

Patterns and controls of nitrous oxide emissions from waters draining a subtropical agricultural valley

John Harrison

Institute of Coastal and Marine Sciences, Rutgers University, New Brunswick, New Jersey, USA

Pamela Matson

Department of Geological and Environmental Sciences, Stanford University, Stanford, California, USA

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[1] Although nitrous oxide (N_2O) emission from agricultural runoff is thought to constitute a globally important source of this greenhouse gas, N_2O flux from polluted aquatic systems is poorly understood and scarcely reported, especially in low-latitude (0° – 30°) regions where rapid agricultural intensification is occurring. We measured N_2O emissions, dissolved N_2O concentrations, and factors likely to control rates of N_2O production in drainage canals receiving agricultural and mixed agricultural/urban inputs from the intensively farmed Yaqui Valley of Sonora, Mexico. Average per-area N_2O flux in both purely agricultural and mixed urban/agricultural drainage systems ($16.5 \text{ ng N}_2\text{O-N cm}^{-2} \text{ hr}^{-1}$) was high compared to other fresh water fluxes, and extreme values ranged up to $244.6 \text{ ng N}_2\text{O-N cm}^{-2} \text{ hr}^{-1}$. These extremely high N_2O fluxes occurred during green algae blooms, when organic carbon, nitrogen, and oxygen concentrations were high, and only in canals receiving pig-farm and urban inputs, suggesting an important link between land-use and N_2O emissions. N_2O concentrations and fluxes correlated significantly with water column concentrations of nitrate, particulate organic carbon and nitrogen, ammonium, and chlorophyll a, and a multiple linear regression model including ammonium, dissolved organic carbon, and particulate organic carbon was the best predictor of $[\text{N}_2\text{O}]$ ($r^2 = 52\%$). Despite high per-area N_2O fluxes, our estimate of regional N_2O emission from surface drainage ($20,869 \text{ kg N}_2\text{O-N yr}^{-1}$; 0.046% of N-fertilizer inputs) was low compared to values predicted by algorithms used in global budgets. **INDEX TERMS:** 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 1615 Global Change: Biogeochemical processes (4805); 1803 Hydrology: Anthropogenic effects; 1860 Hydrology: Runoff and streamflow; **KEYWORDS:** nitrous oxide, greenhouse gas, runoff, land-use, denitrification, nitrification

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1. Introduction

[2] Because nitrous oxide (N_2O) is an important greenhouse gas that also plays a role in the destruction of stratospheric ozone, it has received considerable attention [e.g. Khalil and Rasmussen, 1983; Matson and Vitousek, 1990]. Currently, global atmospheric N_2O concentration is increasing at the rate of 0.2 – 0.3% per year, and fertilization of agricultural fields is thought to be the single most important source of the observed increase [Intergovernmental Panel on Climate Change (IPCC), 2001]. After a decade or more of research, we now have a reasonably good understanding of the relationship between nitrogen (N) fertilization and N_2O flux from soils [de Klein *et al.*, 2001; Harrison and Webb, 2001]. However, much less is known

about the gaseous loss of fertilizer N once it has left agricultural fields in solution or particulate forms. Some researchers have estimated that indirect N_2O emissions (emissions from surface and groundwaters not within agricultural fields) are currently as large as direct emissions from fields [Mosier *et al.*, 1998], and others have projected that increases in N loading to rivers will triple river N_2O production by 2050 [Kroeze and Seitzinger, 1998]. However, uncertainty surrounding estimates of N_2O emissions from indirect sources is large, ranging over one and a half orders of magnitude and accounting for over 60% of the uncertainty in current estimates of total anthropogenic N_2O emissions. This uncertainty is due to a combination of poor understanding regarding the mechanisms controlling N_2O production and a lack of studies of off-site emissions of N_2O from agriculture [de Klein *et al.*, 2001; Brown *et al.*, 2001].

[3] Previous work with sediments and soils has indicated that N_2O is formed principally as a byproduct of two

microbially mediated N transformations: denitrification and nitrification. Denitrification, the microbial reduction of nitrate (NO_3^-) to N_2O and dinitrogen (N_2) under anaerobic conditions, is thought to be controlled by inorganic N availability, organic carbon (C) availability, oxygen (O_2) concentration, and temperature [Nishio *et al.*, 1983; Seitzinger, 1988; Firestone and Davidson, 1989; Robertson, 1989]. Nitrification, the oxidation of ammonium (NH_4^+) to NO_3^- under aerobic conditions (with N_2O as a byproduct), is controlled by NH_4^+ availability, temperature, and redox conditions [Firestone and Davidson, 1989]. Previous work has suggested that the proportion of total denitrification or nitrification emitted as N_2O depends on the relative availability of resources for microbes, as well as ambient redox conditions and temperature [Seitzinger, 1988; Seitzinger *et al.*, 1984; Joergensen *et al.*, 1984]. Consequently, environmental variables such as N availability, organic C availability, temperature, and oxidation-reduction conditions are likely to influence the rate at which N_2O is produced.

[4] In this study, we used a combination of field and laboratory approaches to estimate rates of N_2O production in Yaqui Valley drainage canals and to improve our understanding of the controls on those rates. These approaches included (1) regression analysis examining relationships between measured N_2O fluxes and factors likely to influence N_2O production, (2) in situ sampling of sediment cores, (3) potential nitrification and denitrification assays, and (4) intact core experiments.

2. Site Description

2.1. Watershed

[5] The Yaqui Valley is located between $26^\circ 45' \text{N}$ and $27^\circ 33' \text{N}$ latitude and $109^\circ 30' \text{W}$ and $110^\circ 37' \text{W}$ longitude (Figure 1). Containing 226,000 ha of intensively managed, irrigated, wheat-based agriculture, the Yaqui Valley is the birthplace of the Green Revolution for wheat and one of Mexico's most productive breadbaskets. This valley is considered to be agro-climatically representative of 43% of wheat production in the developing world [Meisner *et al.*, 1992].

[6] Mean annual temperature in the valley is 22.5°C , and mean annual precipitation is 28.7 cm, with 82% of that precipitation occurring during a "wet" season (July–October). Over the course of this 20-month study, total rainfall in the region was just 37.5 cm, and this included only three rain events with greater than 2 cm rainfall in 24 hours (Arizona Meteorological Network). Occasional heavy rain events associated with major tropical storms may play an important role in this system on the several year timescale, but this topic is beyond the scope of this study.

[7] In the Yaqui Valley, the use of fertilizer N has increased markedly in the past 3 decades of development; between 1968 and 1995, fertilizer application rates for wheat production increased from 80 to 250 kg-N ha^{-1} per 6-month wheat crop, and survey results indicate substantial increases in fertilizer inputs in just the past decade [Naylor *et al.*, 2000]. Today the most common farming practice for wheat production in the valley is a pre-planting broadcast application of urea or injection of anhydrous ammonium (at the rate of $150\text{--}200 \text{ kg-N ha}^{-1}$), immediately followed by irrigation.

Smaller allocations of fertilizer ($50\text{--}100 \text{ kg-N ha}^{-1}$) are commonly added later in the crop cycle along with additional irrigation water. These valley-wide fertilization/irrigation events occur in principally in November, and intermittently throughout the winter and early spring. These events lead to large N losses to the atmosphere, groundwater, and surface waters [Matson *et al.*, 1998; Panek *et al.*, 2000; Riley *et al.*, 2001]. Summer crops, primarily maize, are grown when reservoir water storage is high and irrigation water is available; an additional $250\text{--}300 \text{ kg-N ha}^{-1}$ is typically applied to summer maize. However, during this study, summer crops were not planted due to water shortages.

2.2. Drainage Canals

[8] In the Yaqui Valley, surface irrigation runoff, livestock waste, and largely untreated urban sewage enter the coastal zone directly via a system of 5 principal, and 14 smaller, open waterways (hereinafter referred to as "drainage canals" or "canals") (Figure 1). These perennial constructed and natural waterways have muddy to sandy bottom sediments and are lined by shrubby vegetation (mainly *Tamarix sp.* and *Cercidium microphyllum* (palo verde)). Sampling sites were free of macrobenthic flora and fauna. Approximate drainage areas of study canals ranged from 800 to 43,000 ha, and mean annual discharges ranged from 1600 (A3) to 59,000 m^3 (A1), averaging 17,017 m^3 (Table 1). Over the period of this study, flow in these drainage canals was regulated almost entirely by upland water use (taken from a reservoir) because rain events were small and infrequent.

3. Methods

3.1. Measurement Program

[9] We sampled eight drainage canals biweekly for 23 months (November 1999 through September 2001) (Figure 1). In these canals, we measured fluxes of N_2O as well as several environmental variables likely to influence and co-vary with N_2O emission. These variables included dissolved oxygen (DO), NO_3^- , NH_4^+ , temperature, dissolved organic carbon (DOC), particulate organic carbon (POC), particulate organic nitrogen (PON), salinity, chlorophyll a (Chl a), turbidity (NTUs), wind speed and direction, water velocity, and pH. Drainages were chosen to vary widely with respect to the factors likely to influence N-cycling and N_2O flux.

3.2. Gas Collection and Analysis

[10] We estimated gas fluxes using two techniques: floating chambers (as in work by Livingston and Hutchinson [1995]), and headspace equilibration (modified from Robinson *et al.* [1988]). We applied the floating chamber technique in sites A1 and PA1, the two largest drainage canals. In this technique, we fitted 10-cm high, 25-cm-diameter acrylonitrile-butadiene-styrene (ABS) plastic chambers with floating collars and tied them to stakes driven into canal bottoms. We sampled four replicate chambers simultaneously at 10-min intervals, and flux measurements lasted 30 min. During each flux measurement, we measured water flow rates and depth just downstream of each chamber. We calculated concentrations of chamber

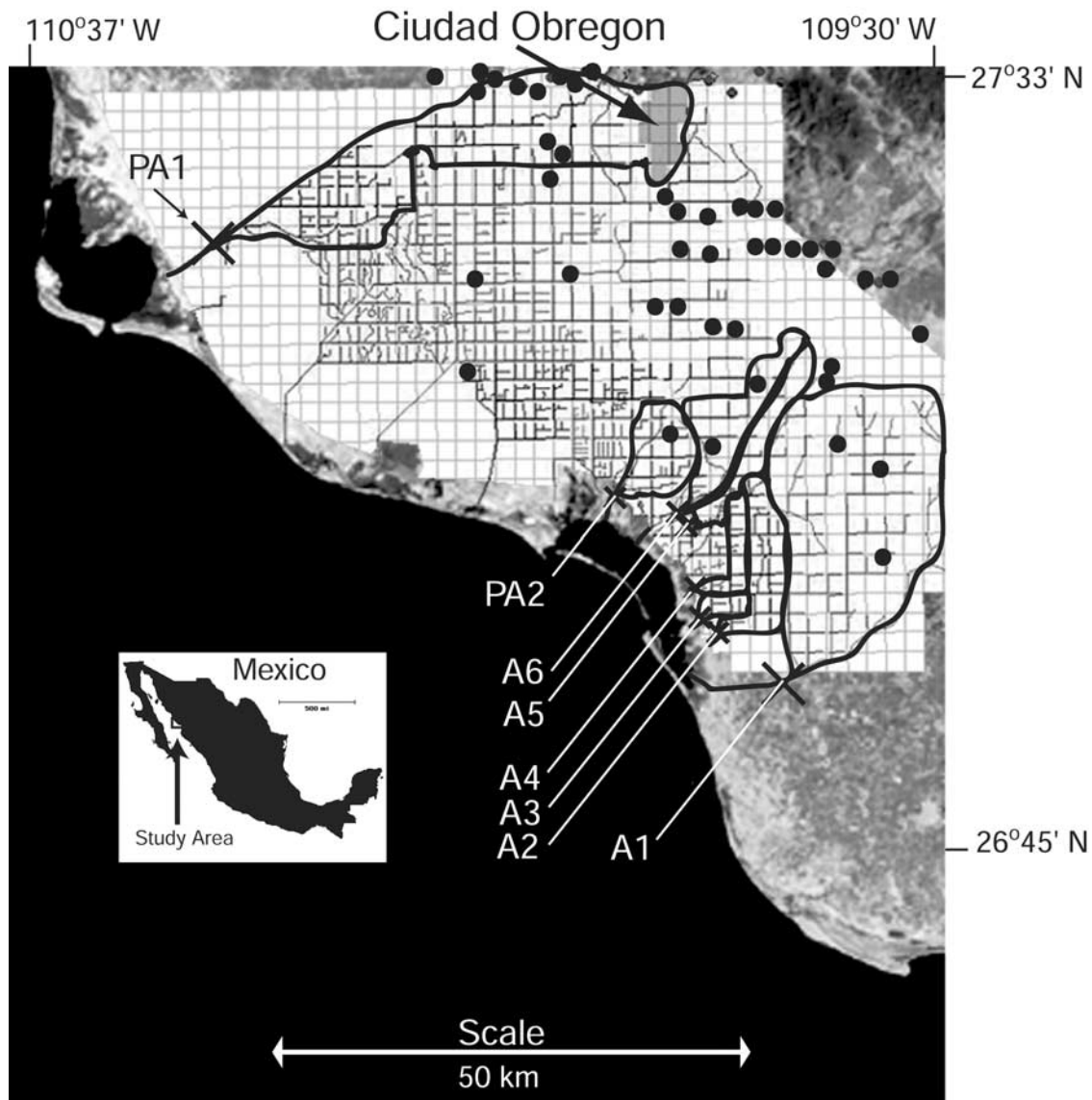


Figure 1. Yaqui Valley, with study drainages outlined in black and drainage canals portrayed as dark rectilinear networks. Water in the Valley generally flows southwest toward the Gulf of California, shown in black. Solid circles represent the locations of pig farms, and the city of Obregón (Pop. 300,000+) is shown in the upper right.

gases using least squares linear regression, and calculated N₂O fluxes by regressing gas concentration within a chamber against sampling time, correcting for temperature and chamber volume as in work by *Matson et al.* [1998]. Minimum detectable flux of N₂O was approximately 0.3 ng N₂O -N cm⁻² h⁻¹.

[11] In addition to the floating chambers, we employed a headspace equilibration technique at all eight sites. For this we pre-sealed 60-mL glass Wheaton bottles with gray butyl stoppers, then evacuated and flushed them with helium. Fifteen-mL aliquots of canal water were injected into bottles, brought back to the laboratory, and gently shaken

Table 1. Canal Watershed Areas, Mean Annual Discharges, and Surface Areas

Canal	Area Served, Ha	Mean Annual Discharge 1987–1996, 1000 m ³	Canal Surface Area, Ha
PA1	22,400	52,000	68–134
PA2	3200	NA	10–19
A1	43,600	59,000	133–262
A2	6400	14,500	19–38
A3	800	1600	2–5
A4	2800	5500	9–17
A5	6400	13,000	19–38
A6	8800	15,500	27–53

for 4 hours at 25°C. Headspace gas was then extracted and analyzed for N₂O, and original [N₂O] was calculated using the appropriate solubility tables [Weiss and Price, 1980]. Ambient air samples were also collected at each site for use in flux calculations.

[12] On several occasions, we compared triplicate samples poisoned with saturated mercuric chloride (HgCl) solution to samples lacking HgCl. There was no detectable difference between poisoned and unpoisoned vials in 24 hours with respect to N₂O. We made all headspace measurements between 4 and 12 hours after sample collection, and most samples were not poisoned.

[13] We measured N₂O using a Shimadzu gas chromatograph configured with electron capture detector (ECD). The ECD contained ⁶³Ni as the isotope source and an argon/methane mixture was used as the carrier gas [Matson *et al.*, 1998]. Standards ranged from 500 ppbv to 500 ppmv N₂O, and 500 and 900 ppb standards bracketed every 15 samples. Coefficients of variation for standards never exceeded 2%.

3.3. Determination of Gas Transfer Coefficient

[14] A gas transfer coefficient was estimated via a triple tracer experiment in PA1 and was validated by comparing chamber fluxes with simultaneously measured N₂O concentration. In the tracer experiment, a pulse of dissolved SF₆ gas (volatile tracer), rhodamine (visual tracer), and bromine (conservative tracer) was added to one of the larger canals (PA1) during a period with minimal wind in a manner similar to Wanninkhof *et al.* [1990]. The slug of tracer was sampled over time, and the difference in rate of loss between the volatile tracer (SF₆) and conservative tracer (bromine) was used to calculate a gas transfer coefficient according to Kilpatrick *et al.* [1989]. In the case of PA1, this transfer coefficient was 4.67 cm hr⁻¹ for N₂O at a Schmidt number of 600, assuming a flat water surface (according to Wanninkhof [1992]). This estimate is in rough agreement with an estimate based on comparisons between N₂O concentration and chamber fluxes (mean = 7.8 cm hr⁻¹ ± 3.5 cm hr⁻¹ (1 S.D.)).

[15] Fluxes were calculated according to [Liss, 1974]

$$F = k*(C_w - C_{eq}), \quad (1)$$

where F is gas flux across the air-water boundary, k is the gas-transfer velocity, C_w is the dissolved gas concentration in the water column, and C_{eq} is the dissolved gas concentration in equilibrium with the atmosphere. Because wind speed can play an important role in regulating gas transfer velocity over the range observed in our study (0.1–7.5 m s⁻¹), we accounted for variation in wind speed using the relationship

$$y = 1.91e^{0.35k}, \quad (2)$$

where y is wind speed in m s⁻¹, and k is the gas transfer velocity in cm hr⁻¹ at a constant Schmidt number (in this case 600) [Raymond and Cole, 2001]. We used on-site wind data after June 26, 2002. Prior to this date, we used wind data from a nearby weather station (<10 km away). We

normalized Schmidt numbers with respect to temperature according to Wanninkhof [1992].

3.4. Other Chemical Analyses

[16] We measured [NO₃-N], [NH₄⁺-N], and [PO₄³⁻-P] on an Alpkem Flow Solution IV autoanalyzer (Techniques P/N 000623, P/N 000156, and DIN P/N 000621 respectively [O/I Analytical, 1999]). Reported [NO₃⁻] is actually [NO₃⁻ + NO₂⁻] due to the cadmium reduction technique utilized. All nutrient samples were filtered through sterile 0.45-μm glass fiber filters on site and frozen until analyzed. Our detection limit for [NO₃-N], [NH₄⁺-N], and [PO₄²⁻-P] was 40 μg l⁻¹.

[17] We determined DOC as non-purgeable organic carbon with a Shimadzu total organic carbon (TOC) analyzer. Samples were pre-acidified with ultra-pure HCl, sparged with O₂ to purge inorganic C, and combusted. We measured extracted Chl a and phaeophytin concentrations with a Turner Designs, model 10-AU fluorometer according to EPA protocol [Arar and Collins, 1997]. One-hundred-fifty-mL aliquots were filtered on site, treated with MgCO₃ as a buffer, frozen, and then subsequently freeze-dried for analysis. We measured POC and PON by filtering 150-mL aliquots of canal water onto pre-ashed, Whatman GF/C filters, and subsequently analyzing them with a Carlo Erba (now CE Elantech, Inc.) NA1500 Series II elemental analyzer (EA) (high temperature combustion direct injection technique [Wangersky, 1975, 1993]).

[18] We measured DO (±0.3 mg L⁻¹), salinity (±0.1 g L⁻¹), and air and water temperature (±0.1°C) with a YSI model 85 oxygen and salinity meter. We measured turbidity (±2%) and pH (±0.04) with a Solomat 803PS multiprobe. We determined wind speed and direction with a handheld Kestrel, propeller anemometer, and water current velocity and depth with a Marsh-McBirney electromagnetic flowmeter and wading staff according to USGS protocol [Rantz *et al.*, 1982a, 1982b].

3.5. Denitrification and Nitrification Potential Assays

[19] To estimate the relative importance of autotrophic nitrification and denitrification as sources of N₂O, and to determine what factors might limit denitrification and N₂O production in surface sediments, we performed potential nitrification and potential denitrification assays on sediments from canal A1.

[20] For denitrification potential experiments (similar to those of Rysgaard *et al.* [1996], Pfenning and McMahon [1997], and many others), 1-g subsamples of hand-sieved (2-mm sieve) sediment were taken from the top 3 cm of 10-cm-diameter cores collected at site A1. Subsamples were placed in 60-mL Wheaton bottles with 15 mL of filtered ambient water, and amended with an addition of NO₃⁻ (+14.0 mg l⁻¹ NO₃-N), organic C (+12 mg l⁻¹ as ethyl acetate-C), a mixture of both NO₃⁻ and organic C (+14 mg l⁻¹ NO₃-N, +12 mg l⁻¹ C), or nothing (control). We also incubated sediments with varying C amendments (+0.28, +0.6, +1.2, and +12 mg l⁻¹-ethyl acetate C) to determine the effect of increasing C availability on N₂O production. After amending the sediments, we sealed, evacuated, and flushed all vials with helium. We then performed an acetylene block, inhibiting the reduction of N₂O to N₂ on half the bottles,

allowing us to estimate potential denitrification in addition to N_2O production. For each treatment, we sampled and analyzed three replicate vials at the beginning of the incubation period, and after 4 hours of gentle shaking at 25°C. We calculated potential denitrification and N_2O production from differences between initial and final N_2O concentrations (both aqueous and gaseous phase N_2O) in C_2H_2 -treated and untreated vials, respectively. These assays were performed on three occasions (July 2000, December 2000, and February 2001), and yielded similar results each time.

[21] We also performed a potential nitrification assay (similar to *Rysgaard et al.* [1996] and many others) in order to determine the potential nitrification rate, estimate the amount of N_2O that could be produced via nitrification, and determine the degree to which nitrification in these systems is influenced by NH_4^+ availability. Sediments for this assay were collected in November 2000 and subsampled similarly to the sediments used in denitrification potential assays. Sediments were amended with additions of PO_4^{3-} (+10 mg PO_4^{3-} -P l^{-1}) and NH_4^+ (+1.05, 2.1, 4.2, and 8.4 mg NH_4^+ -N l^{-1}). One set of bottles was sampled immediately while another was left to incubate for approximately 4 hours at 25°C. When the incubation was complete, headspace was analyzed for N_2O concentration and water was filtered and frozen for subsequent nutrient analysis. Nitrification was calculated as the difference between initial and final $[NO_3^-]$, and N_2O production was determined by difference as well.

3.6. Intact Core Experiments

[22] To determine the impact of $[NO_3^-]$, $[DOC]$, and $[NH_4^+]$ on the production of N_2O under more realistic (non-slurry) conditions, we performed several experiments using intact cores. In these experiments, 10–15 cm of sediment and 25–30 cm of overlying water were collected by hand from canal A1 in 10-cm-diameter X 40-cm-long, clear, polycarbonate cores. These cores were transported to our Yaqui Valley laboratory where they were allowed to settle for 12–14 hours at their original temperature ($\pm 1^\circ C$) in a well-aerated, gently circulating, temperature-controlled water bath consisting of water also collected at site A1. Once cores equilibrated, they were amended with 0.6 mg L^{-1} ethyl acetate-C, 1 mg NO_3^- -N L^{-1} in N_2O production experiments, or, in the case of denitrification experiments C_2H_2 and 12 mg L^{-1} ethyl acetate-C. Following amendments, cores were capped. Incubations were run with at least one blank core (water without sediment), and at least two control cores (water and sediment without amendment). Cores were sampled 4 times over the course of their 6–12 hour incubation period for $[NO_3^-]$, $[NH_4^+]$, $[O_2]$, $[N_2O]$, $[CO_2]$, and $[CH_4]$. Cores were incubated under ambient indoor light conditions, and incubations were ended before $[O_2]$ fell below half saturation.

3.7. Sectioned Core Experiment

[23] To determine where N_2O production was likely to be occurring in the sediment column, we sectioned and analyzed cores for $[NO_3^-]$, $[NH_4^+]$, $[DOC]$, $[POC]$, $[PON]$, and $[N_2O]$ with depth. On two occasions (June 23 and 25, 2001, at A1 and PA1, respectively) we collected 10 replicate

5-cm-diameter X 30-cm-long cores from PA1 and A1. Cores were returned to the laboratory within 2 hours for subsampling. We subsampled five cores at 1- to 2-cm intervals for dissolved N_2O concentrations. We used a 3-mL syringe to extract sediment from holes drilled in the side of each core, which had been covered with waterproof tape until time of sampling. Subsamples were placed in pre-poisoned 60-mL Wheaton Vials, and 15 mL of deionized water was added to each sediment sample. Bottles were capped immediately, shaken, and allowed to equilibrate for 2 hours at 25°C. Headspace gas was then extracted and analyzed for N_2O content. After gas sampling was completed, the five remaining cores were sectioned and analyzed for pore water $[DIN]$ (defined as $NO_3^- + NO_2^-$, and NH_4^+), $[DOC]$, $[PON]$, $[POC]$, and bulk density.

3.8. Statistical Analyses

[24] Gas flux, gas concentration, and independent variables with lognormal distributions were log-transformed prior to statistical analysis using Statview 5.0.1 [*Abacus Concepts*, 1992]. Treatment and interaction effects in potential nitrification, potential denitrification, and intact core experiments were evaluated using a factorial design ANOVA.

[25] Simple and stepwise regression approaches were used to determine the relationships between $[N_2O]$ at all sites, and several factors likely to influence it: discharge, water column $[NO_3^-]$, $[NH_4^+]$, $[DOC]$, temperature, pH, DO, salinity, turbidity, $[POC]$, and $[PON]$. N_2O concentration data were used in regression analyses except in the cases of water velocity and discharge, when chamber flux data were used. For our estimates of regional N_2O flux, both septum vial and chamber flux estimates were used. When both measurements were available, we used chamber-based flux estimates. In order to avoid potentially confounding diel effects [*Harrison and Matson*, 2001], only gas measurements performed between 1000 and 1400 local time were used. Unless otherwise stated, uncertainties are ± 1 standard deviation.

3.9. Regional Flux Estimates

[26] We estimated total annual N_2O -N emission to the atmosphere, F_a ($kg-N yr^{-1}$), from each drainage by time-integrating N_2O fluxes. To this end, we used

$$F_a = \frac{365 \cdot 24 \cdot A \cdot \sum_{i=1}^n D \cdot F_{i-1} + 0.5 \cdot D \cdot (F_i - F_{i-1})}{D_{tot}}, \quad (3)$$

where A is the surface area of each drainage canal, D is the number of days between flux measurements, D_{tot} is the total duration (days) of data set, and F_i is the mean calculated N_2O flux for a particular date ($kg cm^{-2} hr^{-1}$, Figure 2). The results of this method generally agreed with estimates based on mean and median N_2O fluxes, and for the remainder of this paper, only time-integrated estimates are used.

4. Results and Discussion

4.1. N_2O Fluxes

[27] Per-area N_2O fluxes from drainage canals were generally high, and sometimes extremely high (Figure 2).

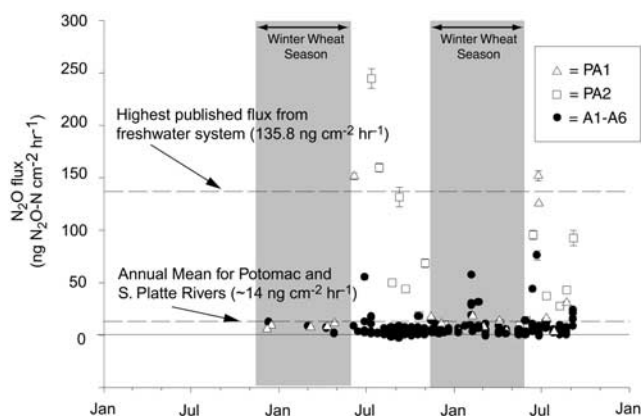


Figure 2. N_2O flux in eight Yaqui Valley drainage canals over two winter wheat cycles (October 1999 through September 2001) determined from supersaturation data. Solid circles represent fluxes from low $[\text{NH}_4^+]$ canals (A1-6), and open triangles and squares represent fluxes from PA1 and PA2, respectively. Shaded areas represent winter wheat seasons when most irrigation and fertilization occurred. Error bars represent ± 1 S.D., and when not visible are smaller than the data point to which they refer. Sample size (n) = 3 for each point.

Mean N_2O flux from the two largest drainage canals (A1 and PA1) was $32.2 \text{ ng cm}^{-2} \text{ hr}^{-1}$, and mean flux from all canals was $16.5 \text{ ng cm}^{-2} \text{ hr}^{-1}$, comparable to fluxes from eutrophic rivers such as the Potomac and the South Platte ($\sim 14 \text{ ng cm}^{-2} \text{ hr}^{-1}$ [McElroy *et al.*, 1978; McMahon and Dennehy, 1999]). At their highest ($244.6 \text{ ng cm}^{-2} \text{ hr}^{-1}$), N_2O fluxes from these drainage canals were greater than the highest reported fluxes from rivers ([Cole and Caraco, 2001; McMahon and Dennehy, 1999]). If anything, these estimates are conservative, as they include only fluxes calculated from concentration data, which were generally slightly lower than floating chamber estimates (slope = 1.08, $R^2 = 0.7$). The highest per-area N_2O fluxes occurred in the canals receiving a mixture of pig-farm and agricultural effluents (PA1 and PA2; Figures 2 and 3), and during summer months when temperatures were high, flows were reduced, and algae blooms were occurring (Figures 2 and 4). Canals with the highest surface areas had the highest rates of N_2O emission watershed-wide (Figure 5 and Table 1), implying an important role for water surface area in determining rates of regional N_2O emission.

4.2. Potential Controls on N_2O Emission

[28] Because sediment processes and water column concentrations appeared to be closely coupled in this system [Harrison and Matson, 2001] (Figure 6), we expected that water column N_2O concentrations, and thus N_2O fluxes, would correlate with water column concentrations of factors controlling N_2O production. In Yaqui Valley drainage canals, many of the factors believed to influence denitrification and nitrification, and hence N_2O production, varied across space and time (Figure 4).

[29] One example of spatial variation was the difference between pig-farm influenced and non-pig-farm influenced canals. The drainage canals in this study could be grouped as two distinct classes with respect to several characteristics. Canals PA1 and PA2 received significant pig-farm and urban inputs whereas watersheds of A1–A6 received primarily agricultural runoff, though A1 and A6 contained a few small pig-farms without direct input into drainage canals (Figure 1). For the remainder of this paper, drainage canals PA1 and PA2 are referred to as pig-farm and agriculture-influenced canals (PA Canals), and canals A1–A6 are referred to as agricultural drainage canals (A Canals). Pairwise comparisons between canals indicated that sites PA1 and PA2 had higher concentrations of $[\text{NH}_4^+]$, $[\text{POC}]$, $[\text{DOC}]$, and $[\text{PO}_4^{2-}]$ than sites A1–A6 (by ANOVA $P < 0.001$ in all cases). Sites PA1 and PA2 also differed from sites A1–A6 with respect to $[\text{NO}_3^-]$, salinity, $[\text{DO}]$, and $[\text{Chl a}]$ ($P = 0.05$, 0.02 , < 0.01 , and 0.01 , respectively). In the following sections, we further describe observed patterns of factors likely to influence $[\text{N}_2\text{O}]$, and evaluate their respective influences on N_2O concentrations in Yaqui Valley drainage canals. We also examine field-based correlations in light of results from laboratory incubations.

4.3. Nitrate

[30] Low NO_3^- availability often limits denitrification in anoxic sediments [e.g., Hinkle *et al.*, 2001; Pfenning and McMahon, 1997]), and N_2O is a product of denitrification, so NO_3^- supplied from the water column to upper layers of the sediment has the potential to exert a strong control on $[\text{N}_2\text{O}]$ in these systems. In our study canals, $[\text{NO}_3^-]$ ranged

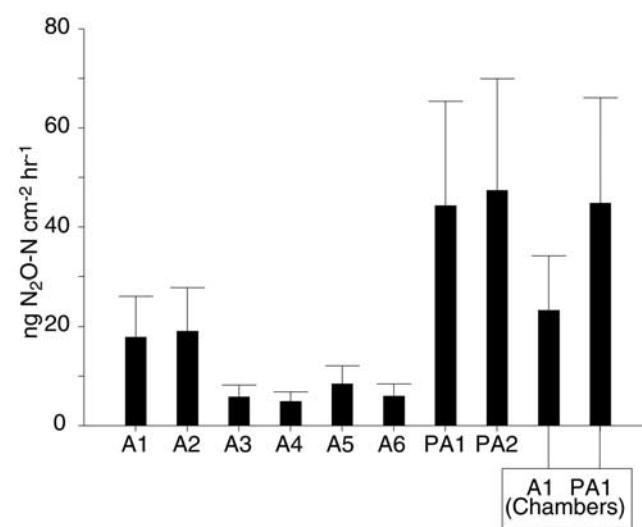


Figure 3. Per-area rates of N_2O flux in study drainage canals ($\text{ng N cm}^{-2} \text{ hr}^{-1}$). Flux estimates based on concentration data are shown on the left, and flux estimates based on floating chambers are shown (legend boxed) to the right for comparison. Error bars represent the sum of uncertainties due to error in flux coefficient ($\pm 45\%$, estimated based on comparison between floating chamber fluxes and measured N_2O super-saturation values) and headspace measurement ($\pm 3.4\%$).

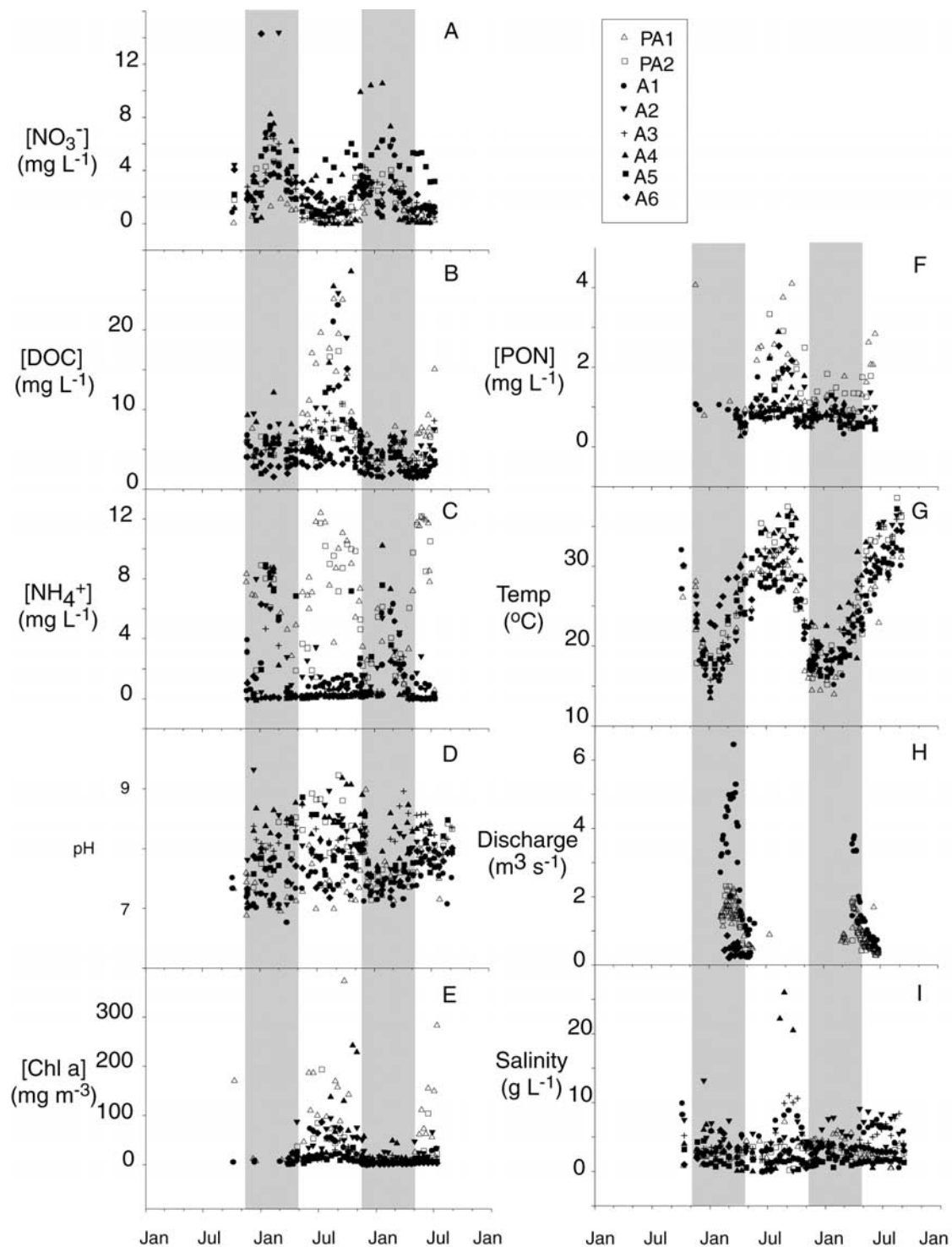


Figure 4. Time series plots of (a) $[\text{NO}_3^-]$ (mg L^{-1}), (b) $[\text{DOC}]$ (mg L^{-1}), (c) $[\text{NH}_4^+]$ (mg L^{-1}), (d) pH, (e) $[\text{Chl a}]$ (mg L^{-1}), (f) $[\text{PON}]$ (mg L^{-1}), (g) Temperature ($^\circ\text{C}$), (h) discharge ($\text{m}^3 \text{s}^{-1}$), and (i) salinity (g L^{-1}). All variables were measured approximately bi-weekly over two winter wheat cycles (October 1999 through September 2002). Distinct drainage canals are represented as different shapes. Shaded areas represent winter wheat seasons when most irrigation and fertilization occur.

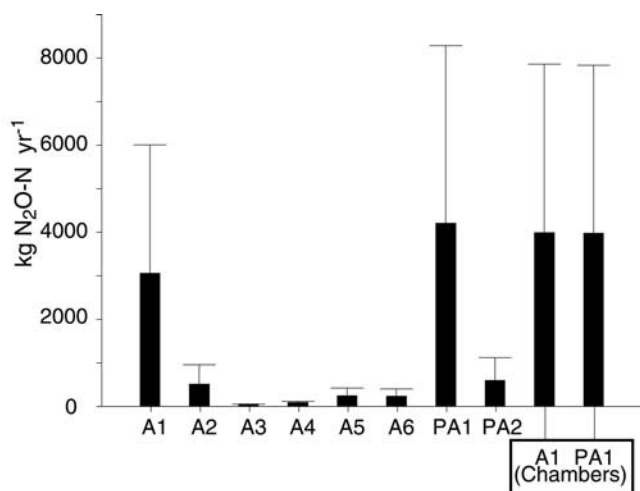


Figure 5. Annual N_2O -N flux from study drainage canals. Flux estimates based on N_2O concentration data are shown on the left, and flux estimates based on floating chambers are shown to the right with a boxed legend. Error bars represent the sum of uncertainties due to error in flux coefficient ($\pm 45\%$, estimated based on comparison between floating chamber fluxes and measured N_2O super-saturation values), headspace measurement ($\pm 3.4\%$), and our estimate of drainage surface area ($\pm 50.6\%$).

from undetectable levels to $14.38 \text{ mg l}^{-1} \text{ NO}_3^-$ -N, and tended to be highest during the winter and spring when auxiliary irrigation events occurred (Figure 4). The high NO_3^- concentrations we observed are very high in comparison to NO_3^- levels in unpolluted systems, and high even in relation to many anthropogenically influenced systems [Meybeck, 1982; Kemp and Dodds, 2002; U.S. Geological Survey, 2002]. Increased $[\text{NO}_3^-]$ was likely due to direct runoff following N-fertilizer application and irrigation or to leaching of NO_3^- remaining in soils following November's principal fertilization/irrigation event (Figure 2). The latter scenario is consistent with an N-leaching model developed for the Yaqui Valley [Riley *et al.*, 2001].

[31] When all drainage canals and seasons were considered, $[\text{NO}_3^-]$ explained only 6.6% of the variability in $[\text{N}_2\text{O}]$ ($P = 0.02$), and when only PA canals were considered, there was no significant relationship between $[\text{NO}_3^-]$ and $[\text{N}_2\text{O}]$ ($P = 0.47$). Nor was there a significant relationship between mean annual $[\text{NO}_3^-]$ and mean annual $[\text{N}_2\text{O}]$, casting doubt on the generally accepted relationship between $[\text{NO}_3^-]$ and N_2O flux. However, in canals A1–A6, $[\text{NO}_3^-]$ explained 17.8% of the variability in $[\text{N}_2\text{O}]$ (Table 2).

[32] Laboratory experiments supported a link between NO_3^- availability and $[\text{N}_2\text{O}]$. Both denitrification potential assays and intact core incubations responded significantly to NO_3^- additions with enhanced N_2O production (Figure 7). In the case of denitrification potential assays, NO_3^- additions increased N_2O production by an order of magnitude. Correlation between $[\text{NO}_3^-]$ and $[\text{N}_2\text{O}]$ was weaker in field data than in laboratory incubations. This may be because NO_3^- only limited N_2O production via denitrification when it was in short supply. When $[\text{NO}_3^-]$ was high, other factors such

as organic C, rather than NO_3^- , may have limited N_2O production due to denitrification.

4.4. Organic Carbon

[33] In study canals, $[\text{DOC}]$ ranged from <1.0 – 27.3 mg L^{-1} with a mean concentration of 5.9 mg L^{-1} (Figure 4). This mean is similar to the global mean $[\text{DOC}]$ for rivers (5.75 according to Meybeck [1982]), and the range of $[\text{DOC}]$ values is greater than the global range of mean annual $[\text{DOC}]$ for large rivers (1.05 – 13.63 mg L^{-1} according to Ludwig *et al.* [1996]).

[34] If organic C limited N_2O production via denitrification when NO_3^- was abundant, we would expect to see a significant relationship between organic C and N_2O in canals with relatively high concentrations of NO_3^- . In canals with $[\text{NO}_3^-] > 1 \text{ mg L}^{-1}$, $[\text{DOC}]$, $[\text{POC}]$, and $[\text{TOC}]$ correlated significantly with N_2O ($r^2 = 0.05$, 0.15 , and 0.089 , and $P = 0.029$, $P < 0.001$, and $P = 0.004$, respectively). Thus, in cases where NO_3^- was plentiful, POC explained almost as much variability in $[\text{N}_2\text{O}]$ as $[\text{NO}_3^-]$. However, at best, organic carbon still only explained 15% of the variation in $[\text{N}_2\text{O}]$.

[35] Results from potential denitrification assays suggested that denitrification and N_2O production in canal A1 were C-limited. In these experiments, organic C increased

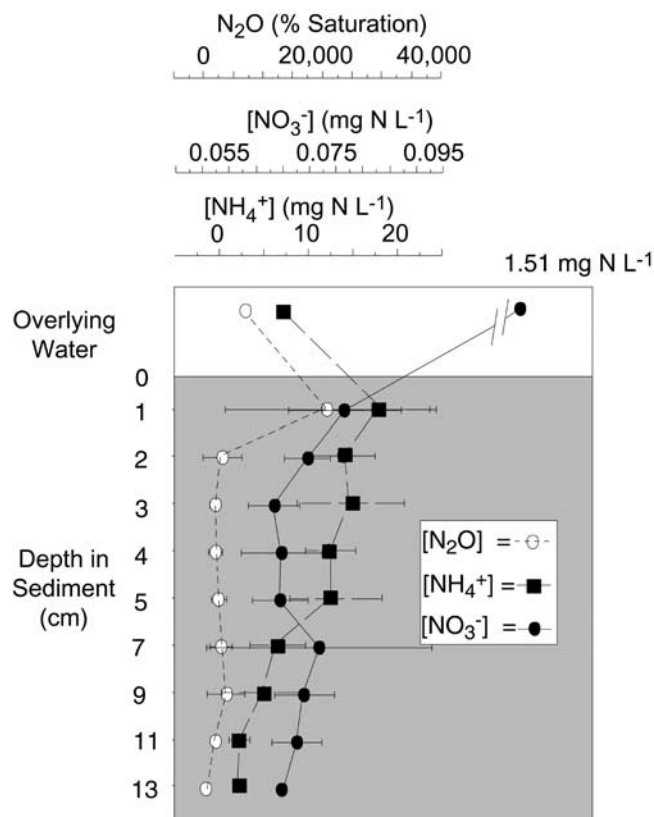


Figure 6. $[\text{N}_2\text{O}]$ (% saturation), open circles; $[\text{NO}_3^-]$ (ppm), solid circles; and $[\text{NH}_4^+]$, solid squares in cores collected from PA1 by depth in cm (Y axis). Sample size (n) = 5 for each point and error bars represent ± 1 S.D. A similar pattern was observed in canal A1.

Table 2. Correlations Between Measured N₂O Concentration (ng-N₂O L⁻¹) and Independent Variables Such as Temperature, Dissolved O₂, Chlorophyll a, Dissolved Inorganic Nitrogen [DIN] Defined as [NO₃⁻ + NO₂⁻ + NH₄⁺], Dissolved Organic Carbon [DOC], Particulate Organic Carbon [POC], Particulate Organic Nitrogen [PON], [NO₃⁻], [NH₄⁺], pH, Salinity, and Turbidity^a

Independent Variable	Stepwise Multiple Regressions						Simple Regressions				
	Step	n	P	r ² (Adj.)	F to enter	F to remove	n	Slope	Int.	P	r ² (Adj.)
<i>All Freshwater sites</i>											
Intercept	0	91		–	–	805.4	–	–	–	–	–
Log [NH ₄ ⁺]	1	91	<0.001	0.446	73.4	77.2	136	0.289	3.332	<0.001	0.362
Log [DOC]	2	91	0.034	0.486	7.9	11.1	137	–	–	NS	–
Log [POC]	3	91	<0.001	0.516	6.5	6.5	119	0.316	3.05	0.002	0.073
Log [DIN]							138	0.486	2.164	<0.001	0.411
Log [PON]							112	0.613	3.238	0.001	0.085
Log [NO ₃ ⁻]							134	0.233	3.255	0.002	0.066
<i>PA Canals (High [NH₄⁺] and [PO₄²⁻])</i>											
Intercept	0	14		–	–	631.9	–	–	–	–	–
Log [Chl a] (μg L ⁻¹)	1	14	<0.001	0.549	16.8	15.0	23	0.382	3.304	<0.001	0.469
Log [NO ₃ ⁻]	2	14	0.08	0.669	5.3	5.3	24	–	–	NS	–
[O ₂]							28	0.045	3.389	<0.001	0.473
pH							29	0.339	1.102	<0.001	0.367
Log [PON]							19	0.720	3.689	0.001	0.436
Log [POC]							19	0.545	3.343	0.002	0.420
Temp (°C)							30	0.233	3.217	0.007	0.206
<i>A Canals (Low [NH₄⁺] and [PO₄²⁻])</i>											
Intercept	0	77		–	–	40.8	–	–	–	–	–
Log [DIN]	1	77	<0.001	0.357	45.0	34.3	114	0.335	2.405	<0.001	0.302
pH	2	77	<0.001	0.422	9.8	9.8	132	-0.375	6.115	<0.001	0.229
Log [NH ₄ ⁺]							111	0.182	3.205	<0.001	0.186
Log [NO ₃ ⁻]							110	0.258	3.092	<0.001	0.171

^aResults of forward stepwise regression analysis with log-transformed N₂O concentration as the dependent variable are shown on left, and results of individual regressions are shown on the right. Non-significant regressions are omitted. For the stepwise multiple regression, criteria for inclusion were: *F* to enter > 4 and *F* to remove < 3.95. Unless otherwise noted, units are in terms of mg L⁻¹.

denitrification and the proportion of denitrification, resulting in N₂O production an order of magnitude more than NO₃⁻ additions alone (Figure 7). Intact core experiments were consistent with potential denitrification assays both in pattern and magnitude of carbon effect (Figure 7). Together, these laboratory results suggest C-limitation of N₂O production. As is likely the case with NO₃⁻, organic C may only limit N₂O production some of the time or its effect may be masked by the fact that organic carbon suspended in the water column may or may not become available to denitrifying organisms. The influence of organic C on N₂O production may also have been masked by nitrification, which may also have played an important role in N₂O production.

4.5. Ammonium

[36] In our study canals, water column [NH₄⁺] ranged from undetectable levels to 12.19 mg L⁻¹ NH₄⁺-N (Figure 4). The highest NH₄⁺ levels were quite high. As a basis for comparison, the range of average [NH₄⁺] concentrations in 681 U.S. streams, some of which are subject to intensive agricultural and urban inputs was just 0–5.5 mg L⁻¹ [Alexander et al., 1996]. In canals A1-6, [NH₄⁺] followed a similar pattern to [NO₃⁻], peaking during winter and spring irrigation and fertilization events. However, in PA canals, [NH₄⁺] remained high year round. Mean [NH₄⁺] was different in the two groups of canals (1.50 ± 2.32 mg L⁻¹ and 6.18 ± 3.73 mg L⁻¹ NH₄⁺-N for A canals and PA canals, respectively; P < 0.0001 by ANOVA).

[37] When all study canals were considered, [NH₄⁺] was significantly and positively correlated with [N₂O] (P < 0.001 and r² = 0.36), and [DIN] was the best single predictor of N₂O production, explaining 41% of the variability in N₂O in all canals (Table 2). This is consistent with a significant nitrification source of N₂O. So is the observed distribution of N₂O in sectioned cores (concentrated in the top few centimeters, Figure 6) and the fact that [O₂] correlated significantly and positively with [N₂O] in PA canals (P < 0.001 and r² = 0.473).

[38] Laboratory assays also suggested that nitrification could play an important role in the production of N₂O. Potential nitrification assays suggested that nitrification could be almost as important a source of N₂O as denitrification in drainage canal sediments (Figure 8), and we observed a significant, positive relationship between [NH₄⁺] and N₂O production via nitrification in potential nitrification experiments (Figure 8 inset).

[39] In addition to acting as a direct source of N₂O, nitrification may also contribute to N₂O production by providing the NO₃⁻ necessary to fuel denitrification, as has been shown to occur in many core studies [e.g., An and Joye, 2001; Laursen and Seitzinger, 2002; Thompson et al., 2000]. However, from our data it is impossible to determine the extent to which coupled nitrification-denitrification contributes to N₂O production.

4.6. Water Column pH

[40] By influencing the activities of nitrifying and denitrifying bacteria, pH has the potential to control N₂O

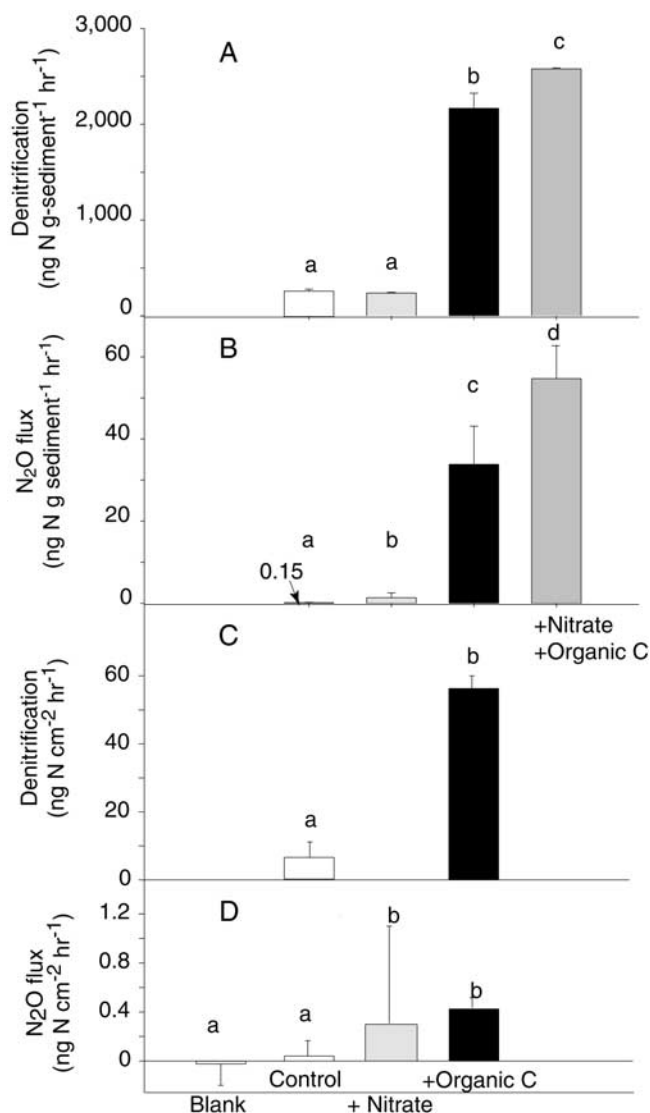


Figure 7. (a, b) Potential denitrification and N₂O production in sediment slurries as a function of NO₃⁻ and Organic C availability. The + Nitrate treatment consisted of a 14 mg L⁻¹ enrichment of NO₃⁻. The + Organic C treatment consisted of a 12 mg L⁻¹ C enrichment with ethyl acetate. All treatments were significantly different from each other by ANOVA ($P < 0.05$) except control and + nitrate treatments with respect to denitrification. Data shown are from December 2, 2000. (c, d) N₂O Production and denitrification in intact cores. Different lower-case letters designate values that are significantly different from each other ($p < 0.05$) Treatments in acetylene block estimate of denitrification: Control (same as in N₂O incubations) and +12 mg L⁻¹ organic C as ethyl acetate. Treatments in N₂O incubations: blank (water without sediment), Control (water and sediment without amendment), +0.6 mg L⁻¹ ethyl acetate-C, or +1 mg L⁻¹ NO₃⁻ enrichments.

production. In pure culture, ammonium oxidizers have been shown to have a pH range of 5.8–8.5 [Watson *et al.*, 1989] with an optimum of 7.8 [Hagopian and Riley, 1998]. Other studies have shown that denitrifiers have an optimum pH of 7.0–8.0 and that denitrification is positively related to pH [Knowles, 1982]. In our study canals, pH was higher in purely agricultural canals (A1–A6; mean = 7.95) than in mixed-input canals (PA1 and PA2; mean = 7.8), and in canals A1–A6 more frequently exceeded the optimal pH range of nitrifiers and denitrifiers. This may explain why we saw a positive correlation between pH and [N₂O] in pig-farm influenced canals, a slightly negative correlation between pH and N₂O in purely agriculture influenced canals, and no effect of pH when all canals were considered (Table 2).

4.7. Temperature

[41] By influencing microbial metabolic rates, temperature can influence the rate at which microbial N transformations occur [e.g., Kadlec and Reddy, 2001]. Temperature has been observed to affect rates of N₂O production in some aquatic systems [Seitzinger, 1988], though not in all [Knowles, 1982]. In our study, water temperatures ranged from 13.5° to 38°C, were highest during July and August, and were relatively uniform across all study canals (Figure 4). Although the effect of temperature was significant in PA canals, ($r^2 = 0.206$ and $P = 0.007$) (Table 2), it was not significant when either canals A1–6, or all canals were considered. The temperature effect in PA canals was most likely due to the correlation between temperature and Chl *a* ($P < 0.001$, $r^2 = 0.399$). Temperature may be less important in this system than in other systems because temperatures are generally within the accepted optimum range for nitrifiers and denitrifiers [Kadlec and Reddy, 2001; Hagopian and Riley, 1998] (Figure 4). Additionally, these canals experience wide day-night temperature swings (up to 10°C), which may preclude narrow temperature-related metabolic maxima within microbial populations. It may also be that

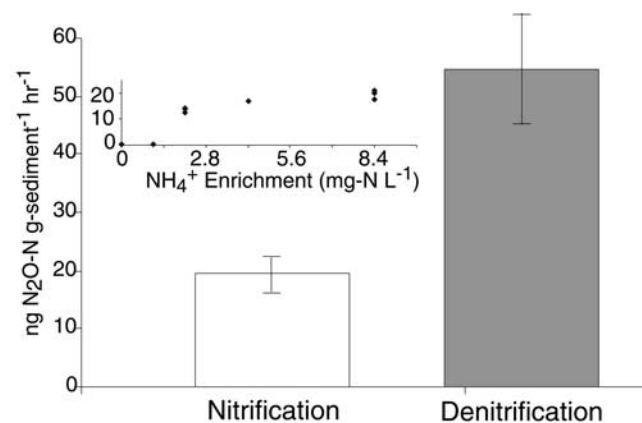


Figure 8. Comparison of potential for nitrification and denitrification to produce N₂O. Error bars represent ± 1 S.D. Inset: NH₄⁺ enrichment versus N₂O production. Sample size (n) = 3 for each NH₄⁺ concentration.

a temperature effect is masked by other factors and their interactions.

4.8. Discharge and Flow Rate

[42] Stream flow velocity and discharge could affect N₂O fluxes by altering rates of material exchange across the sediment-water interface or across the water-air interface, as has been suggested by *Raymond and Cole* [2001] and many others. We tested this hypothesis by attempting to correlate flow rate and discharge with chamber-based flux estimates.

[43] Mid-channel depths ranged from 3 cm during low flow summer months in the smallest canal to 2 m during peak flow in one of the major canals (PA1). Flow velocities were generally low (mean: 0.321 m s⁻¹, range: 0.06–0.568 m s⁻¹ at sites PA1 and A1). Neither comparison of replicate floating chambers subject to different water flow velocities nor stepwise multiple regression including multiple sampling dates indicated a significant relationship between water velocity or discharge and N₂O flux. This is consistent with the findings of *McMahon and Dennehy* [1999], but also may be due to the relatively low range of flows we observed in our study canals.

4.9. Salinity

[44] Some have hypothesized that salinity can influence N₂O production by altering DIN availability, or by influencing the presence of H₂S, an inhibitor of nitrification and the final step in denitrification [*Joye and Hollibaugh*, 1995; *Sorensen et al.*, 1980]. Although the canals in our study were not subject to tidal mixing, they did exhibit a striking salinity range due to seasonal variations in runoff-water salinity and evaporation. Salinities ranged from 0.00 to 26.00 g L⁻¹ with a mean value of 3.16 g L⁻¹, and were inversely correlated with discharge. Highest salinities occurred during low-flow summer months, and generally declined during irrigation events (Figure 4). In this study, salinity didn't significantly correlate with [N₂O] (P > 0.05 in all cases). This may be due to the fact that salinity was almost always sufficient to prevent the formation of large adsorbed N pools. Salinity may exert a stronger control on [N₂O] in systems with lower average salinities.

4.10. Algae Blooms (Chlorophyll a) and Related Variables

[45] Algae blooms have the potential to create extremely favorable conditions for N₂O production. By increasing DOC release to the water column and deposition of POC to sediments, algae growth can remove the organic C limitation on denitrification, while rapid daytime photosynthesis can create the enriched dissolved oxygen environment necessary for rapid nitrification and coupled nitrification-denitrification [*An and Joye*, 2001].

[46] In summer months, when canal water flows decreased, we observed intense algae blooms (up to 373.6 mg Chl a m⁻³), particularly in PA canals (Figure 4). In these canals, [Chl a] was the best single predictor of [N₂O] (r² = 0.47, P < 0.001), and other bloom-related variables such as [O₂], [PON], and [POC] also correlated

significantly with [N₂O] (r² = 0.473, 0.436, and 0.42, and P = <0.001, 0.001, and 0.002, respectively).

4.11. Multiple Regression Models

[47] Though several of the variables tested had some predictive value with respect to [N₂O], none of them stood out as a clearly superior predictor of [N₂O] when considered alone. However, with a multiple regression approach, we were able to explain 52% of the variation in [N₂O] in all canals using [NH₄⁺], [DOC], and [POC] as independent variables (Table 2). When only agriculturally influenced canals were considered, [DIN] and pH explained 50% of the variation in [N₂O]. When only canals receiving a mixture of pig-farm and agricultural inputs were considered, the best regression model for [N₂O] included [Chl a] and [NO₃⁻], and explained 67% of the variation in [N₂O].

[48] In contrast to other studies where [DIN] has correlated strongly with [N₂O] [e.g., *McMahon and Dennehy*, 1999], in our study, multiple factors appeared to control [N₂O], and controls appeared to change with changes in inorganic N availability. Under low [DIN] conditions, DIN probably controlled [N₂O]. However, when DIN was plentiful, control of [N₂O] likely shifted to factors associated with stream productivity, a notion supported by the strong relationship between algae-bloom-related variables and [N₂O] in PA canals described above.

4.12. Regional Significance of Aquatic N₂O Flux and Implications for Global Estimates

[49] Annual N₂O-N fluxes from drainage canals in this study ranged from 13 kg N₂O-N yr⁻¹ in canal A3 to 4,167 kg N₂O-N yr⁻¹ in canal A1 (Figure 5), and the total annual flux from all canals together was 8,678 kg N₂O-N yr⁻¹. By assuming that the fluxes we measured in the study canals were representative of canal fluxes valley-wide, we were able to estimate a valley-wide annual N₂O-N flux from agricultural drainage canals to be 20,869 kg N₂O-N yr⁻¹.

[50] Assuming a relatively conservative valley-wide per-hectare fertilizer application rate of 250 kg N ha⁻¹ wheat or maize crop cycle⁻¹ [*Matson et al.*, 1998; *Naylor et al.*, 2000], and a conservative estimate of wheat and maize crop-area (170,000 ha [*Secretaria de Agricultura*, 2000]), we calculate that 0.046% of the N fertilizer applied to Yaqui Valley fields was lost from drainage waters as N₂O-N. Thus N₂O-N emissions from drainage water were about an order of magnitude lower than emissions from agricultural fields (0.205–1.4% of the applied N in the 1995/96 wheat season [*Matson et al.*, 1998]), and over 2 orders of magnitude less than N leached to surface and groundwaters (8–20% of applied N [*Riley et al.*, 2001]).

[51] It is also possible to compare our measured regional N₂O fluxes with fluxes predicted by global N₂O models. Two such models are described in *Mosier et al.* [1998] and *Seitzinger and Kroeze* [1998].

[52] The model described by *Mosier et al.* [1998] is used as the basis for IPCC calculations of national N₂O emissions. It calculates N₂O emissions from rivers according to

$$N_2O = NLEACH*(EF5 - r), \quad (4)$$

where NLEACH refers to N leached from land to rivers (calculated as $[\text{N-Fertilizer} + \text{N-Excreted as manure}] * [\text{Fraction leached}]$) and EF5-r refers to the sum of the percent of nitrification (0.5%) and denitrification (0.25%) resulting in N_2O emission. Using an N-loading estimate for the Yaqui Valley of $67,842 \text{ Mg N yr}^{-1}$ ($1 \text{ Mg} = 10^6 \text{ g}$) [Rice, 1995] as model input, and an NLEACH ranging from 10 to 80%, we calculate a predicted rate of N_2O emission for Yaqui Valley drainage waters of 51–407 $\text{Mg N}_2\text{O-N}$. This range of predicted N_2O emissions is 2–19 times as high as our measurement-based estimate.

[53] Another model, described by Seitzinger and Kroeze [1998], calculates N_2O emission from rivers according to

$$\text{N}_2\text{O}_{\text{riv}} = \text{EF}_{\text{riv}} * 3 * \text{DINEXPORT}_{\text{riv}}, \quad (5)$$

where EF_{riv} is an emission factor equal to 0.03 or 0.003 depending on N inputs. In systems like the Yaqui Valley, where N inputs exceed 10 kg ha^{-1} , EF_{riv} is assumed to be 0.03, or 3% of the DIN exported by the river. $\text{DINEXPORT}_{\text{riv}}$ is the product of DIN concentration and discharge.

[54] To develop input data for this model, we calculated Yaqui Valley DIN loads using

$$\text{DIN}_{\text{coast}} = [\text{DIN}] * Q_{\text{ann}}, \quad (6)$$

where [DIN] is median DIN concentration over the course of our study and Q_{ann} is mean annual discharge for Yaqui Valley drainage canals over the years 1987–1996 (Comision Nacional del Agua, Sonora, Mexico, unpublished data, 1987–1996). This approach yielded an estimate that the canals included in this study transport 709 Mg of DIN to the coast annually. Scaling up to the whole valley, we estimate that Yaqui Valley drainage canals carry 954–1688 Mg of DIN to the near-coastal zone annually. High and low estimates of N-transfer were achieved by including and excluding pig and urban-influenced canals from valley-wide estimates of N transfer, with high estimates resulting from inclusion of pig and urban-influenced canals. Using our calculated DIN export as model input, the approach of Seitzinger and Kroeze [1998], yields an estimated river N_2O production for the Yaqui Valley of 86–152 $\text{Mg N}_2\text{O-N yr}^{-1}$, or 4–7 times our measurement-based estimate.

[55] Given that Yaqui Valley drainage canals demonstrated some of the highest N_2O fluxes ever measured in a flowing freshwater system, it is surprising that our regional estimates of N_2O emissions are substantially lower than estimates based on global models. One potential explanation for this is that our sampling strategy missed the real hot spots for N_2O production and emission. Reay et al. [2003] suggest that differences between measured and predicted N_2O emissions from agricultural drainage waters may be due to sampling that is performed too far downstream to see the highest rates of N_2O production. However, in our study, we sampled within the agricultural fields, not downstream of them, and the few longitudinal transects we ran (data not shown) showed, if anything, a trend toward increasing N_2O concentrations as one moved downstream.

[56] Another factor that might explain the difference between measured and predicted values is the location of the

Yaqui Valley drainage system with respect to the coast. Water residence time and channel morphology are thought to influence N-processing in rivers, with N-processing, and hence N_2O production, increasing with increasing residence time and decreasing stream size [Seitzinger et al., 2002; Alexander et al., 2000]. The fact that the Yaqui Valley is located close to the coast may mean that N is transformed less en route to the coastal zone than in other systems, leading to lower overall rates of N_2O emission from drainage waters. Globally, most drainage systems are located farther from the coast than the Yaqui Valley system [Vörösmarty et al., 2000].

[57] Finally, it may also be as some have suggested [Nevison, 1999; Reay et al., 2003] that existing models of river N_2O production substantially overestimate N_2O production in agricultural drainage waters. However, further work will be required to determine whether this is the case and, if so, how to improve existing models.

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J. Harrison, Institute of Coastal and Marine Sciences, Rutgers University, 71 Dudley Road, New Brunswick, NJ 08901, USA. (harrison@imcs.rutgers.edu)

P. Matson, Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305, USA. (matson@pangea.stanford.edu)