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Research Article

Effects of a diel oxygen cycle on nitrogen transformations and greenhouse gas emissions in a eutrophied subtropical stream

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Abstract. Rivers and streams constitute a major pathway for material transport from land to sea and an important source of greenhouse gases. Short-term variation in stream chemistry due to day-night oxygen (O_2) fluctuations could significantly affect a stream's capacity to transport nutrients and produce greenhouse gases. Though it is well established that diel cycles are important in controlling O_2 and CO_2 dynamics, the study of diel dynamics of other redox-sensitive elements has been fairly limited. Here we show that a subtropical stream can undergo complete reduction and oxidation sequences in just a few hours. This redox fluctuation has important consequences for downstream transfer of nutrients and for greenhouse gas production. Among these consequences are decreased denitrification rates relative to estimates made using only daytime measurements (17–38% during our observation period), increased downstream nitrogen (N) transfer, a striking change in form of transported N (decreased nitrate and increased ammonium), and decreased estimates of in-stream nitrous oxide (N_2O) flux (36–38% during our observation period). Additionally, methane (CH_4) concentrations doubled and carbon dioxide (CO_2) concentrations rose from 4.6 to 30.7 mg L^{-1} during the 24-hour period of our observations. Diel shifts like the one we describe have implications for our understanding of nutrient transport and greenhouse gas production in eutrophied streams.

Key words. Nitrogen; greenhouse gases; subtropical stream; anoxia; diel; denitrification, redox conditions.

Introduction

Rivers and streams constitute a primary pathway for material transport from land to sea and an important source of greenhouse gases (Meybeck, 1982; Seitzinger and Kroeze, 1998; Richey et al., 2002). Recent evidence indicates that rivers and streams can process nutrients and other chemicals rapidly over short distances (e.g. Peterson et al., 2001), and separate work has shown that diel O_2 cycles due to plant productivity (respiration and photosynthesis) can influence transformations and transfer of trace metals such as arsenic (As), iron (Fe) and manganese (Mn) (Brick and Moore, 1996; Sullivan et al., 1998). However, there has been relatively little work on how short-term O_2 variations affect nutrient transport through streams and production of greenhouse gases by streams.

Many previous studies have documented diel O_2 fluctuation in rivers and streams (e.g. Grimm and Petrone, 1997; Neal et al., 2002; Park et al., 2003), and a few studies have shown evidence of complete nighttime anoxia in river-associated wetlands and stagnant waters (Caraco and Cole, 2002; Venterink et al., 2003). Previous research has also shown significant diel fluctuations in CO_2 in some rivers (Neal et al., 2002) and a few studies have inferred a link between diurnal fluctuations in O_2 and denitrification rates in a river-associated wetland (Ven-

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terink et al., 2003) and sediments heavily colonized by benthic microalgae (e.g. Christensen et al., 1990; Nielsen et al., 1990; Risgaard-Petersen et al., 1994; Lorenzen et al., 1998). One recent study has linked diel patterns in O_2 consumption to patterns of N_2O and N_2 production (Laursen and Seitzinger, 2004). However, no studies have documented a rapid and complete in-stream redox oscillation in the detail we describe here, and none have examined the role or implications of night-onset anoxia for nitrogen cycling and transport in streams or rivers. Here we show that rapid in-stream redox fluctuations can affect a broad spectrum of biologically important nutrients and greenhouse gases over very short timescales, in a manner consistent with thermodynamics-based predictions.

Despite the potential for day-night shifts in O_2 conditions to alter stream chemistry, current conceptual (Fisher et al., 1998) and numerical models (Seitzinger and Kroeze, 1998; Wollheim et al., 1999) of river biogeochemistry ignore diel changes in stream chemical dynamics. Even models which incorporate the ability of rivers to transform nutrients (Fisher et al., 1998; Wollheim et al., 1999), rather than treating them as simple conduits, generally ignore short-term environmental variations despite the fact that diel O_2 fluctuations are relatively common in biologically productive rivers and streams.

Thermodynamics may help predict the response of rivers and streams to diel O_2 cycles. Experiments in terrestrial systems have demonstrated that as flooded soils become increasingly reduced, microbes reduce inorganic compounds in cascading reactions that occur in order from most to least energetically favorable (Table 1) (Morel and Herring, 1993). When soils are drained, reduced species are re-oxidized, also in order of energetic favorability. In this study we examine the extent to which similar dynamics occur in a stream's water column as it becomes increasingly reduced and then re-oxidized over the course of a day-night fluctuation in $[O_2]$.

We also examine whether diel fluctuations in redox conditions can affect downstream transfer of nitrogen and the production of nitrous oxide (N_2O) and other greenhouse gases. Reactive N typically limits primary production in coastal environments (Carpenter et al., 1998), and when present in excess it can lead to negative environmental impacts such as oxygen depletion, toxic and nuisance algae blooms, sedimentation, and biodiversity loss (Steidinger and Haddad, 1981; Carpenter et al., 1998). Rivers are generally important sources of reactive N to coastal ecosystems. However, microbial denitrification in rivers can convert reactive N to inert N_2 gas en-route from sources to the coast, thereby helping to prevent eutrophication of coastal ecosystems. Thus, if diel changes in O_2 conditions affect denitrification rates in rivers, these diel cycles may have important implications for transfer of reactive N to coastal ecosystems. Because redox conditions affect the processes that are responsible for the production and emission of several greenhouse gases (e.g. CO_2, N_2O, and CH_4), we might also expect those gases to be significantly impacted by diel fluctuations in O_2 conditions. We tested the above predictions by monitoring water-column concentrations of several redox-sensitive ions and gases over a 24-hour period in a biologically productive, subtropical stream.

Table 1. Gibbs free energy measured at pH = 7 and molar concentrations of reactants. From Morel (1993).

Reaction	Electron Acceptor	Free Energy Released per mol CH_2O Consumed
Aerobic Respiration	O_2	476 kJ
NO_3^- Reduction	NO_3^-	452 kJ
MnO_2 Reduction	MnO_2	388 kJ
$Fe(OH)_3$ Reduction	$Fe(OH)_3$	187 kJ
SO_4^{2-} Reduction	SO_4^{2-}	82 kJ
CH_4 Formation	CO_2	71 kJ

Study site, materials and methods

Study site and long-term data

Mexico's Yaqui Valley (Fig. 1) was among the first regions in the developing world to experience the suite of changes in agricultural practice known collectively as the "Green Revolution" (Naylor et al., 2000). Beginning in

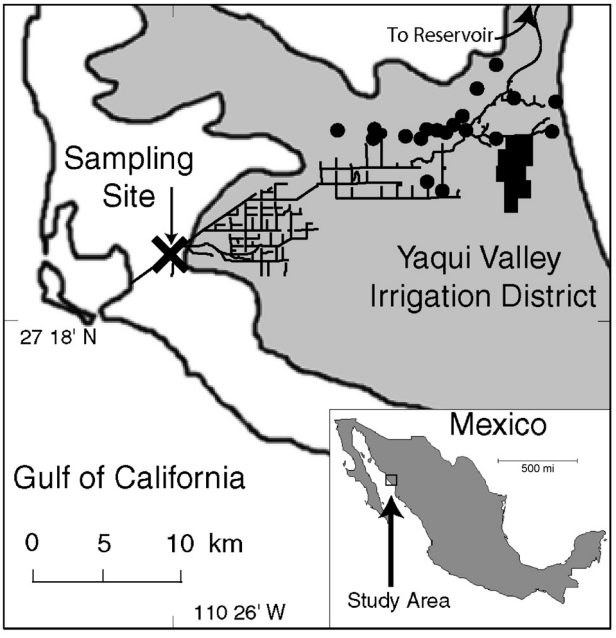

Figure 1. Study site (Yaqui Valley, Sonora, Mexico); Canal Two is shown as a dark, rectilinear network, and our sampling station is marked with an X. Water in the Valley generally flows SW toward the Gulf of California. Shaded area represents agricultural land, dark circles (●) represent the locations of pig farms, and the city of Obregón (Pop. 300,000+) is shown in black in the upper-right.

the 1950s, Green Revolution Technologies greatly increased the Yaqui Valley's agricultural yield, due to improved wheat varieties and rapidly increasing application of nitrogenous fertilizers. Fertilization, together with regional increases in population and hog production (Matson et al., 1998), has greatly increased the amount of reactive N (fixed N) flowing through the valley. Similar patterns of growth and change are common in regions of agricultural intensification throughout the developing world. As a region of rapid change and development, the Yaqui Valley provides a model system that can help us understand, predict, and respond to trends throughout the developing subtropics (Naylor et al., 2000; Harrison and Matson, 2003.)

The Yaqui Valley is drained by a network of natural and man-made streams that carry a mixture of agricultural and urban wastewater to the Sea of Cortez, providing a useful system in which to examine the chemical dynamics of polluted rivers and streams (Harrison and Matson, 2003). Due to their high productivity, some of the Valley's drainage canals exhibit pronounced day-night O_2 fluctuations.

In this study we focused on one stream called Canal Two (Fig. 1), one of the Yaqui Valley's principal drainage streams, for which we have collected extensive, long-term data on hydrologic, nutrient, and trace gas dynamics (Harrison and Matson, 2003). Canal Two is a perennial, channellized, mixed sand and mud-bottomed stream that is influenced by irrigation runoff, livestock waste, and largely untreated urban sewage. The Alvaro Obregon Resevoir, fed by the Yaqui River serves as the principal source of water to this stream. In the Yaqui Valley mean annual temperature is 22.5 °C, and mean annual precipitation is 28.7 cm, with 82% of that precipitation occurring during a "wet" season (July-October). Irrigation patterns, rather than rainfall are the dominant driver of discharge in Yaqui Valley streams. Canal Two is one of eight Yaqui Valley drainage canals that were sampled biweekly for 23 months (November 1999–September 2001) as part of a larger study of Yaqui Valley biogeochemistry (Harrison and Matson, 2003). In these canals, we measured concentrations of N_2O, CO_2, CH_4, O_2, nitrate (NO_3^-), ammonium (NH_4^+), dissolved organic carbon (DOC), particulate organic carbon (POC), particulate organic nitrogen (PON), phosphate (PO_4^{3-}), chlorophyll a (chl a), turbidity (NTUs), wind-speed and direction, water velocity, water depth, channel width, salinity, pH, and temperature. Over the 23-month study period, Canal Two was 15–100 cm deep, 10–15 m wide, free of both macrobenthic organisms and benthic macrophytes, and lined by shrubby vegetation (mostly *Tamarix ramosissima* and *Parkinsonia aculeata*). There was also very little benthic periphyton, most likely because of light limitation in this turbid stream. Sediment organic matter content was 3.9% by weight (Harrison, 2003). Water discharge rates in Canal Two ranged from 0.37 to 2.22 $m^3 s^{-1}$ with high discharges restricted to valley-wide irrigation events and isolated precipitation events. During our diel observation period, Canal Two's discharge was 0.48 $m^3 s^{-1}$, and its mean depth was 15 cm, normal for non-irrigation periods. Over the extended, 23-month study, mid-channel flow rates ranged from 0.018 m s^{-1} to 0.55 m s^{-1} (mean: 0.297 m s^{-1}), and we estimated Canal Two's re-aeration time to be 2–4 hours (Harrison, 2003). The study reach had high dissolved inorganic nitrogen (DIN) concentrations, primarily as NH_4^+ (mean: 7.21 mg/N L^{-1}), and high PO_4^{3-} concentrations (mean: 1.30 mg/P L^{-1}). It also exhibited high DOC concentrations (mean: 8.46 mg C L^{-1}), and a substantial seasonal fluctuation in temperature (range: 14.0–35.3 °C, mean: 24.1 °C). Canal Two also exhibited seasonally high chl a concentrations (range: 2.6–373.6 mg m^{-3}, mean: 69.5 mg m^{-3}).

Sampling, analytical methods and solubility modeling

For our diel observations, Canal Two was monitored from noon on 2 July 2001 to noon on 3 July 2001 and was sampled every 2 hours. All nutrient samples ([NO_3^-], [NH_4^+], and [PO_4^{2-}]) were filtered through sterile 0.45 µm glass fiber filters on-site and frozen until analyzed on an Alpkem Flow Solution IV autoanalyzer (Harrison and Matson, 2003). We measured non-purgeable organic carbon (NPOC) with a Shimadzu total organic carbon (TOC) analyzer. We measured filter-extracted chlorophyll a and phaeophytin concentrations (extracted with 90% acetone) with a Turner Designs, model 10-AU fluorometer according to EPA protocol #445. Aliquots (150 ml each) were filtered on site, treated with $MgCO_3$ to prevent acidification, frozen, and subsequently freeze dried for analysis. We measured POC and PON by filtering 150 ml aliquots of canal water onto pre-ashed GF/C filters, and subsequently analyzed the filters with a Carlo Erba (now CE Elantech, Inc.) NA1500 Series II elemental analyzer (EA)). Total dissolved Fe, Mn, and S were measured after samples were filtered and acidified using inductively coupled plasma-atomic emission spectrometry (ICP-AES) at wavelengths 2599, 2794, and 1807 nm, respectively. Detection limit was 5 µg L^{-1} and precision was ±15 µg L^{-1} for each element. Dissolved O_2 (±3%), salinity (±0.1 g L^{-1}), and air and water temperature were measured with a YSI model 85 oxygen and salinity meter. pH (±0.04) was measured with a Solomat 803PS multiprobe. Water current velocity and depth were measured with a Marsh-McBirney electromagnetic flow meter and wading staff, according to USGS protocol.

Gas concentrations were estimated using a headspace equilibration technique (as in Harrison and Matson (2003)). In this technique, 60 ml glass Wheaton bottles were pre-sealed with gray butyl stoppers, evacuated, and flushed with helium. At each sampling period, six 15 ml

aliquots of canal water were injected into bottles, brought back to the laboratory, and shaken for 4 hours at 25 °C. Injection of 15 ml of water into He-filled bottles resulted in slight over-pressurization of bottles. Headspace gas was then extracted and analyzed for N_2O, CO_2, and CH_4, and original gas concentrations were calculated using the appropriate solubility tables (Weiss and Price, 1980), accounting for slight over-pressurization. Ambient air samples were also collected at each time point for determination of supersaturation. Six vials were collected at each time point. Three were poisoned with saturated mercuric chloride (HgCl) solution, and three were left untreated. Poisoned vials were used for the determination of [CO_2] and [CH_4], and all vials were used for the determination of [N_2O], as there was no significant difference between N_2O concentrations in poisoned versus non-poisoned vials. All headspace measurements were made between 4 and 12 hours after sample collection, and were allowed to equilibrate at a temperature of 25 °C. Concentrations of N_2O, CH_4, and CO_2 were analyzed using a Shimadzu gas chromatograph configured with electron capture (ECD), flame ionization (FID), and thermal conductivity (TCD) detectors. The ECD contained 63 Ni as the isotope source and an argon/methane mixture was used as the carrier gas (Harrison and Matson, 2003). Five hundred and 900 ppbv N_2O, 500 ppmv CO_2, and 900 ppbv CH_4 standards bracketed every 15 samples. Coefficients of variation for standards never exceeded 2%. N_2O standards ranged from 500 ppbv to 500 ppmv. CH_4 standards ranged from 0.9 to 10 ppmv, and a single 500 ppmv CO_2 standard was used. Di-nitrogen to argon ratios (N_2:Ar), used to calculate [N_2] and denitrification rate according to Laursen and Seitzinger (2002), were measured with a Prisma quadrupole mass spectrometer (QMS) as in Kana et al. (1994) (n = 2 for each time point). In this method, variation in [Ar] is assumed to be a function of physical factors (e.g. temperature and salinity), while [N_2] is affected by both physical and biological factors. Thus, variation in N_2:Ar can be used to estimate the change in N_2 due solely to biological N_2 production (denitrification) and uptake (fixation). Equilibrium N_2:Ar was calculated based on temperature conditions two hours prior to N_2:Ar measurements (i.e. half of the calculated re-aeration time for Canal 2 under similar flow conditions (Harrison, 2003)). Predicted temperature-related shifts in solubility were an order of magnitude smaller than observed shifts in N_2:Ar. O_2:Ar was also measured with the QMS and compared well with YSI data, indicating that the samples had been well preserved. We used a multi-element geochemical model (Visual Minteq 4.0) to determine the solubility of Mn (III/IV), Fe (III), HS^-, Mn^{2+}, Fe^{2+}, and SO_4^{2-} over the entire range of pH and temperature conditions we observed in Canal Two during our observations. We also used Visual Mindeq 4.0 to calcuate [Mn^{2+}], [Fe^{2+}], and [SO_4^{2-}] based on measurements of dissolved species.

Determination of diel effect on denitrification and N-transfer

Our estimate of 24-hour denitrification with night-time anoxia (DN_a) in kg N hr^{-1} was calculated as:

$$DN_a = \sum_{i=1}^{n} 2 * DN_i \quad (1)$$

where n is the total number of hours in the study, and DN_i is the instantaneous denitrification rate (mmol N_2 m^{-2} h^{-1}) calculated according to Laursen and Seitzinger (2002), multiplied by 2 because sampling occurred every two hours.

Our estimate of 24-hour denitrification without night-time anoxia (DN_b) in kg N hr^{-1} was calculated as:

$$DN_b = h * DN_{avg} + \sum_{i=1}^{n} 2 * DN_i \quad (2)$$

where h is the number of hours for which denitrification was suppressed (We assumed h was equal to 6–9 hrs based on diel N_2 data.), and DN_{avg} is the mean daytime denitrification rate (1042.4 ng N cm^{-2} hr^{-1}). DN_{avg} was calculated as the mean of calculated daylight DN_i values.

Results and discussion

Oxidation and reduction

During our diel observation period, we recorded a rapid and complete oxidation-reduction sequence (Fig. 2), a phenomenon that has not previously been characterized (beyond O_2 and CO_2 excursions) in a canal, river, or stream setting. At this time, Canal Two was experiencing a phytoplankton bloom (mean [chl a]: 87 mg m^{-3}), and the diel O_2 variation was pronounced (>300% saturated to complete anoxia in just a few hours (Fig. 2)).

In a classic reduction sequence, microbes consume electron acceptors sequentially, generally in the order: $O_2 > NO_3^- > MnO_2 > Fe(OH)_3 > SO_4^{2-} > CO_2$ (Table 1; McBride, 1994). We expected to see similar dynamics in Canal Two as conditions became increasingly reduced throughout the night. As the aforementioned electron acceptors were reduced and depleted, we expected to see increases in concentrations of reduction products: N_2 (and N_2O), Mn^{2+}, Fe^{2+}, H_2S, and CH_4, in that order. Concentrations of reduction products should decrease as their source ions are depleted or as conditions become increasingly oxidized with the onset of daytime photosynthesis.

The chemical dynamics we recorded over the period of our observations were consistent with thermodynamic predictions, and chemical shifts occurred very rapidly (Fig. 2). In the evening, with the cessation of photosynthesis, we observed a decrease in [O_2], followed by decreases in [NO_3^-], and [SO_4^{2-}] (Fig. 2). Along with the consumption of these electron acceptors (which in the case of

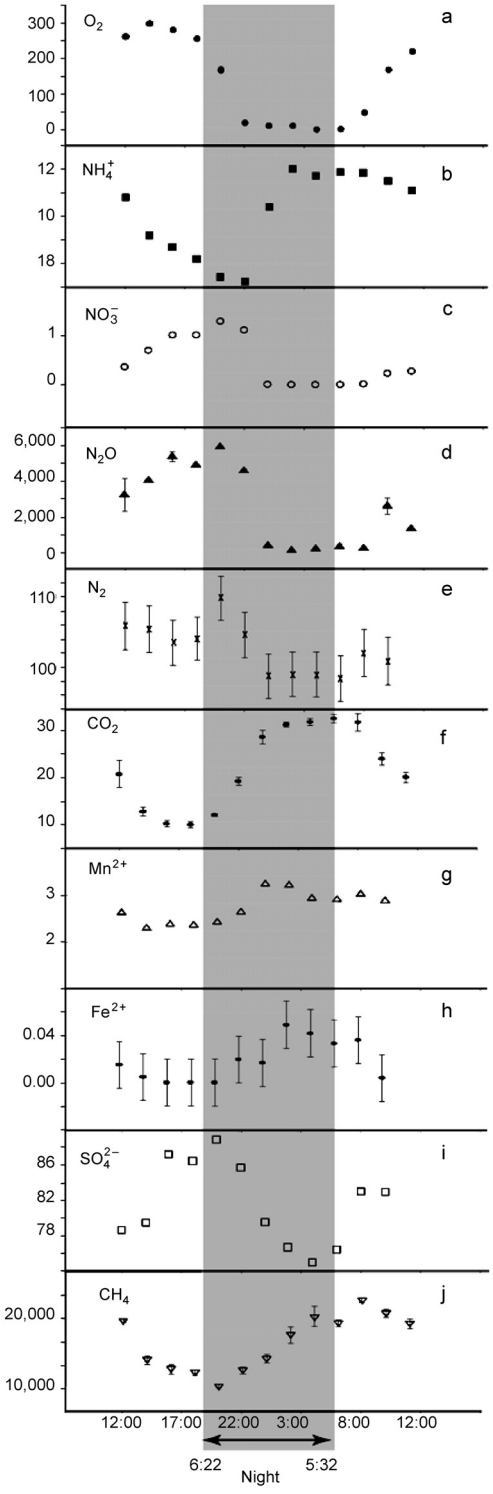

Figure 2. Diel measurements from 2–3 July 2001. a) Dissolved oxygen [O_2], b) Ammonium [NH_4^+], c) Nitrate [NO_3^-], d) Nitrous oxide [N_2O], e) Dinitrogen [N_2], f) Carbon dioxide [CO_2], g) Dissolved manganese [Mn^{2+}], h) Dissolved iron [Fe^{2+}], I) Dissolved Sulfur [SO_4^{2-}], and j) Methane [CH_4]. Except for CO_2, gases (O_2, N_2, and CH_4) expressed in terms of % saturation. CO_2 expressed as concentration (mg-C L^{-1}). Error bars represent ±1 S.D. of triplicate samples (Analytical error). Dissolved species expressed in terms of mg L^{-1}. Dissolved N species (NH_4^+ and NO_3^-) are expressed as mg-N L^{-1}.

NO_3^- may have been enhanced by a cessation of nitrification) we saw increases in the concentrations of reduction products. Carbon dioxide and N_2 concentrations increased first, followed by [Mn^{2+}], [Fe^{2+}], and finally [CH_4] (Fig. 2).

In the morning, with the onset of photosynthesis, we observed an increase in [SO_4^{2-}], followed by an increase in [O_2], and finally an increase in [NO_3^-]. Although the order of appearance of SO_4^{2-} and O_2 conforms to thermodynamic predictions, the timing of [NO_3^-] increase does not. This unexpected lag in [NO_3^-] may have been due to phytoplankton uptake or to the importance of reaction kinetics in determining oxidation rates.

We also observed significant diel changes in pH, temperature, and salinity (Fig. 3). Changes in salinity do not explain the observed chemical dynamics because the timing of peak salinity is not reflected in measured ionic con-

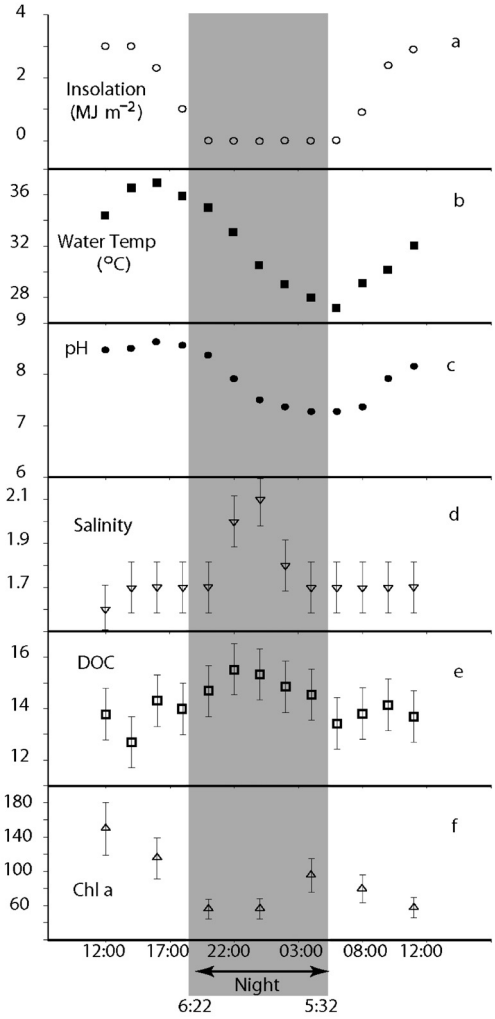

Figure 3. Diel measurements from 2–3 July 2001. a) Insolation expressed as Mjoules m^{-2}, b) Water temperature (°C), c) pH ± 0.01, d) Salinity (g L^{-1}), e) Dissolved organic carbon (mg-C L^{-1}) ± 1 mg L^{-1}, and f) Chl a (mg m^{-3}) ± 1 S.D.. All measurements except chl a were made every 2 hours. Chl a was measured every 4 hours.

centrations of Fe, Mn, or SO_4^{2-} (Fig. 2). For example, if [SO_4^{2-}] were influenced primarily by salinity, we would expect increases in [SO_4^{2-}] to coincide with increases in salinity. However, we observed the opposite pattern. It is also very unlikely that diel patterns in [NH_4^+] or [NO_3^-] resulted from diel changes in inputs due to diel patterns in human activities such as sewage inputs or irrigation return flows. If daytime sewage inputs were the primary source of NH_4^+, we would expect the opposite pattern in [NH_4^+] to what we observed, with high [NH_4^+] during the day and lower [NH_4^+] during the night. However, it is impossible to entirely discount nighttime sewage releases as a source of diel variation in [NH_4^+]. There was no substantial irrigation occurring in the valley during the time of these observations, so irrigation return flows were not a source of diel variation in solute concentrations.

Changes in temperature and pH are also insufficient to explain the chemical shifts we observed. Results from a geochemical model (Gustafsson, 2002) indicate that Mn (III/IV), Fe (III), and HS^- are extremely insoluble over the entire observed pH and temperature range in Canal Two (Solubilities <0.0001, 0.002, and 0.5 mg L^{-1} for each species respectively at maximum pH: 8.5 and minimum temperature: 27 °C). Conversely, Mn^{2+}, Fe^{2+}, and SO_4^{2-} are extremely soluble over the same range of pH and temp (solubilities >5000, >20 mg L^{-1}, and >10000 mg L^{-1} for Mn^{2+}, Fe^{2+}, and SO_4^{2-} respectively). This result indicates that the observed changes in pH and temperature (Fig. 2) are unlikely to have caused the observed patterns in dissolved Mn, Fe, and S.

The rapid, diel change in stream redox conditions we observed has at least two potentially important ramifications. First, it may significantly alter our estimates of reactive N reaching coastal ecosystems. And, second, it may significantly affect our estimates of greenhouse gas emissions from productive aquatic systems like Canal Two. These effects are discussed in following sections.

Nitrogen transfer

Nitrogen transformations are heavily dependent on ambient O_2 conditions. Nitrification, the microbially mediated oxidation of NH_4^+ to NO_3^-, can only occur in the presence of oxygen. Conversely, denitrification, the microbially mediated reduction of NO_3^- to N_2, is favored under anoxic conditions.

The pattern of N species in the water column, especially N_2 (Fig. 2), suggests that denitrification occurred during daylight hours and accelerated shortly after nightfall as conditions for denitrification were enhanced by decreasing O_2. Then, after a brief period of high denitrification activity coincident with consumption of NO_3^- from the water column, denitrification appeared to cease until the following morning. In the morning, denitrification resumed, presumably because morning photosynthesis provided O_2 required for the nitrification portion of coupled nitrification-denitrification.

Denitrification apparently ceased for at least 6 hours during the night, as evidenced by the sustained low N_2 between midnight and 6:00 am (Fig. 2). An estimation of denitrification during our 24-hour study based only on mid-day measurements would therefore overestimate denitrification by 17–38 %, (denitrification rate: 7682 ng N cm^{-2} d^{-1} with a diel cycle vs. 10542 ng N cm^{-2} d^{-1} without a diel cycle).

It is unlikely that nitrogen fixation played an important role over the period of our study. Nitrogen fixation is inhibited by oxygen, so daytime N_2 fixation was likely minimal over the course of our observations. If N_2 fixation were the main mechanism for the nighttime increase in [NH_4^+] and decrease in [N_2], we would expect to see a constant increase in [NH_4^+] throughout the night, not the plateau that occurs at 12 mg L^{-1} (Fig. 2). Furthermore, we believe a major role for N_2 fixation is unlikely in a system like this one where reactive nitrogen is in such constant, abundant supply. However, given available data, it is not possible to rule out some nighttime draw-down of [N_2] via microbial fixation.

In addition to affecting denitrification, and thus the overall amount of downstream N-transfer, diel O_2 swings also appeared to change the *form* in which N is carried downstream. With the onset of night and anoxic conditions, phytoplankton N uptake and nitrification were inhibited, and more NH_4^+ (and less NO_3^-) was carried seaward than during daylight hours. [NO_3^-] decreased from 1.30 mg/N L^{-1} during daylight hours to undetectable levels (<0.04 mg L^{-1}) shortly after the canal became anoxic. [NH_4^+] increased from 7.24 to 12.02 mg L^{-1} over the same period. Considering that total DIN concentrations for most unpolluted rivers are generally less than 1.0 mg L^{-1} (Alexander et al., 1996; Meybeck, 1982), the diel shifts in N speciation we observed were quite large. As plant and phytoplankton species can have differential preferences for NH_4^+ and NO_3^- (e.g. Rosser and Thompson, 2001), this shift may influence the nature of primary producers in Canal Two and its receiving estuary. In addition to the diel effect on N transfer, transport of other elements such as Mn and Fe is likely to be affected as well, with potentially important implications for bioavailability and bio-toxicity of other compounds. Our observations of diel N dynamics are consistent with previous lab based (Venterink et al., 2003) and theoretical studies (Park et al., 2003), but represent the first time such dynamics have been corroborated with direct field observations. Such corroboration is essential because theoretical approaches are subject to large uncertainties, and laboratory approaches (generally based on an acetylene block approach) often misrepresent in situ nitrogen transformations (Seitzinger et al., 1993).

Greenhouse gas production

In addition to their implications for downstream material transfer, the rapidly changing conditions within Canal Two have implications for greenhouse gas production. Concentrations of N_2O, CH_4, and CO_2 were all significantly affected by diel shifts in Canal Two's chemical environment (Fig. 2). Diel cycles in CO_2 are fairly well documented in rivers (e.g. Neal et al., 2002), though the changes in concentration we observed were exceptionally large (4.67 mg L^{-1} – 30.7 mg L^{-1}). Diel changes in [CH_4] have not been reported in river settings, though they are common in terrestrial and wetland environments. In Canal Two [CH_4] approximately doubled over the course of our short-term study (Fig. 2).

Rates of N_2O production also changed significantly, with N_2O production ceasing for at least 8 hours, as indicated by fully equilibrated night-time concentrations in Canal Two (Fig. 2). If we had only sampled daytime N_2O concentrations, we would have over-estimated N_2O flux by 38% (2345 ng N cm^{-2} d^{-1} with no diel cycle vs. 1443 ng N cm^{-2} d^{-1} with a diel cycle). Because high rates of N_2O production tend to coincide with algae blooms in Canal Two (Harrison and Matson, 2003), diel oxygen dynamics could have an important impact on N_2O production over an annual cycle.

Conclusions

The rapid onset of anoxia in Canal Two and its chemical consequences result from several conditions that are occurring in concert and that are increasing as tropical and subtropical populations grow and intensify their agricultural production (e.g. high NH_4^+ and organic matter loads, and high temperatures) (Kroeze and Seitzinger, 1998; Harrison and Matson, 2003). The little available data suggests that N export to coastal regions is already high in the developing tropics and subtropics, particularly in Southern and Southeast Asia (Meybeck, 1982; Seitzinger and Kroeze, 1998). If many of these highly N-enriched systems are subject to the diel shifts similar to the ones we observed in Canal Two, then diel cycles might have a significant impact on the amount and forms of reactive N and other elements reaching coastal regions as well as greenhouse gas production in similar streams. The patterns we observed in this study suggest that by ignoring diel changes in N-cycling, the aquatic biogeochemistry community potentially miscalculates the amount of reactive N reaching the coastal zone and the amount of greenhouse gas production in systems with large O_2 excursions. Measurements of diel O_2 excursions in other high-N streams suggest that the large and rapid O_2 excursions we observed in Canal 2 are quite unusual in temperate zone streams. For example, in the River Kennet, a highly polluted stream in England, Neal et al. (2000) observed diel O_2 excursions of just 20–200% saturated. Similar studies of nitrate-rich streams in the US (Laursen and Seitzinger, 2004) show much smaller diel O_2 excursions. Large diel O_2 excursions may be more common in nutrient-rich subtropical and tropical regions with high temperatures and rapid respiration rates, but very few studies have been done on diel stream dynamics outside of the temperate zone. It is also possible that much smaller O_2 excursions than the one we observed in Canal Two can induce significant changes in the rates of N-gas production and consumption. For example, recent work by Laursen and Seitzinger (2004) indicates that relatively small O_2 excursions in two high-nitrate streams in the Midwest US can result in substantial diel shifts in denitrification and N_2O production rates. Future research will be required to better understand the mechanisms controlling diel N dynamics, both in temperate and tropical streams. For now, we have demonstrated that diel changes in O_2 concentrations cascade down the redox ladder and can influence a wide array of biogeochemically important processes. These diel chemical dynamics should be explored more comprehensively and possibly included in future regional and global models of downstream N transport and river greenhouse gas emission.

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