

Hydrologic effects on methane dynamics in riparian wetlands in a temperate forest catchment

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[1] To understand how hydrological processes affect biogeochemical and methane (CH₄) cycles in temperate riparian wetlands, we measured CH₄ fluxes and dissolved chemical constituents and CH₄ concentrations in groundwater, and monitored several environmental factors in wetlands located within a forested headwater catchment in a warm, humid climate in Japan. Variation in redox components dissolved in groundwater, including nitrate (NO₃⁻), Mn, Fe, and sulfate (SO₄²⁻), depended on temperature and soil-water conditions. Strongly reducing conditions usually occurred in the high-temperature months of July, August, and September. Dissolved CH₄ in groundwater changed with redox conditions and was highest in summer and lowest in winter. CH₄ emissions from riparian wetlands were observed almost throughout the year and displayed clear seasonality. Occasionally in summer, emission rates were more than 4 orders of magnitude greater than hillslope uptake rates. Although CH₄ emissions increased markedly during most of the summer, they were constrained by (1) fluctuation of the water table, which when lowered can shift the subsurface zone to a more oxidized condition, and (2) the oxygen-rich water such as precipitation and lateral subsurface flow from the hillslope. These results suggest that hydrological processes in forest headwater catchments play an important role in supplying oxygen to soils and consequently affect biogeochemical cycles, including CH₄ formation, and that small wetlands in forest watersheds function as large sources of CH₄, especially in regions with warm humid summers.

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1. Introduction

[2] The greenhouse gas methane (CH₄) is the second largest contributor to global warming [Rohde, 1990]. The infrared radiative heating effect of CH₄ is 26 times greater than that of carbon dioxide on a mole-per-mole basis [Lelieveld and Crutzen, 1992]. CH₄ is produced in anoxic environments, including the submerged soils of wetlands and paddy fields, by methanogenic bacteria during the anaerobic degradation of organic matter. Isotopic measurements have revealed that 70 to 80% of atmospheric CH₄ is of biogenic origin, with natural wetlands the largest source [Khalil and Shearer, 1993].

[3] Many reports have shown that subarctic [Moore and Knowles, 1990; Moore et al., 1990], boreal [Crill et al.,

1988; Bubier et al., 1993; Roulet et al., 1993], and temperate [Wilson et al., 1989; Moore and Knowles, 1990; Yavitt et al., 1990] wetlands function as CH₄ sources. However, quantifying global CH₄ fluxes remains difficult because of the high spatial and temporal variability in fluxes [Intergovernmental Panel on Climate Change, 2001]. Whereas CH₄ is mainly eliminated through oxidation by OH⁻ radicals in the troposphere [Watson et al., 1990; Prinn, 1994], microbial oxidation in aerobic soils is considered the next most efficient sink for atmospheric CH₄ [Reeburgh et al., 1993; Intergovernmental Panel on Climate Change, 2001]. Therefore forest soils, a major portion of which is not saturated with water, are assumed to be a major sink of atmospheric CH₄ [Le Mer and Roger, 2001]. Studies of CH₄ flux on the forest floor have focused almost exclusively on CH₄ oxidation. Reported CH₄ oxidation rates in forest floor soils range from 0 to 10 mg CH₄ m⁻² d⁻¹, and CH₄ emission has also been detected [e.g., Ishizuka et al., 2000; Smith et al., 2000]. These oxidation rates are much lower than the usual CH₄ emission rates observed in wet soils. In humid-temperate and tropical climates, wetlands often occur in riparian zones around streams and ponds. For example, the total area of forested wetlands in the United States was 20.7 million ha, more than 10% of all forested land, in 1990 [Tulloch, 1994]. Such wetlands can be ‘hotspots’ of CH₄ emission because of

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the high supply rate of organic matter from the surrounding forests. High small-scale spatial variability in redox conditions can be found within a single soil core [Young and Crawford, 2004], and emissions of trace gas from tiny hotspots (e.g., soil aggregates with high organic content) can account for most of the total emissions from a core [e.g., Parkin, 1987], which makes estimation of trace gas emissions difficult. Such controversial estimations can also affect the calculations of trace gas emissions on larger scales, such as whole forest ecosystems, where hotspots (e.g., wetlands in a forest) can easily affect the total CH₄ budget of a forest ecosystem.

[4] Methanogenic bacteria are active only under anoxic and strongly reducing soil conditions [Takai, 1970; Schütz et al., 1989]. Previous reports have shown that soil water conditions [Bubier et al., 1992; Moore and Roulet, 1993; van den Pol-van Dasselaar et al., 1997, 1999] and temperature [Crill et al., 1988; Bubier et al., 1993] affect CH₄ production in soil and soil surface flux. Variation in soil water conditions and temperature affect the soil redox state, and consequently, the CH₄-production process [Sugimoto and Fujita, 1997; Singh et al., 2000; Singh, 2001]. Although the hydrological processes that regulate the movement of water, which affects the supply and consumption rates of electron donors and acceptors, play an important role in wetland biogeochemical cycles [Mitsch and Gosselink, 2000], detailed information on their effects is required to interpret the biogeochemical and CH₄ cycles.

[5] Our objectives were to understand how hydrological processes in forest watersheds affect biogeochemical reactions and CH₄ dynamics in forested wetlands and to assess the importance of riparian forest wetlands as CH₄ sources. We measured environmental and hydrological factors, such as soil temperature, water table, CH₄ efflux, and dissolved CH₄ concentrations. In addition, we discuss the biogeochemical reactions in each part of the wetland.

2. Materials and Methods

2.1. Site Description and Hydrological Features

[6] We studied the riparian wetlands in the Kiryu Experimental Watershed (KEW; 35° N, 136° E; 190–255 m above sea level; 5.99 ha), located in southeastern Shiga Prefecture, central Japan. The Kiryu watershed covered about 99.3% by semimature Japanese cypress (*Chamaecyparis obtusa* Sieb. et Zucca) forest with some Japanese red pine (*Pinus densiflora* Sieb. et Zucca) and several deciduous species and by 0.67% (400.6 m²) distinct wetland in riparian zones (Figure 1a). Japanese cypress was planted on the hillslope over the watershed in the 1960s. The wetlands we studied, Kiryu Wetland 1 (KW1) and Kiryu Wetland 2 (KW2), were located upstream of check dams constructed across the main stream of the watershed about 100 years ago to prevent soil erosion. There were other natural wetlands in KEW, but all were located in riparian zones along streams and were either always submerged or periodically submerged. The entire watershed was on a base of weathered granitic rock with an abundance of albite. Although several tree species (*Alnus japonica*, *Clethra barvinervis*, *Evodiopanax innovans*, and *Rhus trichocarpa*) and sphagnum grew in and around the wetlands, vegetation in the wetlands was sparse, probably because of occasional sediment transport with surface flow.

[7] Precipitation was measured at a meteorological station within the watershed (Figure 1a). The runoff rate was continuously measured at a gauging weir (Figure 1a). Mean annual air temperatures, precipitation, and runoff were recorded during the observation period (Table 1). The water levels in KW1 and KW2 were measured in wells installed at each CH₄-flux plot. Surface soil temperatures at depths of 0.02 and 0.10 m were also continuously monitored (RT-12, ESPEC MIC, Japan) at each CH₄ flux measurement plot. Piezometer nests were installed along transects (Transect-edge, see below) crossing stream channels and in KW2 (Figure 1b). Piezometers were also installed vertically at KW2-center and KW2-downstream (Figure 1b). The piezometers were constructed from PVC pipe 13.0 mm in diameter slotted by 0.05 m at the bottom. Hydraulic head readings were taken manually at intervals of 2–3 weeks using a water-level indicator.

2.2. Methane Flux Measurements

[8] We measured the CH₄ flux in KW1 and KW2. Three PVC static chambers (diameter, 0.26 m; volume, 0.014 m³) were placed within 1.5 m of each other at each of five observation plots: KW1 (at 1.70 m in soil depth), KW2-upstream (0.25 m), KW2-edge (0.55 m), KW2-center (1.77 m), and KW2-downstream (1.38 m; Figure 1b). The plots at KW2-edge were along the Transect-edge line, and the plots at KW1, KW2-upstream, and KW2-downstream were along a perennial stream (Figure 1b). The surface soils of KW1 and KW2-upstream were sandy, whereas those of KW2-edge, KW2-center, and KW2-downstream were silty with much undecomposed litter. Flux measurements were made from a boardwalk, which reduced disturbance and prevented the ebullition of gases from the soil surface during the measurements. When measuring CH₄ flux, the chamber top was placed gently on the chamber base and covered with aluminum foil to reduce heating during sampling. Four gas samples of chamber air were collected via the septum stopper on the chamber top within 45 min after enclosure at 15-min intervals using a 50-mL syringe. The samples were immediately injected into preevacuated vials (10 mL) fitted with butyl rubber stoppers for laboratory analysis.

[9] CH₄ concentrations were determined using a gas chromatograph (GC; GC-14BPF, Shimadzu, Japan) equipped with a flame ionization detector (FID) and a Porapack Q column (2 m × 3 mm in diameter, Shinwa Chemical Industry, Japan) using N₂ (flow rate, 50 mL min⁻¹) as the carrier gas. The temperatures of the detector and column were 120 and 50°C, respectively. The samples were analyzed within 2 days of collection. Testing revealed that the vacuum inside the vials could be retained for a period of 1 week and the sample integrity could also be maintained for the same duration. CH₄ flux was calculated on the basis of the change in the headspace gas concentration with time, assuming first-order kinetics [Dobbie and Smith, 1996]. Although analyses of the individual time series showed that the slope values for CH₄ versus time were linear, we occasionally observed outliers, which were likely caused by ebullition. In addition, sometimes CH₄ in the initial sample of the time series was much greater than ambient CH₄, indicating that chamber placement disturbed the site. In such cases, the entire time series was discarded. CH₄ flux was measured at intervals of 2–3 weeks. In each plot,

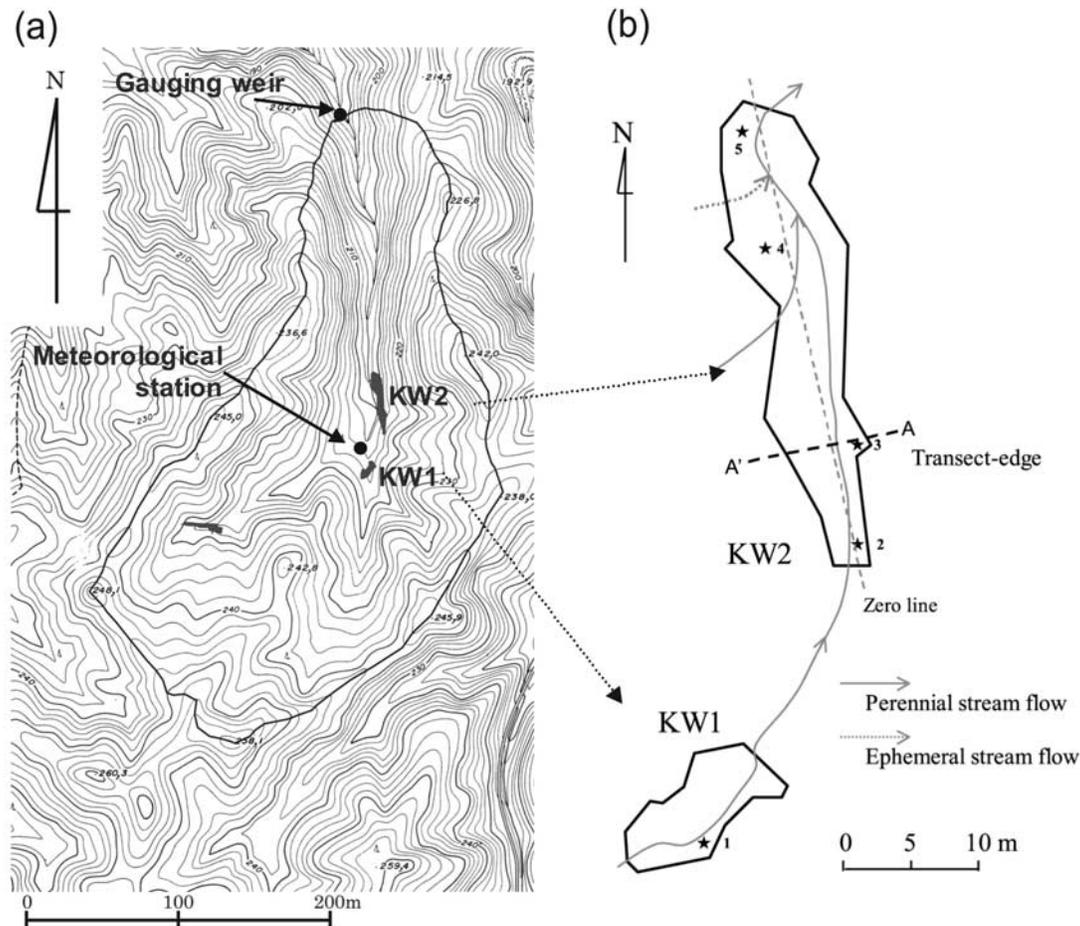


Figure 1. (a) Topographic map of the Kiryu Experimental Watershed and the location of riparian wetlands (gray areas). (b) Locations of the observation plots in the wetlands KW1 and KW2. 1, KW1; 2, KW2-upstream; 3, KW2-edge; 4, KW2-center; 5, KW2-downstream. Dashed line indicates the zero line and the transect for piezometer nests.

the flux was measured once daily, and the other measurements were collected at approximately the same time.

2.3. Groundwater Collection and Analysis

[10] Porewater samples were collected vertically near the flux chambers to measure dissolved gases and water chemistry. The porewater samplers were placed at KW2-edge (at soil depths of 0.10 and 0.25 m), KW2-center, and KW2-downstream (at 0.10, 0.20, 0.30, 0.50, and 0.70 m). The samplers were intended to collect porewater without

degassing and high decompression. To exclude soil and detritus, a double-walled sampler screened with numerous vertically aligned 2-mm holes was constructed by placing a 100-mL polypropylene bottle inside a wide-mouth, 200-mL polystyrene bottle. The samplers were installed near the flux chambers at vertical intervals of least 0.10 m and were equipped with a polyethylene tube and a three-way valve. Immediately after the CH_4 flux measurements, porewater was slowly collected using 50- or 100-mL syringes, taking special care that no bubbles were created while sucking the

Table 1. Mean Annual Air Temperature, Annual and Summer Precipitation, and Annual Discharge in the Kiryu Experimental Watershed^a

	2002	2003	2004	2005	1996–2005
Mean annual air temperature, deg C	13.4	12.9	13.9	13.0	13.2 ^b
Annual precipitation, mm yr ⁻¹	1179.4	1946.8	1796.8	1150.5	1574.1
Summer precipitation, mm ^c	398.5	804.0	500.3	474.0	550.6
Annual discharge, mm yr ⁻¹	405.3	1097.9	948.4	396.8	780

^aUnpublished data from the Laboratory of Forest Hydrology, Kyoto University.

^bAverage of the values obtained from 2000 to 2005.

^cFrom June to August.

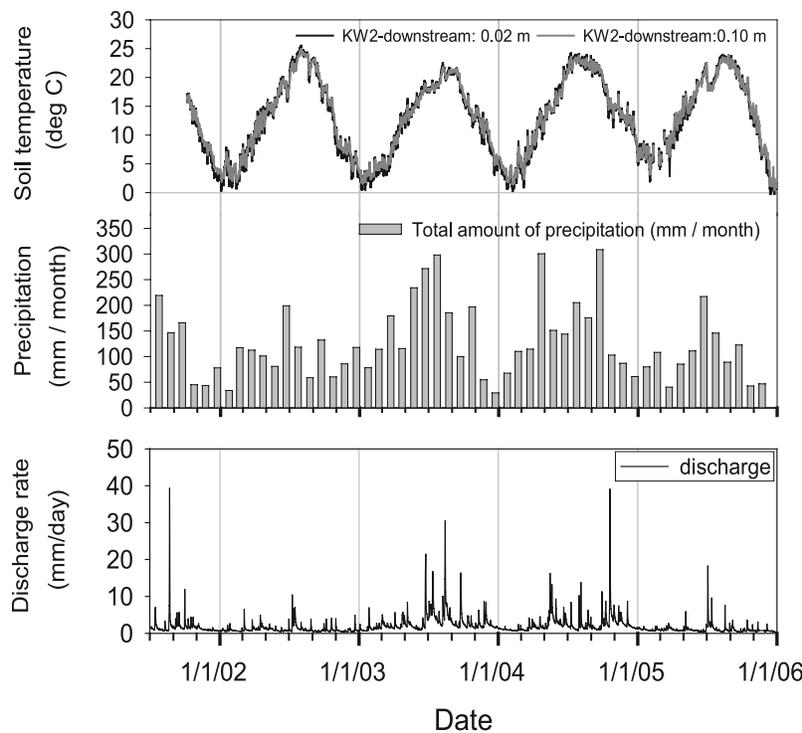


Figure 2. Seasonal patterns of soil temperature measured at KW2-downstream, monthly precipitation measured at the nearby meteorological station, and the runoff hydrograph for the Kiryu Experimental Watershed measured at the gauging weir.

solution, and injected into 20-, 30-, or 50-mL preevacuated vials for the measurement of dissolved CH_4 and CO_2 concentrations without exposure to the atmosphere, and into plastic bottles for other chemical analysis; the vials and plastic bottles were stored in a cooling box (around 4°C) in the field. The water samples for O_2 concentration measurements were collected in 100-mL biological oxygen demand (BOD) bottles and were fixed immediately in the field using the Winkler method. Surface water (KW2-edge and KW2-center) and stream water (KW2-downstream) were also sampled.

[11] In situ measurements, including pH, were also conducted at the time of sampling. Dissolved CO_2 levels in water samples were measured in situ from June 2003 to August 2005 using a portable pCO_2 meter (CGP-1, DKK-TOA, Japan [Ohte *et al.*, 1995]).

[12] Water samples collected for dissolved organic carbon (DOC) analysis were filtered through $0.45\text{-}\mu\text{m}$ PTFE membrane filters and stored in glass vials at 4°C . DOC concentrations were measured using a total organic carbon analyzer (TOC-V, Shimadzu, Japan). Samples for metals analyses, including Fe and Mn, were filtered in situ through $0.45\text{-}\mu\text{m}$ cellulose acetate membrane filters and acidified with ultrapure reagent-grade nitric acid to decrease solution pH (<2). They were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES; SPS1500VR, Seiko, Japan). Nonacidified samples for measuring NO_3^- and SO_4^{2-} concentrations were filtered through $0.20\text{-}\mu\text{m}$ cellulose acetate membrane filters and analyzed using ion chromatography (HIC-6A, Shimadzu, Japan).

[13] Dissolved CH_4 and CO_2 concentrations were determined within 8 h by multiple equilibrations with a headspace of ultra high purity (UHP) helium [McAullife, 1971]. The headspace was prepared in a vial by replacing sample water with UHP helium. The vials were vigorously shaken for 2 min to drive gases from the porewater into the headspace. The headspace gas was withdrawn using a gas-tight syringe and CH_4 concentrations were analyzed using a GC-FID. For CO_2 concentration measurements, samples of the same gas were collected from the headspace and injected into a GC (GC-8APT, Shimadzu, Japan) equipped with a thermal conductivity detector (TCD) and a Shincarbon T column ($6\text{ m} \times 2\text{ mm}$ in diameter, Shinwa Chemical Industry, Japan) using He (flow rate, 50 mL min^{-1}) as the carrier gas. The temperature of both the detector and the column was 200°C . GC measurements of dissolved CO_2 were carried out from February 2005 and confirmed the data obtained by in situ dissolved pCO_2 measurements.

2.4. Soil Sampling and Analysis

[14] Mineral and organic soil samples were collected in triplicate from the surface and each water sampling depth in each plot in January 2006. Topsoil and 10–20 cm interval samples underlying the thin litter layer (0–1 cm thick) were collected. The depths of the organic soil were approximately 5, 15, 40, and 50 cm in KW2-upstream, KW2-edge, KW2-center, and KW2-downstream, respectively. Soils were sieved through a 2-mm mesh sieve to remove coarse fragments and then homogenized. The total C and total N concentrations of soil samples were measured using the

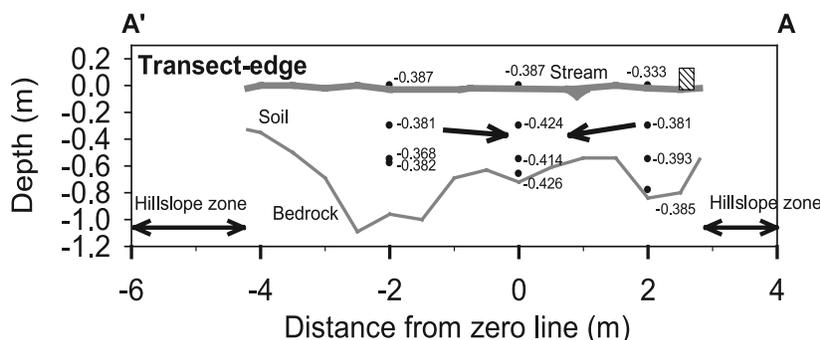


Figure 3. Spatial distribution of hydraulic heads along a cross section of the KW2-edge plot. Head measurements are given in meters, with the elevation of the inlet point near the KW2-upstream plot as an arbitrary datum. Values in the figure are the mean head values for the measurement period (October 2002 to December 2005). The gray lines correspond to the soil surface (thick line) and the bedrock surface (thin line). The dots represent the locations of piezometer openings. Arrows indicate the direction of groundwater flow. The diagonally striped box indicates the location of a flux chamber.

combustion method [Bremner, 1996] in an NC-analyzer (Sumigraph NC-900, Sumigraph Co. Japan).

3. Results

3.1. Hydrological and Environmental Conditions

[15] Seasonal variations in soil temperature at KW2-downstream (0 and 0.10 m), monthly precipitation, and a runoff hydrograph of the KEW are shown (Figure 2). The study site is affected by the Asian monsoon system, which usually results in a summer rainy season. Variation was observed in summer (June, July, and August) precipitation; high amounts of precipitation were recorded in 2003, and low amounts in 2002, 2004, and 2005 (Figure 2). Summer precipitation accounted for 72.4, 146.0, 90.9, and 86.1% of the mean annual precipitation (1574.1 mm for 1996–2005) in 2002, 2003, 2004, and 2005, respectively (Table 1). Runoff from the KEW was affected most by rain intensity; runoff amounts were lower in dry years (2002, 2005) and

heavier during rainy periods (summer 2003 and autumn 2004; Figure 2).

[16] At KW2-edge, the occurrence of a groundwater pathway from the side of the hillslope to a stream was supported by piezometric data (Figure 3). Litter can be supplied from the hillslope, especially with ephemeral surface flow during storm events in this plot. Such litter may accumulate in the surface soils. Soil C concentrations were higher in surface soils than in deeper soil zones (Figure 4). The KW2-center plot was 5 m from the perennial stream flow, and the upper soil layer contained much more organic matter than the other plots (Figure 4). Piezometric data showed that the vertical head gradients were small near the KW2-center plot. Differences in hydraulic head between the depths of 0.30 and 0.50 m were as small as 0.03 m H₂O (n = 21, mean from August 2004 to December 2005). KW1, KW2-upstream, and KW2-downstream were all situated near the perennial stream. The water table in these three plots remained near the soil surface,

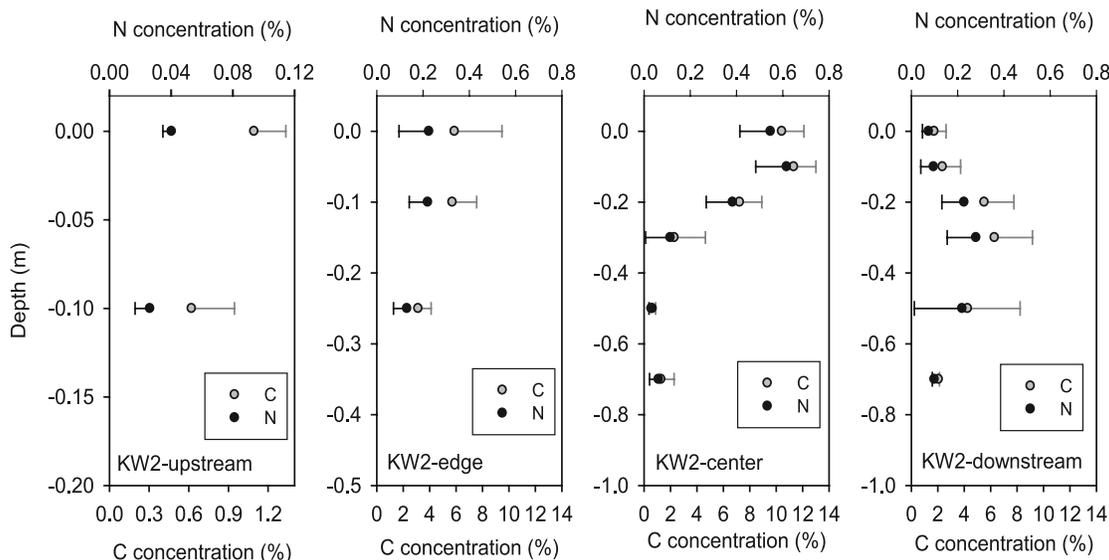


Figure 4. Soil C and N contents at each KW2 sampling plot. The mean ± SD of triplicate samples is shown. Samples were collected in January 2006.

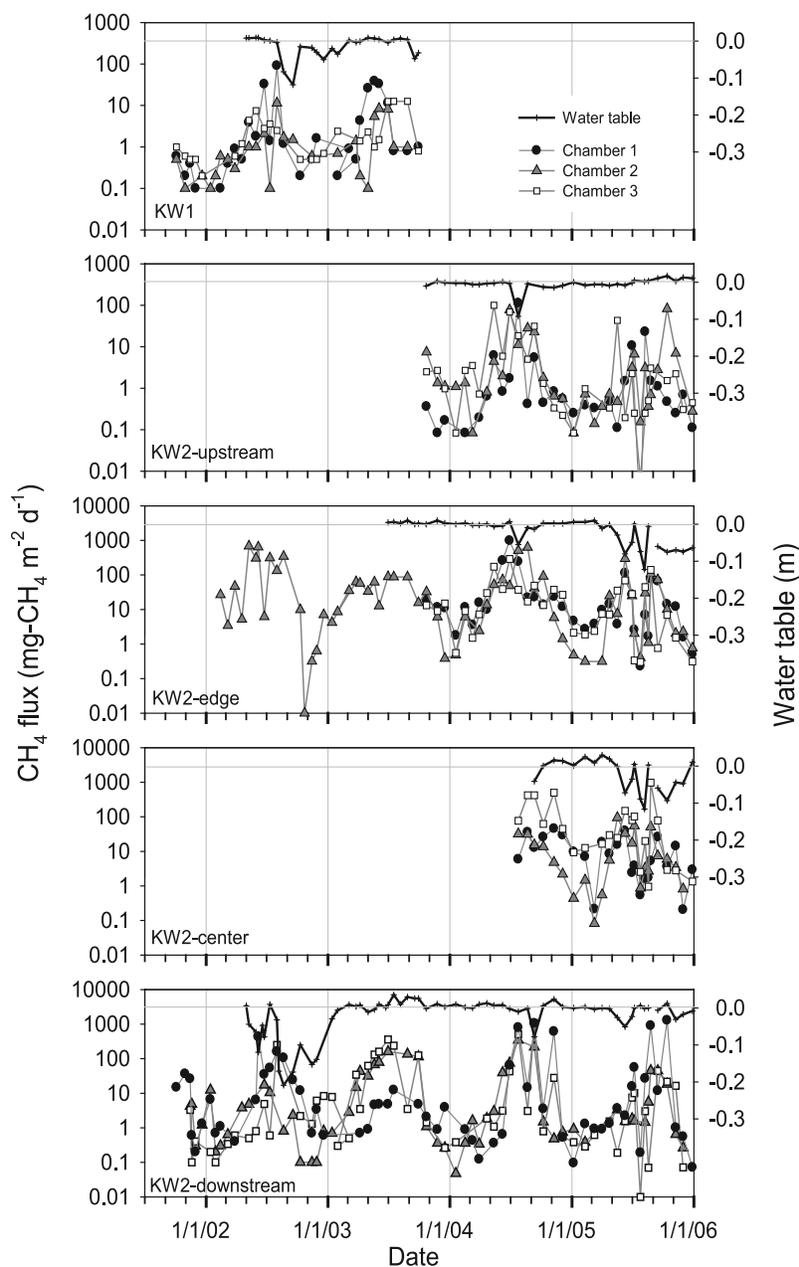


Figure 5. Seasonal patterns of water table level and methane flux in each KW2 plot. Negative flux indicates CH_4 uptake by wetlands.

except in the dry summers of 2002 and 2005 (Figure 5). The surface soils of KW1 and KW2-upstream were similar, i.e., sandy with less organic matter. At KW2-downstream, soil C concentrations were highest at 0.30 m in depth (Figure 4). The piezometric data for the KW2-downstream plot (Table 2; October 2002 to December 2005) indicate that the head gradients were downward within the upper portion of the soil profile (about <0.70 m), suggesting that groundwater flowed downward and stream flow contributed substantially to the underlying groundwater in this plot.

3.2. Methane Flux

[17] The seasonal patterns of CH_4 flux in the wetlands were somewhat similar at all sites; that is, CH_4 was emitted during most of the sampling periods and the emission rates

were generally highest in the summer at all sites (Figure 5). The CH_4 emission rates observed in each plot were considerably higher in the KW2-edge (e.g., maximum; $986.1 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ on 28 June 2004, Figure 5), KW2-center (e.g., $976.6 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ on 25 August 2005), and KW2-downstream (e.g., $1294.4 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ on 13 October 2005) plots, whereas the rates were lower in the KW1 (e.g., $91.2 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ on 1 August 2002) and KW2-upstream (e.g., $113.0 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ on 24 July 2004) plots, which contained less organic matter in the soil (Figure 4). The CH_4 emission rates in summer varied annually in each plot. For example, the CH_4 emission rate in summer 2003 (Chamber 3; maximum, $359.8 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$, 30 June 2003) was much lower than that in 2004 (Chamber 3; $1060.1 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$, 10 September 2004)

Table 2. Vertical Distribution of Hydraulic Heads in Each Plot^a

	Depth, M	Distribution
KW2-edge ^b	0	-0.387
	0.3	-0.396
	0.55	-0.408
	0.78	-0.400
KW2-center ^c	0	-0.851
	0.3	-0.876
	0.55	-0.846
	0.75	-0.817
	1.05	-0.816
	1.35	-0.806
	1.63	-0.912
KW2-downstream ^b	0	-0.698
	0.3	-0.798
	0.55	-0.907
	0.75	-0.927
	1.05	-0.949
	1.35	-0.916

^aHead measurements are given in meters with the elevation of the inlet point near the plot KW2-upstream as an arbitrary datum.

^bAverage of the values obtained from October 2002 to December 2005.

^cAverage of the values obtained from November 2003 to December 2005.

and 2005 (Chamber 1; 1294.4 mg CH₄ m⁻² d⁻¹, 13 October 2005; Figure 5) at KW2-downstream.

3.3. Methane Concentrations and Groundwater Chemistry

[18] The mean pH in all stream water, surface water, and groundwater samples was between 6 and 7; pH decreased

with depth in all plots at most sampling times and did not show clear seasonality (data not shown). Figure 6 shows the seasonal patterns of dissolved O₂ (DO), nitrate (NO₃⁻), manganese (Mn), iron (Fe), sulfate (SO₄²⁻), CH₄, CO₂, and DOC in the wetland groundwater for each sampling plot.

[19] At the edge of the wetland (KW2-edge), DO in groundwater was usually lowest at a depth of 0.10 m (0–2.2 mg L⁻¹, mean 0.2 mg L⁻¹; Figure 6a). DO at 0.25 m decreased in summer 2005 with the lowering of the water table. The ranges of and mean NO₃⁻ were 0.01–0.07 mmol L⁻¹ and 0.04 mmol L⁻¹ for surface water, 0–0.10 mmol L⁻¹ and 0.03 mmol L⁻¹ at 0.10 m, and 0–0.05 mmol L⁻¹ and 0.02 mmol L⁻¹ at 0.25 m, respectively. Both dissolved Mn and Fe increased in summer in ground water, and the mean values were higher at 0.10 m (Mn, 0.5 mg L⁻¹; Fe, 3.0 mg L⁻¹) than at 0.25 m (Mn, 0.2 mg L⁻¹; Fe, 1.8 mg L⁻¹). SO₄²⁻ was usually lowest at 0.10 m (range, 0.01–0.07 mmol L⁻¹; mean, 0.03 mmol L⁻¹) when the water table remained above 0.10 m. SO₄²⁻ at 0.25 m decreased in the dry summer of 2005 more than in the summers of 2003 and 2004 (Figure 6a). Dissolved CH₄ was higher at 0.10 m (0.04–1.45 mmol L⁻¹, mean 0.69 mmol L⁻¹) than in surface water (0–0.12 mmol L⁻¹, mean 0.02 mmol L⁻¹) or at 0.25 m (0.04–1.05 mmol L⁻¹, mean 0.43 mmol L⁻¹). Dissolved CO₂ at 0.10 m (0.09–2.78 mmol L⁻¹, mean 0.81 mmol L⁻¹) and 0.25 m (0.13–2.93 mmol L⁻¹, mean 1.00 mmol L⁻¹) was somewhat similar, both peaking in summer (Figure 6a).

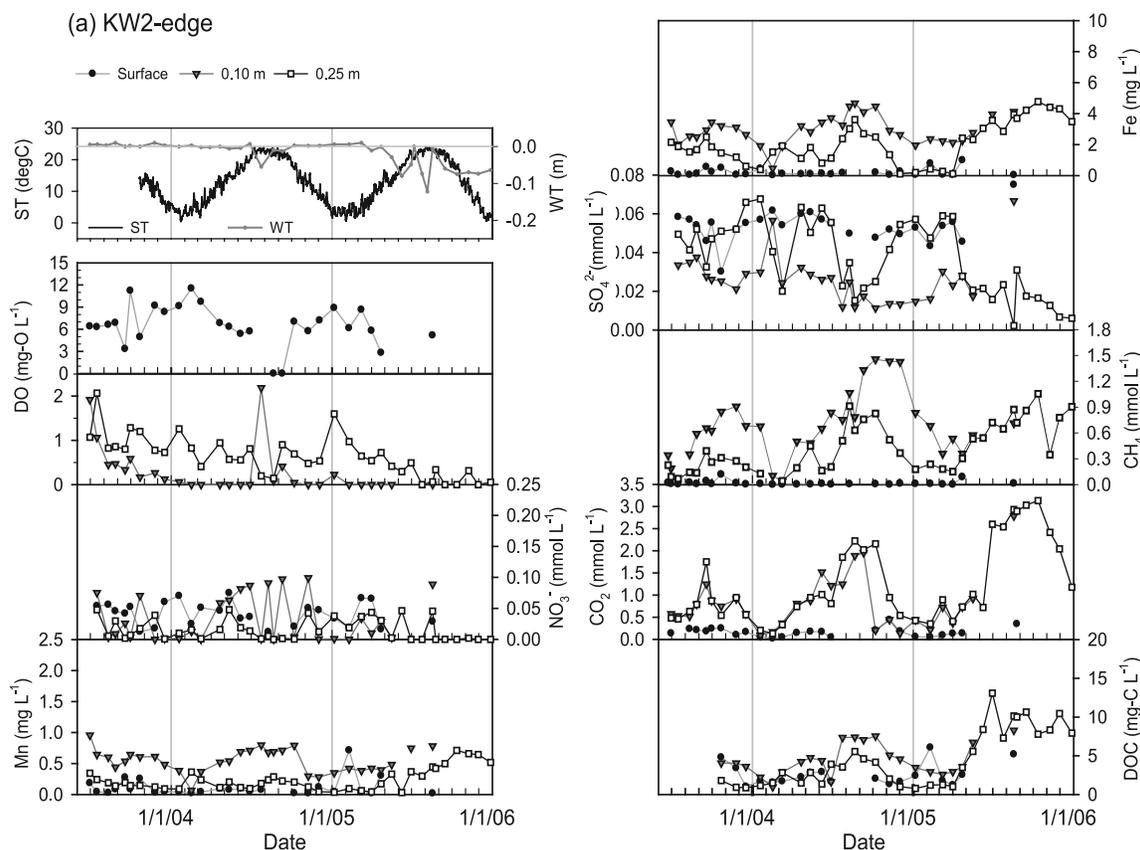


Figure 6. Seasonal patterns of soil temperature (ST), water table level (WT), and dissolved oxygen (DO), NO₃⁻, Mn, Fe, SO₄²⁻, CH₄, CO₂, and dissolved organic carbon (DOC) concentrations in surface water and groundwater in (a) KW2-edge, (b) KW2-center, and (c) KW2-downstream plots.

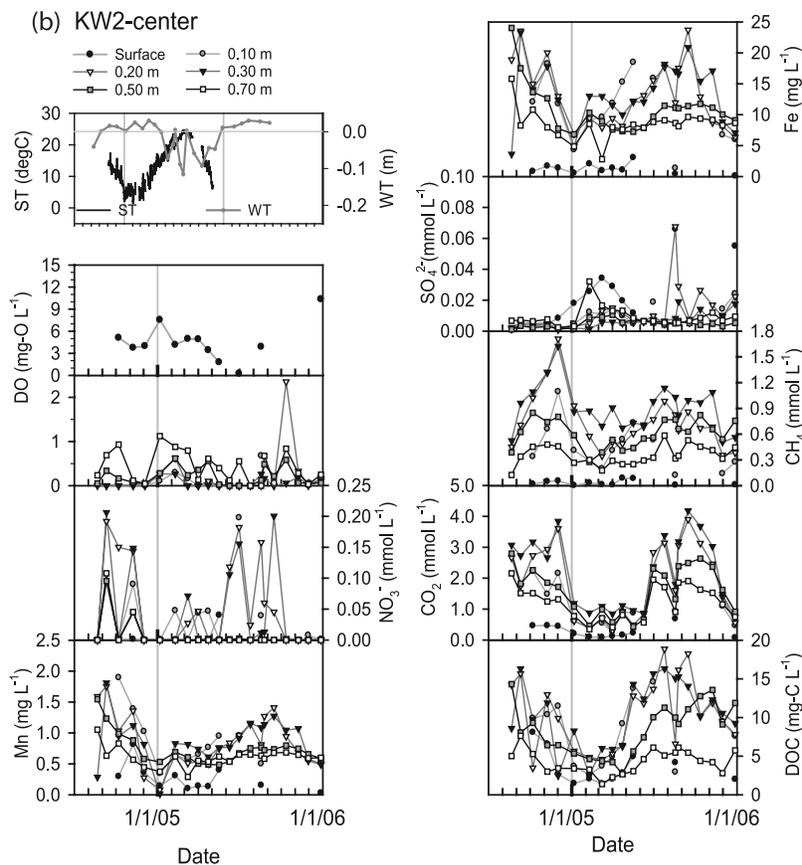


Figure 6. (continued)

Dissolved CO_2 at 0.25 m increased dramatically in the dry summer of 2005. The mean DOC during high water table periods (from October 2003 to April 2005; Figures 5 and 6a) was higher at 0.10 m (4.18 mg C L^{-1}) than at 0.25 m (2.19 mg C L^{-1}).

[20] In the center of the wetland (KW2-center), DO remained low, usually ranging between 0 and 1 mg L^{-1} at all depths (Figure 6b). The highest DO was usually observed at 0.70 m depth. NO_3^- usually remained near zero, and occasionally increased from summer to autumn, especially at shallower depths (0.10–0.30 m). Dissolved Mn and Fe increased from summer to autumn, especially at depths of 0.10–0.50 m. The maximum Fe in this plot exceeded 20 mg L^{-1} (at depths of 0.20–0.50 m in summer 2004 and 0.20–0.30 m in summer 2005) and was much higher than in other plots. SO_4^{2-} remained below 0.02 mmol L^{-1} at all depths above 0.50 m, except in the dry summer of 2005, and the concentrations were much lower than in other plots. Dissolved CH_4 , CO_2 , and DOC were also highest at 0.20–0.30 m in depth, and CH_4 remained relatively high even in winter. The seasonal variation in dissolved CO_2 was higher (mean \pm SD: 0.10 m, $0.97 \pm 0.79 \text{ mmol L}^{-1}$, $n = 13$; 0.20 m, $1.66 \pm 1.24 \text{ mmol L}^{-1}$, $n = 19$) than that of dissolved CH_4 (0.10 m, $0.47 \pm 0.24 \text{ mmol L}^{-1}$, $n = 13$; 0.20 m, $0.79 \pm 0.35 \text{ mmol L}^{-1}$, $n = 19$), especially at shallower depths. The mean DOC concentration (0.10 m, 8.0 mg C L^{-1} ; 0.20 m, 10.5 mg C L^{-1} ; 0.30 m, 10.6 mg C L^{-1}) was much higher than in other plots (Figure 6).

[21] At KW2-downstream, temporal variations in the concentrations of dissolved components were remarkable (Figure 6c). DO was high in winter and low in most summers. However, relatively high DO was observed in the rainy summer of 2003. The NO_3^- at 0.10–0.70 m ranged from 0– 0.06 mmol L^{-1} and averaged 0.01 mmol L^{-1} . Dissolved Mn and Fe were higher in summer and lower in winter. In contrast, SO_4^{2-} decreased in summer. Dissolved CH_4 was similar below 0.20 m. The maximum dissolved CH_4 at each depth varied annually and was considerably higher in 2004 and 2005 than in 2003, especially at the surface. Whereas dissolved CO_2 at all depths increased in summer, the maximum values in 2003 ($<1 \text{ mmol L}^{-1}$) were much lower than those in 2004 and 2005 ($3\text{--}4 \text{ mmol L}^{-1}$). DOC was also higher in summer, and was highest in the dry summer of 2005 at all depths.

4. Discussion

4.1. Temporal and Spatial Variability in Biogeochemical Reactions Controlling CH_4 Dynamics in Different Parts of the Wetland

4.1.1. Edge of the Wetland

[22] At the KW2-edge plot, DO at 0.10 m remained $<0.5 \text{ mg L}^{-1}$, except in the rainy summer of 2003 and in July 2004, when the water table dropped. DO was usually high in deeper zones but was low in the dry summer of 2005 (Figure 6a). These results indicate that a more reducing condition was maintained at shallower depths than at deeper

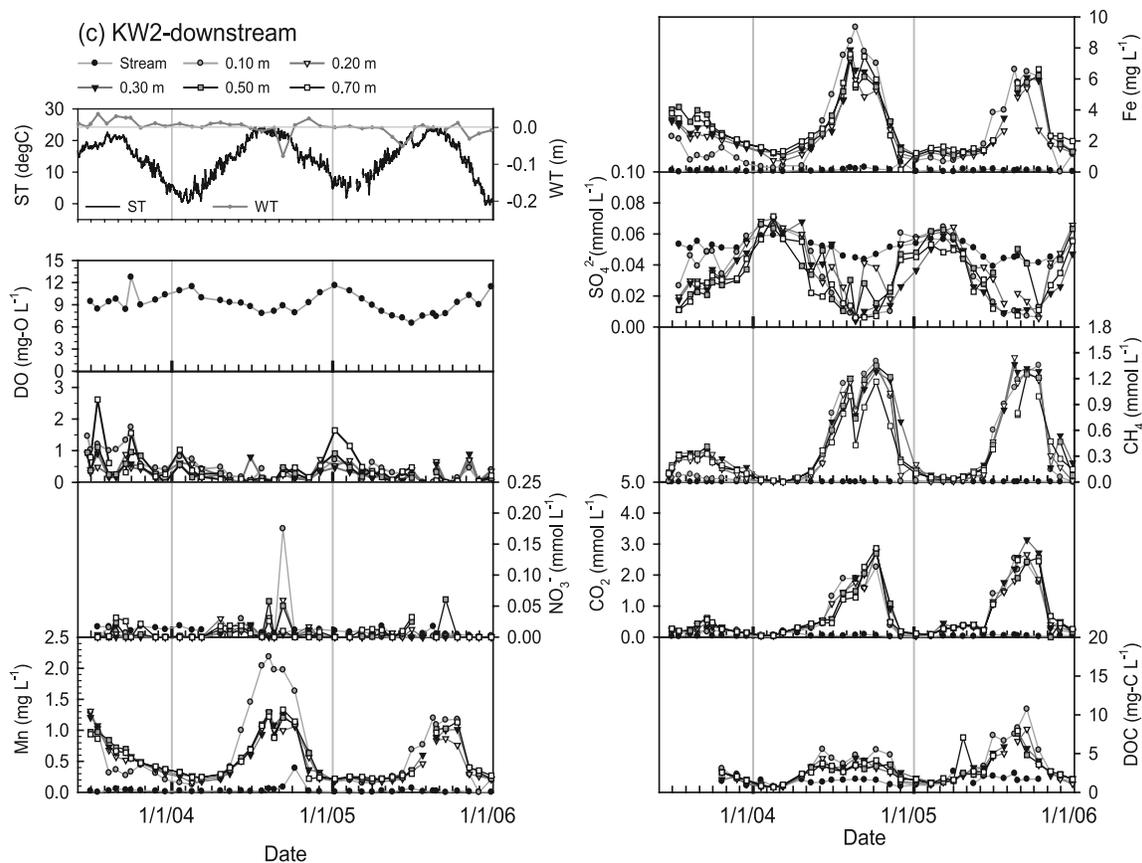


Figure 6. (continued)

depths when the water table was near the soil surface. This suggests that the water in deeper zones was supplied not only by vertical filtration, but also by other water-flow pathways, such as lateral subsurface flow from the hillslope. Indeed, the hydraulic gradient indicated the occurrence of a water pathway from the adjacent hillslope to the wetland groundwater (Figure 3). Such subsurface flow on or through bedrock in a hillslope–riparian buffer has been observed previously [McGlynn *et al.*, 1999; Katsuyama *et al.*, 2005]. Kosugi *et al.* [2006] also suggested, on the basis of hydro-metric observations, the occurrence of saturated lateral flow over the soil–bedrock interface as precipitation increased in a small catchment (0.024 ha) in the KEW. Such lateral subsurface flow may supply relatively large amounts of DO to deeper zones because it does not pass through the highly reduced upper soil layer where oxygen could be consumed rapidly. Assuming that DO supply to groundwater is affected by such subsurface flow, the amount of precipitation should be important for DO and chemical components through the intermediary of controlling flow rate and water chemistry. The supply of electron donors from such lateral flow can create less reducing conditions in the deeper zones than in the shallower zones. To test this hypothesis, the antecedent precipitation index for the preceding 10 days (API₁₀) was calculated as $\Sigma(P_i/i)$, where P_i is the precipitation on day i ($i = 1-10$) prior to the sampling day. There was no significant correlation between API₁₀ and DO at 0.10 m ($n = 16$, $r = 0.068$, $P = 0.81$), but the relationship was

significant at 0.25 m ($n = 24$, $r = 0.704$, $P < 0.001$). This suggests that DO in incoming water fluctuated with precipitation, and the water in deeper zones was more affected by such relatively oxygen-rich lateral subsurface flow.

[23] Vertical profiles of dissolved Mn, Fe, and SO₄²⁻ also showed strong reducing conditions at a depth of 0.10 m in summer (Figure 6a), with the exception of the dry summer of 2005. However, NO₃⁻, which can be consumed even in moderately reducing conditions, changed remarkably at a depth of 0.10 m, where concentrations often exceeded those in surface water. This may have been due to nitrification in wetland surfaces under nitrogen-rich conditions (Figure 4 [e.g., Gribsholt *et al.*, 2005]). Both DOC in groundwater and soil C were higher in shallower zones (Figures 4 and 6a), where a strongly reducing condition could easily occur because of the abundance of substrate for anaerobic metabolism. Therefore the highest levels of CH₄ production can also occur in the soil in shallow zones in periods when the water table is high.

[24] Annual variation in summer precipitation had a noticeable effect on groundwater chemistry. Suppression of CH₄ production at 0.25 m in the rainy summer of 2003 (Figure 7a) was caused by increased lateral subsurface flow, as discussed above. In contrast, higher Mn, Fe, CH₄, CO₂, and DOC and the lowest SO₄²⁻ were observed at 0.25 m in the dry summer of 2005 (Figure 6a). In summer 2005, the difference in hydraulic head between depths of 0.30 and 0.50 m was 0.5 cm H₂O ($n = 8$, mean from June to

November), which was less than in 2003 (0.7 cm H₂O, n = 9) and 2004 (1.2 cm H₂O, n = 7). This implies that there was less vertical infiltration at this plot in the dry summer of 2005 than in 2003 and 2004. These results indicate that in the dry year of 2005, a more reducing condition occurred in the deeper zone because of a decrease in oxygen supply from incoming water. Our results suggest that changes in the quality and quantity of lateral subsurface flow from hillslopes control the variations in redox conditions, and thereby affect CH₄ production in the wetland edge.

4.1.2. Center of the Wetland

[25] At the KW2-center plot, high levels of dissolved Mn, Fe, and CH₄, and low levels of SO₄²⁻ revealed that highly reducing conditions were formed, especially in summer (Figure 6b). In this plot, higher soil C (mean ± SD, g C kg⁻¹ dry soil: 0.10 m, 10.4 ± 1.7; 0.20 m, 11.3 ± 1.7; 0.30 m, 7.25 ± 1.7) and DOC (mean: 0.10 m, 8.0 mg C L⁻¹; 0.20 m, 10.5 mg C L⁻¹; 0.30 m, 10.6 mg C L⁻¹) in shallow zones, as compared to deeper zones, contribute to maintaining the highly reducing conditions. Redox status differed between summers 2004 and 2005, presumably because of differences in hydrological conditions. A higher water table was maintained at KW2-center in summer 2004 than in 2005 (Figure 5). In this period of 2004, dissolved Mn, Fe, and CH₄ remained high, and SO₄²⁻ was extremely low, especially above 0.50 m (Figure 6b); this indicates the occurrence of strongly reducing conditions at shallow depths under low DO. In contrast, in the dry summer of 2005, significant decreases in dissolved Mn, Fe, and CH₄, and an increase in SO₄²⁻ in August showed that more oxic conditions were established at 0.10 and 0.20 m (Figure 6b). However, high levels of dissolved Mn, Fe, CH₄ and low SO₄²⁻ (Figure 6b) indicate that strongly reducing conditions prevailed below the level of the water table (deeper than 0.30 m) in both summer 2005 and 2004. The annual maximum CH₄ in 2004 (0.20 m: 1.71 mmol L⁻¹, 2 December; Figure 6b) was higher than that in 2005 (0.30 m: 1.14 mmol L⁻¹, 25 July) in the shallow zone. This suggests that differences in water conditions between these two summers could control CH₄ production in surface soils. In addition, reoxidation of CH₄ in surface soils [Roslev and King, 1994, 1996] could possibly occur with expansion of the oxic zone under a low water table, as in 2005.

[26] Compared to the other plots, the occurrence of the highest concentrations of Mn, Fe, and CH₄, together with the lowest SO₄²⁻ (Figure 6), indicates that the most reducing conditions were established in this plot. A possible explanation is that the soil C and DOC in groundwater in this plot (mean from 0.10–0.70 m depths: 5.5 g C kg⁻¹ dry soil and 4.30 mg C L⁻¹, respectively) were high compared to those in KW2-edge (mean from 0.10–0.70 m depths: 4.6 g C kg⁻¹ dry soil and 5.15 mg C L⁻¹, respectively) and KW2-downstream (mean from 0.10–0.70 m depths: 3.7 g C kg⁻¹ dry soil and 3.06 mg C L⁻¹, respectively; Figures 5 and 6). These probably serve as a substrate for nitrate-, manganese-, iron-, and sulfate-reducers and methanogens. In fact, much CO₂, the main product of most of the above-mentioned biogeochemical reactions, was produced in summer in this plot. Large quantities of CH₄ could be produced because CO₂ is one of the major substrates for CH₄ [Takai, 1970; Conrad et al., 1989; Schütz et al., 1989]. In addition, acetate, another major substrate, may be produced to some extent.

4.1.3. Downstream of the Wetland

[27] At the KW2-downstream plot, changes in redox status largely depended on changes in temperature when the water table was near the soil surface (–0.08 to 0.03 m, mean 0 m, June 2003 to December 2005; Figure 6c). Simple linear regression analyses of the mean values of dissolved component concentrations in the groundwater column (depths of 0.10–0.70 m) showed that Mn (n = 38, r = 0.7502, P < 0.001), Fe (n = 38, r = 0.7206, P < 0.001), SO₄²⁻ (n = 37, r = –0.8264, P < 0.001), CH₄ (n = 39, r = 0.5914, P < 0.001), CO₂ (n = 36, r = 0.5800, P < 0.001), and DOC (n = 31, r = 0.7964, P < 0.001) were related to soil temperature (0.10 m). Constantly low NO₃⁻ (mean for 0.10–0.70 m, 0.01 mmol L⁻¹) during the observation period suggest that either little nitrification could occur in this plot or that most NO₃⁻ was consumed by denitrification under reducing conditions. In summer, depletion of DO and SO₄²⁻, and increases in Mn, Fe, CH₄, and CO₂ were observed simultaneously (Figure 6c), indicating that production of soluble Mn and Fe and CH₄ were activated at the same time. This trend was most obvious in summer 2004 (Figure 6c), when CO₂ increased dramatically. Significant relationships between CO₂ and CH₄ concentrations in groundwater (mean values of 0.10–0.70 m depths; R² = 0.8228) suggest that increased concentrations of CO₂ strongly contributed to CH₄ production in this plot.

[28] Noting the interannual variation, mean DO in groundwater in the rainy summer of 2003 (mean for depths of 0.10–0.70 m, from June to November: 0.70 mg O L⁻¹) was much higher than in 2004 (0.16 mg O L⁻¹) and 2005 (0.19 mg O L⁻¹). There are two conceivable explanations for the high DO observed in summer 2003: (1) more precipitation may have resulted in increased oxygen supply to groundwater, and (2) less oxygen consumption may have occurred owing to the lower temperature of surface soil (Figure 2). The activity of microorganisms, including methanogens, under reducing conditions may have been suppressed by the lower temperatures [Dunfield et al., 1993]. Dissolved CH₄ in groundwater was also considerably lower in summer 2003 (0.50 m, maximum on 18 September 2003: 0.41 mmol L⁻¹; Figure 6c) than in 2004 (0.10 m, 7 October 2004: 1.40 mmol L⁻¹) and 2005 (0.20 m, 18 August 2005: 1.45 mmol L⁻¹). On the basis of these results, the seasonal patterns of hydrological processes affected by the pattern of precipitation changed the redox conditions in this streamside plot, thereby affecting CH₄ production.

[29] In addition, the hydraulic data show the occurrence of faster horizontal groundwater flow below 0.60 m than in shallower zones at KW2-downstream (M. Katsuyama et al., unpublished data, 2005). This indicates that the residence time of deeper groundwater is relatively short in this plot because of sedimentation of sandy soil in the deep zone. Under such conditions, it is possible that the discharge of retained components, including CH₄, with deep groundwater flow could occur. These conditions can also explain the clear seasonality of redox components and contribute to the rapid decrease in CH₄ concentration in this plot (Figure 6c). Our results show that hydrologic conditions can form ‘hot spots’ and ‘hot times’ of CH₄ production in small riparian wetlands by controlling the chemistry of groundwater.

4.2. Linking Mechanisms of CH₄ Production and Flux

[30] Variability in CH₄ production pathways, i.e., acetate fermentation and CO₂ reduction, may be controlled by seasonal changes in biogeochemical processes affecting microbial decomposition, and this variability seems to extend to wetland environments [Cicerone *et al.*, 1992; Tyler *et al.*, 1994; Delwiche and Cicerone, 1993; Shannon and White, 1996]. Studies with stable isotopes show intra-site and intersite variability in the relative importance of acetate dissimilation and CO₂ reduction in peatland ecosystems [Kelley *et al.*, 1992; Lansdown *et al.*, 1992; Martens *et al.*, 1992]. In our site, however, vigorous microbial decomposition of organic matter must occur in anaerobic wetland soils because CO₂, a main product of these reactions, increased dramatically with temperature in all plots (Figure 6). Moreover, the CO₂ in groundwater usually equaling or exceeding CH₄ at high temperatures, and the correlations between groundwater CH₄ and CO₂ in each plot ($R^2 = 0.3171$, KW2-edge, 0.10–0.25 m; $R^2 = 0.3959$, KW2-center, 0.10–0.70 m; $R^2 = 0.8228$, KW2-downstream, 0.10–0.70 m) indicate that CO₂ was an important substrate for CH₄ production in this wetland.

[31] Figure 7a shows the relationship between dissolved CH₄ in surface groundwater (0.10 m) and CH₄ emission rates in all plots (means of three chambers in each plot) in summer (June–October) and in the rest of the year (November–May), categorized by soil temperature. Dissolved CH₄ at 0.10 m in all plots was lower in summer 2003 (0.01–0.85 mmol L⁻¹, mean 0.27 mmol L⁻¹; June–October) than in summer 2004 (0.22–1.46 mmol L⁻¹, mean 0.85 mmol L⁻¹) and 2005 (0.07–1.36 mmol L⁻¹, mean 0.79 mmol L⁻¹; Figure 6). CH₄ emissions were lower in both 2003 and 2005 than in 2004 (Figures 5 and 7).

[32] Depletion of CH₄ emissions with the lowering of the water table has been reported from column experiments with peat [e.g., Moore and Roulet, 1993] and from field flux measurements [e.g., Macdonald *et al.*, 1998; van den Pol-van Dasselaar *et al.*, 1999]. These studies showed strong relationships between the water table and CH₄ emissions; however, most of the work has been done on larger temporal and spatial scales and on ombrotrophic systems, such as bogs, or on fens. In these sites, although there is an influence of the groundwater table, the pattern of CH₄ flux is dominated by the initial water table. Similarly, most laboratory studies have used peat columns in which there is no lateral flow of water [e.g., Roslev and King, 1996]. In our system, and small riparian wetlands like our site, the properties of the groundwater are important, through the transport of oxygen and other constituents that affect rates of CH₄ production and consumption. Thus the traditional dependence of flux on water table position may not apply to these situations.

[33] In our study wetland, although the water table was usually maintained above the soil surface in the summer 2003 and 2004, larger quantities of CH₄ in surface groundwater (Figures 6 and 7a) and higher CH₄ emissions were observed only in 2004 (Figures 5 and 7b). Formation of an oxic zone in the soil by precipitation in 2003 could have led to a decrease in CH₄ production and emission. This indicates that whereas the water tables were at the same level, hydrological conditions can change redox conditions, the amount of CH₄ produced, and, consequently, the CH₄

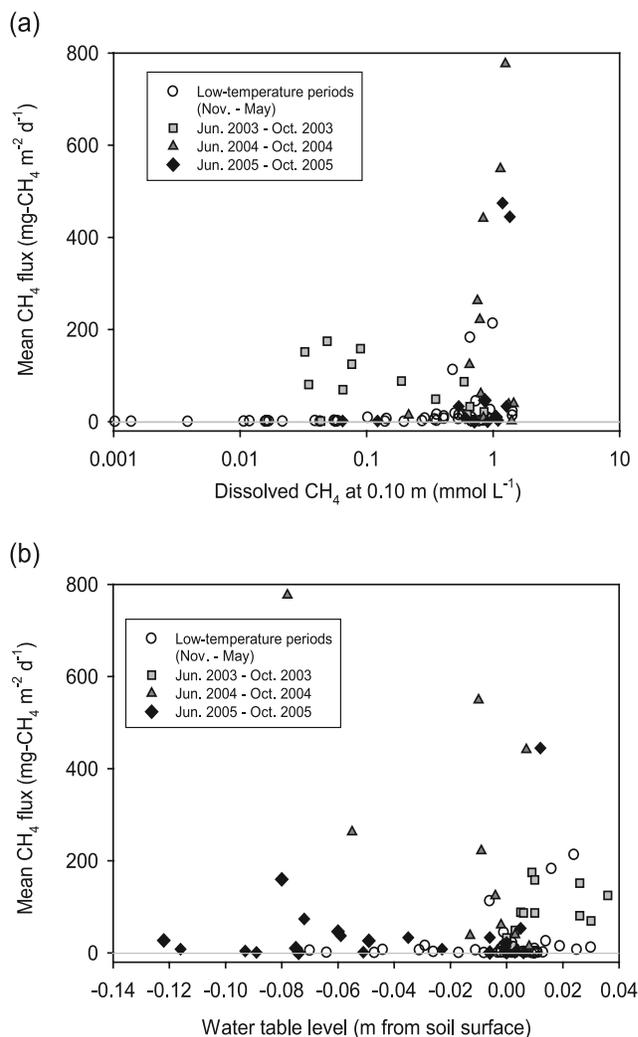


Figure 7. Relationships between mean CH₄ flux and (a) dissolved CH₄ concentration at a depth of 0.10 m and (b) water table level.

emission rate. On the other hand, although dissolved CH₄ was similar in the deeper zones of all plots, dissolved CH₄ in surface soils and CH₄ emission rates were considerably lower in summer 2005 than in 2004 (Figures 6 and 7a). An obvious difference between these two summers was the water table level (Figures 5 and 7b). According to Grable [1966], who reported that $D_{\text{water}}/D_{\text{air}}$ (where D is the diffusion coefficient) for O₂ is 1.13×10^{-4} , a drop in the water table could gradually mitigate reducing conditions from the surface to deeper layers by facilitating oxygen transport from the atmosphere to the soil. A decrease in CH₄ emissions with lowering of the water table was also observed at KW1 and KW2-downstream in summer 2002 [Itoh *et al.*, 2005] (Figure 5). The reason for the decreasing CH₄ emissions in summer 2002 is thought to be the shift of surface soil to an oxic condition (e.g., increase in DO and Eh) with a lowering of the water table [Itoh *et al.*, 2005]. Indeed, the isotopic composition of CH₄ emitted from KW2-edge was ¹³C-enriched relative to that of dissolved CH₄ in groundwater (0.25 m) in the dry summer of 2005

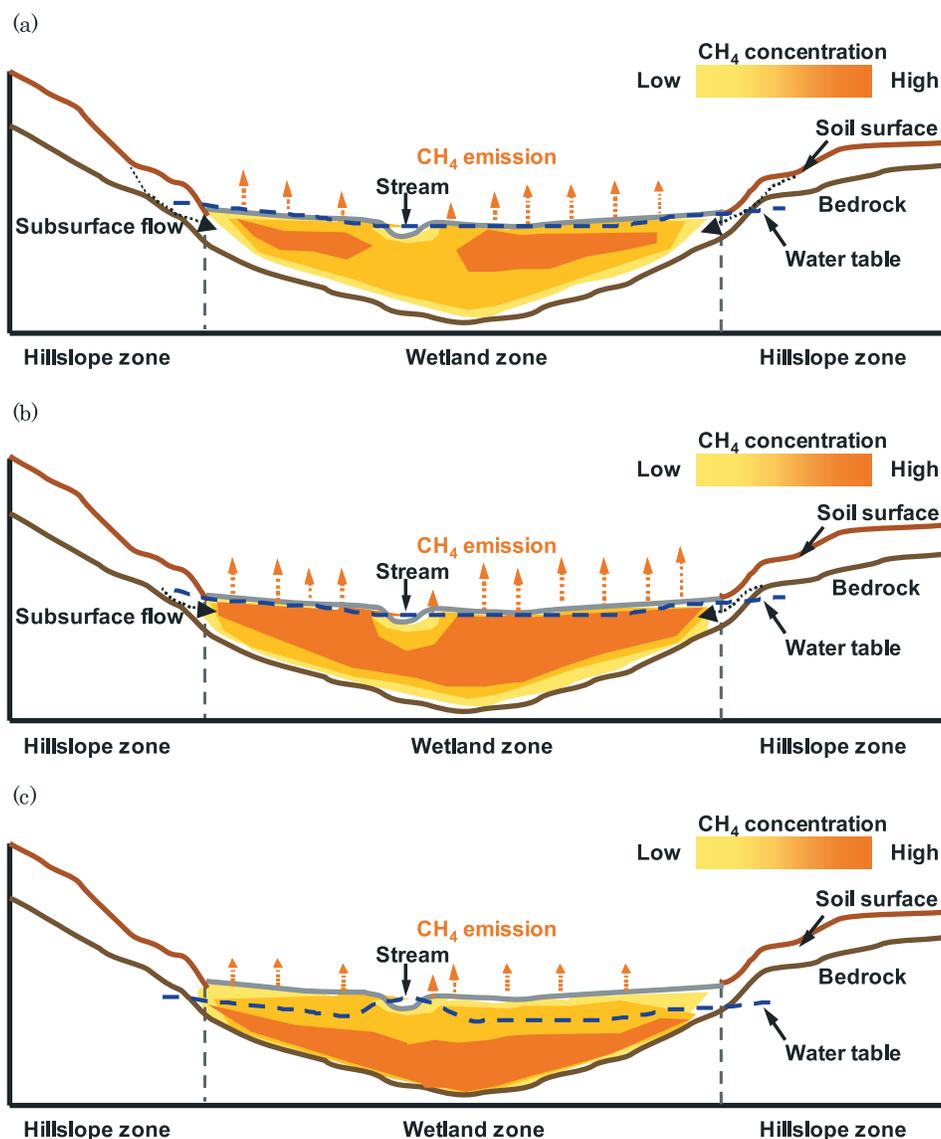


Figure 8. Schematic diagrams of CH_4 dynamics in the study wetlands with (a) above-, (b) near-, (c) and below-mean summer precipitation. Gray and black arrows indicate the direction of potential seepage and CH_4 emissions, respectively. Arrow length indicates the strength of CH_4 emissions.

(25 August 2005) (N. Suzuki, personal communication, 2005; M. Itoh et al., unpublished data, 2005). This indicates the occurrence of CH_4 oxidation with transport from groundwater to the atmosphere through the surface soil, given that a light isotope (^{12}C) is preferentially oxidized to CO_2 [Coleman et al., 1981]. Liptay et al. [1998] found similar results in landfill cover soil, suggesting the importance of this reoxidation process.

[34] Itoh et al. [2005] reported that increased CH_4 emissions from riparian wetlands in summer could change the catchment-scale CH_4 budget from a CH_4 sink to a source. Our results show that CH_4 emission from the riparian wetland was greater in normal- than in high- and low-precipitation summers, suggesting that this interannual difference in CH_4 emission can control the CH_4 budget on a catchment scale. Indeed, CH_4 emission from riparian wetlands can be more than 4 orders of magnitude greater than the summer hillslope uptake rate reported by Itoh et al.

[2005]. These results indicate the importance of considering the effects of precipitation patterns on CH_4 emission to assess the CH_4 budget on a catchment level. Estimating a more reliable catchment-scale CH_4 budget using our hydrologic and chemical data is the next step. In addition, our field measurements can provide information for testing and improving some topographically based hydrologic and biogeochemical models [e.g., Creed and Band, 1998], as suggested by Mitchell [2001].

[35] In summary, we present diagrams of CH_4 dynamics in three types of summer (Figure 8). Overall, in a high-precipitation summer (such as 2003; Figure 8a), the increased oxygen supply from more frequent incoming water (Figure 2) results in a less reduced condition than in normal- and reduced-precipitation years (2004 and 2005, respectively). Therefore the amount of CH_4 produced and retained in groundwater decreases; consequently, CH_4 emissions from the soil surface are not as high (Figure 7). In a summer with

a normal amount of precipitation (as in 2004; Figure 8b), strongly reducing conditions are formed, particularly in the upper soil layer, because of both the high water table and high soil temperature. Under such conditions, activated CH₄ production induces a large quantity of CH₄ accumulation in surface soils. This high CH₄ in surface soils results in high CH₄ emissions. In a low-precipitation summer (like that in 2005; Figure 8c), water table depletion induces the formation of an aerobic (oxic) layer in surface soils and an anoxic, reducing condition in deeper zones where oxygen is not supplied by water from above. Under such conditions, CH₄ emissions are suppressed because of the aerobic surface layer, despite high CH₄ concentrations in deeper zones. Our results illustrate that hydrological processes create 'hot spots' (typically waterlogged in warm temperature seasons) and 'hot times' (typically in years of average precipitation and warm temperatures) of CH₄ production and of CH₄ emission.

5. Conclusions

[36] Our results show that hydrological variation affecting oxygen inflow with water movement results in spatial and temporal heterogeneity (hot spots and hot times) in CH₄ dynamics by controlling the redox conditions in a forested riparian wetland. During a rainy summer, increased water (both stream and groundwater) movement formed oxic conditions and depressed CH₄ production in soil because of the large supply of relatively oxygen-rich water. In a dry summer, water table depletion facilitated oxygen transport from the atmosphere to the surface soil and resulted in a more oxic surface soil layer that had accumulated less CH₄. In the deeper zones, however, a strongly reducing condition was formed, and much CH₄ was produced as the residence time of deep groundwater increased. This implies that the effects of precipitation on water movement are important for biogeochemical reactions in soil with regard to oxygen supply and consumption.

[37] CH₄ emissions from the soil surface were highest in summer and were physically affected by changes in the water table. Although CH₄ emission rates markedly increased during most of the summer, they were constrained in both high- and low-precipitation summers because of the decrease in CH₄ production and accumulation in the surface layer.

[38] Our results indicate that riparian wetlands in forested catchments can be significant CH₄ sources and that the strength of the source is affected by hydrological factors. Therefore it is important to assess CH₄ production and emission from riparian wetlands and to consider the hydrological features of individual parts of wetlands.

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