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DIVERGENT CONTROLS ON STREAM GREENHOUSE GAS CONCENTRATIONS
ACROSS A LAND USE GRADIENT

BY

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B.A. Chemistry, Environmental Studies, St. Olaf College, 2016

THESIS

Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirements for the Degree of

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in

Natural Resources: Soil and Water Resource Management

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ACROSS A LAND USE GRADIENT

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ABSTRACT

DIVERGENT CONTROLS ON STREAM GREENHOUSE GAS CONCENTRATIONS ACROSS A LAND USE GRADIENT

By

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University of New Hampshire

Inland waters can be significant sources of carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) to the atmosphere. However, considerable uncertainty remains in regional and global estimates of greenhouse gas (GHG) emissions from freshwater ecosystems, particularly streams. Controls on GHG production in fluvial ecosystems, such as water chemistry and sediment characteristics, are also poorly understood. The main objective of this study was to quantify spatial and temporal variability in GHG concentrations in 20 streams across a landscape with considerable variation in land use and land cover. Stream water was consistently supersaturated in CO₂, CH₄, and N₂O, suggesting that small streams are potentially large sources of GHGs to the atmosphere in this landscape. Results show that concentrations of dissolved CO₂, CH₄ and N₂O differed in their spatial and temporal patterns and in their relationship to stream chemistry. Both bivariate and multivariate analyses revealed a unique combination of predictor variables for each gas, suggesting variation in the landscape attributes and in-stream processes that control GHG concentrations. We also provide evidence suggesting that stream sediments play an important role in fluvial CH₄ dynamics. Developing an understanding of the factors controlling GHG dynamics in streams can help assess and predict how fluvial ecosystems will respond to changes in climate and land use and can be used to incorporate emissions from streams into regional and global GHG emission inventories.

CHAPTER 1: INTRODUCTION

Freshwater ecosystems can be important sources of greenhouse gases (GHGs) to the atmosphere due to their ability to actively process and transform terrestrial inputs of organic matter and other solutes (Battin et al., 2009; Cole et al., 2007). Although the terrestrial landscape is generally considered an important carbon (C) sink, with recent estimates suggesting a net uptake of 3.6 Pg C per year (Keenan & Williams, 2018), streams and rivers may provide sufficient emissions of GHGs to offset the terrestrial C sink. Streams are frequently supersaturated not only in carbon dioxide (CO₂), but also in methane (CH₄, Bastviken et al., 2011; Stanley et al., 2016) and nitrous oxide (N₂O, Audet et al., 2017; Baulch et al., 2011; Beaulieu et al., 2011; Schade et al., 2016; Wilcock & Sorrell, 2008).

Although streams are sources of all three greenhouse gases, recent flux estimates are largely focused on the outgassing of CO₂. One of the first estimates of outgassing of C from fluvial ecosystems by Cole et al. (2007) was an admittedly conservative 0.8 Pg C per year. Over the following decade, this estimate was revised upward to 1.8 Pg C per year (Raymond et al., 2013) and then again to 3.9 Pg C per year (Drake et al., 2018). Estimates of the global extent of rivers and streams (i.e. total surface area) were also recently revised upward (Allen & Pavelsky, 2018). Collectively, these revised estimates suggest that fluvial ecosystems play a larger role in fluxes of GHGs than is represented by current global carbon budgets. Although the magnitude of CH₄ and N₂O emissions is generally lower than that of CO₂, they are more effective at trapping heat and thus aggregate GHG emissions from streams and rivers have the potential to offset the terrestrial carbon sink.

In order to improve estimates of GHG emissions from fluvial ecosystems, it is important to develop a cohesive understanding of the multiple factors driving gas production.

Distinguishing controls on GHGs is complex given the interactive nature of C and nitrogen (N) cycling and the large number of biotic and abiotic factors that might control GHG concentrations. Broadly, CO₂ concentrations are controlled by the tradeoff between respiration and primary production, and the factors that fuel these processes (e.g. oxygen (O₂) and organic C availability; Cole et al., 2007). Methane concentrations are strongly controlled by redox conditions (Stanley et al., 2016), and N₂O concentrations are tightly linked to the factors that influence N cycling processes (e.g. O₂, nitrate (NO₃⁻) availability; Burgin & Hamilton, 2007; Quick et al., 2019). Various studies have begun to investigate controls on GHGs in fluvial ecosystems but results to date are varied and often contradictory. For example, many studies have observed the expected relationship between NO₃⁻ and N₂O concentrations with both nitrification and denitrification being evoked as controlling processes (Audet et al., 2017; Baulch et al., 2011; Beaulieu et al., 2011; Harrison & Matson, 2003; Schade et al., 2016; Turner et al., 2016). In contrast, controls on CH₄ dynamics are more uncertain. A study on drivers of GHGs in temperate forest streams found that organic C availability drives overall gas flux, but that concentrations of NO₃⁻ regulate the magnitude of N₂O and CH₄ production, with higher NO₃⁻ concentrations resulting in lower fluxes of CH₄ (Schade et al., 2016). However, no effect of NO₃⁻ on concentrations and fluxes of CH₄ was found in predominantly agricultural streams (Crawford & Stanley, 2016). This suggests that drivers and inhibitors of CH₄ production may not be universal across sites and biomes, and underscores the need to untangle the complicated relationships between C and N cycling processes that affect greenhouse gas dynamics (Stanley et al., 2016).

Given the uncertainty regarding controls on greenhouse gas dynamics in lotic ecosystems, our objective was to identify drivers of spatial and temporal variability in dissolved

greenhouse gas concentrations in small streams. Twenty study streams were selected across a land use gradient to provide a range of water chemistry, and environmental and physical conditions. Developing an improved understanding of greenhouse gas dynamics in fluvial ecosystems will allow us to better incorporate streams and rivers into global emissions inventories and into biogeochemical models of GHG production and emission.

CHAPTER 2: METHODS

Study area

The 20 streams chosen for study came from a database of streams within the Great Bay watershed, New Hampshire, U.S.A., compiled by the Water Quality Analysis Lab (WQAL) of the University of New Hampshire (UNH) (Figure 1). Site selection was based on land use information and previously collected water quality data. The twenty study streams encompassed a wide range of land use and land cover throughout southeastern New Hampshire (U.S.A) with sites dominated by forest (up to 99% cover), wetlands (up to 34% cover), agricultural activities (up to 51% cover), or urban development (up to 54% cover) representing a considerable range in concentrations of dissolved inorganic nitrogen ($0.005\text{--}3.72\text{ mg N L}^{-1}\text{ NO}_3^-$; $3\text{--}2000\text{ }\mu\text{g L}^{-1}\text{ NH}_4^+$, Table 1).

Water chemistry and dissolved gases

We collected surface water samples monthly at each stream. Water chemistry samples were collected in acid-washed syringes and field filtered through pre-combusted glass fiber filters ($0.7\text{ }\mu\text{m}$; Whatman GF/F) into 60 mL acid washed HDPE bottles and amber vials. Samples were put on ice until returned to the lab and then frozen or refrigerated for subsequent analysis. We analyzed each sample for concentrations of NO_3^- , ammonium (NH_4^+), total dissolved nitrogen (TDN), dissolved organic carbon (DOC), soluble reactive phosphorus (SRP), specific ultraviolet absorbance (SUVA_{254}), and major cations and anions. Dissolved organic nitrogen (DON) concentrations were determined from the difference of TDN and dissolved inorganic nitrogen concentrations ($\text{DIN} = \text{NO}_3^- + \text{NH}_4^+$). Analyses were conducted in the WQAL at UNH. Samples were analyzed for TDN and DOC using high temperature catalytic oxidation (Shimadzu TOC-L with a TNM-1 nitrogen analyzer), for NO_3^- and major anions and cations using ion

chromatography with suppressed conductivity detection (Anions/Cations Dionex ICS-1000), for NH_4^+ using automated colorimetry (Unity Scientific SmartChem 200 discrete analyzer), and for soluble reactive phosphorus (SRP) using automated colorimetry (AQ2 discrete analyzer). Ultraviolet absorbance was measured using high-performance liquid chromatography with a photo diode array detector (Shimadzu SPD-20A) that scanned from 200 to 700 nm in 1-nm intervals. The absorbance at wavelength of 254 nm was used to determine specific ultra-violet absorbance (SUVA, $\text{L mg}^{-1} \text{C}^{-1} \text{m}^{-1}$). SUVA was determined following the methods of Weishaar et al. (2003). Humification index (HIX), which describes the extent of humification of dissolved organic matter (DOM), was determined as the ratio between the area under the 435-480 nm emission spectra peak and the sum of the peak areas between 330-345 and 435-490 nm (Ohno, 2002). Fluorescence index (FI) is used to help identify sources (allochthonous vs. autochthonous) of DOM (McKnight et al., 2001). Fluorescence index was determined as the ratio of 470 to 520 nm fluorescence intensities at an excitation of 370 nm. Log transformed absorption spectra in the ranges of 275-295 and 350-400 nm were fit non-linearly to an exponential function to determine spectral slope (S ; Helms et al., 2008). Slope ratio (S_R) was calculated as the ratio of slopes for the 275-295 and 350-400 nm ranges. Slope ratio provides insights into molecular weight and aromaticity of DOM (Helms et al., 2008). Handheld measurements of dissolved O_2 (percent saturation), specific conductance ($\mu\text{S cm}^{-1}$), pH, water temperature ($^{\circ}\text{C}$), and turbidity (FNU) were recorded at the time of collection using a YSI multiparameter probe (YSI ProDSS, Yellow Spring, OH).

We collected dissolved gas samples in triplicate at each stream using acid-washed 60mL polypropylene syringes fitted with two-way stopcocks. Syringes were filled to 30mL with stream water, cleared of air bubbles, and emptied and refilled to 30 mL underwater (again clearing air

bubbles). Syringes were returned to the WQAL where 30 mL of helium was introduced to each sample. Upon introduction of helium, syringes were shaken for 5 minutes to equilibrate gases between the water and headspace. The 30 mL equilibrated head space of each syringe was then injected into 20 mL evacuated, airtight vials. Gas samples were analyzed for concentrations of CO₂, CH₄, and N₂O using a Shimadzu GC-2014 gas chromatograph. A thermal conductivity detector (TCD) was used to detect CO₂, a flame ion detector (FID) to detect CH₄, and an electron capture detector (ECD) to detect N₂O. Standards of CO₂ (1.8% error), CH₄ (1.7% error), and N₂O (2.2% error), are analyzed at the beginning of each run and after every 12 samples. Headspace gas concentrations (in ppmv) were converted to the partial pressure of dissolved gas in the initial water sample (in μ atm) using the Bunsen Solubility Coefficient following the methods of Mulholland et al. (2004).

Porewater samples

At a subset of sites (n = 9) we collected sediment porewater and gas samples using a porewater extracting device. The sampler is made of 3.175 mm o.d. stainless-steel tubing with fine holes at the sampling end which allows porewater to enter the sampler. The top of the sampler is fitted with a two-way stopcock. The sampling end of the device was inserted into the sediment to the point of refusal (and at multiple depths at sites with deep sediments), and porewater samples were extracted using a syringe. Porewater samples were collected by attaching an acid-washed 60 mL syringe to the two-way stopcock and pulling the syringe plunger to extract the sample. Samples were analyzed for the same analytes as the surface water and dissolved gas samples.

Sediment analyses

Channel and sediment attributes were characterized at the main sampling location, and at an additional cross section 5-10 m upstream from the main location. Estimates of the depth of fine sediments overlying the coarse layer were made by measuring depth to refusal following the methods of Lisle and Hilton (1992). Five measurements were taken at each cross section.

Sediment samples were collected at the primary sampling location and at a location ~20 m upstream. Sediment samples were dried at 60°C for several days. Dried samples were sieved (1 mm) to remove larger rocks and pebbles. Remaining sediment was finely ground using a mortar and pestle in preparation for elemental analysis. Samples were run for weight percent carbon and nitrogen using a Perkin Elmer 2400 Series II CHNS/O analyzer. C:N ratios were determined using the mass of each element.

Statistical analyses

Data that exhibited high levels of skewness, kurtosis, and failed the Shapiro-Wilk tests for assumptions of normality were normalized using logarithmic or square root transformations. We assessed bivariate relationships between dissolved gas concentrations and metrics of stream chemistry using linear regression analysis with each sampling month at each stream treated as a separate data point. We then used partial least squares (PLS) analysis to identify multivariate relationships between gas concentrations and predictor variables, given the ability for PLS to account for multicollinearity among predictor variables (Carrascal et al., 2009). PLS provides variable importance on projection (VIP) scores that represent each variable's influence on the model. A VIP score threshold of 0.8 is generally recommended to identify those variables which exert strong influence on the model, with larger VIP scores having a greater influence on the model (Carrascal et al., 2009). PLS models were created for CO₂, CH₄, and N₂O with all metrics

of stream chemistry and land-use entered into the model (see Table 1). The top five predictor variables, as ranked by VIP score, were then used in linear mixed-effect models (LMMs) to assess how well these most influential variables predict gas concentrations when considered together while also accounting for heterogeneity among sites. Response variables CO₂, CH₄, and N₂O were analyzed separately as a function of the top five predictor variables for each respective gas as fixed effects, with site as a random effect. Linear mixed-effects models were created using the package lme4 in R (Bates et al., 2015). Stepwise multiple regression was used to determine which predictive factors, delineated through PLS VIP scores, significantly influenced measured gas concentrations. Variables from each model were excluded in a backward direction when the AIC values of the alternative models were lower, and the variables involved were significant (based on analysis of variance). We used the MuMIn package (<https://cran.r-project.org/web/packages/MuMIn/MuMIn.pdf>) to determine the amount of variance (R^2) explained by fixed effects alone (marginal, R^2_m) and together with the random effect (conditional, R^2_c) (Nakagawa & Schielzeth, 2013). The level of significance for all analyses was 0.05. All statistical analyses, other than the LMMs, were performed using JMP (JMP®, Version 14. SAS Institute Inc., Cary, NC, 1989-2019).

CHAPTER 3: RESULTS

Water chemistry and dissolved gases

Concentrations of dissolved gases were highly variable across our 20 sites. Dissolved CH₄ concentrations ranged from < 1 to > 300 μatm (mean = 15.41 μatm) across sites over the 12 sampling months, with dissolved N₂O concentrations ranging from < 0.2 to > 19 μatm (mean = 1.23 μatm), and dissolved CO₂ concentrations ranging from ~900 to > 14,000 μatm (mean = 3772 μatm , Table 2). All streams were consistently supersaturated in CO₂, with the majority of streams also supersaturated in both CH₄ and N₂O across sampling months (Table 2).

Carbon dioxide, N₂O, and CH₄ concentrations exhibited temporal variability yet differed in their seasonal patterns (Figure 2, Table 2). Concentrations of CO₂ showed large peaks in January and during the summer (Figure 3). Nitrous oxide concentrations peaked in January, followed by two spikes in late spring and fall consistent with periods of elevated NO₃⁻ concentrations (Figure 3). Peak CH₄ concentrations occurred in the summer, during conditions of lower flows and higher temperatures (Figure 3).

The 20 study streams were variable in water chemistry and other watershed characteristics (Table 1). Streams ranged from nutrient-poor (0.005 mg NO₃-N L⁻¹) to relatively enriched (3.72 mg NO₃-N L⁻¹) and spanned a range of carbon availability (DOC range = 1.08 to 26.96 mg C L⁻¹; mean 6.7 mg C L⁻¹, Table 1). Optical properties of dissolved organic matter (DOM) generally showed a small range of variability across study streams (e.g. FI range = 1.24 – 1.62; mean 1.36, Table 1). Sediment characteristics (depth of fine sediments and C and N content) were variable across study sites. Average depth to refusal was shallow (10.9 cm; range = 0-38 cm) and average sediment C:N ratio was 18.3 (range = 2.1-38.8, Table 1).

Drivers of greenhouse gas concentrations

Simple linear regression analyses revealed significant relationships between both N₂O and CO₂ concentrations and individual solutes, but we found no significant bivariate relationships between any predictor variables and CH₄ concentrations. Across sites, CO₂ concentrations showed a significant, negative relationship with dissolved O₂ (% saturation, $r^2 = 0.70$, $p < 0.0001$, Figure 4). Dissolved N₂O was positively related to NO₃⁻ concentrations ($r^2 = 0.34$, $p < 0.0001$, Figure 5). We also found a significant, positive relationship between potassium (K⁺) and N₂O ($r^2 = 0.34$, $p < 0.0001$, Figure 6).

The partial least squares analysis for CO₂ identified 11 predictor variables with VIP scores ≥ 0.8 , with the top five being DO (% saturation), DOC and NH₄⁺ concentrations, FI, and percent forest (Table 3). The N₂O PLS model resulted in 14 predictor variables above the 0.8 threshold. Percent agriculture, NO₃⁻ and K⁺ concentrations, temperature, and percent forest were the top five predictors influencing the N₂O model (Table 3). Partial least squares analysis for CH₄ identified 15 predictor variables with the top five being percent agriculture, percent developed, NH₄⁺ concentration, specific conductance, and percent forest (Table 3). For all linear mixed-effects models, site was an important factor when considering the influence of the fixed effects, as shown by the increase in the amount of variation explained (R^2_c) when including site as a random effect. The results of the LMM for CO₂ indicate that three predictors (DO, DOC, and FI) explain 81% of the variance. Concentrations of DOC and FI positively influence CO₂ concentrations and DO% has a negative relationship with CO₂ concentrations (Figure 4). Model results for N₂O identified that NO₃⁻, temperature, and percent agriculture account for 88% of the variability in N₂O concentrations. Beta values indicate a positive influence of NO₃⁻ concentrations and % agriculture, while temperature shows a negative relationship with N₂O

concentrations (Table 4). Land use, % agriculture and forest, accounted for 76% of the variance in CH₄ concentrations when site was included as a random effect. Both % agriculture and % forest were negatively related to CH₄ concentrations (Table 4).

Sediment porewater

Across sites, CO₂ concentrations were consistently higher in the sediments (mean = 16,501 μ atm, range ~1,500-80,000 μ atm) than the surface water (mean ~ 3000 μ atm, range ~1000-7000 μ atm), while N₂O concentrations were on average higher in the surface water (mean = 0.95 μ atm, range 0.23-4 μ atm) than the sediments (mean = 0.70 μ atm, range ~0-5 μ atm; Figure 7). Methane concentrations were variable by site, with some having larger concentrations in the surface water (mean = 24, range 0.29-89 μ atm) and others having higher concentrations in the sediment porewater (mean = 712 μ atm, range ~1-9000 μ atm Figure 7).

Surface water to porewater ratios for each gas allow us to compare the magnitude of gas concentrations between the sediments and surface water. Ratios greater than one indicate higher concentrations in the surface water relative to the sediments, and those less than one indicate higher concentrations in the sediments. The mean ratio for CO₂ was 0.34 ± 0.29 , 4.0 ± 5.3 for N₂O, and 4.7 ± 9.1 for CH₄. Across sites, porewater CH₄ concentrations were positively correlated to the ratio of NH₄:NO₃ (Figure 9).

CHAPTER 4: DISCUSSION

Our results confirm that streams are likely to be considerable sources of greenhouse gases to the atmosphere, as they are frequently supersaturated relative to atmospheric concentrations. We found that no single, measured predictor variable was sufficient to estimate collective greenhouse gas concentrations from streams. Although our results corroborate previous findings that NO_3^- concentrations drive N_2O production (e.g. Baulch et al., 2011; Beaulieu et al., 2011), other factors (temperature, % agriculture, K^+ concentrations) provide additional explanatory power in characterizing temporal and spatial variability in N_2O concentrations. Our results support the growing body of literature suggesting that CH_4 concentrations are extremely variable in space and time and may be highly dependent on local controls (Crawford et al., 2017; Stanley et al., 2016). The particularly strong vertical gradients we observed in CH_4 concentrations with depth in the stream sediments suggests that hyporheic conditions may be particularly important in controlling CH_4 concentrations in stream water.

Streams as sources of GHGs

Our measured gas concentrations are comparable to previously reported values across ecosystems. Mean dissolved CO_2 concentrations ($2021 \mu\text{g C L}^{-1}$) and consistent supersaturation in our study streams (280-1903%, mean = 920%) are similar to what has been shown in previous studies from the midwestern USA (mean $1713 \mu\text{g C L}^{-1}$; Crawford & Stanley, 2016) and higher than those reported for interior Alaska (mean = $759 \mu\text{g C L}^{-1}$; Crawford et al., 2013). Nitrous oxide concentrations in our study, which averaged $0.77 \mu\text{g N L}^{-1}$, were very similar to those reported in a study of streams draining a predominantly agricultural landscape in the midwestern USA (range $0.15\text{-}5.13 \mu\text{g N L}^{-1}$, mean $0.81 \mu\text{g N L}^{-1}$; Beaulieu et al., 2008) and slightly lower than those reported for different sites in an agricultural catchment in Sweden (range $0.16\text{-}10.3 \mu\text{g}$

N L⁻¹, mean 2.7 µg N L⁻¹; Audet et al., 2017). Many previous studies on N₂O production and emissions from headwater streams have been conducted in predominantly agricultural settings and have shown that these heavily impacted systems can be considerable sources of N₂O (e.g. Audet et al., 2017; Baulch et al., 2011; Beaulieu et al., 2008; Wilcock & Sorrell, 2008). Our data thus provide evidence that even streams draining temperate and forested catchments with modest levels of agriculture (averaging 12% among our study watersheds; Table 1) and relatively low stream water N concentrations can produce considerable amounts of dissolved N₂O. Methane concentrations in our 20 streams (mean = 8.3 µg C L⁻¹) fall within the broad range, though slightly less than the average, of global CH₄ concentrations compiled by Stanley et al. (2016), which encompasses > 900 sites across multiple biomes (range 0-4636 µg C L⁻¹, mean = 16 µg C L⁻¹). The majority of our streams were supersaturated with CH₄ (59-2,876%, mean = 831%), consistent with growing evidence that fluvial ecosystems are generally supersaturated and thus are sources of CH₄ to the atmosphere (Stanley et al., 2016).

Temporal variability in stream GHG concentrations

The temporal variability in concentrations of CO₂, N₂O, and CH₄ provides insight into potential controlling mechanisms across our study watersheds. Peaks in dissolved CO₂ follow periods of increased allochthonous inputs of organic matter, namely leaf litter in the fall, and snowmelt runoff in the spring, suggesting that CO₂ concentrations are driven largely by net heterotrophy (Borges et al., 2015; Cole et al., 2007; Figure 3). These winter and spring peaks are also concomitant with periods of high CH₄ and N₂O, respectively (Figure 3). The increase in N₂O concentrations that we observed in winter suggests that this may be a period of increased nitrification, when oxygen levels were near saturation and NH₄⁺ concentrations (mean > 70 µg N L⁻¹) were higher than other times of the year. In contrast, the spikes in N₂O in the summer and

fall parallel pulses of NO_3^- and occur at times of lower O_2 saturation, which suggests that denitrification might be the dominant pathway for production of N_2O at these times. These temporal patterns in N_2O concentrations suggest that there may be a seasonal switch in the primary N-cycling processes that drive concentrations of N_2O . Our temporal patterns are consistent with other studies that observed increases in N_2O production and emission during the winter (Baulch et al., 2011; Beaulieu et al., 2008, 2009); however, others found peak N_2O concentrations in late spring and summer (Audet et al., 2017; Borges et al., 2018), suggesting that drivers and pathways of N_2O production may differ across systems, further complicating management strategies that aim to remove excess N while avoiding gaseous loss as N_2O (Davis et al., 2019).

Highest CH_4 concentrations occur in August, when flow and oxygen levels are low, NO_3^- and sulfate (SO_4^{2-}) concentrations are at their minimum, and water temperatures are high (Figure 3). The combination of the depletion of more favorable electron acceptors (NO_3^- and SO_4^{2-}), higher temperatures and lower oxygen availability provide conditions suitable for methanogenesis. Although some previous studies have also observed peak CH_4 concentrations in summer and lower concentrations in winter (Borges et al., 2018; Dinsmore et al., 2013), others have observed no clear seasonal pattern (Dawson et al., 2004). The lack of a consistent seasonal pattern across temperate zone streams suggests that no single factor such as temperature or oxygen availability is consistently related to CH_4 concentrations (Stanley et al., 2016). The summer peak in CH_4 concentrations also provides evidence that denitrification is the source of summer N_2O peaks, given the thermodynamic favorability of denitrification over methanogenesis.

Drivers of stream GHG concentrations

Each gas exhibited unique bivariate and multivariate controls, suggesting that future models will require multiple predictors to estimate all three greenhouse gases. The strong negative relationship between dissolved oxygen and CO₂, identified through bivariate analysis, is indicative of the tradeoff between respiration and primary production, which may be happening *in situ* or in the surrounding riparian soils (Borges et al., 2015; Hotchkiss et al., 2015; Figure 4). Although our data do not allow us to tease apart whether metabolism is occurring *in situ* or on the landscape, recent work has shown that the origin of CO₂ in headwater streams is often dominated by the lateral flux of CO₂ from the landscape (Campeau et al., 2019).

The positive relationship between N₂O and NO₃⁻ is consistent with many previous studies (Audet et al., 2017; Baulch et al., 2011; Beaulieu et al., 2011; Harrison & Matson, 2003; Schade et al., 2016; Turner et al., 2016), supporting the importance of the role of denitrification as a source of N₂O. Although a positive relationship between NO₃⁻ and N₂O concentrations is generally attributed to denitrification, it could also be interpreted as the accumulation of the products of nitrification (Peterson et al., 2001). Thus, future work should investigate the proportion of N₂O concentrations coming from denitrification versus nitrification. The unexpected positive relationship between K⁺ and N₂O concentrations has, to our knowledge, not been observed in other studies (Figure 6). While we cannot dismiss the possibility that this correlation is simply a byproduct of other in-stream processes and changing environmental conditions which could influence concentration of K⁺ (e.g. pH levels, cation exchange), there are lines of evidence that suggest that K⁺ may play an active role in enhancing N₂O production. Potassium was shown to be an effective catalyst in the reduction of NO to N₂O and has also been found to increase N reductase enzyme activity in plants; the same family of enzymes which are

involved in catalyzing the sequential steps of denitrification (Kapteijn et al., 1984; Khanna-Chopra et al., 1980; Villora et al., 2003). Given that our data do not allow us to untangle the mechanism by which K^+ is influencing N_2O concentrations, the relationship between K^+ and N_2O should be interpreted with caution, and we hope future work will provide insight into interactions between K^+ concentrations and N cycling processes.

Contrasting our results for CO_2 and N_2O , the variability in CH_4 concentrations across sites was unexplained by any single predictor variable. While others have found a positive relationship between DOC and CH_4 , suggesting that C availability drives CH_4 production (Crawford et al., 2016; Schade et al., 2016), our data show no clear influence of DOC on CH_4 dynamics. We also expected elevated NO_3^- concentrations to inhibit CH_4 production, due to either thermodynamic favorability or toxicity of denitrification byproducts (Bodelier & Steenbergh, 2014), but no distinct relationship could be established between NO_3^- and CH_4 . Given the contrasting results among various studies, further research is needed to disentangle the relationship between CH_4 production and NO_3^- concentrations (Crawford & Stanley, 2016; Schade et al., 2016) as well as to derive predictors of spatial and temporal variability in CH_4 concentrations.

Our multivariate approach using linear mixed-effects models allows us to explore relationships between water chemistry and land use (fixed effects) and gas concentrations, while also accounting for differences among sites (random effect). For all three gases, including site as a random effect improves the variance explained by the LMMs by 30-44% (Table 4). The increase in explained variation for each model, resulting from the inclusion of site as a random effect, indicates that variability in unmeasured site-level characteristics plays an important role in

gas responses. Characteristics influencing evasion rates and connectivity to the surrounding landscape are possible factors influencing site-level variability.

Collectively, our results suggest that the quantity of DOC available for respiration is more important than the composition. The negative relationship with DO% shown in both bivariate and multivariate analyses, along with the positive influence of DOC and FI, shows that CO₂ dynamics are driven by net heterotrophy (Borges et al., 2015; Cole et al., 2007; Table 4, Figure 4). The influence of DOC concentrations and FI indicates that both the concentration and composition of DOC affect CO₂ concentrations. Values of FI ranging from 1.2-1.5 indicate allochthonous terrestrially sourced DOM, and values between 1.7-2.0 indicate autochthonous DOM (McKnight et al., 2001). Although we see a positive relationship, indicating higher FI values predict higher CO₂ concentrations, our small range of FI values fall within the range of allochthonous sources, suggesting a strong landscape influence on CO₂ dynamics (Tables 1, 4).

The positive relationship between both % agriculture and NO₃⁻ concentrations suggests that land use is an important driver of N₂O concentrations and is consistent with previous studies (Audet et al., 2017; Beaulieu et al., 2009; Schade et al., 2016). Although we generally expect a positive influence between temperature and respiration byproducts, the negative influence of temperature is consistent with our temporal patterns of peak N₂O in the winter months.

We found no strong relationships between any of the expected controls on surface water CH₄ concentrations (e.g. DO%, C availability, NO₃⁻) suggesting that CH₄ dynamics are difficult to predict, and that controls on CH₄ concentrations are not consistent across sites, in agreement with the lack of predominant global-scale drivers observed by Stanley et al. (2016).

Geomorphological characteristics are thought to be important drivers of methanogenesis (Stanley et al., 2016), however, we found no relationship between sediment characteristics and surface

water CH₄ concentrations among our 20 study sites. The only variables that significantly influenced the LMM for CH₄ were % agriculture (-) and % forest (-) (Table 4). Streams draining agricultural landscapes are often associated with elevated concentrations of N and other nutrients. Thus, the negative relationship between % agriculture and CH₄ may be due to the presence of excess nutrients that should inhibit production of methane. The negative relationship with % forest suggests that as watersheds become more developed, higher amounts of CH₄ can be expected. However, the relationships to land use do not allow us to assign specific drivers or inhibitors of CH₄.

Porewater as an indicator of CH₄ production

Sediment porewater data provide evidence that variability in stream sediments may play an important role in controlling CH₄ production. Our range of surface water to porewater ratios for CH₄ shows that while some sites have higher concentrations in the surface water, many have considerably higher CH₄ concentrations in the deeper sediments (Figure 7). To explore this potential relationship, we developed a depth profile from one of our study sites which shows the influence of redox conditions similar to what we expected to see in the surface water (Figure 8). Moving from the surface water (depth = 0 cm) to the deeper sediments, concentrations of NH₄⁺ and CH₄ increase. In contrast to the increase in NH₄⁺ and CH₄, our depth profile shows a general decline in concentrations of NO₃⁻, N₂O, and SO₄²⁻ (Figure 8). The concurrent depletion of NO₃⁻ and N₂O suggests that denitrification becomes limited by NO₃⁻ availability. And although our sampling technique did not allow for measurements of oxygen at depth, increases in NH₄⁺ with concurrent declines in NO₃⁻ can serve as an indicator of the extent of reducing conditions. The depletion of oxygen and other more thermodynamically favorable terminal electron acceptors (NO₃⁻ and SO₄²⁻) creates conditions suitable for methanogenesis. In addition to the porewater

depth profile (which could only be explored at one site), CH₄ concentrations were also predicted by porewater NH₄:NO₃ ratios ($r^2 = 0.82$, $p < 0.0001$), with increased CH₄ concentrations at higher ratios (Figure 9).

Results from our porewater analysis suggest spatial segregation of biogeochemical processes (e.g. denitrification and methanogenesis) due to differences in solute, energy, and oxygen availability between the surface water and varying hyporheic depths, as has been proposed in previous studies (Crawford & Stanley, 2016). This could explain why relatively high CH₄ concentrations and fluxes are observed in streams even when inhibitory conditions exist in the surface water (e.g. high NO₃⁻ concentrations). These porewater results also explain the lack of expected predictive relationships with between CH₄ and other surface water measurements.

CHAPTER 5: CONCLUSION

We propose a conceptual framework for small streams in which N_2O production is largely occurring in the surficial sediments, CH_4 production happening in deep sediments, while CO_2 concentrations are largely influenced by the surrounding landscape (Figure 10). The porewater depth profile in combination with the relationship between porewater CH_4 and $\text{NH}_4\text{:NO}_3$ ratios confirms that the more reduced environment of the porewater and depletion of NO_3^- in the deeper sediments creates hot-spots of CH_4 generation. This supports the over-arching hypothesis of strong thermodynamic controls on CH_4 in the sediments and is consistent with the lack of significant relationships within the surface water-based predictor variables.

Our results suggest that CO_2 concentrations are largely a result of metabolism, which may be happening in-stream or in the surrounding terrestrial landscape. Optical DOM data suggests that stream DOC is derived from an allochthonous source, highlighting the importance of the surrounding landscape in fueling CO_2 dynamics. Additionally, many other studies have highlighted the importance of connectivity to the terrestrial landscape, as well as landscape features, in driving CO_2 dynamics in small streams (Campeau et al., 2019; Hotchkiss et al., 2015; Rocher-Ros et al., 2019). Our results corroborate previous work highlighting the importance of benthic-hyporheic N_2O production in small streams (Marzadri et al., 2017), and identify the surficial sediments as particularly important, given the relationships to water chemistry in the overlying surface water. Lastly, the lack of expected controls on CH_4 in the surface water yet tight thermodynamic controls observed in the porewater suggest that CH_4 production dominates as we move deeper into the hyporheic zone.

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TABLES

Table 1. Stream and watershed characteristics across the 20 study sites.

	Mean	Minimum	Maximum
NO ₃ ⁻ (mg N L ⁻¹)	0.52	0.005	3.72
DOC (mg C L ⁻¹)	6.69	1.08	26.96
TDN (mg N L ⁻¹)	0.79	0.03	3.83
NH ₄ ⁺ (µg N L ⁻¹)	45.80	2.50	2000
DON (mg N L ⁻¹)	0.24	0.00	1.58
Cl (mg Cl L ⁻¹)	92.24	2.07	397
SO ₄ ²⁻ (mg S L ⁻¹)	2.69	0.02	7.73
Acetate (mg L ⁻¹)	0.12	0.03	0.69
PO ₄ ³⁻ (µg P L ⁻¹)	15.42	0.50	337.54
Na (mg Na L ⁻¹)	55.57	1.67	321.83
K (mg K L ⁻¹)	2.86	0.01	11.14
Mg (mg Mg L ⁻¹)	4.10	0.06	14.06
Ca (mg Ca L ⁻¹)	18.72	0.10	64.31
pH	6.7	3.8	8.6
Specific Conductance (µs cm ⁻¹)	394.9	17.2	1658.0
Dissolved O (% saturation)	85.0	18.8	108.3
Temperature (°C)	8.9	-0.1	25.5
SUVA	3.90	0.01	5.97
FI	1.36	1.24	1.62
HIX	0.90	0.32	0.99
Slope Ratio	0.86	0.62	2.01
% Developed	21%	0%	54%
% Agriculture	12%	0%	51%
% Forest	54%	31%	99%
% Wetland	7%	0%	34%
% Impervious	17%	1%	33%
Depth to refusal (cm)	10.9	0.0	38.0
Sediment %C	1.0%	0.2%	5.6%
Sediment %N	0.1%	0.0%	0.3%
Sediment C:N	18.3	2.1	38.8

Table 2. Mean dissolved greenhouse gases at each site. Units are μatm . Standard deviations in parentheses.

Site	CH ₄	N ₂ O	CO ₂
BDC	5.87 (2.78)	8.97 (4.74)	4994 (1976)
BNR	1.1 (0.91)	0.76 (0.16)	1146 (105)
BRB	27.19 (20.28)	0.66 (0.29)	7802 (1856)
CSB02	8.11 (5.51)	3.23 (1.27)	6617 (1788)
DCF03	4.88 (2.37)	0.33 (0.1)	1700 (455)
FSB	3.47 (1.57)	0.57 (0.26)	2327 (632)
GRBK	18.94 (12.48)	0.55 (0.27)	4709 (1552)
HVH	47.69 (86.73)	0.39 (0.07)	4267 (2038)
JMY	23.43 (24.45)	0.7 (0.15)	5418 (1678)
MLB01	53.79 (20.31)	0.86 (0.2)	3886 (743)
PB02.7	17.33 (5.79)	0.48 (0.13)	2604 (494)
PIK	36.72 (15.54)	0.64 (0.13)	2322 (424)
PKB	4.19 (1.94)	0.83 (0.54)	3339 (998)
PST	14.93 (6.67)	1.04 (0.31)	3942 (1152)
RMB04	6.28 (2.21)	0.48 (0.28)	2299 (893)
SBM0.2	1.12 (1.02)	0.35 (0.14)	5182 (4403)
TPB	9.15 (5.18)	0.4 (0.18)	1736 (387)
TWB	5.3 (2.72)	2.08 (0.76)	3594 (873)
WEB	17.99 (6.28)	0.42 (0.07)	5037 (1384)
WHB01	3.42 (2.13)	0.83 (0.36)	2552 (2344)
Mean	15.41	1.23	3771
Atmospheric Concentration	1.87	0.33	410

Table 3. Variable importance on projection (VIP) scores (≥ 0.8) of predictor variables for carbon dioxide (CO₂), nitrous oxide (N₂O), and methane (CH₄) via partial least squares (PLS) analysis. Higher VIP scores represent a greater influence on the model.

Predictor	CO ₂	N ₂ O	CH ₄
DO (%)	2.84*	—	1.02
DOC (mg C L ⁻¹)	1.44*	—	0.91
% Forest	1.06*	1.32*	1.27*
NH ₄ ⁺ (μg N L ⁻¹)	1.04*	0.88	1.44*
FI	1.02*	—	—
log PO ₄	1.02	1.18	0.89
pH	1.02	0.99	0.95
% Wetland	0.98	—	—
K ⁺ (mg K L ⁻¹)	0.93	1.58*	1.08
DON	0.87	—	—
SO ₄ (mg S/L)	0.86	1.16	0.99
% Agriculture	—	1.85*	1.68*
NO ₃ ⁻ (mg N L ⁻¹)	—	1.65*	0.86
Temp (°C)	—	1.26*	0.94
% Developed	—	0.92	1.57*
% N	—	0.89	—
C:N	—	0.86	—
Spec Cond	—	0.83	1.32*
% C	—	0.82	—
Slope ratio	—	—	0.83
HIX	—	—	0.81
Number of factors	4	13	5
R ² X	50.4	82.8	57.81
R ² Y	77.8	82.2	54.49

*Asterisks and bold-face denote top five VIP scores for each model (see Table 4).

Table 4. Results from linear mixed-effects models (LMMs) with fixed effects and the random effect of site (not shown) for dissolved gas concentrations. The fixed effects included in each initial model were selected based on the five highest variable importance on projection (VIP) scores as identified through partial least squares (see Table 3). Fixed effects that did not significantly improve the model were dropped through pairwise deletion. β values provide a measure of how strongly, and in which direction, each predictor influences the model. Akaike information criterion (AIC) values estimate the relative quality of each model, with lower values indicating a better model. Marginal coefficient of determination (R^2_m) shows variation explained by fixed effects alone, while the conditional coefficient of determination (R^2_c) accounts for variation explained by both fixed and random effects.

Response	Initial Model	Final Model	β_{final}	AIC _{initial}	AIC _{final}	R^2_{final}	
						R^2_m	R^2_c
CO ₂ (μatm)	DO (%)						
	DOC (mg C L ⁻¹)	DO (%)	-0.01				
	FI	DOC (mg C L ⁻¹)	0.15	-173.7	-279.0	0.51	0.81
	% Forest	FI	0.40				
N ₂ O (μatm)	NH ₄ ($\mu\text{g N L}^{-1}$)						
	NO ₃ ⁻ (mg N L ⁻¹)						
	Temperature (°C)	NO ₃ ⁻ (mg N L ⁻¹)	0.28				
	% Agriculture	Temperature (°C)	-0.05	-0.8	-192.5	0.54	0.88
	K ⁺ (mg K L ⁻¹)	% Agriculture	1.56				
CH ₄ (μatm)	% Forest						
	% Agriculture	% Agriculture	-2.27	276.2	136.2	0.32	0.76
	% Developed	% Forest	-1.71				
	Spec Cond ($\mu\text{S cm}^{-1}$)						
	NH ₄ ($\mu\text{g N L}^{-1}$)						

FIGURES

Figure 1. Map of study streams located in southeastern New Hampshire.

Figure 2. Boxplot panels representing CO_2 (A), N_2O (B, log scale), and CH_4 (C) concentrations across 12 months at 20 sites. Ordered by decreasing N_2O concentrations.

Figure 3. Mean CO₂ (A), N₂O (B), CH₄ (C), and concentrations across 20 sites over time. The dashed line represents standard error.

Figure 4. Linear regression between CO_2 and dissolved oxygen (% saturation) across sites ($r^2 = 0.70$, $p < 0.0001$).

Figure 5. Linear regression between N_2O (log transformed) and NO_3^- (square root transformed) concentrations across sites ($r^2 = 0.34$, $p < 0.0001$).

Figure 6. Linear regression between N_2O (log transformed) and K^+ (square root transformed) concentrations across sites ($r^2 = 0.34$, $p < 0.0001$).

Figure 7. Ratio of surface water to porewater concentrations for each gas ($n_{\text{sites}} = 9$, for CO_2 and CH_4 $n_{\text{samples}} = 25$, for N_2O $n_{\text{samples}} = 23$). Values above one indicate gas concentrations are higher in the surface water relative to the porewater and values below one indicate higher concentrations in the sediment porewater.

Figure 8. Depth profile of sediment porewater and dissolved gas concentrations at one site (PIK). Samples at depth 0 cm represent surface water samples. Greater depths represent sediment depth at which samples were extracted.

Figure 9. Linear regression between porewater CH_4 concentrations and porewater $\text{NH}_4:\text{NO}_3$ ratios ($r^2 = 0.82$, $p < 0.0001$; $n_{\text{sites}} = 9$). Lower ratios indicate a more oxidized environment (more NO_3^-) while higher ratios indicate an environment more reduced (more NH_4^+).

Figure 10. Conceptual framework for small streams. N_2O production is largely occurring in the surficial sediments, CH_4 production happening in deep sediments, while CO_2 concentrations are largely influenced by the surrounding landscape.

APPENDICES

APPENDIX A

Coordinate locations and original WQAL identification number or abbreviation of all study sites.

Site	Original ID	Latitude	Longitude
BDC	BDC	43.09332	-70.98911
BNR	38247	43.201438	-71.1747
BRB	39258	43.035069	-70.768906
CSB02	CSB02	43.133544	-70.970557
DCF03	DCF03	43.136202	-71.181731
FSB	39248	43.040584	-70.852712
GRBK	39770	42.97225	-70.93027
HVH	37787	43.27848	-70.90695
JMY	37676	43.30098	-70.91571
MLB01	MLB01	43.075449	-70.939182
PB02.7	PB02.7	43.135112	-70.925128
PIK	37816	43.26847	-70.966913
PKB	39659	42.9949	-70.92521
PST	39806	42.973495	-70.845501
RMB04	RMB04	43.053432	-71.033041
SBM0.2	SBM0.2	43.170400	-71.217305
TPB	TPB	43.317758	-71.167497
TWB	39934	42.96217	-71.200988
WEB	37598	43.31928	-70.68723
WHB01	WHB01	43.122284	-71.004873

APPENDIX B

Porewater $\delta^{13}\text{C}$ -CH₄ data. Porewater gas samples were analyzed for C isotopes using infrared absorption spectroscopy (Quantum Cascade Laser Spectrometer) in the University of New Hampshire Trace Gas Lab.

UNH ID #	Collection Date	Sample Name	Site	$\delta^{13}\text{C}$ -CH ₄ (per mil)	CH ₄ (μatm)
159043	16-Feb-18	GRBK_PW	GRBK	-51.6132	367.99
161869	16-May-18	CSB02 PW	CSB02	-61.0565	55.58
161870	16-May-18	GRBK PW	GRBK	-57.3256	589.84
161879	18-May-18	PIK PW 1	PIK	-58.5971	971.75
161880	18-May-18	PIK PW 2A	PIK	-55.6512	1137.93
161881	18-May-18	PIK PW 2B	PIK	-58.4964	1448.42
163291	18-Jul-18	CSB02 PW	CSB02	-66.0115	44.14
163292	18-Jul-18	GRBK PW	GRBK	-57.3608	1062.47
163312	19-Jul-18	PIK PW 1	PIK	-64.3192	5212.51
163313	19-Jul-18	PIK PW 2	PIK	-72.4261	3.68
163651	02-Aug-18	DCF03 PW	DCF03	-55.0967	18.01
166701	26-Oct-18	CSB02 PW	CSB02	-62.6721	70.13
166702	26-Oct-18	BNR PW	BNR	-61.3274	756.02
166704	26-Oct-18	PIK PW	PIK	-61.5076	626.58

APPENDIX C

Land use percentages and watershed area for each site.

Site	% Developed	% Agriculture	% Forest	% Wetland	% Impervious	Watershed Area (km ²)
BDC	5%	51%	31%	8%	9%	0.29
BNR	21%	25%	50%	0%	18%	0.51
BRB	45%	0%	47%	4%	33%	0.39
CSB02	5%	29%	53%	8%	7%	3.99
DCF03	0%	6%	82%	4%	2%	7.03
FSB	29%	24%	36%	2%	21%	1.09
GRBK	32%	2%	46%	14%	21%	0.39
HVH	30%	4%	53%	7%	13%	4.77
JMY	17%	19%	49%	13%	11%	1.03
MLB01	36%	3%	52%	0%	31%	0.89
PB02.7	54%	3%	36%	3%	32%	1.42
PIK	35%	5%	53%	3%	25%	2.49
PKB	9%	23%	44%	18%	17%	4.85
PST	42%	7%	32%	11%	29%	1.12
RMB04	7%	13%	66%	7%	10%	4.92
SBM0.2	0%	0%	99%	0%	1%	0.30
TPB	0%	0%	89%	6%	N/A	N/A
TWB	32%	4%	58%	3%	20%	1.14
WEB	4%	7%	45%	34%	5%	17.54
WHB01	17%	13%	62%	4%	17%	1.02

APPENDIX D

Mean water chemistry and dissolved gas concentrations across the twelve sampling months for each site.

Site	CH ₄ (μ atm)	N ₂ O (μ atm)	CO ₂ (μ atm)	NO ₃ ⁻ (mg N L ⁻¹)	DOC (mg C L ⁻¹)	NH ₄ ⁺ (μ g N L ⁻¹)	TDN (mg N L ⁻¹)	SO ₄ ²⁻ (mg S L ⁻¹)	PO ₄ ³⁻ (μ g P L ⁻¹)	K ⁺ (mg K L ⁻¹)	DO (% sat)
BDC	5.87	8.97	4994	1.17	14.01	286.2	1.97	3.69	124.5	8.85	76.33
BNR	1.10	0.76	1146	1.00	1.68	12.4	1.12	2.13	9.3	3.52	96.58
BRB	27.19	0.66	7802	0.29	12.13	38.8	0.57	4.42	10.6	3.24	64.99
CSB02	8.11	3.23	6617	0.60	6.29	30.5	0.85	2.72	14.0	2.72	77.37
DCF03	4.88	0.33	1700	0.04	7.48	17.3	0.28	0.66	9.9	0.61	94.20
FSB	3.47	0.57	2327	0.60	5.37	19.0	0.91	3.29	13.9	2.34	93.93
GRBK	18.94	0.55	4709	0.43	6.47	33.1	0.72	2.85	8.8	2.50	80.27
HVH	47.69	0.39	4267	0.08	5.56	20.9	0.28	2.14	3.7	1.96	80.53
JMY	23.43	0.70	5418	0.48	8.24	49.4	0.80	2.35	13.5	2.81	76.81
MLB01	53.79	0.86	3886	0.64	2.30	44.5	0.79	4.13	8.2	4.35	90.06
PB02.7	17.33	0.48	2604	0.39	7.28	79.8	0.77	3.39	14.2	5.34	91.51
PIK	36.72	0.64	2322	1.26	2.73	78.6	1.50	2.55	6.0	2.25	92.18
PKB	4.19	0.83	3339	0.30	7.37	19.1	0.59	2.89	11.1	2.57	87.31
PST	14.93	1.04	3942	1.37	5.19	28.7	1.74	3.99	7.7	3.37	85.53
RMB04	6.28	0.48	2299	0.18	6.01	26.6	0.43	2.96	9.4	2.37	91.85
SBM0.2	1.12	0.35	5182	0.09	1.83	13.9	0.08	1.31	5.1	0.51	72.73
TPB	9.15	0.40	1736	0.04	4.41	17.7	0.16	0.83	5.1	0.17	93.96
TWB	5.30	2.08	3594	0.66	7.16	30.8	0.96	3.34	7.5	4.31	88.07
WEB	17.99	0.42	5037	0.09	16.29	25.9	0.51	1.10	10.4	1.05	70.57
WHB01	3.42	0.83	2552	0.57	5.71	10.9	0.75	3.40	13.6	1.43	94.64