranged from only 0.005 to 0.1 mgCH_4-C/L. Similarly methane evasion was also low from these streams varying from 0 to 5.7 mgCH_4-C$\cdot$m$^{-2}\cdot$d^{-1}. The effects of organic matter and temperature on methanogenesis were further examined by experimentally manipulating POM and temperature in stoppered flasks filled with hyporheic sediments and stream water. Methane production significantly increased with all independent variables. Methane production is greatest in bank sediments that are relatively isolated hydrologically and lowest in hyporheic and parafluvial sediments that are interactive with the surface stream.

Key words: methane, methanogenesis, arid-lands, Sonoran Desert, streams, hydrologic exchange

Introduction

Ecosystem respiration requires a supply of organic matter and terminal electron acceptors. In desert streams, ecosystem respiration is high and fueled by luxuriant in-stream algal production (Busch & Fisher 1981; Grimm 1987). This high respiration is not restricted to the benthos, but extends into the underlying sediments (Grimm & Fisher 1984). Labile organic matter from the stream surface is transported into sediments at regions of hydrologic downwelling where rapid respiration is supported (Jones et al. 1995). Dissolved oxygen is also transported into sediments via downwelling zones (Valett 1993), and as a result organic matter is decomposed largely aerobically (Jones et al. 1994).

While rapid flux of organic matter and oxygen from the surface to subsurface supports high aerobic respiration, desert stream sediments have potential for substantial anaerobic metabolism (Jones et al. 1994). As water downwells from the surface into sediment interstices, aerobic respiration can rapidly reduce available oxygen (Holmes et al. 1994). In Sycamore Creek, a Sonoran Desert stream, anoxia is common where sediments are relatively isolated from surface flow such as at a depth of one-meter below the surface channel (Valett et al. 1990) and in sediments lateral to surface flow (Jones et al. 1994; Stanley & Boulton 1995).

The extent of anaerobic metabolism in streams is of significance not only for decomposition but also for global warming. In highly reducing environments, methanogenesis is a major anaerobic pathway in freshwater ecosystems (Whiticar et al. 1986; Oremland 1988). Currently, more methane in the atmosphere than at any time in the past 160,000 years (Chappellaz et al. 1990). Atmospheric methane concentration has increased as fast as 1% per year (Rasmussen & Khalil 1984; Cicerone 1988), although in recent years the rate of methane accumulation has slowed (Steele et al. 1992). This increase of atmosphere methane is estimated to contribute 15% (Rodhe 1990; Denmeade 1991) to a predicted increase in mean global temperature of 0.8 to 4.1 °C by 2030 (Levine 1992). Methane production and emission are strongly influenced by temperature (Kelly & Chynoweth 1981; Crill et al. 1988; Wilson et al. 1989); freshwater ecosystems of the arid southwestern United States are commonly 25 to 30 °C (Fisher et al. 1982), and thus have potential for high methane emission. Moreover, arid and semi-arid lands occupy one-third of the earth's land surface (Crawford & Gosz 1982; Graf 1988), yet have received little attention as a source of atmosphere methane.

This research focused on three questions: 1) what is the extent and importance of methanogenesis; 2) what factors control methane production and emission; and 3) what is the rate of methane evasion from streams of arid and semi-arid Arizona? Intensive study of the extent of anaerobic metabolism and factors controlling methanogenesis was conducted in one stream, Sycamore Creek, Arizona, USA. Methane evasion from other arid and semi-arid streams was examined by surveying emission from four additional streams in southern Arizona.

Study sites

Precipitation in central and southern Arizona occurs primarily during the winter and summer, whereas stream discharge is typically greatest during winter and spring (Grimm 1992). Streams are characterized by sparse canopies and broad channels. Within broad active channels, streams are typically 'underfit' in that the wetted perimeter occupies only part of the active channel and the surface stream is bounded laterally by expansive gravel bars. Active channel sediments are composed of sand to gravel-sized sediments that are frequently reworked by flash floods (Graf 1988). Further lateral is a riparian zone that is elevated compared with the active channel and inundated only during larger floods.

The primary study site, Sycamore Creek, is typical of the streams studied. Sycamore Creek is an intermittent stream located 32 km northeast of Phoenix, Arizona (stream 1; Fig. 1). The stream drains a 505-km^2 mountainous watershed that ranges in elevation from 427 to 2164 m. The catchment is composed of igneous and metamorphic rock with shallow overlying soils and unconsolidated sediments (Thomsen & Schumann 1968). Ponderosa pine and piñon-juniper woodlands predominate at higher elevations and Sonoran desert scrub at lower elevations. Stream channels are bordered by a cottonwood-willow riparian zone. Precipitation is bimodal between winter and summer with annual means of 58 and 34 cm at higher and lower elevations, respectively (Thomsen & Schumann 1968).

The single 100-m study reach of sandy run at ca. 650 m elevation typified lower to mid-elevation reaches (ranging in elevation from 600 to 760 m) of Sycamore Creek. Here the wetted channel was shallow (5 cm) and wide (5–6 m) and bounded by a broad active channel ($\sim$ 20 m) of alluvial sediments, and lateral bank sediments rich in organic matter and frequently anoxic (Jones et al. 1994). Stream substrata in mid-elevation runs consist primarily of sand and fine gravel with a mean depth above bedrock of 62 cm (Valett et al. 1990). Riparian cover is sparse and set back from the stream. Consequently, the stream receives full sunlight most of the day and has in-stream gross primary production as high as 12 $gO_2 \cdot m^{-2} \cdot d^{-1}$. Aerobic respiration is also high with a benthic rate as great as 7 $gO_2 \cdot m^{-2} \cdot d^{-1}$ (Grimm 1987) and a subsurface rate as rapid as 16 $gO_2 \cdot m^{-2} \cdot d^{-1}$ (Jones et al. 1995).

Methanogenesis was studied in three subsystems: sediments beneath the wetted channel (hyporheic zone), gravel bars within the active channel and lateral to the wetted channel (parafluvial zone), and the interface between the active channel and riparian zone (bank sediments). Sediments in all three subsystems were below the water table and thus saturated. Sediments located within the active channel (hyporheic and parafluvial zones) had little vegetation, were composed of coarse-sandy sediments, were poorly structured, and appeared oxic. In contrast, bank sediments were vegetated, composed of fine particles, highly structured, and frequently appeared black and reducing.

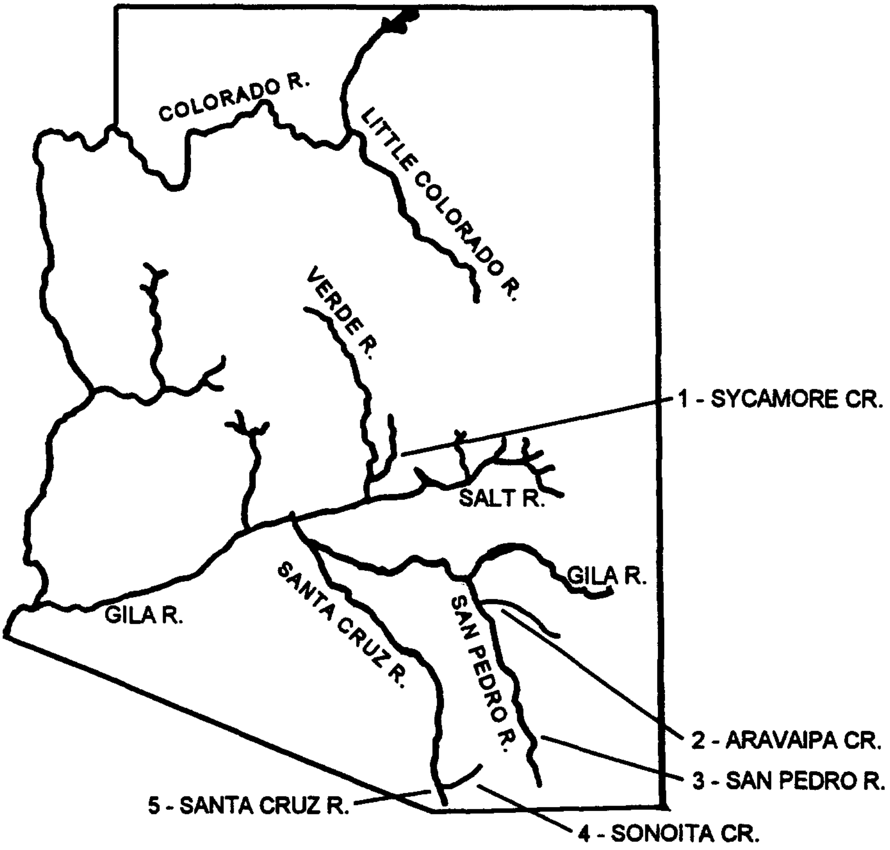

Fig. 1. Location of sample sites and streams in Arizona, USA. Sycamore Creek (1) 30 km upstream from Verde River; Aravaipa Creek (2) 8.3 km upstream from San Pedro River; San Pedro River (3) at Fairbanks, AZ; Sonoita Creek (4) at Patagonia, AZ; Santa Cruz River (5) at Nogales, AZ.

Methods

Interstitial methane and methane evasion in Sycamore Creek

The Sycamore Creek study site was mapped in June 1993 to determine areal extent of the wetted and active channels, extent of anoxia, and concentration of interstitial methane throughout the reach. Extent of anoxia (measured by the presence of ferrous iron; Stookey 1970; Dahm et al. 1991) and methane concentration were determined by sampling subsurface water every 2 m along 21 transects located every 5 m across the stream channel throughout the 100 m reach (124 sample points total; Fig. 2). Water for ferrous iron and methane determination was collected by drawing a continuous column of

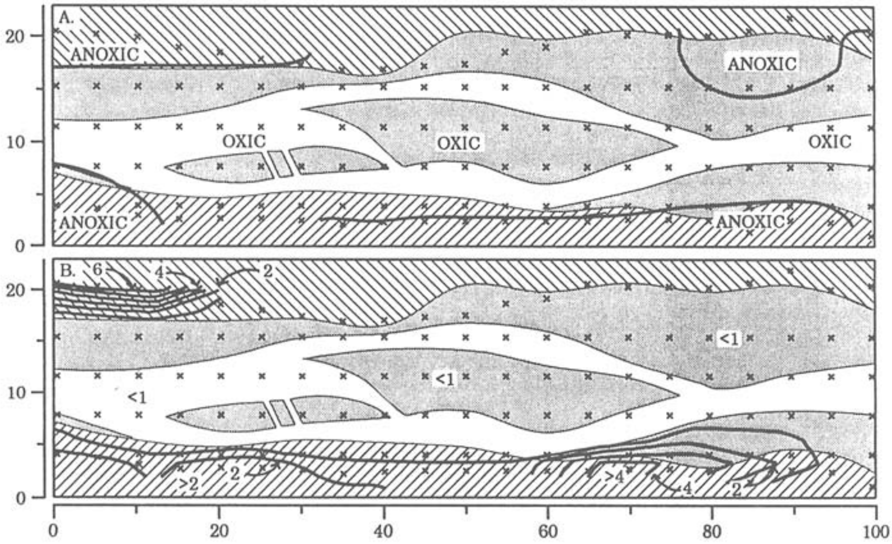

Fig. 2. Extent of anoxia (panel a) and interstitial methane concentration (mgCH$_4$-C/L; panel b) in the Sycamore Creek study reach. Stream flow is from left to right. Open fill = surface stream/hyporheic zone; stippled fill = parafluvial zone; diagonal fill = bank sediments. Crosses denote sample locations and axes are distance (m).

water from a piezometer inserted 25 cm into sediments. Ferrous iron samples were immediately filtered and injected into Vacutainer® tubes (n = 3 per sample point) pre-injected with ferrozine reagent (Stookey 1970) and methane samples were injected into sterile Vacutainer® tubes (n = 3 per sample point; 2 ml sample into 5 ml tube). Samples were stored on ice for transport to the laboratory. Ferrous iron was analyzed colorimetrically; we defined anoxic regions as sediments with greater than 1 mg Fe^{2+}/L. Methane was measured by withdrawing a gas sample from the headspace of Vacutainer® tubes and analyzing on a Varian Model 3300 gas chromatograph equipped with a flame ionization detector (detection limit = 5 μg CH$_4$-C/L). The distributions of anoxia and methane were mapped by Kriging analysis (Geo-EAS software; Delhomme 1978; Journal & Huijbregts 1978; Englund & Sparks 1991). The areal extent of oxic and anoxic regions was determined from the Kriged maps; the proportion of stream composed of anoxic sediments was based upon the area bounded by the sample locations (Fig. 2).

Methane evasion, interstitial methane, dissolved organic carbon (DOC) and particulate organic carbon (POC) were measured in Sycamore Creek on three sample dates from late spring to early autumn (10 June 1993, 18 August 1993 and 23 October 1993) in three subsystems: hyporheic, parafluvial and bank sediments. Methane evasion was measured using static chambers (n = 6 chambers per location) constructed of white plastic pipe capped on one end (10 cm diameter, 30 cm high). The same chambers were used for both air-soil and air-water interfaces and were positioned by gently placing chambers on the substrate. Methane flux was determined as increase in methane concentration between initial and final gas samples collected in Vacutainer® tubes (5 ml) over a 45-minute period. No attempt was made to control temperature within chambers. The air and soil temperature within chambers was potentially elevated relative to ambient conditions and may have influenced methane evasion rate (Matthias et al. 1980). Incubation times, however, were kept short to reduce chamber heating effects.

Samples for DOC were collected by drawing a continuous column of water from a piezometer inserted 25 cm into sediments using a peristaltic pump and filling three previously acid-washed polyethylene bottles (n = 3 sample locations per subsystem, n = 3 replicates per sample location). Samples were stored at 4°C, filtered in the laboratory (Whatman GF/F glass fiber filters) and analyzed within 48 h by high temperature oxidation on a Shimadzu Model 5000 total organic carbon (TOC) analyzer (n = 3 replicates per sample location). The standards for DOC analysis were 0, 2, 4 and 8 mgC/L potassium biphthalate solutions. TOC analyzer response was linear across standards. The standard curve was shifted through the origin which in effect assumes the background output from the analyzer is zero. The detection limit was 0.1 mgC/L and precision was 0.04 mgC/L. Sediments for POC analysis were collected from a depth of 2–15 cm using a trowel and frozen until analyzed. POC was measured by sealing sediments (<1 mm size class separated by dry sieving) into glass ampules, digesting with persulfate and measuring resulting CO_2 on an Oceanography International Model 700 TOC analyzer (Menzel & Vaccaro 1964; n = 4 replicates per sample location). This method underestimates refractory organic matter, thus values obtained are minimum estimates of POC. Effects of subsystem and date (sample date) on methane evasion, interstitial methane, DOC, and POC were assessed by ANOVA (SYSTAT, Inc.; Wilkinson 1990). Tukey's method of multiple comparison was used to assess differences in treatment level effects. Effects of DOC, POC, and interstitial methane on methane evasion were assessed by linear regression (Wilkinson 1990).

Survey of interstitial methane and methane evasion in southern Arizona streams

Methane evasion and interstitial methane were measured in four streams in southern Arizona (streams 2–5; Fig. 1) in gravel bars and bank sediments during one sampling trip in later winter (14–16 March 1994). Within gravel bars of these streams methanogenesis was further studied by sampling at two points along parafluvial flowpaths to examine the effect of water residence time in sediments (0.5 and 5 m from the point where water from the stream surface flows into sediments). Interstitial methane and methane evasion were measured using methods previously described except that incubation periods for methane evasion lasted 3 h ($n = 5$ chambers and $n = 3$ water samples per sample point and/or subsystem). Effects of sample location and stream on interstitial methane and methane evasion were assessed by ANOVA (Wilkinson 1990).

Factors controlling methane production

The effects of particulate organic matter (POM), temperature, and incubation time on methane production were further examined experimentally in the laboratory. Erlenmeyer flasks (250 ml) were filled with sediments (100 g wet mass) and stream water (100 ml) and sealed with rubber stoppers ($n = 5$ flasks per treatment). Flasks were amended with POM (live green algae collected from Sycamore Creek) to produce three treatments: 0, 5 and 10 mg POM added, and then incubated at either 24 or 32 °C. POM amendments were approximately equal to 0, 23 and 45 mgC/kg sediment (assuming organic matter is 50% carbon). Average POC content of sediments in Sycamore Creek is 20 mgC/kg sediment (Jones et al. 1995). The effects of incubation time were studied by incubating flasks for 96 h with the same stream water and sampling every 24 h. At the end of an incubation period (i.e., 24 h) a gas sample was withdrawn from each flask by inserting a needle through the rubber stopper, and analyzed by gas chromatography. Oxygen was not measured in flasks but was probably consumed within 16 to 48 hours based upon aerobic respiration rate in the hyporheic zone of Sycamore Creek (Jones et al. 1995). Effects of POM, temperature, and time on methane production were assessed using a repeated measure ANOVA (time repeated measure; Wilkinson 1990).

Results

Methane emission in Sycamore Creek

Anoxia was common in sediments of Sycamore Creek, particularly lateral to the surface stream and accounted for 5% of stream area (Fig. 2a). The hyporheic zone and mid-channel parafluvial gravel bars, areas with high hydrologic exchange with the surface stream, were oxic throughout. Parafluvial and bank sediments lateral to the surface stream, which had reduced hydrologic exchange with oxygenated surface water, were frequently anoxic.

Interstitial dissolved methane tended to be associated with anoxia (Fig. 2a and 2b). In oxygenated hyporheic and parafluvial sediments methane was always less than 1 $mgCH_4$-C/L and commonly less than 0.05 $mgCH_4$-C/L, whereas methane in anoxic parafluvial and bank sediments was abundant, typically ranging from 1 to 6 $mgCH_4$-C/L.

POC in hyporheic and parafluvial sediments was low and constant temporally ($p \geq 0.05$; Fig. 3) averaging only 94 mgC/kg sediment. In contrast, bank sediment POC was high and varied significantly between sampling dates ($p < 0.001$) ranging from a mean of 500 mgC/kg sediment in June and August to 2500 mgC/kg sediment in October. Interstitial DOC was also greater in bank sediments than hyporheic and parafluvial zones ($p < 0.001$). Temporally, however, DOC increased in hyporheic and parafluvial subsystems from 1.6 to 3.4 mgC/L between August and October ($p < 0.001$; Fig. 3). Methane patterns were similar to DOC and POC in that hyporheic and parafluvial sediments averaged only 0.03 $mgCH_4$-C/L, whereas bank sediments averaged 1.5 $mgCH_4$-C/L ($p < 0.05$; Fig. 4). Furthermore, methane only accounted for 0.4% of DOC (CH_4-C ÷ [CH_4-C + DOC]) in hyporheic and parafluvial sediments but 18% in bank sediments ($p < 0.001$).

Methane emission from Sycamore Creek was closely coupled to higher interstitial methane, DOC, and POC concentration in anoxic bank sediments. Emission from bank sediments averaged 170 $mgCH_4\text{-}C{\cdot}m^{-2}{\cdot}d^{-1}$ and was significantly greater than in hyporheic and parafluvial sediments where methane evasion was only 3.7 $mgCH_4\text{-}C{\cdot}m^{-2}{\cdot}d^{-1}$ ($p < 0.001$; Fig. 4). Interstitial methane explained 65% of the variation in methane emission (linear regression; $p < 0.05$), DOC accounted for 27% of the variation ($p < 0.05$), and POC was not significant ($p \geq 0.05$). Overall methane emission from the active channel of Sycamore Creek (sum of methane emission from subsystems weighted by areal extent of subsystems) was 16, 17 and 5.6 $mgCH_4\text{-}C{\cdot}m^{-2}{\cdot}d^{-1}$ during June, August and October, respectively, and averaged 13 $mgCH_4\text{-}C{\cdot}m^{-2}{\cdot}d^{-1}$ across the three study dates. More than 80% of the total emission of methane from Sycamore Creek was from bank sediments.

Methane in streams of southern Arizona

Methane emission was much lower in streams of southern Arizona compared with Sycamore Creek, although stream temperatures were much cooler. The temperature of surveyed streams (streams 2–5; Fig. 1) was only 8 to 13 °C as opposed to 20 to 28 °C in Sycamore Creek. In contrast to the distinct pattern between subsystems of Sycamore Creek, interstitial methane concentration did not differ among subsystems or between streams in southern Arizona (Fig. 5), averaging 0.02 $mgCH_4$-C/L in all four streams ($p \geq 0.05$). Interstitial methane concentration was highly variable, however, ranging from 0.005 to

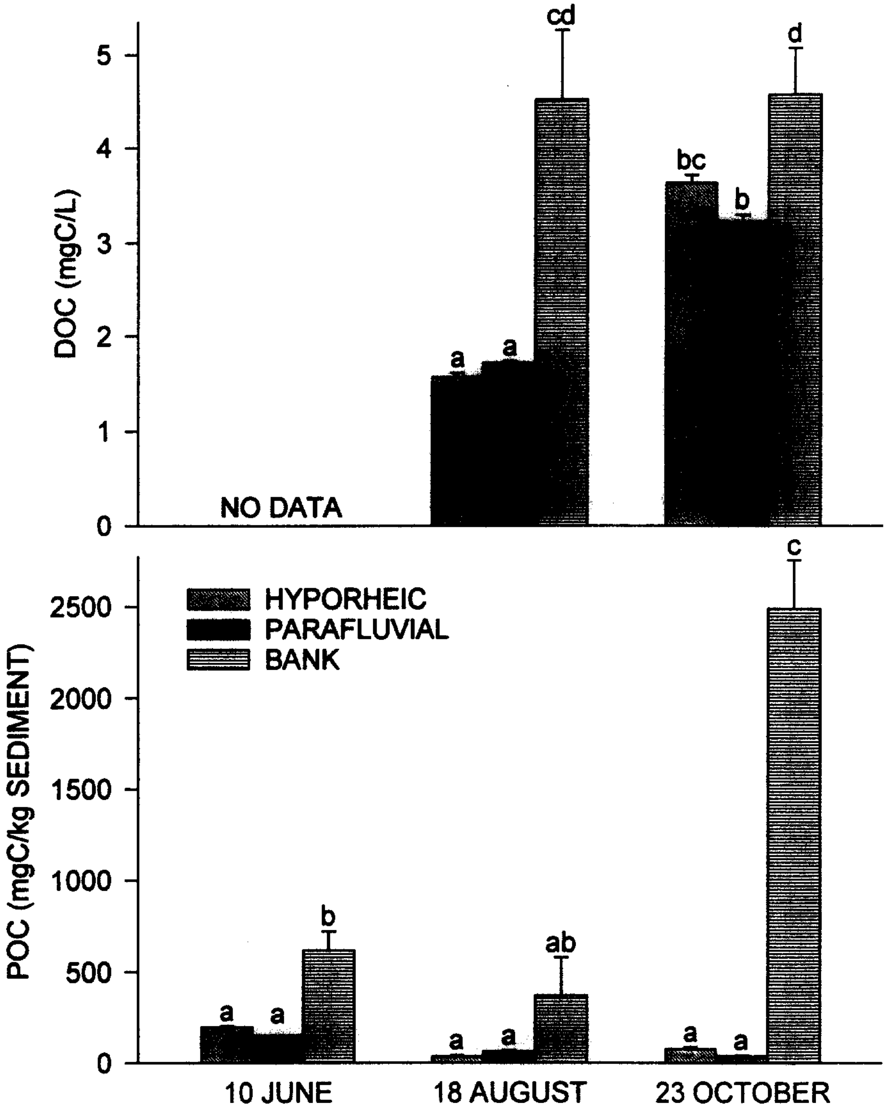

Fig. 3. Dissolved organic carbon (DOC) and particulate organic carbon (POC) concentrations in hyporheic, parafluvial and bank sediments of Sycamore Creek. Data are mean ± SE (n = 3). Bars having the same letter designation have means indistinguishable by Tukey's multiple comparison ($\alpha = 0.05$).

0.1 mgCH$_4$-C/L. Similarly, methane emission was constant and low across streams and subsystems averaging only 0.8 mgCH$_4$-C·m^{-2}·d^{-1} ($p \geq 0.05$), except from Sonoita Creek bank sediments (stream 4; Fig. 1) where evasion was 5.7 mgCH$_4$-C·m^{-2}·d^{-1} ($p < 0.01$).

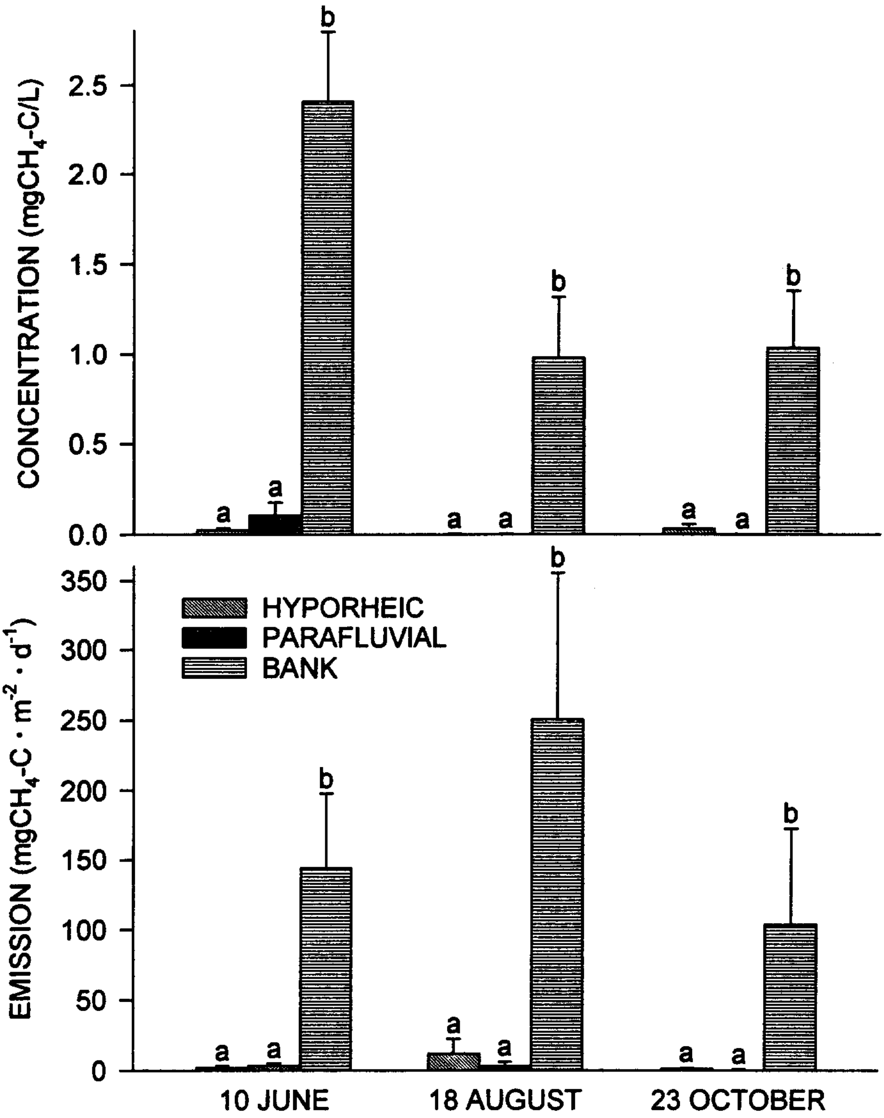

Fig. 4. Interstitial methane concentration and methane emission in hyporheic, parafluvial and bank sediments of Sycamore Creek. Data are mean ± SE ($n = 6$). Bars having the same letter designation have means indistinguishable by Tukey's multiple comparison ($\alpha = 0.05$).

Factors controlling methane emissions

Temperature, POM, and incubation time all significantly affected methane production (Fig. 6). Methane production increased 21-fold from 21 to 450 $mgCH_4\text{-}C{\cdot}kg\ sediment^{-1}{\cdot}d^{-1}$ with an increase of temperature from 24 °C to

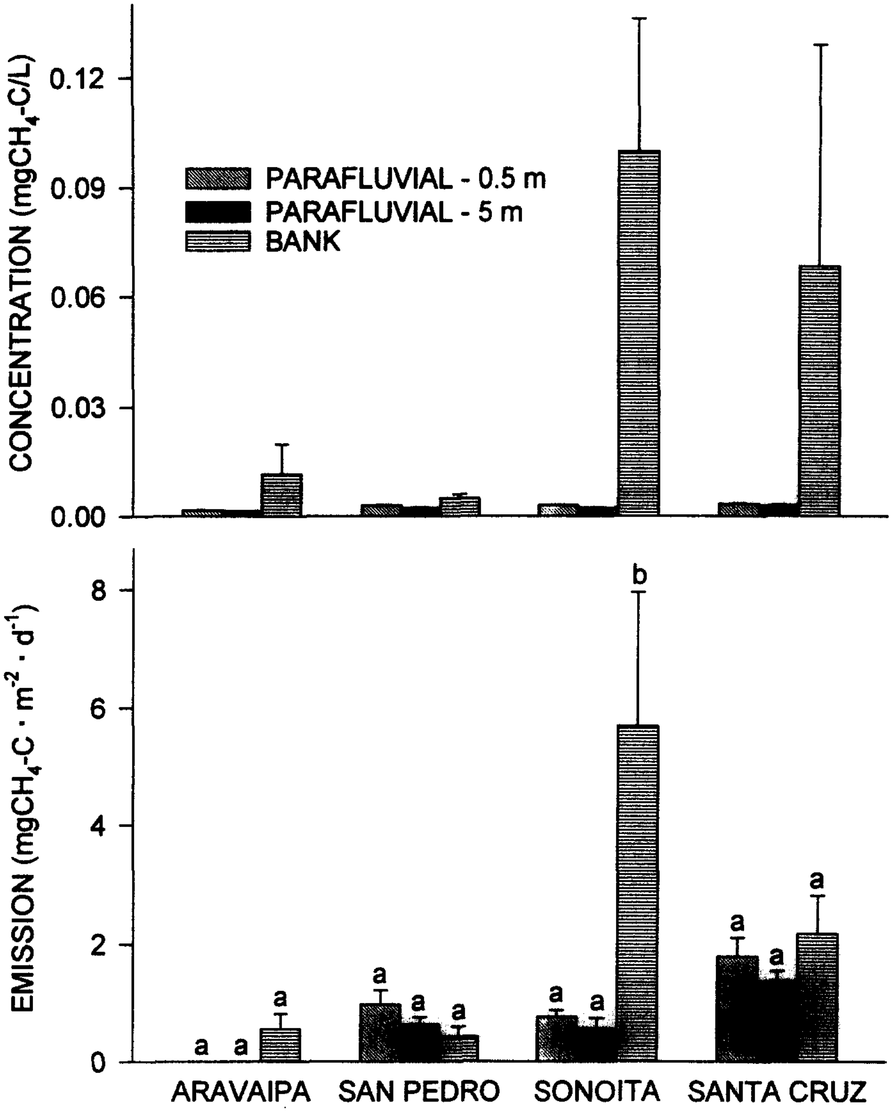

Fig. 5. Interstitial methane concentration and methane emission in parafluvial and bank sediments of four streams in southern Arizona. Data are means ± SE ($n = 5$). Bars having the same letter designation have means indistinguishable by Tukey's multiple comparison ($\alpha = 0.05$).

32 °C ($p < 0.001$). The addition of 10 mg POM to flasks had a dramatic effect, elevating methane production 18 times from 22 to 402 mgCH$_4$-C·kg sediment^{-1}·d^{-1}, respectively ($p < 0.001$). Similarly, the time sediments and water remained within flasks significantly affected methane production;

methane production after four days was 604 $mgCH_4$-C·kg sediment^{-1}·d^{-1} as compared with only 10 $mgCH_4$-C·kg sediment^{-1}·d^{-1} after one day ($p < 0.001$). Additionally, POM, temperature, and time all had significant interactions ($p < 0.001$). As a consequence, for example, the increase in methane production rate over time was greater at 32 °C than 24 °C, and with 10 mg POM than 0 mg POM.

Discussion

Factors controlling methanogenesis in streams

Subsurface metabolic processes in streams are tightly coupled to vertical hydrologic exchange and advective transport through sediments (White 1990; Hendricks & White 1991). In streams, hydrologic exchange from the surface stream to sediments is a primary determinant of the spatial distribution and extent of subsurface metabolic pathways (Holmes et al. 1994). As surface water downwells into the hyporheic zone, labile organic matter (Jones et al. 1995) and oxygen (Stanley & Boulton 1995) are transported into sediments. This labile organic matter fuels a high respiration rate (Jones et al. 1995) resulting in decline of dissolved oxygen. Downstream along subsurface flowpaths, as oxygen is consumed by respiration, redox potential drops and eventually methanogenesis develops (Jones et al. 1994).

Regions of anoxia develop in the sediments when import of dissolved oxygen through hydrologic exchange is slower than total respiratory demand along a flowpath. Extent of anoxia primarily depends on subsurface flowpath lengths, interstitial flow rate, and sediment respiration. In Sycamore Creek, much of the hyporheic zone is oxic (Fig. 2; Valett et al. 1990; Stanley & Boulton 1995) in spite of high sediment respiration (Grimm & Fisher 1984; Jones et al. 1995), suggesting frequent hydrologic exchange between surface and subsurface. Hyporheic respiration in Sycamore Creek averages 0.79 mgO_2·L sediment^{-1}·h^{-1} (range 0.05 to 4.41 mgO_2·L sediment^{-1}·h^{-1}; Grimm & Fisher 1984; Jones et al. 1995) which would deplete oxygen in 3 h (range 0.5 to 45 h; assuming sediment porosity of 0.3 and surface oxygen of 7.5 mgO_2/L; Jones et al. 1995). Interstitial flow rate is high, averaging 2.2 m/h (Valett et al. 1990), and thus for hyporheic sediments to remain oxic, flowpaths cannot be longer than about 7 m. Anoxia in Sycamore Creek occurs in deep hyporheic sediments (Valett et al. 1990), the parafluvial zone (Fig. 2; Stanley & Boulton 1995) and where interstitial flow rate is very low (Jones et al. 1994).

Physicochemical attributes of the environment such as organic matter, redox potential, and temperature, as well as biotic interactions between microorganisms, further affect methanogenesis and must also be incorporated into conceptualizations of stream hydrology and anaerobiosis. As redox potentials decline a number of terminal electron acceptors are used before metabolism ultimately shifts to methanogenesis including nitrate, manganic manganese, ferric iron, and sulfate. Nitrate is present in hyporheic sediments but absent in anoxic bank sediments, presumably consumed by denitrifying bacteria (Duff & Triska 1990). Ferrous iron concentration is high in bank sediments, some of which is likely generated anaerobically. Methanogenic bacteria are dependent upon end-products of fermentation, typically H_2 and acetate (Winfrey & Zeikus 1979), for a metabolic substrate (Yavitt et al. 1987). Sulfate reducing bacteria compete with methanogens for metabolic substrates (Winfrey & Zeikus 1977; Sorensen et al. 1981; Kristjansson et al. 1982) and can reduce substrate concentration below those required by methanogenic bacteria (Lovley and Klug 1983, 1986). Previous research in lake ecosystems has demonstrated a vertical zonation of sulfate reduction and methanogenesis (Cappenberg 1974; Reeburgh & Heggie 1977; Winfrey & Zeikus 1977; Lovley & Klug 1982). In lakes, sulfate diffuses into sediments from the overlying water. Sulfate reduction consequently excludes methanogenesis in upper sediments, whereas sulfate concentration declines deeper in sediments due to respiration, resulting in a transition to methanogenesis. A similar segregation likely exists in stream sediments; however, zones of sulfate reduction and methanogenesis will align longitudinally along hydrologic flowpaths, and sulfate reduction will occur up-flowpath of methanogenesis. Lovley & Klug (1983, 1986) predicted that sulfate reducers would out-compete methanogens for metabolic substrates when sulfate concentration is greater than 1 to 2 mgSO_4-S/L. Sulfate in Sycamore Creek averages 31 mgSO_4-S/L (Fisher et al. 1982), suggesting that sulfate reduction is likely an important anaerobic pathway. As evidence for sulfate reduction in Sycamore Creek, anoxic bank sediments were typically black, presumably due to ferrous sulfide. Thus, zones of methanogenesis are likely shifted downstream along subsurface flowpaths due to competing microorganisms and, consequently, total methane emission from the stream is probably reduced.

In contrast to the inhibiting effect of alternative terminal electron acceptors on methane production, organic matter has a positive effect on methanogenesis (Molongoski & Klug 1980; Kelly & Chynoweth 1981; Wilson et al. 1989). Organic matter stimulates methanogenesis by first increasing aerobic respiration rate and extent of anoxia along flowpaths and, second, stimulates fermentation and production of methanogenic substrates in anoxic zones. In Sycamore Creek, POC storage in bank sediments is high (0.14% mass/mass as compared to only 0.005% in hyporheic and parafluvial sediments; Jones et al. 1994) and, consequently, fermentation and production of methanogenic substrates is also likely high. Furthermore, our laboratory study showed a clear-cut effect of POM on methane production. Methane emission measured *in situ*, however, was not significantly correlated with POC, which previous authors have interpreted to indicate that methanogenesis is not limited by metabolic substrates (Kelly & Chynoweth 1981; Naiman et al. 1991).

Methane emission is also strongly influenced by temperature (Fig. 6; Zeikus & Winfrey 1976; Baker-Blocker et al. 1977; Harriss et al. 1982; Yavitt et al. 1987; Crill et al. 1988; Wilson et al. 1989). Temperature directly affects aerobic respiration and thus extent of anoxia along flowpaths, and stimulates fermentation and methanogenesis in anoxic regions. In fact, Crill et al. (1988) reported methane emission from a bog in Minnesota to increase from only 4.5 to 400 $mgCH_4\text{-}C{\cdot}m^{-2}{\cdot}d^{-1}$ as mean soil temperature increased from 5 °C during spring to 16 °C in early summer. As stream temperature changes across seasons, the areal extent of anoxia likely expands and contracts, and rate of methane production within anoxic zones increases and decreases. Temperature in sediments of Sycamore Creek during the study ranged from 20 to 28 °C and in the laboratory experiment, temperature had a strong effect on methane production (Fig. 6). Methanogenesis is low or non-detectable, however, in many aquatic ecosystems during winter, presumably due to low temperature (King & Wiebe 1978; Chanton & Martens 1988; Chanton et al. 1989; Sorrell & Boon 1992). Methane evasion from the southern Arizona streams surveyed was quite low and may have been due to lower winter temperatures (8 to 13 °C).

Methane production along subsurface flowpaths can also feed back on surface stream functioning. Interstitial water in bank sediments is high in methane, with methane accounting for 18% of total DOC ($CH_4\text{-}C \div [CH_4\text{-}C + DOC]$), and is potentially a source of labile organic carbon to the surface stream. As anoxic interstitial waters mix with oxic surface water methane is readily consumed and may support high methanotrophic production. Moreover, methanotrophs ultimately regulate the emission rate of methane to the atmosphere. Previous studies have reported methane oxidation to consume a sizable fraction of methane production with estimates ranging from 11 to 100% (Holzapfel-Pschorn et al. 1985; Megraw & Knowles 1987; Yavitt et al. 1988; Yavitt et al. 1990; Pulliam 1993). In Sycamore Creek, methane production in anoxic bank sediments is equal to aerobic respiration in oxic hyporheic and parafluvial zones (Jones et al. 1994) averaging 3500 $mgC{\cdot}m^{-2}{\cdot}d^{-1}$. Methane emission from bank sediments, however, was only 170 $mgCH_4\text{-}C{\cdot}m^{-2}{\cdot}d^{-1}$ suggesting that more than 95% of methane production is consumed by methanotrophic bacteria.

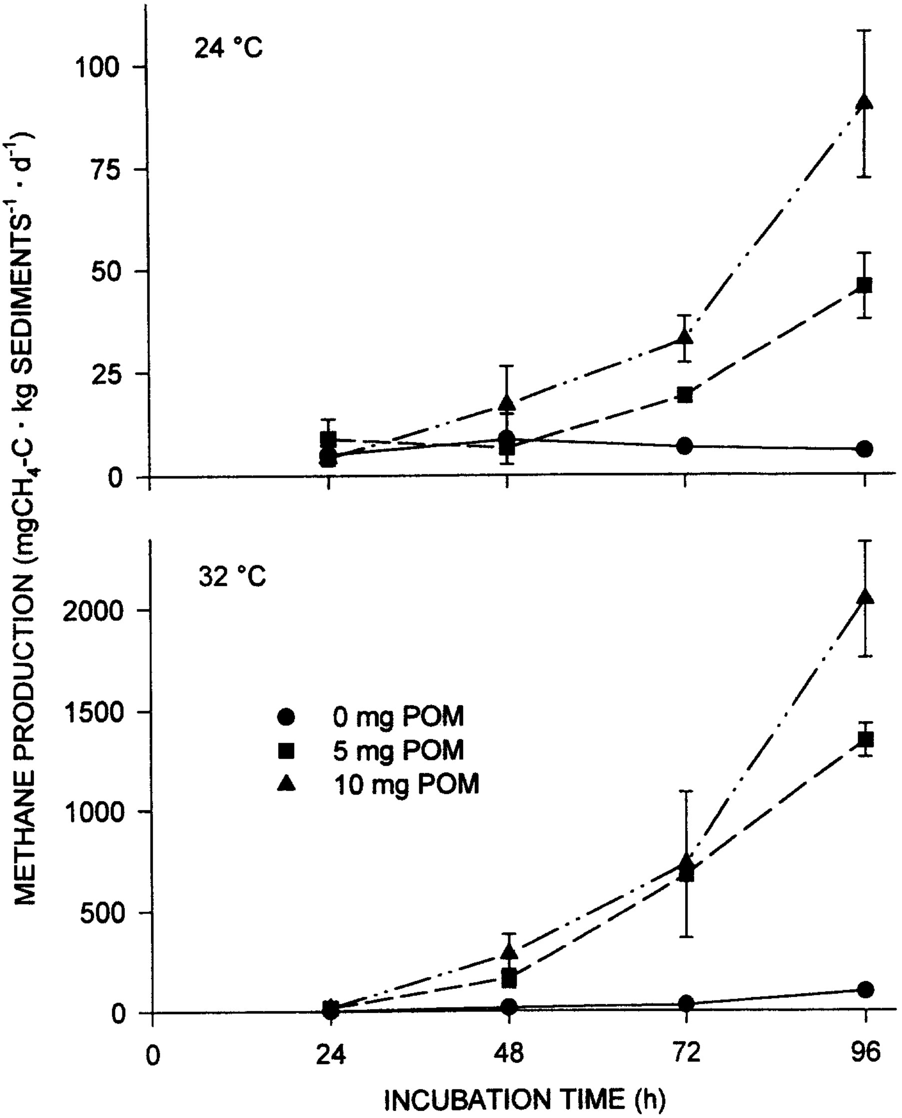

Fig. 6. Methane production versus particulate organic matter (POM) and temperature in sediments. Data are means ± SE ($n = 5$).

Methane evasion from arid-land streams

Methane emission from anoxic bank sediments in Sycamore Creek was high compared with evasion from other freshwater ecosystems. Mean annual methane evasion from freshwater ecosystems of North America ranges from 19 to 440 mgCH_4-C·m^{-2}·d^{-1} with most reported rates less than 100 $mgCH_4\text{-}C{\cdot}m^{-2}{\cdot}d^{-1}$ (see Pulliam 1993) as compared with 170 $mgCH_4\text{-}C{\cdot}m^{-2}{\cdot}d^{-1}$ from bank sediments of Sycamore Creek. Similarly, Boon & Sorrell (1991) and Sorrell & Boom (1992), reported high rates of methanogenesis and methane emission in billabongs (lentic floodplain water bodies) of arid-land rivers in southeastern Australia. Billabongs are rich in organic matter, have low redox potential, and as a result harbor distinct microbial communities as compared to adjacent rivers (Boon 1991). Anoxic bank sediments of Sonoran Desert streams may be functionally analogous to billabongs in that both subsystems probably have reduced hydrologic exchange with the mainstream and long water residence. Overall methane emission from the Sycamore Creek study reach, however, was only 13 $mgCH_4\text{-}C{\cdot}m^{-2}{\cdot}d^{-1}$ (sum of methane emission from subsystems weighted by areal extent of subsystems), quite low compared with other aquatic ecosystems. Methane evasion from southern Arizona streams surveyed was even lower, with all sites emitting less than 6 $mgCH_4\text{-}C{\cdot}m^{-2}{\cdot}d^{-1}$, albeit at low temperatures. Thus, in spite of the potential for high methane emission from arid-land streams, overall evasion was low.

Acknowledgments

Thanks to M. Mallett, B. Harper, S. Clinton, N. Drake, and K. Petrone for help in the laboratory and field. Thanks also to Drs. C. Dahm, J. Elser and W. Minckley for constructive comments on the manuscript. This research was supported by National Science Foundation's Ecosystem Studies Program (grants DEB-9224059 to JBJ and SGF, and DEB-9108362 and DEB-9306909 to SGF and NBG).

References

Baker-Blocker A, Donahue TM & Mancy KH (1977) Methane flux from wetland areas. Tellus 29: 245–250

Boon PI (1991) Bacterial assemblages in rivers and billabongs of southeastern Australia. Microbial Ecology 22: 27–52

Boon PI & Sorrell BK (1991) Biogeochemistry of billabong sediments. I. The effects of macrophytes. Freshwater Biol. 26: 209–226

Busch DE & Fisher SG (1981) Metabolism of a desert stream. Freshwater Biol. 11: 301–307

Cappenberg TE (1974) Interrelations between sulfate-reducing and methane-producing bacteria in bottom deposits of a fresh-water lake. I. Field observations. Antonie van Leeuwenhoek 40: 285–295

Chanton JP & Martens CS (1988) Seasonal variation in ebullitive flux and carbon isotopic composition of methane in a tidal freshwater estuary. Global Biogeochemical Cycles 2: 289–298

Chanton JP, Martens CS & Kelly CA (1989) Gas transport from methane saturated, tidal freshwater and wetland sediment. Limnol. Oceanogr. 34: 807–819

Chappellaz J, Barnola JM, Raynaud D, Korotkevich YS & Lorius C (1990) Ice-core record of atmospheric methane over the past 160,000 years. Nature 345: 127–131

Cicerone RJ (1988) Methane linked to warming. Nature 334: 198

Crawford CS & Gosz JR (1982) Desert ecosystems: their resources in space and time. Environmental Conservation 9: 181–195

Crill PM, Bartlett KB, Harriss RC, Gorham E, Verry ES, Sebacher DI, Madzar L & Sanner W (1988) Methane flux from Minnesota Peatlands. Global Biochemical Cycles 2: 371–384

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

Delhomme JP (1978) Kriging in the Hydrosciences. Advances in Water Resources 1: 251–266

Denmeade OT (1991) Sources and sinks of greenhouse gases in the soil-plant environment. Vegetatio 91: 73–86

Duff JH & Triska FJ (1990) Denitrification associated with stream periphyton: chamber estimates from undisrupted communities. J. Environ. Qual. 13: 514–518

Englund E & Sparks A (1991) Geostatistical Environmental Assessment Software: User's Guide. United States Environmental Protection Agency, Las Vegas, Nevada, USA

Fisher SG, Gray LJ, Grimm NB & Busch DE (1992) Temporal succession in a desert stream ecosystem following flash flooding. Ecol. Monogr. 52: 92–110

Graf WL (1988) Fluvial Processes in Dryland Rivers. Springer-Verlag, New York, New York, USA

Grimm NB (1987) Nitrogen dynamics during succession in a desert steam. Ecology 68: 1157–1170

Grimm NB (1992) Implications of climate change for stream communities. In: Kareiva PM, Kingsolver JG & Huey RB (Eds) Biotic Interactions and Global Change (pp 293–314). Sinauer Associates, Sunderland, Massachusetts, USA

Grimm NB & Fisher SG (1984) Exchange between interstitial and surface water: implications for stream metabolism and nutrient cycling. Hydrobiologia 111: 219–228

Harriss RC, Sebacher DI & Day FD, Jr. (1982) Methane flux in the Great Dismal Swamp. Nature 297: 673–674

Hendricks SP & White DS (1991) Physicochemical patterns within a hyporheic zone of a northern Michigan river, with comment on surface water pattern. Can. J. Fish. Aquat. Sci. 48: 1645–1654

Holmes RM, Fisher SG & Grimm NB (1994) Parafluvial nitrogen dynamics in a desert stream ecosystem. Journal of North American Benthological Society 13: 468–478

Holzapfel-Pschorn A, Conrad R & Seiler W (1985) Production, oxidation and emission of methane in rice paddies. FEMS Microbial Ecology 31: 343–351

Jones JB, Jr., Fisher SG & Grimm NB (1995) Vertical hydrologic exchange and ecosystem metabolism in a Sonoran Desert stream. Ecology 76: 942–952

Jones JB, Jr., Holmes RM, Fisher SG & Grimm NB (1994) Chemoautotrophic production and respiration in the hyporheic zone of a Sonoran Desert stream. In: Stanford JA & Valett HM (Eds) Proceedings of the Second International Conference on Ground Water Ecology (pp 329–338). American Water Resources Association, Herndon, Virginia, USA

Journal AG & Huijbregts CH (1978) Mining Geostatistics. Academic Press, London, England

Kelly CA & Chynoweth DP (1981) The contributions of temperature and of the input of organic matter in controlling rates of sediment methanogenesis. Limnol. Oceanogr. 26: 891–897

King GM & Wiebe JW (1978) Methane release from soils of a Georgia salt marsh. Geochim. Cosmochim. Acta 42: 343–348

Kristjansson JK, Shönheit P & Thauer RK (1982) Different K_s values for hydrogen of methanogenic bacteria and sulfate reducing bacteria: an explanation for the apparent inhibition of methanogenesis by sulfate. Arch. Microbiol. 131: 278–282

Levine JS (1992) Global Climate Change. In: Firth P & Fisher SG (Eds) Global Climate Change and Freshwater Ecosystems (pp 1–25). Springer-Verlag, New York, New York, USA

Lovley DR & Klug MJ (1982) Intermediary metabolism of organic matter in the sediments of a eutrophic lake. Appl. Environ. Microbiol. 43: 552–560

Lovley DR & Klug MJ (1983) Sulfate reducers can outcompete methanogens at freshwater sulfate concentrations. Appl. Environ. Microbiol. 45: 187–192

Lovley DR & Klug MJ (1986) Model for the distribution of sulfate reduction and methanogenesis in freshwater sediments. Geochim. Cosmochim. Acta 50: 11–18

Matthias AD, Blackmer AM & Bremner JM (1980) A simple chamber technique for field measurements of emission of nitrous oxide from soils. J. Environ. Qual 9: 251–256

Megraw SR & Knowles R (1987) Methane production and consumption in a cultivated humisol. Biology and Fertility of Soils 5: 56–60

Menzel DW & Vaccaro FR (1964) The measurement of dissolved and particulate organic carbon in seawater. Limnol. Oceanogr. 9: 138–142

Molongoski JJ & Klug MJ (1980) Anaerobic metabolism of particulate organic matter in the sediment of a hypereutrophic lake. Freshwater Biol. 10: 507–518

Naiman RJ, Manning T & Johnston CA (1991) Beaver population fluctuations and tropospheric methane emissions in boreal wetlands. Biogeochemistry 12: 1–15

Oremland RS (1988) Biogeochemistry of methane production. In: Zehnder AJB (Ed) Biology of anaerobic microorganisms (pp 641–705). John Wiley and Sons Publishers, New York, New York, USA

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

Rasmussen RA & Khalil MAK (1984) Atmospheric methane in the recent and ancient atmospheres: concentrations, trends, and interhemispheric gradient. J. Geophys. Res. 89: 11599–11605

Reeburgh WS & Heggie DT (1977) Micorbial methane consumption reactions and their effect on methane distributions in freshwater and marine environments. Limnol. Oceanogr. 22: 1–9

Rodhe H (1990) A comparison of the contribution of various gases to the greenhouse effect. Science 248: 1217–1219

Sorensen J, Christensen D & Jorgensen BB (1981) Volatile fatty acids and hydrogen as substrates for sulfate-reducing bacteria in anaerobic marine sediments. Appl. Environ. Microbiol. 42: 5–11

Sorrell BK & Boon PI (1992) Biogeochemistry of billabong sediments. II. seasonal variations in methane production. Freshwater Biol. 27: 435–445

Stanley EH & Boulton AJ (1995) Hyporheic processes during flooding and drying in a Sonoran Desert stream. I. Hydrologic and chemical dynamics. Arch. Hydrobiol. 134: 1–26

Steele LP, Dlugokencky EJ, Lang PM, Martin RC & Masarie KA (1992) Slowing down of the global accumulation of atmospheric methane during the 1980s. Nature 358: 313–316

Stookey LL (1970) Ferrozine: a new spectrophotometric reagent for iron. Anal. Chem. 42: 779–781

Thomsen BW & Schumann HH (1968) Water resources of the Sycamore Creek watershed, Maricopa County, Arizona. U. S. Geological Survey Water-Supply Paper 1861

Valett HM (1993) Surface-hyporheic interactions in a Sonora Desert stream: hydrologic exchange and diel periodicity. Hydrobiologia 259: 133–144

Valett HM, Fisher SG & Stanley EH (1990) Physical and chemical characteristics of the hyporheic zone of a Sonoran Desert stream. Journal of the North American Benthological Society 9: 201–215

White DS (1990) Biological relationships to convective flow patterns within stream beds. Hydrobiologia 196: 149–158

Whiticar MJ, Faber E & Schoell M (1986) Biogenic methane formation in marine and freshwater environments: CO_2 reduction versus acetate fermentation – isotopic evidence. Geochim. Cosmochim. Acta 50: 693–709

Wilkinson L (1990) SYSTAT: The System for Statistics. SYSTAT, Inc., Evanston, Illinois, USA

Wilson JO, Crill PM, Bartlett KB, Sebacher DI, Harriss RC & Sass RL (1989) Seasonal variation of methane emissions from a temperate swamp. Biogeochemistry 8: 55–71

Winfrey WR & Zeikus JG (1977) Effect of sulfate on carbon and electron flow during microbial methanogenesis in freshwater sediments. Appl. Environ. Microbiol. 33: 275–281

Winfrey WR & Zeikus JG (1979) Anaerobic metabolism of immediate methane precursors in Lake Mendota. Appl. Environ. Microbiol. 37: 244–253

Yavitt JB, Downey DM, Lang GE & Sexstone AJ (1990) Methane consumption in two temperate forest soils. Biogeochemistry 9: 39–52

Yavitt JB, Lang GE & Downey DM (1988) Potential methane production and methane oxidation rates in peatland ecosystems of the Appalachian Mountains, United States. Global Biogeochemical Cycles 2: 253–268

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

Zeikus JG & Winfrey MR (1976) Temperature limitation of methanogenesis in aquatic sediments. Appl. Environ. Microbiol. 31: 99–107