

Controls on methane concentrations and fluxes in streams draining human-dominated landscapes

JOHN T. CRAWFORD^{1,3} AND EMILY H. STANLEY²

¹U.S. Geological Survey, National Research Program, 3215 Marine Street, Boulder, Colorado 80303 USA

²Center for Limnology, University of Wisconsin-Madison, 680 North Park Street, Madison, Wisconsin 53706 USA

Abstract. Streams and rivers are active processors of carbon, leading to significant emissions of CO₂ and possibly CH₄ to the atmosphere. Patterns and controls of CH₄ in fluvial ecosystems remain relatively poorly understood. Furthermore, little is known regarding how major human impacts to fluvial ecosystems may be transforming their role as CH₄ producers and emitters. Here, we examine the consequences of two distinct ecosystem changes as a result of human land use: increased nutrient loading (primarily as nitrate), and increased sediment loading and deposition of fine particles in the benthic zone. We did not find support for the hypothesis that enhanced nitrate loading down-regulates methane production via thermodynamic or toxic effects. We did find strong evidence that increased sedimentation and enhanced organic matter content of the benthos lead to greater methane production (diffusive + ebullitive flux) relative to pristine fluvial systems in northern Wisconsin (upper Midwest, USA). Overall, streams in a human-dominated landscape of southern Wisconsin were major regional sources of CH₄ to the atmosphere, equivalent to ~20% of dairy cattle emissions, or ~50% of a landfill's annual emissions. We suggest that restoration of the benthic environment (reduced fine deposits) could lead to reduced CH₄ emissions, while decreasing nutrient loading is likely to have limited impacts to this ecosystem process.

Key words: agriculture; urbanization; sediments; streams; nutrients; methane; climate.

INTRODUCTION

Streams are active processors of organic matter, often resulting in supersaturated concentrations of the products of respiration (CO₂ and CH₄). Recognition of the role of drainage networks as hotspots in the landscape for organic matter breakdown (Cole et al. 2007, Aufdenkampe et al. 2011) has underscored the need to develop a mechanistic understanding of the spatial and temporal distribution of these respiratory products, and substantial progress is being made in this direction for CO₂ (e.g., Raymond et al. 2013, Rawlins et al. 2014). This has not been the case for CH₄, however. While ecosystem respiration in streams is likely dominated by aerobic breakdown of organic matter, anaerobic pathways are not unusual and often support key ecological processes beyond the realm of energy flow. Indeed, many of these pathways are arguably better understood in terms of their biogeochemical contribution to ecosystem processes, as is well demonstrated by the case of denitrification. With respect to methanogenesis, there is growing evidence that generation of CH₄ in (or import to) streams may provide an unexpectedly large contribution to autotrophy (via its oxidation;

Shelley et al. 2014) to consumers in lotic food webs (Trimmer et al. 2009a, Smits et al. 2015), and at a larger scale, to the atmospheric CH₄ pool (Stanley, E.H., N.J. Casson, S.T. Christel, J.T. Crawford, L.C. Loken, and S.K. Oliver, *in press*).

Concentrations in, and emissions of CH₄ from streams are products of several interacting influences that include hydrologic and geomorphic control of the habitats appropriate for anaerobic respiration, availability of ample supplies of organic matter (OM), and depletion of alternative electron acceptors (e.g., nitrate or sulfate) to pave the way for this less energetically favorable form of respiration (Stanley et al. *in press*). In the case of streams draining agricultural and urban landscapes, all of these potential drivers are subject to modification, leading to the question: What are the magnitudes and determinants of CH₄ concentrations and emissions in human-influenced streams?

While the diversity and intensity of changes that can be wrought by agriculture and suburban/urban development vary widely, we focus our attention on the potential effects of two ubiquitous consequences of human land use on stream CH₄ dynamics. First, fertilizer use, manure spreading, urban runoff, and point-source discharges all contribute to widespread nutrient enrichment of aquatic ecosystems, particularly of nitrate (NO₃⁻) (Mayer et al. 2002, Carpenter et al. 2011). The presence of NO₃⁻ should suppress less thermodynamically favorable pathways of

Manuscript received 16 July 2015; revised 4 November 2015; accepted 6 November 2015. Corresponding Editor: C. Nilsson.

³E-mail: jtcrawford@usgs.gov

anaerobic metabolism, such as sulfate reduction and methanogenesis, and shunt respiration toward denitrification (Hedin et al. 1998, Megonigal et al. 2004). Consistent with this expectation, increased NO_3^- loading has been associated with reduced concentrations of CH_4 in lakes (McCrackin and Elser 2011) and lower CH_4 production or emissions from wetlands (Dodla et al. 2009), rice paddies (Klüber and Conrad 1998), and salt marsh soils (Balderston and Payne 1976). Alternatively, inhibition of methanogenesis associated with excess NO_3^- loading may be due to toxic effects of byproducts of its reduction, namely nitrite (NO_2^-) and nitrous oxide (N_2O) (Bodelier and Steenbergh 2014). Regardless of the specific mechanism, the interaction between C and N cycles leads to the hypothesis (H1) that CH_4 concentration and emission are constrained by NO_3^- in human-influenced streams, either due to its toxic or thermodynamic effects. Thus, N-rich streams should be relative cold spots on the landscape for CH_4 generation and efflux.

The second widespread modification to streams associated with agricultural land use and other human activities such as road or housing construction is often dramatic increases in sediment loading. Delivery and accumulation of sediments in stream and river channels far outpace the natural rate of erosion (Wilkinson and McElroy 2007) and this is most certainly the case in the Midwestern United States, where riverine loads remain elevated despite soil conservation measures and declining alluvial sediment accretion (Trimble 1999). Delivered sediments are transported downstream eventually, but depending on the geomorphic conditions (e.g., presence of dams or woody debris that facilitate sediment trapping) can be stored for varying lengths of time. Materials delivered to and stored within the channel are often relatively fine-grained (Wilson et al. 2004) and contain a high percentage of organic matter (Wood and Armitage 1997), so sediment deposition may provide habitat and energy essential for the persistence of methanogenic Archaea. Presence of such fine-grained, OM-rich materials has been associated with high rates of CH_4 generation and ebullition in both agricultural (Sanders et al. 2007, Baulch et al. 2011) and relatively pristine, nutrient-poor (Crawford et al. 2014b) streams. These results lead to an alternative hypothesis (H2) that CH_4 concentration and emission are primarily driven by availability of appropriate habitat for its generation. If so, and in contrast with H1, increased loading and storage of fine sediments could result in CH_4 enrichment of agricultural and urban streams.

To determine patterns and controls of CH_4 concentrations and fluxes in human-dominated streams, and specifically to evaluate the two divergent hypotheses (H1 and H2), we (1) conducted a survey of physical and chemical conditions in several southern Wisconsin streams to identify the best predictors of CH_4 concentrations and fluxes; and (2) undertook a laboratory experiment to directly evaluate the effects of NO_3^- and organic



FIG. 1. Photograph of a representative stream in a heavily agricultural landscape of southern Wisconsin, USA. Credit: Nick Gubbins

C on net CH_4 production. Given the possibility that agricultural practices may enhance CH_4 fluxes, we also (3) measured ebullition and dissolved CH_4 concentrations from a subset of streams in southern Wisconsin over four months as a relatively simple indicator of the magnitude and persistence of these sites as atmospheric CH_4 sources. In order to contextualize CH_4 patterns in human-dominated systems, we compare this data set to pristine streams in northern Wisconsin for which we have extensive measurements made using identical methods. Finally, drawing on these results, we suggest potential strategies to decrease stream and river CH_4 production in human-dominated landscapes in the event that this issue warrants attention from policymakers at local and national levels of government.

METHODS

Stream sites

We surveyed 23 streams during summer 2014 in Dane County, Wisconsin, USA. Sites included urban, agricultural, mixed use, and semi-forested catchments (Fig. 1). Streams were selected in a random stratified design to cover the range of land cover and variations in landscape geomorphology (Fig. 2; unglaciated regions, prairie, drumlins, etc.). To supplement these one-time sampling events, we continued a sampling regime at four streams for the remainder of the summer at irregular intervals. These sites (Sites 7, 32, 50, 53) were selected to represent the variability of stream CH_4 that was encountered in our survey, and the general patterns of land cover in the study region of southern Wisconsin.

Water chemistry and channel attributes

In order to test hypotheses and to explore CH_4 relationships with different water quality parameters, we

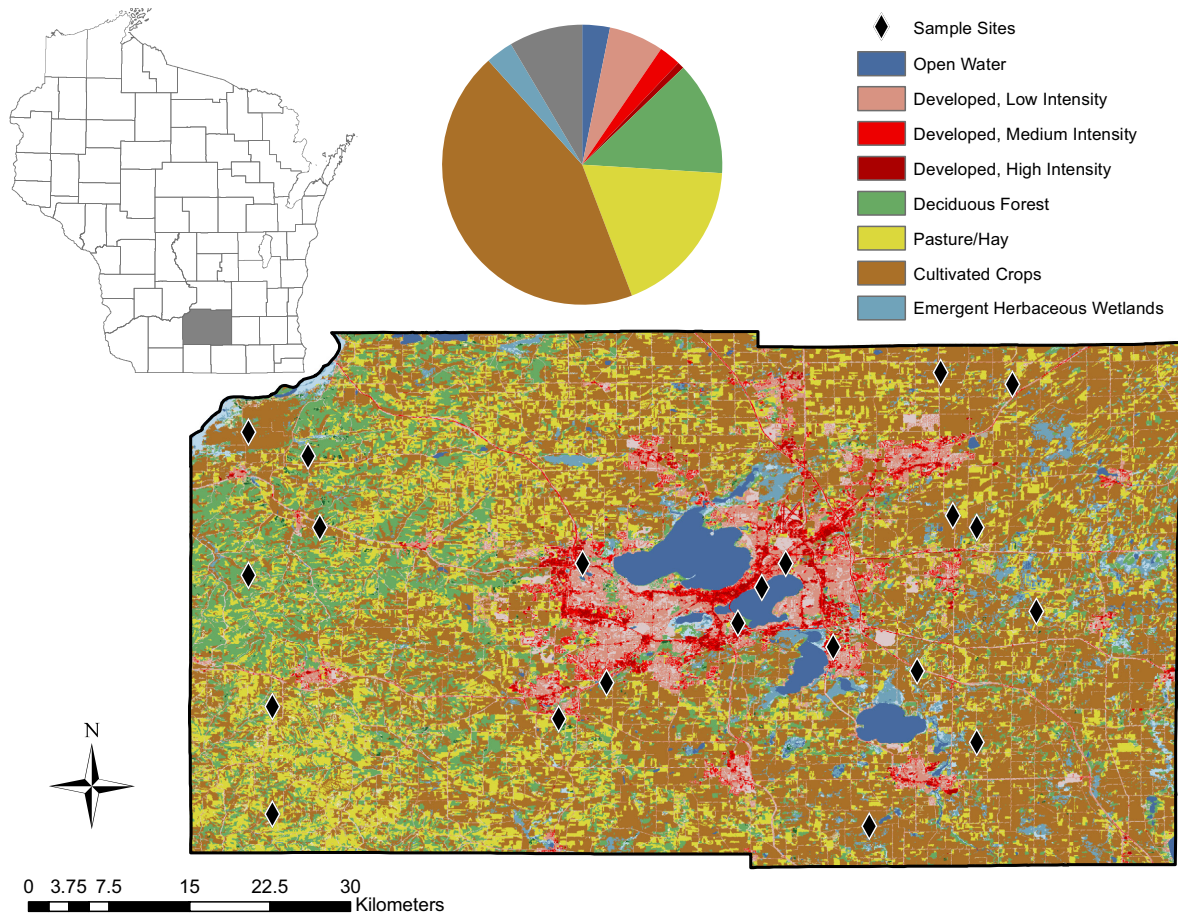


FIG. 2. Map of stream survey sites and land cover in Dane County, Wisconsin; pie chart indicates the total relative cover of individual land cover types (see key).

collected water samples for chemical analysis at each of the 23 survey sites. Water was filtered in the field (0.45- μ m glass fiber filter), distributed into appropriate acid-washed bottles, and subsequently analyzed for dissolved organic carbon (DOC, mg/L), $\text{NO}_3 + \text{NO}_2$ ($\mu\text{g/L}$; hereafter referred to as $\text{NO}_3\text{-N}$ for brevity), ammonium ($\text{NH}_4\text{-N}$, $\mu\text{g/L}$), soluble reactive phosphate (SRP, $\mu\text{g/L}$), and sulfate (SO_4^{2-} , mg/L). In addition, unfiltered samples were collected for laboratory analysis of total nitrogen (TN, $\mu\text{g/L}$), and total phosphorus (TP, $\mu\text{g/L}$), and $\text{NO}_2\text{-N}$ ($\mu\text{g/L}$) was determined at roughly one-half of the sites. All analyses were done following protocols established by the North Temperate Lakes Long Term Ecological Research program. $\text{NO}_2\text{-N}$ was determined manually within 24 h using the sulfanilamide-dihydrochloride method (APHA 1998). Ancillary field measurements of specific conductivity ($\mu\text{S/cm}$), dissolved oxygen (percent saturation), pH, and water temperature ($^{\circ}\text{C}$) were made using a YSI multiparameter sonde (YSI, Yellow Springs, Ohio, USA).

Channel and sediment attributes were characterized along a 100-m reach at each site as part of the summer

survey. We measured depth to refusal (DTR) as a means of approximating the depth of fine sediments overlying hard mineral sediments using methods of Lisle and Hilton (1992). Five measurements were made along three replicate channel cross-sections and a 20-cm sediment core (fine sediments + mineral bed if present at this depth) was collected at each of the three transects for bulk density and loss on ignition (LOI). Replicate cores were taken from the right, center, and left locations of the channel and returned to the laboratory where they were dried for several days at 50°C . Homogenized subsamples were then weighed for bulk density and heated at 500°C for 4 h to determine LOI.

Gas concentrations and fluxes

At each of the 23 sites, we measured dissolved CH_4 and CO_2 and made direct flux measurements using a suspended chamber technique (Crawford et al. 2013). Partial pressure of CH_4 ($p\text{CH}_4$) and CO_2 ($p\text{CO}_2$) were measured simultaneously in the field with a Los Gatos Research ultraportable greenhouse gas analyzer connected to a

membrane gas equilibrator (Liqui-Cel, Membrana, Charlotte, North Carolina, USA). Water was pumped through the equilibrator for a minimum of 10 min and the equilibrium concentrations of CH_4 and CO_2 were recorded in the field. Gas concentrations (ppmv) were converted to partial pressure by multiplying by barometric pressure (atm; 1 atm = 1.01325×10^5 Pa). Simultaneous measurements of air–water gas exchange were also made with the greenhouse gas analyzer using a plastic chamber attached to a portable crane. The flux of CH_4 (or CO_2) J was calculated using Eq. 1:

$$J_{\text{CH}_4} = dC/dt * h \quad (1)$$

where dC/dt is the gas concentration change over time ($\text{mol} \cdot \text{m}^{-3} \cdot \text{time}$) and h is the height of the plastic chamber (m).

In addition to repeated samples for dissolved gases, we installed 16 funnel-style traps at each of the four monitoring streams (four traps per site) to estimate CH_4 emissions via bubbling (i.e., ebullition; Molongoski and Klug 1980, Baulch et al. 2011). Bubble traps were installed on 10 July 2014, and were sampled until the end of October 2014, when freezing conditions prevented collection of accurate measurements. Each trap had a bottom surface area of $\sim 500 \text{ cm}^2$ that narrowed at the top into a graduated (1-mL resolution) syringe and three-way stopcock. Traps were attached to steel poles that were pounded into the stream bed. Traps were almost completely submerged and contained no head-space at deployment. Bubble traps were sampled by carefully approaching them to avoid induced ebullition. Volume of accumulated gas in the trap was based on the graduated syringe, and volumes $< 1 \text{ mL}$ were recorded as zero. We estimated the daily mass flux of CH_4 by multiplying the bubble flux rate (mol gas/d), according to the ideal gas law, by bubble composition (mole fraction, percentage by volume). Bubble composition was

assessed from fresh bubbles collected manually from the sediments using a smaller version of the bubble traps. We elected to analyze fresh bubbles as opposed to the gas composition in deployed traps in order to avoid possible exchange and oxidation in the water. Samples were analyzed with gas chromatography. We assumed that temperature of the bubble was equal to the stream water temperature at the time of sampling and that total pressure was equal to the barometric pressure at the surface of the water.

Sediment experiment

As a second test of the two hypotheses, and to determine if CH_4 was produced within the active stream channel (rather than being imported to the channel via groundwater discharge), we conducted a laboratory experiment using benthic sediments from the four long-term sites. We ran 24-h incubations in order to determine whether these sediments were active CH_4 producers, as CH_4 production over such short time periods would only be expected if these communities were viable. Four replicate sediment samples were collected from the top $\sim 20 \text{ cm}$ using a plastic corer at each site. Sediments were sealed in plastic bags after eliminating as much air from the bags as possible then transported to the laboratory and refrigerated overnight. Sediments were then distributed into 150-mL glass containers ($\sim 45 \text{ g}$ dry sediments), amended with 50 mL of a treatment solution, immediately flushed with N_2 gas for 5 min, and sealed with a gas-tight screw cap equipped with a septum. Following collection of an initial head-space gas sample, containers were placed on a shaker table in the dark. Treatments were as follows: deionized water (control), water amended with acetate (40 mg C/L) to assess potential C limitation of methanogens, an NO_3^- amendment (20 mg

TABLE 1. Summary chemical and physical data for streams in Dane County, Wisconsin, USA.

	Mean	Minimum	Maximum
Dissolved organic C (DOC; mg/L)	4.15	0.63	7.01
$\text{NH}_4\text{-N}$ ($\mu\text{g/L}$)	103.7	11	543
$\text{NO}_3\text{-N}$ ($\mu\text{g/L}$)	2270	9	6650
$\text{NO}_2\text{-N}$ ($\mu\text{g/L}$)	32	2	124
Soluble reactive phosphate (SRP; $\mu\text{g/L}$)	60	4	266
Total N ($\mu\text{g/L}$)	4554	307	12657
Total P ($\mu\text{g/L}$)	176	38	564
SO_4^{2-} (mg/L)	23.6	3.6	85.3
Conductivity ($\mu\text{S/cm}$)	786	201	1606
Discharge (L/s)	608	0	5578
Dissolved O (saturation; %)	88.6	4.6	181.9
pH	7.54	6.45	8.7
Water temperature ($^{\circ}\text{C}$)	18.6	12.14	24.81
$p\text{CH}_4$ (μatm)	268	5.56	523
$p\text{CO}_2$ (μatm)	3199	266.5	6825
Depth to refusal (cm)	32	6	91

N/L) to test for possible NO_3^- suppression, and a combination of both acetate (40 mg C/L) and NO_3^- (20 mg N/L) to consider interactive treatment effects. Initial and final sample headspace CH_4 concentrations were determined by extracting a headspace gas sample from each replicate and injecting it directly into a Varian 3800 gas chromatograph equipped with a HayeSep N column and a flame ionization detector. The final gas sample was collected after 24 h of incubation. Headspace volume was measured for each replicate and a water sample was extracted and filtered for determination of $\text{NO}_3\text{-N}$. Sediments were then transferred to individual aluminum pans for dry mass and LOI determination.

Statistical analysis

All statistical analyses were performed using R (R Core Team 2014). We analyzed the results of the sediment experiment with a two-way ANOVA including interactions. We further analyzed the sediment experiment for the influence of uncontrolled covariates (sediment organic matter content) using ANCOVA. Ordinary least squares modeling was used to identify potential relationships between CH_4 and chemical and physical site attributes. The level of significance for all statistical tests was set to 0.05.

RESULTS

Stream survey

Streams in southern Wisconsin encompassed a wide range of chemical conditions, from nutrient-poor ($\text{NO}_3\text{-N}$ and SRP concentrations of 9 and 4 $\mu\text{g/L}$, respectively) to extremely enriched (>6000 $\mu\text{g NO}_3\text{-N/L}$) systems (Table 1). Similarly, conductivity, which is an indicator of water source and solute load also spanned a wide range (201 to 1606 $\mu\text{S/cm}$; mean of 786 $\mu\text{S/cm}$). The depth and organic matter content of fine benthic sediments also varied substantially among the 23 survey sites. Average DTR was 32.1 cm (range = 6–91 cm). This ubiquitous fine sediment was also relatively OM rich, with average LOI values of 8.5% (range = 2.0–33%).

Both dissolved oxygen and $p\text{CO}_2$ were well within the range of previously reported values in streams, averaging 88.6% saturation, and 3199 μatm , respectively (Table 1). Dissolved CH_4 , on the other hand, was very high and variable and averaged 268 μatm . The lowest concentration (5.56 μatm) was found in a stream in a predominantly forested area, and the highest (523 μatm) was at a site ~750 m downstream from a eutrophic lake.

The $p\text{CH}_4$ was highly correlated with a number of physical and chemical parameters, but was not significantly related to any N oxides, although we did observe a weak

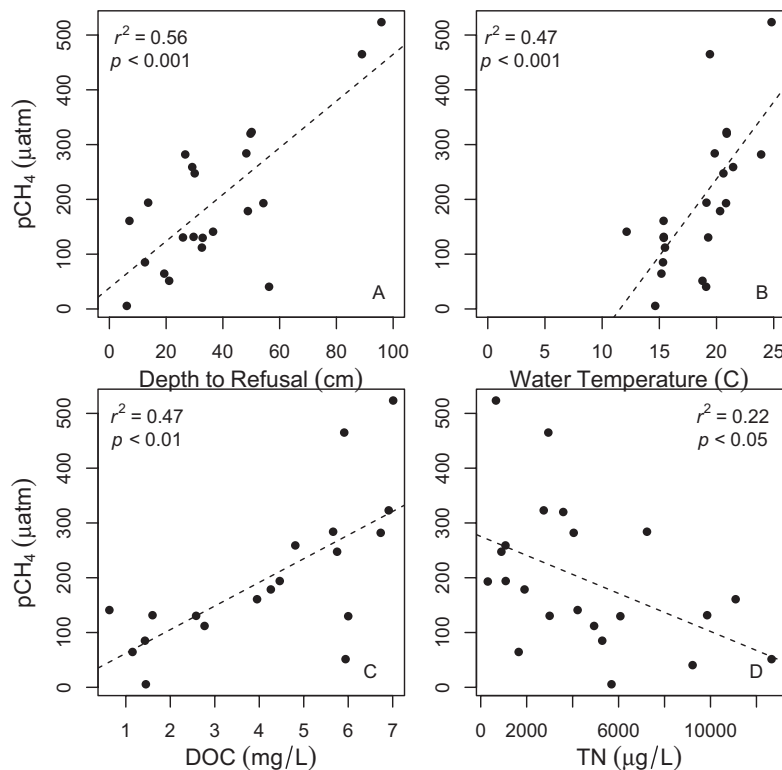


FIG. 3. Relationships between stream partial pressure of CH_4 ($p\text{CH}_4$) and (A) depth to refusal, (B) water temperature, (C) dissolved organic carbon (DOC), (D) and total nitrogen (TN).

negative but significant correlation with TN. Reach-averaged depth to refusal (DTR) was positively correlated with $p\text{CH}_4$ (Fig. 3A, $P < 0.001$, $r^2 = 0.56$, slope = 4.26, standard error [SE] = 0.84). Additionally, water temperature (Fig. 3B, $P < 0.001$, $r^2 = 0.47$, slope = 28.1, SE = 6.62), DOC (Fig. 3C, $P < 0.001$, $r^2 = 0.48$, slope = 43.2, SE = 10.9), and TN (Fig. 3D, $P < 0.05$, $r^2 = 0.22$, slope = -0.017 , SE = 0.007) were also related to $p\text{CH}_4$.

Consistent with the observed supersaturation of CH_4 and CO_2 , chamber measurements confirmed that streams were always sources of CH_4 and CO_2 to the atmosphere via diffusion across the air–water interface. Average diffusive CH_4 flux was $27.2 \text{ mmol CH}_4 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (range = 0.019–180, standard deviation [SD] = 48.0, $n = 19$), and average diffusive CO_2 flux was $466 \text{ mmol CO}_2 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (SD = 551.9, $n = 22$). Visual analysis of dC/dt plots for replicate chamber measurements revealed nonlinearity in some instances for CH_4 (but not for CO_2), indicating possible ebullition during chamber measurements. In only a few cases were replicate measurements discarded. Despite these potential deviations from linearity, we considered the flux estimates to be acceptable. Model fits of dC/dt over the 5-min deployments had r^2 values averaging 0.75 and 0.87, for CH_4 and CO_2 , respectively.

Temporal patterns

Temporal measurements of four Dane County streams showed that supersaturated CH_4 conditions were not limited to early summer. Stream $p\text{CH}_4$ was consistently supersaturated with respect to the atmosphere from June to October (average = $95.1 \mu\text{atm}$), and although the temporal sampling effort was irregular, there was no obvious trend. In addition to the ubiquitous pattern of CH_4 supersaturation, CH_4 -rich bubbles were present in traps throughout the summer

and fall, demonstrating that sites were also releasing CH_4 via ebullition. Average bubble rates were $623 \text{ mL gas} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (range = 0–4890 $\text{mL} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$). CH_4 composition of bubbles varied substantially ($< 2 \text{ ppm}$ to 62% CH_4 by volume), with an average of 11.4% CH_4 by volume. Conversion to CH_4 efflux rates based on observations of bubble emission and bubble composition suggested an average areal flux via bubbles of $4.19 \text{ mmol CH}_4 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (Fig. 4). Average CH_4 ebullition was not significantly correlated with sediment bulk density ($P > 0.1$), nor with average depth to refusal ($P > 0.1$).

Laboratory sediment experiment

Net sediment CH_4 production over 24 h was not significantly affected by addition of acetate or NO_3^- , either alone or in combination, but did vary among sites (Table 2). These results did not support H1 that NO_3^- constrains CH_4 production. Post-hoc analysis (Tukey's HSD test) identified Site 50 as significantly different from the other three sites ($P < 0.05$). Simply plotting accumulated CH_4 per g dry sediment against OM (%) of the sediments indicated a distinct increase in CH_4 generation for samples with OM $> 8\%$, regardless of treatment type or stream site (Fig. 5). Further analysis of the experiment data with ANCOVA using OM as a covariate led to similar results in which only among-site differences were significant. Although we did not measure denitrification activity specifically (e.g., using a procedure such as the acetylene block method), we did observe presence of NO_2^- and nearly complete NO_3^- depletion from the water overlying the sediments in NO_3^- -amended replicates over the course of the experiment (average reduction = 19.92 mg N/L , 99.6% removal).

DISCUSSION

Streams in human-dominated landscapes of southern Wisconsin had remarkably high summertime CH_4 concentrations in the presence of oxygen-rich surface waters. Compared to forested and wetland streams in northern Wisconsin (Crawford et al. 2014b), average Dane County stream $p\text{CH}_4$ documented in our survey ($268 \mu\text{atm}$) was greater than the highest value ($191.8 \mu\text{atm}$) and approximately double the average value ($100.2 \mu\text{atm}$). High diffusive effluxes resulted from these elevated concentrations, averaging $27.2 \text{ mmol CH}_4 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, over threefold greater than summertime rates from the northern Wisconsin streams ($8.5 \text{ mmol CH}_4 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$; Crawford et al. 2014b) and the best available global estimate ($8.2 \text{ mmol CH}_4 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$; Stanley et al. *in press*). When including ebullition, the estimate of average emission increased to $31.4 \text{ mmol CH}_4 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$. In contrast to CH_4 , CO_2 concentrations and fluxes in Dane County streams were unremarkable. Average $p\text{CO}_2$ ($3199 \mu\text{atm}$) was slightly higher than an estimate for headwater streams in the Midwest (~ 2000 – $3000 \mu\text{atm}$; Butman and Raymond

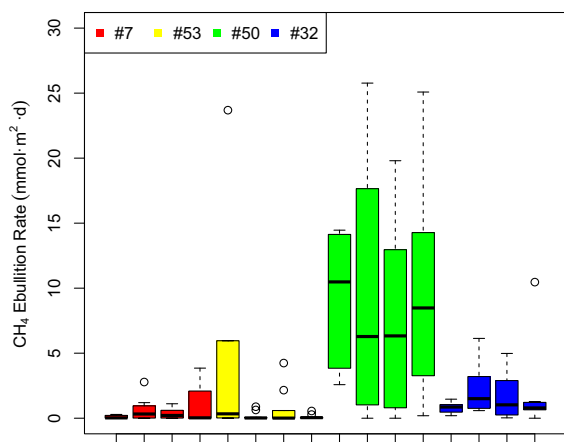


FIG. 4. CH_4 bubbling rates from four monitored streams (7, 53, 50, 32) that were selected based on variation in dissolved CH_4 from the Dane County stream survey.

TABLE 2. Two-way ANOVA results of laboratory CH₄ production experiment; significant differences ($P < 0.05$) were observed at the site level, but no differences were observed among treatments (added NO₃⁻, acetate, both NO₃⁻ and acetate, or deionized water controls).

	df	Sum of squares	Mean square	<i>F</i>	<i>P</i>
Site	3	137.72	45.91	10.437	2.12×10^{-5}
Treatment	3	11.69	3.9	0.886	0.455
Site:Treatment	9	35.94	3.99	0.908	0.526
Residuals	48	211.13	4.4		

2011) and the average diffusive CO₂ flux of 466 mmol CO₂m⁻²d⁻¹ from our summer survey is consistent with the Butman and Raymond (2011) estimate for temperate zone streams and rivers (~540 mmol CO₂m⁻²d⁻¹), even after we converted their reported annual rate to a daily time scale. While far from conclusive, these comparisons between CO₂ and CH₄, and between more pristine and human-influenced streams in Wisconsin suggest a differential enhancement of methanogenesis over total CO₂ production in these latter systems.

Summer surveys and continued fall sampling at a subset of streams failed to reveal strong relationships between NO₃⁻ and *p*CH₄. Combined with sediment experiments in which NO₃⁻ additions did not significantly affect CH₄ production, these results fail to support the hypothesis that CH₄ concentration and emission are constrained by NO₃⁻ in human-influenced streams. The positive correlation between the thickness of the loose sediment layer (DTR) and CH₄ provides support for H2, that CH₄ concentration and evasion are strongly affected by the extent of habitat appropriate for methanogenesis (anoxic, high organic matter content; Stanley et al. *in press*).

The lack of a NO₃⁻ effect either in the sediment experiment or in streams themselves is possible if NO₃⁻ and its attendant transformations are spatially segregated from CH₄ generation. Even within sediment assays

subject to initial thorough mixing followed by moderate shaking during incubation, the fine texture of the sediments likely favored development of separate zones, with NO₃⁻ reduction at the top of sediments and methanogenesis a few centimeters (or less) below. Formation and persistence of distinct patches supporting different biogeochemical rates or transformations are favored when hydrologic connectivity diminishes (Powers et al. 2012). These different patches may occur as orderly layers (i.e., along a redox gradient) if sediments are relatively homogeneous (e.g., fine lake sediments; Lovley and Klug 1986), or be highly variable in their distribution and extent if sediment composition is heterogeneous, as has been suggested for stream beds (Baker et al. 1999, Morrice et al. 2000, Clilverd et al. 2008). In both cases, hydrologic isolation, and thus biogeochemical divergence, is facilitated by presence of fine-grained sediments. In Dane County streams, deposits of these fine-grained, OM-rich materials appear to be sufficiently widespread to overcome their limited hydrologic connectivity and deliver substantial loads of CH₄ first to the water column, and then to the atmosphere.

The hypothesis of NO₃⁻ constraint on CH₄ was based on two possible mechanisms: either the thermodynamic efficiency of denitrification over methanogenesis (denitrifiers simply outcompete methanogens when NO₃⁻ is present), or the intermediary products of NO₃⁻ reduction are toxic to methanogenic Archaea; but CH₄ production in the presence of NO₃⁻ could potentially occur if denitrification does not proceed at a meaningful rate (i.e., denitrifiers are scarce so Archaea do not have to compete for organic substrates). The sediment experiment demonstrated that NO₃⁻ was subject to transformation, as it was rapidly depleted during the 24-h incubation. An alternative fate for NO₃⁻ is reduction to ammonium (dissimilatory nitrate reduction to ammonium; DNRA). It is becoming increasingly clear that this pathway may be responsible for a substantial fraction of observed NO₃⁻ depletions in many aquatic systems (Burgin and Hamilton 2007, Giblin et al. 2013). Yet often-high stream NO₃⁻ concentrations and the high enrichment rate of the NO₃⁻ treatment suggest that there should still be ample NO₃⁻ to support denitrification (and thus potentially inhibit methanogenesis) even if as much as half of the NO₃⁻ was subject to DNRA. Further, if the mechanism of N suppression is not thermodynamic but instead is due to toxic effects of NO₃⁻ reduction products (e.g., NO₂⁻, which is pervasive

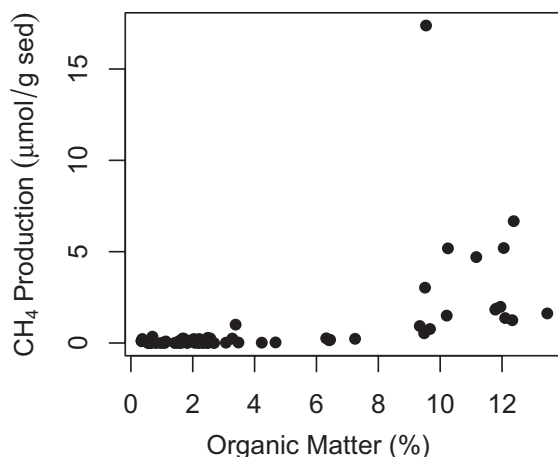


FIG. 5. Plot of the relationship between organic matter content (as measured by loss on ignition) and CH₄ production over 24 h for all replicates in a laboratory experiment

in N-rich Wisconsin streams; Stanley and Maxted 2008), then the pathway of NO_3^- may not be relevant. Thus, we favor the explanation of co-occurrence of NO_3^- reduction and CH_4 generation in streams due to finer-scale spatial separation of these two processes.

While H1 was inspired by first principles supported by observations of N suppression of methanogenesis in a variety of aquatic settings (Balderston and Payne 1976, Roy and Conrad 1999, Granberg et al. 2001), other investigations have also documented amplified CH_4 production under elevated N conditions (e.g., Liu and Greaver 2009). In the Florida Everglades (USA), for example, nitrogen fertilizers were found to enhance acetate-based methanogenesis (Holmes et al. 2013). In fact, N enrichment has the potential to create a cascade of increased primary production and respiration, and if anoxic habitats develop, followed by high production of both N_2O and CH_4 (e.g., Rajkumar et al. 2008). With respect to managing CH_4 production in human-dominated streams, results of this study suggest that reduction of point and non-point source loading of NO_3^- and other terminal electron acceptors is not likely to be effective. The alternative is to manage the sediments either by removal (or their storage mechanism) or reducing the sediment load to streams.

Missing from our investigation are the potential links between human-driven nutrient and sediment enrichment and changes to the organic carbon pool available to methanogens and other anaerobic bacteria. The positive correlation between surface water DOC concentrations and $p\text{CH}_4$ (Fig. 3C) and the threshold increase in CH_4 production for sediments with $>8\%$ OM in our experiment (Fig. 5) suggest potential C controls on CH_4 production. However, a lack of dissolved C control of CH_4 production was partially supported by laboratory incubations of anoxic sediments. A massive C addition in the form of acetate (a precursor molecule in one methanogenesis pathway) either exclusively, or combined with substantial amounts of NO_3^- failed to elicit changes to CH_4 production potential in the laboratory. It is unlikely that methanogens in these stream sediments were limited by the availability of acetate. However, we do not know the pathway by which CH_4 is typically produced in these sediments (acetoclastic vs. hydrogenotrophic). Perhaps other C molecules such as algal-derived C (West et al. 2012) or carbohydrates may be limiting H_2 production in sediments (Conrad 1999), thus limiting the rate of hydrogenotrophic methanogenesis. The role of organic substrates on CH_4 production in stream sediments is a clear research need. Alternatively, elevated CH_4 and DOC concentrations in highly sedimented streams could both be indicative of reducing conditions, which are known to control DOC exchange between sediments, pore waters and the overlying water column.

The legacy of land conversion, intensive erosion, and resultant deposition and storage of fine sediments has restructured streams in urban and agricultural landscapes in southern Wisconsin (and elsewhere), with

subsequent changes to CH_4 production and emissions. Somewhat surprisingly, the role of anthropogenic river sediments as a direct control on CH_4 emissions has been known (and perhaps forgotten) since at least the 1930s (Moens 1957). In Dutch canals, thick, silty “schlamm” (sludge) sediments were strongly related to CH_4 emissions via bubbling, and emissions were greatly reduced following sediment removal and reductions of sewage discharges to surface waters (Moens 1957). In many streams in southern Wisconsin, accumulation of post-settlement alluvium, resultant woody encroachment into previous wet meadow/sedge riparian habitats and resultant channel debris loading has greatly altered channel hydrology, form, and composition (Knox 1977, Booth et al. 2009). Large woody debris from riparian vegetation facilitates trapping and storage of fine-grain sediments through a variety of woody debris “jam” types, including dams and deflectors (Wallerstein and Thorne 2004, Skalak and Pizzuto 2010). Low channel gradients and macrophyte development also favor sediment retention, with the end result that porous, oxygen-rich sand and gravel stream beds become buried by organic-rich, oxygen-depleted sediments in many regional streams. We observed extensive fine sediment deposits in Dane County streams, which were typically associated with wood and other channel debris. In fact, the average stream in urban and agricultural catchments in our survey contained nearly as much fine sediment (by volume) as it did water overlying the larger-grain bed.

Although fine sediment accumulation and its concomitant effects on biogeochemistry and stream biota (Wood and Armitage 1997) result from longstanding changes in land use, restoration of these ecosystems may be effective in reducing some of these changes. Various streams in southern Wisconsin have been the target of restoration activities designed to return channels and riparian areas to historical, pre-settlement conditions and to improve benthic habitats through removal of post-settlement alluvium and woody debris (Booth et al. 2009). This strategy is a more involved variation on traditional farm ditch management in which ditches are routinely dredged to remove accumulated materials (Leece et al. 2006, Needelman et al. 2007). The potential effectiveness of sediment removal could be estimated based on the relationship between depth to refusal and $p\text{CH}_4$ given in Fig. 3A. One could expect a decrease of $4.2 \mu\text{atm}$ of CH_4 for every 1 cm of fine sediments removed from stream channels. The intercept of this relationship suggests that complete restoration to larger caliber mineral sediments could achieve $p\text{CH}_4 < 40 \mu\text{atm}$. However, streams would likely persist as small sources of CH_4 to the atmosphere given that relatively pristine streams in the northern part of the state emit a substantial quantity of CH_4 to the atmosphere (Crawford et al. 2014a). Additionally, the fate of dredged sediments would need to be considered, as burial or storage under anaerobic conditions could simply relocate CH_4 emissions to another environment.

Other past restoration efforts in southern Wisconsin streams can provide further insight into potential CH₄ responses to altered geomorphology. For example, the removal of a small dam and transition from a sediment-filled reservoir to a more typical stream state resulted in decreased ecosystem capacity to remove NO₃, sulfate, NH₄, and SRP (Powers et al. 2013), indicating the substantial (and anaerobic) biogeochemical capacity of agricultural sediments. While no dissolved gas data were available from this restoration, we suspect that substantially decreased fine sediments also led to decreased CH₄ production as evidenced by prevalent reductions in other anaerobic processes. While not as conspicuous as a concrete dam or a sediment-filled reservoir, small debris dams (Wallerstein and Thorne 2004, Harrison et al. 2012) and other geomorphic features that enhance storage of fine-grained sediments can be understood as such. Given that net retention of nitrogen is determined by sediment–water interactions (via anaerobic denitrification) in impounded (Stanley and Doyle 2002) and sediment-impacted streams in agricultural landscapes (Trimmer et al. 2009b), the logical leap to sediment controls of CH₄ production is not hard to fathom, and is in fact defensible in other agricultural landscapes (Sanders et al. 2007, Baulch et al. 2011). Additionally, early equivalents of whole ecosystem experiments indicate that reducing the depth of fine-grained sediments and reduction of direct organic inputs can reduce aquatic CH₄ emissions in human dominated landscapes (Moens 1957).

To understand the potential benefits of managing stream CH₄ emissions as a result of sedimentation controls, we can place stream fluxes into the context of other major CH₄ sources in the region. Using conservative assumptions that streams cover 0.25% of total surface area in Dane County (see Downing et al. 2012) and emit 31 mmol CH₄m⁻²d⁻¹ (diffusion+ebullition) throughout 275 d of open water, total stream CH₄ flux is estimated to be 7.05×10^7 mol CH₄/yr. Landfills and dairy cattle are likely regional anthropogenic sources of CH₄. For example, Dane County holds ~50000 dairy cattle (National Agricultural Statistics Service 2013), which emit $\sim 3.42 \times 10^8$ mol CH₄/yr based on reported livestock emission inventories (Lassey 2007). Similarly, a single large landfill in Dane County emits $\sim 1.24 \times 10^8$ mol CH₄/yr (EPA 2014). Lakes and wetlands are other probable sources in the county but we do not currently have estimates for these environments. Complete elimination of stream CH₄ flux would be similar to the removal of >10000 cattle from the county or a >50% reduction of one landfill's annual emissions. While these calculations contain much uncertainty, they indicate the relative magnitude of stream CH₄ emissions and can be used as a starting point for future decision-making.

ACKNOWLEDGMENTS

Nick Gubbins and Ryan Hassemer assisted with field work and laboratory analyses. Partial funding was provided by the

U.S. Geological Survey Water, Energy, and Biogeochemical Budgets Program and the U.S. Geological Survey Land Carbon Program. Any use of trade or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government. Support for this study was provided by funding from the North Temperate Lakes LTER program, NSF DEB-0822700.

LITERATURE CITED

- APHA [American Public Health Association]. 1998. Standard methods for the examination of water and wastewater, Twentieth edition. American Public Health Association, Washington, D.C., USA.
- Aufdenkampe, A. K., E. Mayorga, P. A. Raymond, J. M. Melack, S. C. Doney, S. R. Alin, R. E. Aalto, and K. Yoo. 2011. Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. *Frontiers in Ecology and the Environment* 9:53–60.
- Baker, M. A., C. N. Dahm, and H. M. Valett. 1999. Acetate retention and metabolism in the hyporheic zone of a mountain stream. *Limnology and Oceanography* 44:1530–1539.
- Balderston, W. L., and W. J. Payne. 1976. Inhibition of methanogenesis in salt marsh sediments and whole-cell suspensions of methanogenic bacteria by nitrogen oxides. *Applied and Environmental Microbiology* 32:264–269.
- Baulch, H. M., P. J. Dillon, R. Maranger, and S. L. Schiff. 2011. Diffusive and ebullitive transport of methane and nitrous oxide from streams: Are bubble-mediated fluxes important? *Journal of Geophysical Research* 116: doi:10.1029/2011JG001656.
- Bodelier, P. L. E., and A. K. Steenbergh. 2014. Interactions between methane and the nitrogen cycle in light of climate change. *Current Opinions in Environmental Sustainability* 9–10:26–36.
- Booth, E. G., S. P. II Loheide, and R. D. Hansis. 2009. Postsettlement alluvium removal: A novel floodplain restoration technique (Wisconsin). *Ecological Restoration* 27:136–139.
- Burgin, A. J., and S. K. Hamilton. 2007. Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. *Frontiers in Ecology and the Environment* 5:89–96.
- Butman, D., and P. A. Raymond. 2011. Significant efflux of carbon dioxide from streams and rivers in the United States. *Nature Geoscience* 4:839–842.
- Carpenter, S. R., E. H. Stanley, and M. J. Vander Zanden. 2011. State of the world's freshwater ecosystems: physical, chemical, and biological changes. *Annual Review of the Environment and Resources* 36:75–99.
- Cilverd, H. M., J. B. Jr Jones, and K. Kielland. 2008. Nitrogen retention in the hyporheic zone of a glacial river in interior Alaska. *Biogeochemistry* 88:31–46.
- Cole, J. J., et al. 2007. Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. *Ecosystems* 10:171–184.
- Conrad, R. 1999. Contribution of hydrogen to methane production and control of hydrogen concentrations in methanogenic soils and sediments. *FEMS Microbiology Ecology* 28:193–202.
- Crawford, J. T., R. G. Striegl, K. P. Wickland, M. M. Dornblaser, and E. H. Stanley. 2013. Emissions of carbon dioxide and methane from a headwater stream network of interior Alaska. *Journal of Geophysical Research Biogeosciences* 118:482–494.

- Crawford, J. T., N. R. Lottig, E. H. Stanley, J. F. Walker, P. C. Hanson, J. C. Finlay, and R. G. Striegl. 2014a. CO₂ and CH₄ emissions from streams in a lake-rich landscape: Patterns, controls, and regional significance. *Global Biogeochemical Cycles* 28:197–210.
- Crawford, J. T., E. H. Stanley, S. A. Spawn, J. C. Finlay, L. C. Loken, and R. G. Striegl. 2014b. Ebullitive methane emissions from oxygenated wetland streams. *Global Change Biology* 20:3408–3422.
- Dodla, S. K., J. J. Wang, R. D. Delaune, and G. Breitenbeck. 2009. Carbon gas production under different electron acceptors in a freshwater marsh soil. *Chemosphere* 76:517–522.
- Downing, J. A., J. J. Cole, C. M. Duarte, J. J. Middelburg, J. M. Melack, Y. T. Prairie, P. Kortelainen, R. G. Striegl, W. H. McDowell, and L. J. Tranvik. 2012. Global abundance and size distribution of streams and rivers. *Inland Waters* 2:229–236.
- EPA. 2014. Facility level information on greenhouse gases tool. <http://ghgdata.epa.gov/>. Accessed December 1, 2014.
- Giblin, A. E., C. R. Tobias, B. Song, N. Weston, G. T. Banta, and V. H. Rivera-Monroy. 2013. The importance of dissimilatory nitrate reduction to ammonium (DNRA) in the nitrogen cycle of coastal ecosystems. *Oceanography* 26:124–131.
- Granberg, G., I. Sundh, B. H. Svensson, and M. Nilsson. 2001. Effects of temperature, and nitrogen and sulfur deposition, on methane emission from a boreal mire. *Ecology* 82:1982–1998.
- Harrison, M. D., P. M. Groffman, P. M. Mayer, and S. S. Kaushal. 2012. Microbial biomass and activity in geomorphic features in forested and urban restored and degraded streams. *Ecological Engineering* 38:1–10.
- Hedin, L. O., J. C. von Fischer, N. E. Ostrom, B. P. Kennedy, M. G. Brown, and G. P. Robertson. 1998. Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. *Ecology* 79:684–703.
- Holmes, M. E., J. P. Chanton, H. Bae, and A. Ogram. 2013. Effect of nutrient enrichment on $\delta^{13}\text{CH}_4$ and the methane production pathway in the Florida Everglades. *Journal of Geophysical Research Biogeosciences* 119:1267–1280.
- Klüber, H. D., and R. Conrad. 1998. Effects of nitrate, nitrite, NO and N₂O on methanogenesis and other redox processes in anoxic rice field soil. *FEMS Microbiology Ecology* 25:301–318.
- Knox, J. C. 1977. Human impacts on Wisconsin stream channels. *Annals of the Association of American Geographers* 67:323–342.
- Lassey, K. R. 2007. Livestock methane emission: From the individual grazing animal through national inventories to the global methane cycle. *Agricultural and Forest Meteorology* 142:120–132.
- Leece, S. A., P. A. Gares, and P. P. Pease. 2006. Drainage ditches as sediment sinks on the coastal plain of North Carolina. *Physical Geography* 27:447–463.
- Lisle, T. E., and S. Hilton. 1992. The volume of fine sediment in pools: an index of sediment supply in gravel-bed streams. *Water Resources Bulletin* 28:31–383.
- Liu, L., and T. L. Greaver. 2009. A review of nitrogen enrichment effects on three biogenic GHGs: the CO₂ sink may be largely offset by stimulated N₂O and CH₄ emission. *Ecology Letters* 12:1103–1117.
- Lovley, D. R., and M. J. Klug. 1986. Model for the distribution of sulfate reduction and methanogenesis in freshwater sediments. *Geochimica et Cosmochimica Acta* 50:11–18.
- Mayer, B., et al. 2002. Sources of nitrate in rivers draining sixteen watersheds in the northeastern U.S.: Isotopic constraints. *Biogeochemistry* 57:171–197.
- McCrackin, M. L., and J. J. Elser. 2011. Greenhouse gas dynamics in lakes receiving atmospheric nitrogen deposition. *Global Biogeochemical Cycles* 25: doi:10.1029/2010GB003897.
- Megonigal, J. P., M. E. Hines and P. T. Visscher. 2004. Anaerobic metabolism: linkages to trace gases and aerobic processes. Pages 317–424 in W. H. Schlesinger, editors. *Biogeochemistry*. Elsevier-Pergamon, Oxford, UK.
- Moens, N. L. W. 1957. Untersuchungen über den Schlamm und die Gasbildung in den Amsterdamer Grachten in den Jahre 1929 bis 1931. *Hydrobiologia* 9:13–24.
- Molongoski, J. J., and M. J. Klug. 1980. Anaerobic metabolism of particulate organic matter in the sediments of a hypereutrophic lake. *Freshwater Biology* 10:507–518.
- Morrice, J. A., C. N. Dahm, H. M. Valett, P. V. Unnikrishna, and M. E. Campana. 2000. Terminal electron accepting processes in the alluvial sediments of a headwater stream. *Journal of the North American Benthological Society* 19:593–608.
- National Agricultural Statistics Service. 2013. 2013 Wisconsin Agricultural Statistics. Madison, WI. http://www.nass.usda.gov/Statistics_by_State/Wisconsin/Publications/Annual_Statistical_Bulletin/bulletin2013_web.pdf
- Needelman, B. A., P. J. A. Kleinman, J. S. Strock, and A. L. Allen. 2007. Improved management of agricultural ditches for water quality protection: An overview. *Journal of Soil and Water Conservation* 62:171–178.
- Powers, S. M., R. A. Johnson, and E. H. Stanley. 2012. Nutrient retention and the problem of hydrologic disconnection in streams and wetlands. *Ecosystems* 15:435–449.
- Powers, S. M., J. P. Julian, M. W. Doyle, and E. H. Stanley. 2013. Retention and transport of nutrients in a mature agricultural impoundment. *Journal of Geophysical Research: Biogeosciences* 118:91–103.
- R Core Team. 2014. R: A language and environment for statistical computing. R Core Team. Vienna, Austria.
- Rajkumar, A. N., J. Barnes, R. Ramesh, R. Purvaja, and R. C. Upstill-Goddard. 2008. Methane and nitrous oxide fluxes in the polluted Adyar River and estuary, SE India. *Marine Pollution Bulletin* 56:2043–2051.
- Rawlins, B. G., B. Palumbo-Roe, D. C. Gooddy, F. Worrall, and H. Smith. 2014. A model of potential carbon dioxide efflux from surface water across England and Wales using headwater stream survey data and landscape predictors. *Biogeosciences* 11:1911–1925.
- Raymond, P. A., et al. 2013. Global carbon dioxide emissions from inland waters. *Nature* 503:355–359.
- Roy, R., and R. Conrad. 1999. Effect of methanogenic precursors (acetate, hydrogen, propionate) on the suppression of methane production by nitrate in anoxic rice field soil. *FEMS Microbiology Ecology* 28:49–61.
- Sanders, I. A., C. M. Heppell, J. A. Cotton, G. Wharton, A. G. Hildrew, E. J. Flowers, and M. Trimmer. 2007. Emission of methane from chalk streams has potential implications for agricultural practices. *Freshwater Biology* 52:1176–1186.
- Shelley, F., J. Grey, and M. Trimmer. 2014. Widespread methanotrophic primary production in lowland chalk rivers. *Proceedings of the Royal Society B: Biological Sciences* 281: doi:10.1098/rspb.2013.2854.
- Skalak, K., and J. Pizzuto. 2010. The distribution and residence time of suspended sediment stored within the channel margins of a gravel-bed river. *Earth Surface Processes and Landforms* 35:435–446.

- Smits, A. P., D. E. Schindler, and M. T. Brett. 2015. Geomorphology controls the trophic base of stream food webs in a boreal watershed. *Ecology* 96:1775–1782.
- Stanley, E. H., and M. W. Doyle. 2002. A geomorphic perspective on nutrient retention following dam removal. *BioScience* 52:693–701.
- Stanley, E. H., and J. T. Maxted. 2008. Changes in the dissolved nitrogen pool across land cover gradients in Wisconsin streams. *Ecological Applications* 18:1579–1590.
- Stanley, E.H., N.J. Casson, S.T. Christel, J.T. Crawford, L.C. Loken, and S.K. Oliver. *In press*. The ecology of methane in streams and rivers: patterns, controls, and global significance. *Ecological Monographs*. <http://onlinelibrary.wiley.com/doi/10.1890/15-1027/full>
- Trimble, S. W. 1999. Decreased rates of alluvial sediment storage in the Coon Creek basin, Wisconsin. *Science* 285:1244–1246.
- Trimmer, M., A. G. Hildrew, M. C. Jackson, J. L. Pretty, and J. Grey. 2009a. Evidence for the role of methane-derived carbon in a free-flowing, lowland river food web. *Limnology and Oceanography* 54:1541–1547.
- Trimmer, M., I. A. Sanders, and C. M. Heppell. 2009b. Carbon and nitrogen cycling in a vegetated lowland chalk river impacted by sediment. *Hydrological Processes* 23:2225–2238.
- Wallerstein, N. P., and C. R. Thorne. 2004. Influence of large woody debris on morphological evolution of incised, sand-bed channels. *Geomorphology* 57:53–73.
- West, W. E., J. J. Coloso, and S. E. Jones. 2012. Effects of algal and terrestrial carbon on methane production rates and methanogen community structure in a temperate lake sediment. *Freshwater Biology* 57:949–955.
- Wilkinson, B. H., and B. J. McElroy. 2007. The impact of humans on continental erosion and sedimentation. *GSA Bulletin* 119:140–156.
- Wilson, A. J., D. E. Walling and G. J. L. Leeks. 2004. In-channel storage of fine sediment in rivers of southwest England. Pages 291–299 *in*: V. Golosov, V. Belyaev, and D. E. Walling, editors. *Sediment Transfer through the Fluvial System*. IAHS Publication 288, Wallingford, England.
- Wood, P. J., and P. D. Armitage. 1997. Biological effects of fine sediment in the lotic environment. *Environmental Management* 21:203–217.