# A synthesis of nitrogen transformations and transfers from land to the sea in the Yaqui Valley agricultural region of northwest Mexico

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[1] Intensification of agricultural systems represents one of the most significant land use changes of the last century. High fertilizer inputs have been a key component of intensification and have contributed to increases in crop yield in most areas, but they can also cause profound alterations in the biogeochemical functioning of the soil, water, and air resources of these systems, particularly with regard to the nutrient nitrogen (N). Comprehensive studies linking field-scale fertilization with regional N fates and consequences for water resources are surprisingly sparse, particularly in the rapidly developing tropics and subtropics. Here we synthesize 15 years of research in wheat fields, drainage canals, estuaries, and coastal waters of the Yaqui Valley region of Sonora, Mexico. Although a relatively low proportion (<4%) of total N inputs are exported via surface water to the coast, the episodic nature of these losses can have significant ecological consequences. For instance, gaseous and dissolved N fluxes from agricultural fields are among the highest observed, and N-rich runoff from the Yaqui Valley fuels phytoplankton blooms in coastal waters. Reductions in N losses with improved timing of fertilizer application relative to crop demand are possible without negatively affecting crop yield or quality and may help to move this and similar regions closer to sustainability.

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## 1. Introduction

[2] The conversion of natural ecosystems to agroecosystems is the most pronounced land use/land cover change driven by human activity. Nearly 40% of the earth's land surface has been converted to croplands or rangelands, and the management intensity on these systems has steadily increased over the last 40 years [*Foley et al.*, 2005]. Agriculture directly influences water resources by the appropriation of runoff and groundwater for irrigation [*Postel et al.*, 1996], and intensive agriculture strongly affects water resources by degrading water quality [*Vitousek et al.*, 1997]. In particular, dramatic changes in the biogeochemistry of aquatic and marine systems are a direct result of extensive and intensive use of nitrogenous fertilizers.

[3] Although remarkable increases in agricultural productivity have been driven by nitrogen (N) fertilizer, only ~50% of applied N ends up in harvested crops; the remainder accumulates in soil or is lost from agroecosystems [*Smil*, 1999]. Primary loss pathways (in addition to harvest) include leaching to subsurface horizons and aquifers, surface runoff, erosion, and gaseous emissions, and these losses have important and unintended consequences for the atmosphere, water systems, oceans, and human health [*Beman et al.*, 2005; *Carpenter et al.*, 1998; *Galloway et al.*, 2003; *Matson et al.*, 1998; *Townsend et al.*, 2003]. Comprehensive efforts to document the amounts and pathways by which N is lost from agroecosystems in all of its forms are, however, surprisingly limited in number. Although numerous studies have quantified aqueous N losses (see Section 4), few if any have also examined gaseous N losses from both soils and surface waters. To our knowledge, no such efforts have targeted developing world agricultural systems, although many of these systems are following a rapid trajectory of intensification.

[4] For the last 15 years we have been building an understanding of the social, economic and environmental sustainability of the Yaqui Valley of Sonora, Mexico. Much of our work has focused on water and nitrogen, including a broad range of studies focused on gaseous N emissions from soils [*Matson et al.*, 1998; *Panek et al.*, 2000] and streams [*Harrison and Matson*, 2003; *Harrison et al.*, 2005], leaching losses [*Riley et al.*, 2001], the importance of N management for yield variability [*Lobell et al.*, 2004; *Lobell et al.*, 2005], development of N simulation models [*Christensen et al.*, 2006; *Riley and Matson*, 2000], regional water management [*Addams*, 2005; *Schoups et al.*, 2006a, 2006b], in-stream N transformations [*Harrison et al.*, 2005], coastal algal blooms exacerbated by agricultural runoff [*Beman et al.*, 2005], and system-wide vulnerability [*Luers et al.*, 2003; *Turner et al.*, 2003a; *Turner et al.*, 2003b]. Here we integrate this information in order to gauge the

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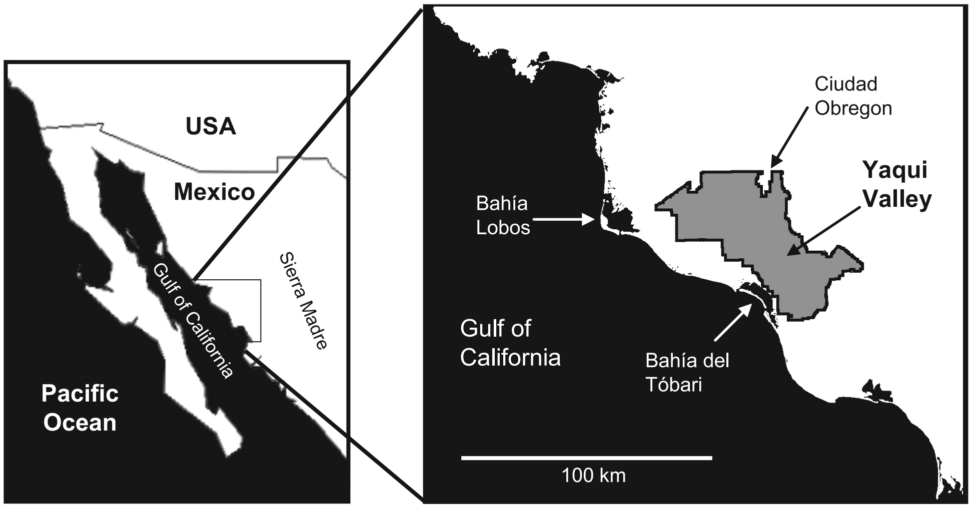


**Figure 1.** Yaqui Valley, Sonora, Mexico. Included within the inset are limits of the Yaqui Valley irrigation district, the locations of the two major estuaries (Bahía Lobos and Bahía del Tóbari), and the valley's largest city, Ciudad Obregon. The Yaqui Valley is situated between 26°45′–27°33′N latitude and 109°30′–110°37′W longitude.

sustainability of N management in the Yaqui Valley, and possibly other high-input semitropical agricultural regions.

## 2. Valley Overview

[5] The Yaqui Valley is an alluvial coastal valley located in Sonora, Mexico, bordered to the east by the Sierra Madre foothills, and to the west by the Gulf of California (Figure 1). The Valley includes approximately 363,000 inhabitants, with an economy based primarily on agriculture, fishing, aquaculture and livestock industries and support sectors. Mean annual precipitation over the last 25 years is 320 mm, with most falling during the summer monsoon season (June–September; a description of seasonal rainfall patterns and regional drought can be found in work by *Nicholas and Battisti* [2008]). Minimum and maximum temperatures during the primary growing season (January–April) average 9.6°C and 27.3°C, respectively. Mean potential evapotranspiration ($\sim$2000 mm $a^{-1}$) greatly exceeds precipitation. Soils are predominantly vertisols with low organic matter (<1%) or aridisols with slightly higher organic matter; most are mixed montmorillonite clays, silty clays and clay loams.

[6] The Yaqui River watershed encompasses $\sim$80,000 km$^2$, and three reservoirs on the Yaqui River and its tributaries are the major source of irrigation water to the valley. A network of irrigation canals delivers water from these reservoirs to serve 233,000 ha of irrigated agriculture, with 15% of irrigation water lost from fields as surface water runoff [*Schoups et al.*, 2005]. Approximately 330 wells are used primarily as a supplemental source for irrigation water, and most access a deep aquifer that varies from 30 to 100 m from the surface [*Schoups et al.*, 2005]. A shallow aquifer varies in depth by season and can rise to 1–2 m from the surface during period of high recharge [*Schoups et al.*, 2005]. Surface water runoff is carried by a series of drains that empty into small lagoons or one of two larger estuaries (Bahía Lobos in the north and Bahía del Tóbari in the south) before entering the Gulf of California (Figures 1 and 2). Further details of the valley's hydrology are discussed by *Addams* [2005] and *Schoups et al.* [2005, 2006a, 2006b].

## 3. Nitrogen Transformations and Transfers in the Yaqui Valley

### 3.1. Nitrogen Inputs to the Valley

[7] There are multiple sources of N to the Yaqui Valley, but clearly the most important input is via fertilization of agricultural fields. For much of the last century, irrigated agriculture has been a focus of development in the Yaqui Valley. In the early 1940s, an agricultural research station that would prove to be a precursor to the current International Maize and Wheat Improvement Center (CIMMYT) agricultural research station was established; under CIMMYT, this station went on to be one of the leading institutions for the development of high-yielding dwarf cultivars of wheat during the "green revolution" of the 1960s and 1970s. The newly developed cultivars were highly responsive to inputs of N fertilizers, and strong fertilizer subsidies through the early 1990s contributed to fertilization rates that continue to be among the world's highest [*Naylor et al.*, 2001]. Wheat has remained the most widely planted crop, and has received the more fertilizer than other crops in the valley for much of the last 50 years (Figure 3). Other locally important crops include maize, soybeans, safflower and cotton. Wheat dominates planting area in the winter season. Soybean was the most significant summer crop but was virtually eliminated because of a whitefly infestation in 1994–1995; it was replaced by corn and cotton, leading to nearly a doubling of annual fertilizer inputs in the valley [*Naylor et al.*, 2001]. For the past 8 years, however, water scarcity has limited planting of many crops in the summer.

[8] In addition to agriculture, several other sectors have also developed rapidly in recent decades, each with increasing N demands. The human population has expanded more than fivefold since 1950, with >60% now concentrated in

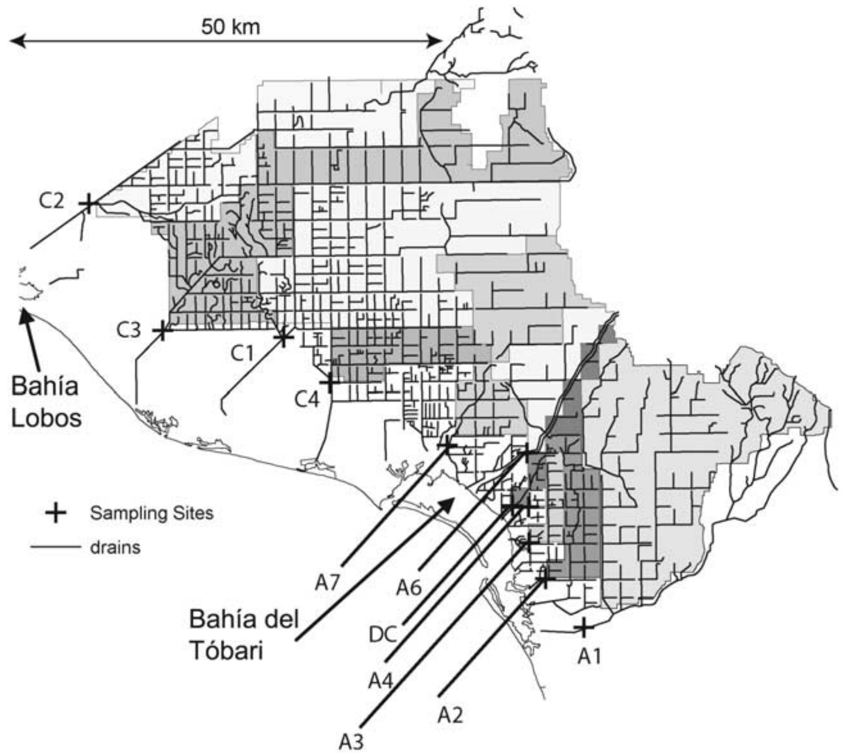


**Figure 2.** Locations of the 11 canal sampling stations. Shaded regions indicate the portions of the valley served by each of the sampled drainage canals. The Yaqui Valley is situated between 26°45′–27°33′N latitude and 109°30′–110°37′W longitude.

Ciudad Obregon, the valley's largest city. Livestock operations, led by pork production, have also increased in the valley throughout the past 20 years. Animal wastes in the valley's livestock production facilities are typically held in open lagoons for weeks to months before they are discharged into canals, and this N-rich waste likely places local N burdens on canals and groundwater. Shrimp aquaculture has also become an important industry in the area in the last 30 years, and N is introduced to shrimp ponds both in feed and directly as N fertilizer.

[9] Overall, we have estimated that ~8200 Mg N are introduced to the Yaqui Valley for human consumption, livestock operations and aquaculture combined, compared to almost seven times that amount for agriculture (Table 1 and Figure 4) (T. D. Ahrens et al., Nitrogen in the Yaqui Valley: Sources, transfers, and consequences, manuscript in preparation, 2008). Wheat agriculture is by far the largest single source of N inputs to the Yaqui Valley, contributing ~41,100 Mg N of the estimated 54,900 Mg N total inputs to agriculture in 2006 (Table 1). Although N management in other sectors may be locally important now and regionally important in the future, understanding the fates of N applied to wheat fields is critical. Here we discuss how

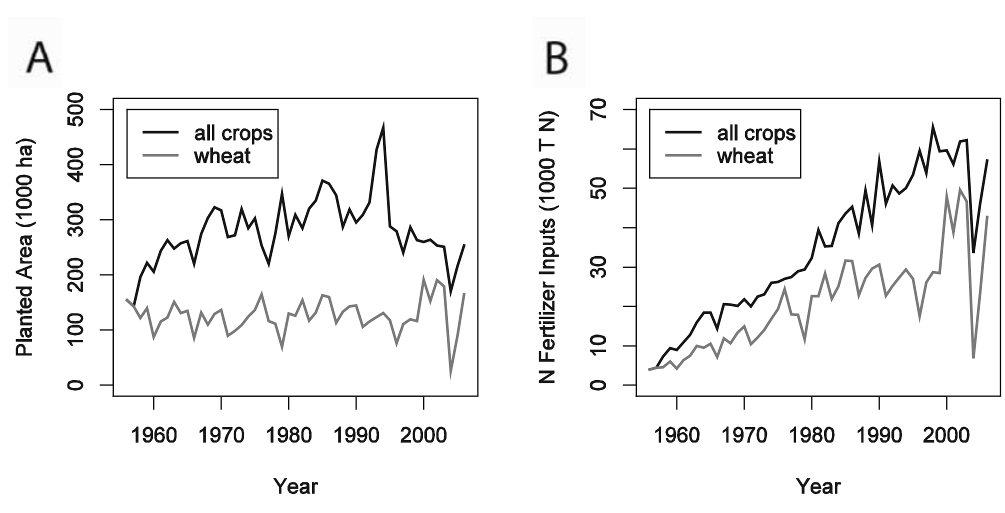


**Figure 3.** Trends in (a) planted area and (b) N fertilizer use in Yaqui Valley from 1956 to 2006.

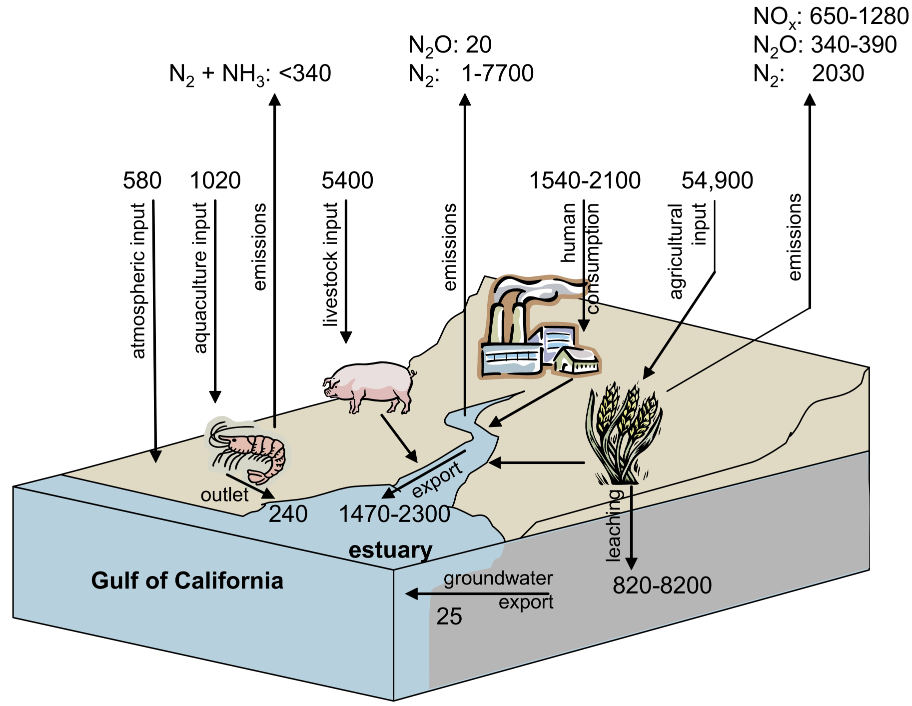


**Figure 4.** Major fluxes of N to and from agriculture, aquaculture, livestock production, and human consumption in the Yaqui Valley (reproduced from Ahrens et al. (submitted manuscript, 2007)). Units for all numbers are reported in Mg N $a^{-1}$. Sources used to estimate each flux are given in Table 1. Groundwater N export to the ocean was calculated using the average modeled groundwater outflow from 1974 to 1997 [*Schoups et al.*, 2005] with mean DIN in wells sampled in 2004 (2.11 mg N $L^{-1}$ (Jewett, unpublished data, 2004)).

N is processed and transported from wheat fields, through drainage canals, and on to coastal and marine systems, in an attempt to understand the effects of agricultural intensification on air and water resources at a regional scale.

### 3.2. Transformations and Transfers in Wheat Fields

[10] Yaqui Valley wheat fields receive on average 250 kg N $ha^{-1}$ $cycle^{-1}$, with two thirds of the total amount most commonly applied as broadcast urea ($(NH_2)_2CO$) several weeks before planting. While high compared to U.S. wheat, similar rates are now common in China [*Ju et al.*, 2004]. Over the last decade, we designed several studies to measure controls on N cycling within farmers' fields and to measure fluxes through the soil-crop system to the atmosphere, groundwater, and canals. One of the first studies was a four-treatment randomized block experiment run for two seasons (1994–1995 to 1995–1996) at the CIMMYT research station to measure soil N retention, gaseous emissions, N leaching rates, and crop growth from wheat crops managed under typical management and three

**Table 1.** Nitrogen Inputs and Outputs From the Yaqui Valley[a]

| | Form of N | Agriculture | Livestock[b] | Shrimp | Human Consumption and Sewage | Drainage Canals | Total |
|---|---|---|---|---|---|---|---|
| Input | N | 54,900 | 5400 | 1020 | 1540–2100 | | 63,500–64,000 |
| Gaseous losses | $NO_x$ | 650–1280 | | | | | 650–1280 |
| | $N_2O$ | 340–390 | 4 | | | 20 | 370–420 |
| | $NH_3$ | | | <340 | | | <340 |
| | $N_2$ | 2030 | | <340 | | 0.7–7700 | 2030–10,070 |
| Leaching losses | $NO_3^-$ | 820–8200 | | | | | 820–8200 |
| Coastal loading | DIN | <1690 | <1690 | <240 | <1690 | 660–1690 | 660–1930 |
| | TN | <2060 | <2060 | 240 | <2060 | 1230–2060 | 1470–2300 |

[a]Values are in Mg N; 1 Mg N = $10^3$ kg. It is not known how much of the N in feed for livestock and human consumption was from intravalley sources; thus estimates may include double counting. The calculation of each estimate is explained in detail by Ahrens et al. (submitted manuscript, 2007). Area planted to each crop, livestock production, and area under active shrimp production were taken from the most recent year available (2004) at www.siap.gob.mx. Fates of N in agriculture and drainage canals are explained in this paper. N dynamics in shrimp ponds drew heavily from *Paez-Osuna et al.* [1997], and human consumption was estimated on the basis of per-person protein intake estimates [*Smil*, 2002; *Socolow*, 1999] and does not include other N in the production waste stream. Atmospheric deposition of inorganic N is not shown in the table but is included in the estimated total input. Deposition was estimated to be 583 Mg N (~2.5 kg N $ha^{-1}$, on the basis of *Holland et al.*'s [2005] estimate of the sum of wet and dry deposition in sparsely populated regions of the West Coast).

[b]Livestock is hogs and cattle.

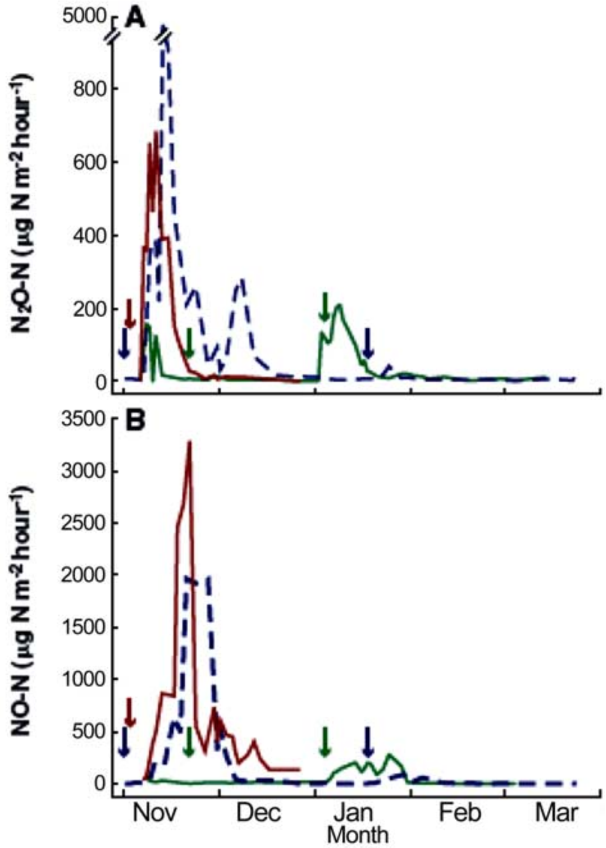


**Figure 5.** Emissions of (a) $N_2O$ and (b) NO from wheat fields managed with typical farmer practices in 1994–1995 (blue) and 1995–1996 (red) and with best alternative management practices in 1995–1996 (green). Arrows indicate fertilizer applications (color coded by year and treatment). From *Matson et al.* [1998]. Reprinted with permission from AAAS.

reduced-N alternatives. Experimental studies were supplemented with a similar sampling regime in three farmers' fields; patterns and magnitudes of fluxes were similar to the experimental plots (P. A. Matson, unpublished data, 1996).

#### 3.2.1. Gaseous N Losses From Soils

[11] Under typical management and the three alternatives, gaseous emissions of nitrous oxide ($N_2O$) and nitric oxides ($NO_x$) were measured along with changes in soil N pools and processes over daily to weekly sampling frequencies. $N_2O$ acts as a greenhouse gas and is involved in the reactions that destroy stratospheric ozone [*Crutzen*, 1970; *Prather and Ehhalt*, 2001], and agriculture is one of the largest sources of $N_2O$ [*Bouwman*, 1996; *Isermann*, 1994; *Mosier et al.*, 1998]. $NO_x$ catalyzes the formation of tropospheric ozone [*Crutzen*, 1970], which is harmful to plant growth and human health [*Benton et al.*, 2000; *Townsend et al.*, 2003]. $N_2O$ fluxes were determined by measuring increased concentrations (via gas chromatography) in the headspace of static chambers placed over soil. $NO_x$ emissions were measured using static chambers and $NO_x$ fluxes determined via chemoluminescence [*Matson et al.*, 1998]. Spatially averaged daily fluxes of NO and $N_2O$ from fields under typical management were variable, with extremely high emissions occurring in the days and weeks following fertilization, dropping to low rates in later in the growing season (Figure 5); individual fluxes ranged up to 650 ng cm$^{-2}$ h$^{-1}$ for $N_2O$-N and 550 ng cm$^{-2}$ h$^{-1}$ for NO-N, among the highest fluxes ever reported. Over the growing season, $N_2O$ and $NO_x$ emissions together accounted for 2.6–4.5% of applied fertilizer [*Matson et al.*, 1998]. Measured season-long emissions rates generally fell within broad ranges of a small number of previously published studies of trace gas emissions from agriculture. *Mosier et al.* [1996] reported that 90% of $N_2O$ emission estimates were likely within a range of 1.25 ± 1% of fertilizers applied to soils, and *Davidson and Kingerlee* [1997] suggested mean NO emissions of 4 kg NO-N ha$^{-1}$ for tropical cultivated land based on a small number (seven) of studies. In the Yaqui Valley, most of the season's gaseous losses occurred during the preplanting period immediately after fertilizer application, when high levels of inorganic N occurred in the absence of plant demand. NO emissions at this time totaled over 1–2 million kg N over the month following fertilization, leading to concentrations that could potentially drive smog events in the downwind urban center (Matson, unpublished data, 1996).

[12] Emissions from native vegetation were not measured, but several published studies suggest that emission rates from wheat fields were considerably higher than those from natural semiarid systems. Background NO emissions from natural systems in the Chihuahuan Desert in New Mexico, USA were estimated to be 0.12 kg NO-N ha$^{-1}$ a$^{-1}$ [*Hartley and Schlesinger*, 2000]. *Guilbault and Matthias* [1998] estimated an annual flux of 0.4 kg $N_2O$-N ha$^{-1}$ a$^{-1}$ on the basis of limited daytime measurements during a 10-week period, but this estimate is at the upper limit of a range of $N_2O$ emissions from semiarid soils compiled by *Galbally et al.* [2008].

[13] NO and $N_2O$ are both released as byproducts or intermediates during the microbially mediated processes of nitrification (the oxidation of $NH_4^+$ to $NO_3^-$ under aerobic conditions) and denitrification (the reduction of $NO_3^-$ to $N_2$ under anaerobic conditions). During the 1995–1996 growing season, an experiment using $^{15}$N-labeled $NH_4^+$ and $NO_3^-$ was designed to determine the magnitude and duration of $N_2O$ emissions from each process. Following irrigation, denitrification dominated over nitrification for 2 days until soils became aerobic, creating conditions favorable for nitrification [*Panek et al.*, 2000]. Emissions from nitrification were higher during drier periods, and over the entire season, both processes contributed equally to seasonal $N_2O$ emissions from Yaqui Valley soils [*Panek et al.*, 2000].

[14] Ammonia fluxes, measured using sulfuric acid traps, were also extremely high (Matson, unpublished data, 1996). While this method cannot be used to make quantitative per-area emission estimates, volatilization losses could represent an important flux of fertilizer N from farmer fields.

#### 3.2.2. Aqueous N Losses From Soils

[15] Estimates of N in soil solution leached below the rooting zone were obtained using weekly to monthly collections of water from zero tension lysimeters installed a meter in depth. Total fluxes were estimated using a process-based N simulation model developed and tested in the Yaqui Valley (NLOSS) [*Riley et al.*, 2001; *Riley and Matson*, 2000]. NLOSS simulates water flow in one dimension and major N processes including decomposition, min-

eralization, nitrification, denitrification, solute transport, and trace gas emissions. Irrigation water leached below the rooting zone carried 2–5% of the applied N fertilizer in research plots under typical management, and much higher amounts (14–26%) in farmer fields [*Riley et al.*, 2001]. High nitrification rates, especially following the preplanting fertilization, led to high concentrations of mobile $NO_3^-$. A majority of N leaching occurred rapidly in the first few days following each irrigation event, and virtually all of the N leached through the soil profile was in the form of $NO_3^-$ [*Riley et al.*, 2001]. The large range of leaching rates from research plots and farmers' fields (2.6–26% of applied N) was similar to variability measured in temperate systems in the U.S. and UK [*Di and Cameron*, 2002].

[16] In rainfed temperate systems, a significant portion of annual leaching losses may occur outside of the growing season in regions where water fluxes and mineralization of organic N co-occur, leading to leaching losses in the absence of crop demand [*Di and Cameron*, 2002]. In the Yaqui Valley, losses during the growing season occurred within days of irrigation events [*Harrison and Matson*, 2003; *Riley et al.*, 2001]. Leaching losses during the nongrowing season were not measured, and it is possible that significant leaching events occurred during occasional intense fallow season rain events in the valley's summer monsoonal, semiarid climate.

#### 3.2.3. Alternative Management Practices

[17] In the 1994–1996 study, alternative management practices that better matched fertilizer supply with crop demand were successful in reducing both gaseous and leaching losses. The most successful alternative treatment involved applying a reduced rate of fertilizer (180 compared to 250 kg N $ha^{-1}$) split between planting (1/3) and at the first postplant irrigation (2/3). Elimination of the high preplant fertilization resulted in 0.74 kg N $ha^{-1}$ in seasonal NO + $N_2O$ evolution, compared to 11.3 kg N $ha^{-1}$ from the treatment with typical farmer practice [*Matson et al.*, 1998]. Yield and grain quality did not differ in these two treatments, which led to an estimated 12–17% increase in profit to farmers due to reduced fertilizer costs [*Matson et al.*, 1998]. Leaching rates also decreased from 2% of applied N in fields under typical research station management to 0.1% in the 180 kg N $ha^{-1}$ alternative in 1997–1998 [*Riley et al.*, 2001]. In addition to improving the timing of fertilization and reducing fertilization rates, other management strategies have also been shown to reduce leaching in temperate agroecosystems, including fallow season cover crops, limiting fertilization during period of high precipitation, tillage timing, and the use of technologies that allows for site-specific nutrient management (SSNM) [*Di and Cameron*, 2002].

[18] Current SSNM trials in the Yaqui Valley can lead to reductions in N use similar to those in the alternative management treatments in the 1994–1996 study. Handheld sensors (GreenSeeker$^{TM}$) are being used to generate fertilizer recommendations on the basis of a comparison between the greenness of heavily fertilized strips to strips initially fertilized at typical on-farm rates [*Ortiz-Monasterio and Raun*, 2007]. Thirteen on-farm validation trials resulted in an average savings of 69 kg N $ha^{-1}$ and U.S.\$62 $ha^{-1}$ without any reduction in crop yield or quality. Such sensor-based approaches allow for two major changes in management that reduce N applications: better timing of crop demand and fertilizer addition, and differential fertilization rates depending on residual N supply available to a crop. If both changes are employed, further reductions in N losses beyond the alternative management practice in *Matson et al.*'s [1998] field experiments are possible. Recent field studies in rice and wheat systems in southeast Asia, China, and India have also shown the potential for increased profit and decreased N use using SSNM [*Dobermann et al.*, 2002; *Khurana et al.*, 2008; *Khurana et al.*, 2007; *Peng et al.*, 2006].

#### 3.2.4. Patterns of N in the Subsurface

[19] The dynamics of N in subsurface flow paths below the rooting zone have not been directly measured in Yaqui Valley. Limited sampling of Valley aquifers suggests that portions of the valley have elevated $NO_3^-$ concentrations in groundwater that exceed Mexico's drinking water standard of 10 mg $NO_3^-$-N $L^{-1}$. Forty of the valley's ~330 operational wells [*Schoups et al.*, 2006b] were sampled during 1993–1994, and a quarter of sampled wells had $NO_3^-$ concentrations >10 mg $NO_3^-$-N $L^{-1}$, with 5 wells that were >30 mg $NO_3^-$-N $L^{-1}$ (B. Hungate, unpublished data, 1994). In 2004, a smaller number of wells in the central portion of the valley were sampled (n = 14), including the most contaminated well of the 1993–1994 sampling campaign (>100 mg $NO_3^-$-N $L^{-1}$), and none exceeded 5 mg $NO_3^-$-N $L^{-1}$ (P. K. Jewett, unpublished data, 2004). Ammonium concentrations were generally low in all wells during both years of sampling, with concentrations rarely exceeding 0.5 mg $NH_4^+$-N $L^{-1}$. Nitrate concentrations are variable across the valley, however, and may respond to changes in N loading in an individual season. For example, the low $NO_3^-$ concentrations in 2004 may be explained by restricted wheat planting and lower N inputs during a drought the preceding year.

[20] Several studies have reported high natural subsurface $NO_3^-$ concentrations in semiarid regions [*Barnes et al.*, 1992; *Walvoord et al.*, 2003]. It is possible that early changes in the Yaqui Valley hydrologic regime led to increased mobility of such a $NO_3^-$ reserve, but the valley has now been actively irrigated for more than a half century. Irrigation water supplied an average of 2900 MCM from 1974 to 1997 to the valley as irrigation water for fields or as seepage from irrigation canals [*Schoups et al.*, 2005]. Nine percent of the irrigation water infiltrates to the deep aquifer (30–100 m below the surface) and is repumped to the surface through wells [*Schoups et al.*, 2005], and an additional, limited amount (<1%) of groundwater is discharged to coastal estuaries [*Schoups et al.*, 2005]. Such changes in the valley's hydrologic regime make it difficult to determine whether potential natural $NO_3^-$ reserves continue to contribute to current groundwater $NO_3^-$ concentrations. Similarly, microbial processing and plant uptake of N is also possible as lateral subsurface flows carry water and nutrients through riparian zones to drains [*Hill*, 1996; *Naiman and Decamps*, 1997; *Sabater et al.*, 2003], but riparian processes remain unquantified in the valley. We have instead focused on N fluxes and transformations in the large drainage canal network that transfers runoff from the Yaqui Valley to the coast.

### 3.3. Cycling and Transport in Drainage Canals

[21] Nitrogen from Yaqui Valley agricultural fields, livestock production facilities, and urban centers flows downstream to the coast through a network of mostly unlined

open canals (Figure 2). These canals serve as both conduits for N transfer and sites of important microbial N transformations. Some transformations result in gaseous losses of N, potentially attenuating the flux of N from land to sea. Two monitoring programs were implemented to understand patterns of N transport and controls on microbial N transformations in the canal system. The first monitoring program (1999–2001) included biweekly sampling of 8 watersheds (canals A1–A7 and C2; Figure 2). The second program (2004–2005) was expanded to include additional sites, with regular sampling from canals that drained more than 95% of the valley's agricultural land. Multiple forms of N ($NO_3^-$, $NH_4^+$, total dissolved N) were measured throughout both programs, along with environmental variables likely to covary with or control N fluxes, including water temperature, flow rates, pH, dissolved organic carbon, conductivity, and dissolved oxygen. These measurements, along with several experiments on intact cores and sediment slurries, were used to determine factors controlling N transformations within the canals and canal sediments [*Harrison and Matson*, 2003]. Altogether, monitoring of these canals allowed us to determine the proportion of N emitted to the atmosphere relative to transport to coastal systems, as well as temporal and spatial variability in land to sea N transport. As part of this work, fluxes of the greenhouse gas $N_2O$ were also quantified and compared with losses from agricultural fields and to total gaseous N losses from canals.

#### 3.3.1. Gaseous N Losses From Canals

[22] Recent global syntheses estimate that approximately 13–16% of all land-based N sources are removed from rivers via denitrification, although individual river systems exhibit considerable variation in the proportion input N that is denitrified [*Mulholland et al.*, 2008; *Seitzinger et al.*, 2006]. Small, low-order streams are particularly important with respect to denitrification [*Alexander et al.*, 2000; *Peterson et al.*, 2001], although the potential for N removal in small streams may decrease with increasing N loading [*Mulholland et al.*, 2008]. Drainage canals may play a role similar to small streams in agricultural systems, serving as important sites for transformation and removal of N [*Harrison et al.*, 2005; *Peterson et al.*, 2001].

[23] Denitrification rates were measured using an array of approaches, including intact cores, acetylene inhibition assays, and whole stream estimates of $N_2$ production from 1999 to 2001 in 8 Yaqui Valley drainage canals [*Harrison and Matson*, 2003]. Measured denitrification rates ranged widely (5–5700 $\mu$mol $m^{-2}$ $h^{-1}$; [*Harrison and Matson*, 2003; *Harrison et al.*, 2005]) depending on the measurement method, canal, and time of year. The upper range of these estimates is comparable to denitrification rates measured in agriculturally influenced streams and rivers in the temperate zone [*Laursen and Seitzinger*, 2005]. Combining maximum denitrification rates with estimated drain surface area (600–1100 ha), we calculated a maximum for in-stream denitrification of 4200–7700 Mg N $a^{-1}$. These data suggest that the magnitude of potential denitrification is comparable to leached N (see Table 1); however, this calculation does not account for the substantial temporal and spatial heterogeneity in N cycling and transport.

#### 3.3.2. Temporal and Spatial Patterns of N Export

[24] Rates of N transport through the valley drainage canals vary across hourly to annual timescales. During a summer phytoplankton bloom in one canal (C2; Figure 2), rapid changes in N cycling were observed following swift shifts in dissolved $O_2$ concentrations [*Harrison et al.*, 2005]. Diel $O_2$ swings appeared to change the form in which N was carried downstream, in addition to affecting denitrification and the overall amount of downstream N transfer. 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. Nitrate concentrations decreased from 1.30 mg N $L^{-1}$ during daylight hours to undetectable levels shortly after the canal became anoxic, while $NH_4^+$ concentrations 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. Denitrification rates were also measured using $N_2$ to argon ratios ($N_2$:Ar) using with a Prisma quadrupole mass spectrometer (QMS) [*Kana et al.*, 1994; *Laursen and Seitzinger*, 2002]. Variation in $N_2$:Ar can be used to estimate denitrification and uptake (fixation) because both [$N_2$] and [Ar] are influenced by physical factors (e.g., temperature and salinity), but only [$N_2$] is affected by biological factors. We estimated that within one 24-hour period, failing to measure nighttime N fluxes would have led to an overestimation of N gas emissions and a 17–38% underestimation of N export from one of the Yaqui Valley watersheds [*Harrison et al.*, 2005].

[25] Total N export from Yaqui Valley canals was dominated by $NH_4^+$, which accounted for two thirds of total dissolved N export. However, the dominance of $NH_4^+$ over $NO_3^-$ was not uniform in all canals. In the two northernmost canals (C2 and C3; Figure 2), more than 98% of DIN was in the form of $NH_4^+$. In each of the canals in the southern half of the valley (A1–A6), $NO_3^-$ accounted for the majority (~60%) of the N load. The proportion of N exported annually as dissolved organic N (DON) ranged by drain from 11 to 23% of total dissolved N export, with no strong spatial trends. Valley-wide, DON export represented 14% of the annual dissolved N flux. The dominance of DIN over DON export is consistent with findings by *Caraco and Cole* [2001] that N export from catchments with high population densities (>20 people $km^{-2}$) were dominated by DIN in both mesic and xeric systems. Throughout the valley, $NO_3^-$ yield (kg N $km^{-2}$ $a^{-1}$) correlated ($r^2$ = 0.40 or higher) with discharge, area planted to wheat, irrigation water permitted to wheat, and basin agricultural land. Crop-related factors did not correlate strongly with $NH_4^+$ export from Valley canals, suggesting that other sources, such as livestock operations and municipal and industrial wastes, may contribute significant amounts of $NH_4^+$ to northern Valley canals (P. K. Jewett and T. D. Ahrens, unpublished data, 2004).

#### 3.3.3. $N_2O$ Production

[26] Emissions of $N_2O$ from agricultural drainage canals in the Yaqui Valley were measured using floating chambers and were among the highest reported for any freshwater system per unit area [*Harrison and Matson*, 2003]. Large diel swings in emission rates were also observed, particularly in $NH_4^+$-rich canals [*Harrison et al.*, 2005]. Although per-area $N_2O$ fluxes were remarkably high, fluxes from surface drainage waters were small compared to other sources of $N_2O$ in the valley because of the small surface

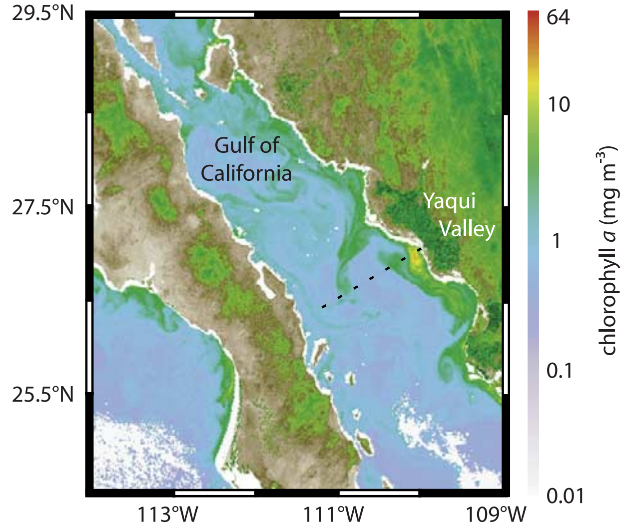


**Figure 6.** Chlorophyll *a* concentrations in the Gulf of California determined by SeaWiFS on 6 April 1998, combined with a MODIS-Aqua vegetation image (normalized difference vegetation index) of vegetation on land taken on 4 April 2003. The SeaWiFS image was taken 1 day after peak irrigation, and an intense phytoplankton bloom can be seen to the west of the productive agricultural fields of the Yaqui Valley. The location of the remote sensing transect used in Figure 7 is shown crossing the bloom. From *Beman et al.* [2005].

area of the drainage network. Emissions from drainage water (0.05% of the applied N in the 1995–1996 wheat season) were about an order of magnitude lower than emissions from agricultural fields (0.2–1.4% of applied N [*Matson et al.*, 1998]), and over 2 orders of magnitude less than N leached to surface and groundwaters (2–26% of applied N [*Riley et al.*, 2001]). This result is in agreement with other recent studies that have examined the regional importance of in-stream $N_2O$ production. *Cole and Caraco* [2001] found that the Hudson River (United States) was a consistent source of $N_2O$, but total in-stream production was only a small portion of total emissions from the watershed. *Clough et al.* [2007] also found high per-area fluxes in a New Zealand river, but similar to canals in the Yaqui Valley, total fluxes were lower than estimates using IPCC methodologies.

### 3.4. Transfers and Transformations in Estuaries and Coastal Waters

[27] Nitrogen leaving the Yaqui Valley is eventually transferred to and potentially transformed in the estuaries and coastal waters of the Gulf of California. Many of the larger canals draining the central portions of the Yaqui Valley (e.g., C1, C3, and C4; Figure 2) enter small lagoons along the coast, while the drainage systems in the north and south lead to two larger estuaries, Bahía Lobos and Bahía del Tóbari. The Yaqui Valley's estuaries provide a final opportunity for removal of agricultural N before being transported to the Gulf of California. Rates of N removal in estuaries cover a broad range of input N (e.g., 10–80% [*Seitzinger*, 1988]), however water residence time generally correlates with N removal ($r^2$ = 0.88 [*Nixon et al.*, 1996]), with shorter residence times resulting in less N removal.

[28] Depending on the form of N entering estuaries (i.e., $NH_4^+$ versus $NO_3^-$), N removal occurs either via direct denitrification of $NO_3^-$ to $N_2$ under anaerobic conditions in estuarine sediments, or via denitrification that is coupled to the nitrification of $NH_4^+$ to $NO_3^-$, presumably in aerobic surface sediments. Although other microbial processes may be important [*Francis et al.*, 2007], current evidence indicates that these are the two dominant pathways by which inorganic N is removed from estuaries. Measurements of both dissolved species in Bahía del Tóbari found $NH_4^+$ to be the dominant form of dissolved N, consistent with what is found in Yaqui Valley drainage canals, and that N concentrations were high [*Beman and Francis*, 2006].

#### 3.4.1. N Transport Through Estuaries

[29] Two independent estimates of N removal were made for Bahía del Tóbari, located in the southeastern portion of the Yaqui Valley (Figure 1). First, a "top-down" estimate was made using *Nixon et al.*'s [1996] simple relationship between water residence time and N removal in estuaries:

$$\%\text{N Exported} = -27.0 * \log(\text{residence time in months}) + 64.8 \quad (1)$$

On the basis of comprehensive measurements in Bahía del Tóbari, M. E. Cruz-Colin et al. (manuscript in preparation, 2008) estimated that water residence time in the estuary is 5–10 days. This estimate corresponds to N export of 78–86% of N inputs, or to removal of 14–22%.

[30] A "bottom-up" approach employed data from potential denitrification assays, which measure rates of denitrification under idealized conditions. Similar to our findings for drainage canals, denitrification rates in the sediments of Bahía del Tóbari varied widely (0.01 to 1.2 mol N $m^{-2}$ $a^{-1}$); however these rates were comparable to rates measured in other estuarine systems [*Piña-Ochoa and Álvarez-Cobelas*, 2006; J. M. Beman et al., Denitrification and nirS-type denitrifier diversity in subtropical estuarine sediments of Bahía del Tóbari, Mexico, submitted to *Environmental Microbiology*, 2008], and indicate that up to 15–30% of N entering Bahía del Tóbari may be removed via denitrification. On the basis of the agreement among these estimates, a significant percentage (70–85%) of N entering Bahía del Tóbari is exported to coastal waters.

#### 3.4.2. Nitrogen Transfers to Coastal Waters

[31] The large throughput of N in Bahía del Tóbari suggests that N may have important effects in the Gulf of California downstream. On the other hand, the total amount of N exported is relatively low (Table 1), and this excess N is transported to the nutrient-rich and highly productive waters of the Gulf. The Gulf of California is characterized by active upwelling along the eastern margin in winter and western margin in summer that brings nutrients from depth to sunlit surface waters [*Alvarez-Borrego*, 2002]; in surface waters, these nutrients sustain elevated rates of primary productivity, discernible as increased chlorophyll *a* concentrations in satellite imagery [*Beman et al.*, 2005; *Kahru et al.*, 2004; *Pegau et al.*, 2002].

[32] In analyzing 5 years of SeaWiFS ocean color imagery (1998–2002) along a 100 km transect from Bahía del Tóbari across the Gulf, we found a significant relationship between irrigation/fertilization events in the Yaqui Valley and increased chlorophyll concentrations, indicative of

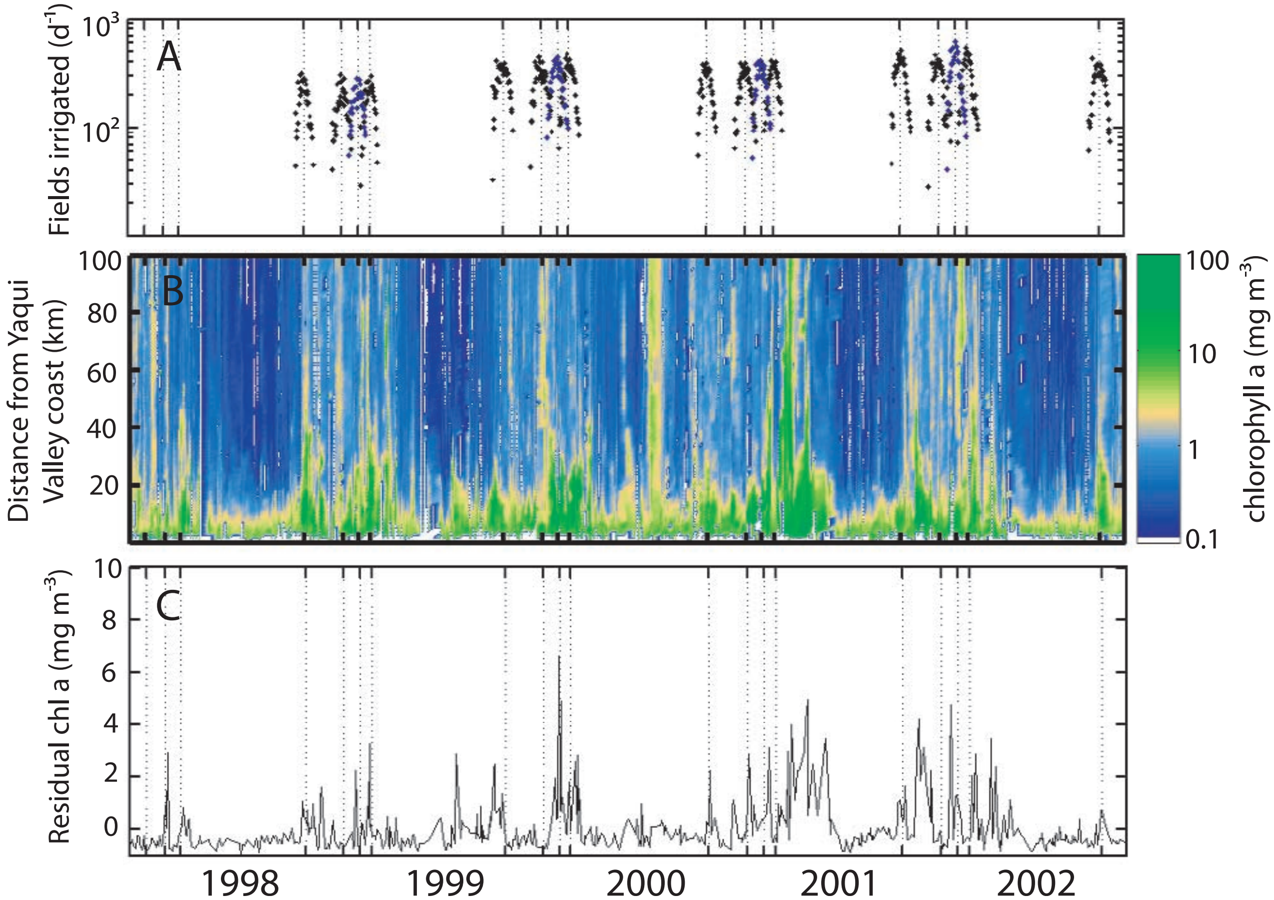


**Figure 7.** A 5-year time series of (a) irrigation allotment, (b) SeaWiFS chlorophyll *a* concentrations, and (c) residual chlorophyll values from a best fit generalized linear model. Dotted lines and tick marks along the horizontal axis denote peak irrigation periods. From *Beman et al.* [2005].

large-scale phytoplankton blooms, in the Gulf of California (Figures 6 and 7) [*Beman et al.*, 2005]. Sea surface temperature data were used to account for the possible influence of upwelling in driving these blooms, yet even after accounting for upwelling, 70% of Valley-wide irrigation events were associated with phytoplankton blooms that occurred within days of irrigation. Blooms varied in size from 57 to 577 km$^2$, which closely matched the potential bloom size on the basis of the N deficit in the Gulf of California and N export from the Yaqui Valley [*Beman et al.*, 2005]. Nitrogen concentrations in the Gulf are depleted relative to other key macronutrients, particularly phosphorus [*Alvarez-Borrego et al.*, 1978], and this appears to render the Gulf particularly vulnerable to N inputs from runoff [*Beman et al.*, 2005]. Both ocean surface waters and upwelled waters are relatively depleted in N, so runoff may act to both directly induce blooms and augment naturally occurring blooms.

[33] N loss pulses from the Yaqui Valley are detectable in fields as gaseous forms, in canals as dissolved losses, and, eventually, dissolved N pulses elicit a biological response in the Gulf of California. It seems unlikely that relatively low-N export spread evenly through time would have such an acute effect in coastal waters. Natural variability associated with precipitation and subsequent runoff from the valley may also be a significant but unquantified factor in bloom dynamics, but the relative simplicity of how the Yaqui Valley is managed could allow these different sources of variability to be separated and N-rich runoff to be reduced.

## 4. Yaqui Valley Nitrogen Transformations and Transfers Placed in Context

[34] From the point N is applied to Yaqui Valley fields, it can undergo multiple transfers and transformations, and integrating across studies in the Yaqui Valley produces an unusually complete picture of the fate of N in the region, from fields to drainage canals to the coast. Here N export from the Yaqui Valley is compared to global models and published studies of N transport from watersheds to the coastal zone. These comparisons place the Yaqui Valley in a broader context by highlighting similarities with other systems that may be general properties, as well as drawing attention to important differences that may have implications for sustainable management of water resources.

[35] Previously published studies have reported a wide range of percent N export from watersheds, ranging from 7% to 97% [*Billen and Garnier*, 1999; *Goolsby et al.*, 1999; *Howarth et al.*, 1996; *McKee and Eyre*, 2000; *Valiela et al.*, 1997]. A recent synthesis of watersheds throughout the eastern U.S. found that N export declined systematically with decreasing latitude and increasing watershed temperature, and was as low as 5% in southern watersheds [*Schaefer and Alber*, 2007]. Significant relationships between N export

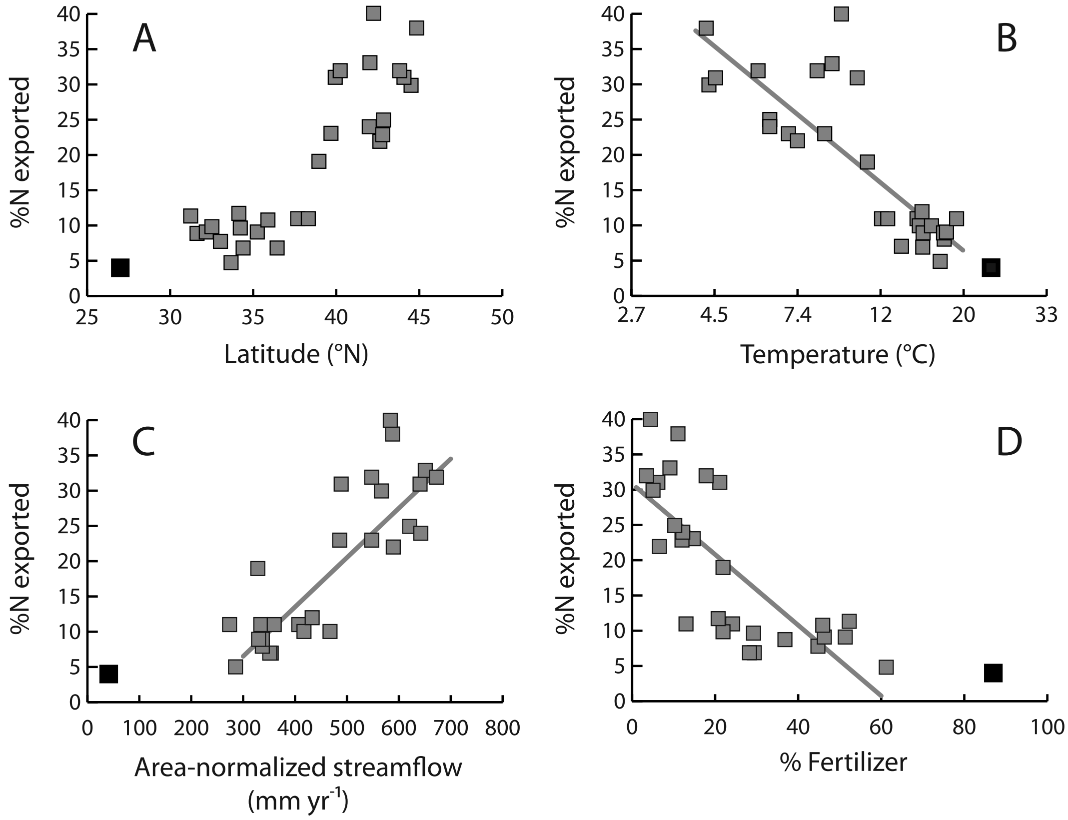


**Figure 8.** Percent of N inputs that are exported from the Yaqui Valley (black data point) in comparison with watersheds of the eastern United States (gray data points). Percent N exported as total N as a function of (a) latitude, (b) mean annual temperature, (c) area-normalized streamflow, and (d) percent of N inputs coming from fertilizer. Data for other watersheds replotted from *Schaefer and Alber* [2007]; the gray lines represent the relationships reported in that study. Note that mean annual temperature is plotted on a logarithmic scale.

and area-normalized streamflow and the percentage of the watershed N input coming from fertilizer were also identified: lower percent export was associated both with lower area-normalized streamflow and with higher percentages of N from fertilizer [*Schaefer and Alber*, 2007].

[36] Overall, the percentage of total dissolved N exported from the Yaqui Valley is low: ~4% of the 63,500 Mg of N inputs is delivered to coastal waters in drainage canals, shrimp pond effluent, and groundwater combined (Ahrens et al., submitted manuscript, 2007). At 27° latitude, the valley experiences mean annual temperatures of 23.7°C. Precipitation is limited (320 mm $a^{-1}$) relative to potential evapotranspiration (2000 mm $a^{-1}$), and streamflow in Yaqui Valley is probably driven in large part by irrigation [*Schoups et al.*, 2005, 2006a, 2006b]. Total N input is dominated by fertilizer, which represents ~87% of inputs. Combined with N export from the valley, these watershed characteristics place the Yaqui Valley at the extremes of the relationships identified by *Schaefer and Alber* [2007] (Figure 8). This is likely due to a combination of higher soil N retention, due to lower flushing rates under limited rainfall, and more N processing in streams, leading to higher gaseous losses and lower export to receiving water bodies [*Caraco and Cole*, 2001].

[37] On the basis of data from monitoring programs, total N yield of dissolved inorganic N (DIN) from the valley to surface water systems was 346 kg DIN-N $km^{-2}$ $a^{-1}$. This per unit area DIN yield is high compared to other watersheds, and only exceeded in densely populated and intensively cultivated landscapes in North America, Europe and Asia [*Dumont et al.*, 2005]. Although the DIN yield is high, models designed to predict $NO_3^-$ export from large rivers solely on the basis of population density [*Peierls et al.*, 1991] and by incorporating sewage loads, atmospheric deposition and inorganic fertilizer inputs [*Caraco and Cole*, 1999; *Caraco et al.*, 2003] estimated much higher $NO_3^-$ yields (Table 2). A large portion of DIN export from the Yaqui Valley was in the form of $NH_4^+$, and predicted DIN export from the NEWS-DIN model [*Dumont et al.*, 2005] was more similar to measured export in the valley. It may be that as point sources take on a more important role in xeric systems, a greater proportion of N export occurs as $NH_4^+$.

[38] Taken together, these comparisons indicate that the percentage of N exported from the Yaqui Valley is consistent with patterns found across different watersheds, while DIN yields are not easily predicted by global models. Limitations in our sampling regime may also have contributed to an underestimation of regional N export. Subsurface groundwater discharge from the valley to the Gulf of California was estimated to contribute <3% of surface discharge [*Schoups et al.*, 2005], and was not thought to be a major source of N to coastal waters. However, periodic

**Table 2.** Estimates of N Export From Three N Loading Models Developed With Large Global Data Sets

| Equation | Source | Estimate for Yaqui Valley ($km^{-2}$ $a^{-1}$) |
|---|---|---|
| $\log(NO_3^-) = 1.15 + 0.62 * \log(\text{population density})$ | *Peierls et al.* [1991] | 366 kg $NO_3^-$-N |
| $NO_3^-$ export = 0.7 * [(Sew + $F$WS$_{export}$ *(Atm + Fert))][a] | *Caraco and Cole* [1999], *Caraco et al.* [2003] | 839 kg $NO_3^-$-N |
| DIN = $FE_{riv}$ * [$DIN_{sew}$ + ($FE_{ws}$*$TN_{dif}$)][b] | *Dumont et al.* [2005] | 500 kg DIN-N |
| Field measurements | this paper | 63 kg $NO_3^-$-N |
| | | 346 kg DIN-N |

[a]Sew, sewage loads; Atm, atmospheric deposition; Fert, inorganic fertilizer loading.
[b]$FE_{riv}$, the fraction of DIN inputs to the river exported to the coast; $DIN_{sew}$, DIN inputs from sewage; $FE_{ws}$, the fraction of watershed N inputs exported to the river; $TN_{dif}$, diffuse sources of N not removed in harvest or grazing.

flushing events (e.g., after a hurricane or intense summer monsoon rainfall) were not captured in our sampling regime, and may be important drivers of N loss from the valley. The sampling campaign in 2004–2005 also followed a year in which wheat plantings in the valley were significantly reduced because of water shortages (only 26,000 ha of wheat were planted in 2003–2004, compared to 180,000 ha the year prior and 89,000 in 2004–2005). If residual N plays an important role for N processing and export, Valley soils may have had lower-than-normal residual N reserves during the 2004–2005 season, leading to lower N export. Lower flushing rates, higher soil retention, increased in-stream processing, temperature effects on N processing, and limitations in field sampling (especially the lack of rain event-based sampling) are all probable factors in explaining why estimates of percent N export from the Yaqui Valley are relatively low.

## 5. Importance and Implications of Temporal Variability

[39] Temporal variability characterized many transformations and fluxes of N from the time of fertilizer application in farmers' fields to its export from the valley in gaseous or dissolved forms. Nitrification and denitrification in the first days following fertilizer additions and irrigation led to high gaseous and leaching losses. Large diel swings in dissolved $O_2$ in Valley canals led to nighttime denitrification events that disproportionately contributed to $N_2O$ emissions from surface waters. Finally, N exported to the coast following frequent Valley-wide irrigations contributed to large phytoplankton blooms in nearshore waters. Relatively high temporal variability may be a fundamental characteristic of this and other low-latitude systems, yet global models often only predict mean annual export and do not generally incorporate seasonal or shorter-term variations in N export (except see *Green et al.* [2004]), suggesting an important area for future research. Monitoring efforts in the Yaqui Valley clearly highlight the importance of considering temporal dynamics. When summed over time, fluxes from the valley to land, water, or air were not extreme, yet individual pulses had significant consequences for the environment of the region.

[40] Ultimately, the temporally variable transformations and transport of N in the fields, canals, and coastal waters of the Yaqui Valley reflect the pulsed nature of fertilizer and irrigation in its fields. While fertilizers distributed in small amounts that are carefully timed to crop requirements have been shown to dramatically reduce N losses [e.g., *Matson et al.*, 1996], such management is unlikely to be economically viable for the relatively low value crops grown in the Yaqui Valley. Nonetheless, management practices that better synchronize crop demand and N application are possible; we have shown that reduced application rates with a higher proportion of N applied later in the growing season can reduce emissions of trace gases and leached $NO_3^-$ by an order of magnitude without reducing crop yield or farmer profit. Reduced leaching losses would also reduce N exported to surface waters, dampening denitrification events and $N_2O$ emissions in Valley drains, and N export events to estuaries and the Gulf of California. The episodic nature of the N cycle in the Yaqui Valley provides a target for abatement and mitigation that could be addressed in order to achieve a transition to sustainable management of water and nutrient resources in the Yaqui Valley agricultural system.

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