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ORIGINAL ARTICLE

Nitrous oxide fluxes and dissolved N gases (N_2 and N_2O) within riparian zones along the agriculturally impacted San Joaquin River

Sarra E. Hinshaw · Randy A. Dahlgren

Abstract Riparian buffer zones play an important role in reducing nitrogen inputs to surface waters, but may contribute to the greenhouse effect by emitting N_2O. This study investigated N_2O fluxes within three abundantly vegetated riparian zones within the agriculturally impacted San Joaquin River, California. Fluxes were measured in the dry season of 2010 and 2011 at four positions perpendicular to the river: outside riparian zone, inside riparian zone, river bank and benthic sediments. Subsurface dissolved N_2/Ar and N_2O concentrations were measured from groundwater wells in the riparian zone simultaneously with N_2O fluxes. Mean N_2O fluxes from the outside riparian zone (6.5 mg ± 2.3 N_2O m^{-2} d^{-1}), were higher than the inside riparian zone (2.7 ± 0.7 mg N_2O m^{-2} d^{-1}) and four times higher than bank sediments (1.6 ± 0.2 mg N_2O m^{-2} d^{-1}). Fluxes from benthic sediments were similar to the outside riparian zone averaging 4.4 ± 1.0 mg N_2O m^{-2} d^{-1}. Dissolved excess N_2 (relative to Ar) and N_2O concentrations in groundwater ranged from 1.53 to 10.2 mg L^{-1} and 0.0–6.0 μg L^{-1}, respectively. A spatial trend was evident along the river flowpath with higher N_2O concentrations at upstream sites. The mean N_2O–N/NO_3^-–N ratio was 0.024 with a peak of 0.34. Variations in riparian soils were complex and N_2O fluxes were primarily controlled by soil pH, %WFPS, NH_4^+ and NO_3^-, while benthic N_2O fluxes were regulated by variations in dissolved oxygen and river flow. Higher fluxes in the riparian soils in 2011 were attributed to several months of flooding that significantly impacted groundwater tables and nutrient availability. Dissolved N_2O from groundwater within the riparian zones was not found to be a significant factor contributing to atmospheric fluxes. These results suggest that riparian zones within the agriculturally impacted San Joaquin River were a significant source of N_2O when elevated NO_3^- was present. Different controlling factors for fluxes within benthic sediments suggested that riparian vegetation did not play a role in NO_3^- concentrations or fluxes within the surface water.

Keywords Nitrate · Denitrification · N_2O · Groundwater · Riparian

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Introduction

Anthropogenic activity has drastically altered the global nitrogen (N) cycle resulting in greater exports

of this primary limiting nutrient to freshwater and marine ecosystems (Vitousek et al. 1997; Caraco and Cole 2001; Howarth and Marino 2006; Hakanson et al. 2007). In particular, N fertilization has led to degradation of water quality, depletion of oxygen and decreases in species abundance and richness (Rabalais et al. 2002; Morrisey et al. 2003; USEPA 2013). Vegetated riparian buffer zones, located at the interface between terrestrial and aquatic ecosystems, are one management strategy that can play a key role in mitigating nitrogen inputs into waterways (Jordan et al. 1993; Cey et al. 1999; Pinay et al. 2007).

When N-enriched surface runoff and groundwater interact with carbon-rich riparian soils, denitrification becomes an important process for nitrate (NO_3^-) removal (Triska et al. 1993; Pinay et al. 1993; Hill et al. 2004). The process of denitrification involves reduction of NO_3^- to nitrous oxide (N_2O) gas and dinitrogen gas (N_2) by heterotrophic bacteria (Knowles 1982). Though removal of NO_3^- by denitrification is advantageous from a water quality perspective, N_2O may contribute to adverse environmental effects (Weller et al. 1994; Groffman et al. 1998).

N_2O is a potent greenhouse gas with a global warming potential ~ 298 times greater than CO_2 (Forster et al. 2007). N_2O from soils contribute $\sim 60\%$ of the total atmospheric N_2O flux and has risen by an estimated 17 % over the past 30 years, primarily due to an increase in N fertilizer use (Smith et al. 2007). Since N_2O is a powerful greenhouse gas, scientists have questioned whether restoration and rehabilitation of riparian zones is reducing one environmental pollutant (NO_3^-) by transforming it into another (N_2O) (Hefting et al. 2003; Dhondt et al. 2004).

Denitrification in agricultural soils transforms ~ 56 Tg N yr^{-1} (range = 22–87 Tg N yr^{-1}) with ~ 5.3 Tg N yr^{-1} emitted as N_2O (Van Drecht et al. 2003; Hofstra and Bouwman 2005; Syakila and Kroeze 2011). Bouwman et al. (2013) estimated that riparian zones alone contributed 0.9 Tg N_2O–N yr^{-1} in 2000, a disproportionately high N_2O flux relative to their surface area. Measured N_2O fluxes span a wide range in riparian ecosystems including agricultural fields (Hefting et al. 2006; Scheer et al. 2008; Li et al. 2013), riparian zones with high nitrate (Soosaar et al. 2011), wetlands (Hernandez and Mitsch 2006), tropical zones (Couwenberg et al. 2012; Kachenchart et al. 2012) and

grasslands (Yan-Fen et al. 2003; Verchot et al. 2006; Carter 2007).

Large spatial and temporal variability exists in soil denitrification and N_2O fluxes (e.g., hot spots and hot moments, Groffman et al. 2000; Machefert et al. 2004; Hunt et al. 2007; DeSimone et al. 2010). While numerous studies have investigated N_2O production in the laboratory (e.g., Hill et al. 2004; Hunt et al. 2007), uncertainties remain in N_2O fluxes when influenced by the interaction of multiple environmental factors in the field setting. Some key parameters influencing denitrification include organic carbon inputs associated with plant materials, temperature, ammonium (NH_4^+), moisture content, pH, NO_3^- and soil/sediment particle size (Hill et al. 2000; Lin et al. 2002; Hoffmann et al. 2006; Cuhel et al. 2010). It is well understood that N_2O fluxes are controlled by NO_3^- concentrations (Lin et al. 2010; Beaulieu et al. 2011). When NO_3^- is non-limiting, reduction of N_2O to N_2 becomes less favorable because it is more energy efficient for microbes to reduce NO_3^- compared to N_2O (Firestone et al. 1980). N_2O fluxes generally increase with increasing soil moisture (Adviento-Borbe et al. 2006; Liu et al. 2007), but moisture content associated with maximum N_2O fluxes are reported between 30 and 80 % water-filled pore space (Granli and Bockman 1994; Ciarlo et al. 2007). In addition, other microbial processes can contribute to N_2O production, including nitrification and nitrifier denitrification (Kaplan 1983; Wrage et al. 2001). N_2O is formed through nitrification as a byproduct of NH_3 oxidation or incomplete oxidation of NH_2OH and is favored in aerobic soils with the presence of NH_4^+ (Lohse et al. 1993; Bateman and Baggs 2005). These varies processes and conditions demonstrate the complexity of processes and environmental factors affecting N_2O emissions.

Hydrological controls on nitrate transport through groundwater riparian zones can also play a key role in N transformations. Shallow groundwater flowpaths that interact with carbon-rich riparian soils have been shown to support high rates of denitrification with a lower proportion of N_2O (N_2O:N_2 ratio, Bernal et al. 2003; Hill and Cardaci 2004; Ernfors et al. 2007). Thus, one design strategy would be to focus on riparian expansion and restoration, resulting in greater NO_3^- consumption and less N_2O production (Abell 1989; Tangen et al. 2015).

It is also important to assess contributions of N_2O from groundwater denitrification to atmospheric N_2O

fluxes. McPhillips et al. (2015) found that longer residence time of groundwater flow increased denitrification rates while promoting lower $N_2O:N_2$ ratios. Some studies have concluded that N_2O fluxes from groundwater are not an appreciable contribution to the atmosphere (Clough et al. 1999; Weymann et al. 2009). During diffusion through the saturated zone, N_2O may be further reduced to N_2, reducing the potential for N_2O emissions from groundwater to the atmosphere. However, other studies have concluded that greater than 20 % of total N loss may be attributed to N_2O emissions from shallow groundwater (Minamikawa et al. 2011; Anderson et al. 2014).

Over the past century, many riparian woodlands along the San Joaquin River (SJR), California were converted to agricultural production (Abell 1989; Moise and Hendrickson 2002). Since 1989, several programs have focused on riparian restorations in the Central Valley of California with improving water quality as an important ecosystem service goal (Furman 1989; CDWR 2009; Griggs 2009). Agricultural discharge transported through sediments, groundwater and surface runoff is a major concern in the SJR (Kratzer et al. 2011; Clayton and Muleta 2012) due to the potential for wide spread hypoxia in the downstream Sacramento–San Joaquin Delta-Estuary (Jassby and Van Nieuwenhuyse 2005; Zamora et al. 2012). Nitrate concentrations in surface waters of the SJR can range up to 4 mg NO_3^-–N L^{-1}, whereas groundwater within these riparian zones have reported nitrate concentrations as high as 14 mg L^{-1} (Zamora et al. 2012) and up to 30 mg L^{-1} in groundwater from nearby dairy fields (Esser et al. 2009). While nitrate concentrations in the regional groundwater surrounding the SJR commonly exceed the drinking water standard of 10 mg NO_3^-–N L^{-1}, it was found that groundwater NO_3 concentrations beneath the bed of the San Joaquin River were typically less than detection (<0.01 mg NO_3^-–N L^{-1}) (Zamora et al. 2012). These findings implicated the riparian zone as an anoxic barrier for nitrate transport to the surface waters of the SJR through efficient NO_3 removal by riparian zone denitrification. While several studies have highlighted the importance of riparian zones for removal of surface and groundwater N (Peterjohn and Correll 1984; Groffman et al. 1998; Vidon and Hill 2004) it is crucial to investigate the importance of N_2O

in groundwater and riparian zones within the SJR to optimize management strategies that mitigate N loads while minimizing the potential for N_2O emissions.

This study presents the first measurements of dissolved nitrogen gases (N_2O and N_2) in groundwater and N_2O fluxes within riparian zones along the eutrophic San Joaquin River. It was hypothesized that N_2O fluxes from riparian zones would be high if soil NO_3^- concentrations reflected the surrounding agricultural groundwater and surface water concentrations (i.e., N_2O production). It was also hypothesized that if dissolved N_2O was present within shallow groundwater, it would diffuse upward and contribute to N_2O fluxes from the surface soil (i.e., N_2O fate/transport). The aims of this study were to (i) measure N_2O fluxes along a topographic gradient from upland riparian zone soils to riverine benthic sediments, (ii) measure dissolved N_2O and N_2 concentrations in groundwater wells within the riparian zones and surface water, and (iii) investigate environmental factors contributing to N_2O fluxes and dissolved N gases.

Materials and methods

Study sites

Three study sites were chosen along a 30 km agricultural reach of the San Joaquin River in the Central Valley, California (Fig. 1): Newman (NW), east of the river (37°21′ 04.76″N, 120°58′ 34.71″W), Crows Landing (CL), west of the river (37°25′ 50.78″N, 121°00′ 50.07″W) and Patterson (PT), east of the river (37°29′ 39.98″N, 121°04′ 49.71″W). The climate is Mediterranean with average minimum and maximum temperatures of 5.3–16.9 °C in the wet season (November–April) and 13.1–30.5 °C in the dry season (May–October) (WRCC 2012). The average rainfall is 278 and 37 mm for the wet and dry seasons, respectively. The two dominant vegetation types within the riparian zone were Fremont cottonwood (*Populus fremontii*) and Goodding's black willow (*Salix gooddingii*). Understory mostly consists of herbaceous vegetation and young willows and cottonwoods. The surrounding land use is mostly dairy operations, row and orchard crops, pastures, and minor wetlands (Kratzer et al. 2004). The SJR receives agricultural
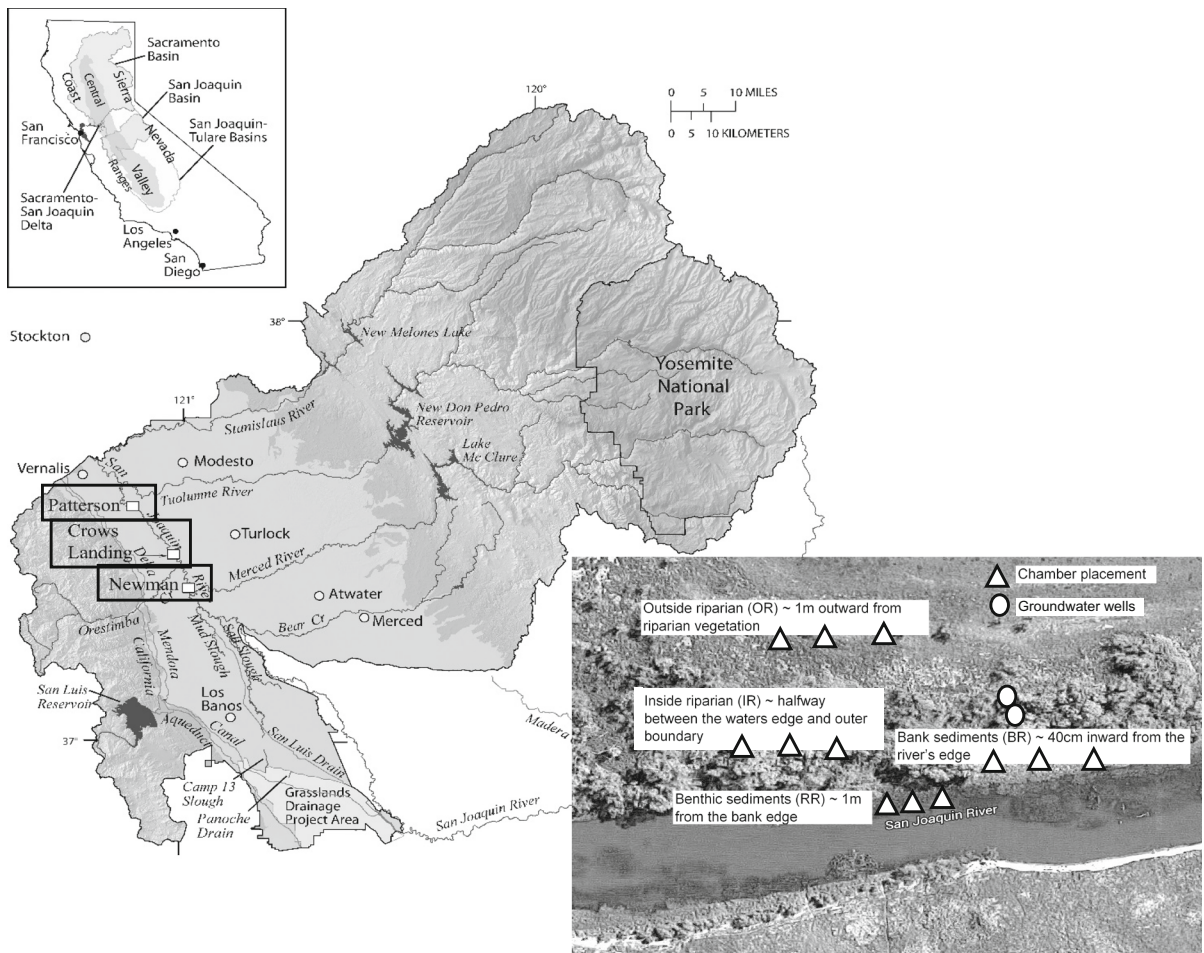
Fig. 1 Location of study sites along the San Joaquin River in Central Valley, California. Insert represents schematic diagram of sampling scheme

drainage during the irrigation season (April–October). For further details on SJR water quality and the study sites see Kratzer et al. (2004) and Zamora et al. (2012).

Sampling was conducted during two sampling periods in each of two years between July 27 to October 3 in 2010 and July 29 to September 19 in 2011. Due to high river flows, measurements between October 2010 and May 2011 were unattainable in either sampling year. River discharge at the three sites between July and October in 2010 and 2011 ranged from 9.1 to 209.1 m^3 s^{-1} whereas discharge between November 2010 to June 2011 ranged from 18.2 to 659.2 m^3 s^{-1} (SJRRP 2011). Bank full width and depth within the study period averaged 60.2 and 0.97 m in 2010 and 90 and 1.6 m in 2011. Selected

soil/sediment physio-chemical properties are presented in Table 1 and Table S1.

Field procedures

Measurements of N$_2$O fluxes

N$_2$O fluxes were measured using the static chamber method (Livingston and Hutchinson 1995). Cylindrical polypropylene chambers (diameter = 30 cm, height = 30 cm) were inserted into the soil to a depth of 5 cm creating a headspace volume of 17.6 L. To quantify spatial variation in gas fluxes, three replicate chambers were placed in four positions along the topographic gradient at each site. Chambers were

Table 1 Soil properties at the three riparian study sites

Site	PS	N$_2$O (mg m^{-2} h^{-1}) Range	Mean	SE	Temperature (°C) Range	Mean	SE	%WFPS Range	Mean	SE	DOC (mg kg^{-1}) Range	Mean	SE	NH$_4^+$–N (mg kg^{-1}) Range	Mean	SE	NO$_3^-$–N (mg kg^{-1}) Range	Mean	SE	pH Range	Mean	SE
NW	OR	0.33–26.4	6.17	2.4	27.9–37.5	32.4	0.9	0.51–28.9	7.80	2.8	48–839	409	61	2.10–30.4	12.3	2.9	0.10–6.54	2.3	0.7	5.2–6.5	5.9	0.1
	IR	0.03–19.5	3.77	1.7	24.8–37.7	31.3	1.3	0.72–30.0	7.61	2.4	64–598	331	45	0.72–43.0	15.6	4.4	0.05–2.54	0.9	0.2	4.8–7.9	6.2	0.3
	BR	0.23–8.68	1.81	0.7	21.4–31.0	24.8	0.8	39.1–86.9	62.6	5.1	41–1978	538	168	1.60–114	22.3	9.9	0.04–1.92	0.3	0.2	4.8–7.7	6.5	0.3
	RR	0.45–6.38	2.63	0.6	18.7–23.9	22.2	0.5	40.3–72.4	61.1	2.3	19–364	190	36	1.38–19.3	9.46	1.6	0.08–6.77	1.5	0.7	5.4–7.5	6.1	0.2
CL	OR	0.05–1.83	0.86	0.1	20.6–35.1	29.0	1.4	0.21–29.1	4.85	2.0	61–543	240	43	2.01–25.2	9.05	1.7	0.20–15.3	2.8	1.1	5.1–7.2	6.3	0.2
	IR	0.19–4.06	0.91	0.3	22.3–45.3	30.7	2.1	0.12–10.2	3.31	1.0	64–393	164	24	1.62–23.5	6.96	1.4	0.41–38.0	5.4	2.5	5.1–7.8	6.4	0.2
	BR	0.19–5.02	1.43	0.4	19.9–50.5	30.1	2.8	0.18–66.6	27.9	5.6	55–492	162	31	1.64–31.3	6.60	2.2	0.11–4.38	1.3	0.3	6.1–7.4	6.9	0.1
	RR	0.13–5.27	1.66	0.4	18.3–27.2	22.6	0.8	28.8–82.1	48.2	3.9	28–234	120	15	0.71–10.8	5.09	0.8	0.06–2.60	0.5	0.2	6.3–8.1	6.9	0.1
PT	OR	0.43–54.4	11.2	5.7	22.0–43.2	31.5	2.4	0.04–58.4	11.0	5.7	69–799	284	63	1.03–39.2	11.4	3.7	0.23–4.90	1.6	0.4	5.0–6.8	5.9	0.2
	IR	0.13–12.9	3.08	1.3	19.1–36.3	29.7	1.4	0.04–38.9	11.8	3.9	68–619	255	49	0.75–32.8	10.6	3.0	0.27–10.6	3.4	0.9	5.0–7.3	5.7	0.2
	BR	0.16–5.22	1.25	0.4	18.7–27.1	22.0	0.9	0.72–72.1	38.6	7.5	74–632	267	50	2.06–17.0	9.02	1.6	0.07–26.2	3.7	2.3	5.4–7.9	6.3	0.2
	RR	0.42–19.8	5.88	1.6	18.7–22.5	21.1	0.4	40.0–79.9	61.7	3.1	41–356	191	34	2.09–17.1	8.93	1.5	0.07–0.58	0.2	0.0	6.1–7.7	6.8	0.2

The values presented are the range and mean ± SE (n = 12)

randomly placed at each topographic position to ensure a representative sampling of each position. The four topographic positions were as follows: 1 m outward from the outer boundary of the riparian vegetation, outside riparian (OR); halfway between the river edge and the outer boundary, inside riparian (IR); 40 cm from the river edge in bank sediments (BR); and 1 m into the river for benthic sediments (RR). The distance and slope gradient of the riparian zone from the river bank to the outer riparian boundary was 29 m and 4.2 % at NW, 30 m and 2.4 % at CL and 24 m and 4.7 % at PT. Between the 2010 and 2011 sampling periods, many trees were removed at CL due to flooding that resulted in the riparian zone being covered by weeds and grasses during the 2011 sampling periods.

Gas samples were collected at 15 min intervals from the chambers for a 1 h collection period between the hours of 10:30 and 14:00. A 30 ml syringe was inserted into a one-way valve connected to a rubber stopper fitted to the side of the chamber. Gas samples (20 ml) were taken and injected into a pre-evacuated 12 ml Labco vial (Labco Unlimited, UK; Hutchinson and Mosier [1981]). For benthic chambers, 60 ml of water was collected and 30 ml expelled and replaced with ambient air. The syringe was shaken vigorously for 2 min to equilibrate the gas and water phases and 20 ml of headspace was injected into the vials. A comparison of the in-stream chambers measurements with and without air headspace confirmed that both techniques produced equivalent N$_2$O fluxes (paired t test $P > 0.05$). Therefore, the water headspace equilibrium was used for benthic chambers because the slope at the river edge presented difficulties for maintaining the stability of the chambers when trying to collect air headspace samples. Samples were analyzed within 24 h of collection using a gas chromatograph (HP/Agilent 6890, μECD using 10 % CH$_4$ in Ar as the carrier gas). Gas fluxes (ppmv h^{-1}) were converted to mg N$_2$O m^{-2} d^{-1} and calculated using linear regression to determine the slope (acceptable if the R$^2 \geq 0.95$) of gas concentration in the chamber headspace versus time with respect to air temperature and the chamber volume.

Groundwater sampling

Groundwater samples were collected at each site from permanent nested wells screened at ~3 and ~30 m

depths (Zamora et al. 2012; Fig. 1). Groundwater depth, dissolved N_2O–N and N_2–N concentrations and general water chemistry were measured from each well on the same day as soil N_2O flux measurements. Prior to collecting groundwater, water depth was recorded with an electronic water level recorder. Wells were then pumped with a submersible pump (LVM Congo, 32 lpm Submersible Pump) to replace a minimum of three well casings of water. Samples were collected after dissolved oxygen concentrations reached a constant value (measured by YSI 556 with flow-through cell). For dissolved N_2 and N_2O analyses, three replicate groundwater samples were collected directly from the groundwater pump into a 60 ml syringe. Samples were then placed in 20 ml Wheaton crimp top, glass vials with the stopper overlaying the top of the vial to ensure minimal contact with the atmosphere. Three replicate samples for dissolved N_2O and N_2 analyses were also collected from surface waters on the same day as groundwater collection. All samples were preserved with 300 µL of $ZnCl_2$ (50 % w/v) and stored at 4 °C until completion of analysis. No air bubbles formed in sample vials during sample storage. In addition to dissolved N_2O and N_2O fluxes, the contribution of dissolved N_2O from groundwater to surface fluxes were investigated by calculating fluxes using Fick's law (Sweerts et al. 1991; Equation S1).

N_2O was measured using the headspace equilibrium method by replacing 6 ml of water with ultra-high purity helium. Vials were shaken for 1 h and N_2O was analyzed by gas chromatography as described above. Excess dissolved N_2, presumed to originate from denitrification, was measured with a membrane inlet mass spectrometer (MIMS, Kana et al. 1994). Three replicated signal readings (m/z) were recorded for N_2:Ar with a mean precision of <0.001 %. N_2:Ar ratios were converted to excess N_2–N mg L^{-1} based on equations from Kana et al. (1994) and Harrison et al. (2005). Values above the expected atmospheric N_2:Ar equilibrium were considered excess N_2 and reported as excess N_2–N (Heaton and Vogen 1981).

Soil and water analysis

Soil and air temperatures were recorded at the beginning and end of each N_2O flux measurement event. At the completion of each sampling event, soil/

sediment was collected from directly beneath each chamber to a depth of 5 cm, immediately placed on ice and stored at 4 °C. A 1:5 soil:deionized water suspension was prepared for pH measurements using a Accumet Basic AB15/Thermo-Orion pH probe (Rayment and Higginson 1992). Soil moisture content was determined by oven drying soil at 105 °C for 36 h and bulk density was calculated from oven-dried sediment collected with intact soil cores (2 cm × 5 cm) taken under each chamber. Water-filled pore space (%WFPS) was calculated from measured bulk density and soil moisture (Blake and Hartge 1986). Sediment particle size was analyzed by sieving to the smallest mesh size of 53 µm (ASTM 2009).

Nitrate and NH_4^+ were determined in soil extracts obtained by adding 40 ml of 2 M KCl to 8 g of oven-dried soil. Dissolved organic carbon (DOC) was extracted by adding 50 ml of deionized water to 5 g of soil (Keeney and Nelson 1987). Samples were shaken for 1 h, centrifuged and the supernatant was filtered through a 0.45 µm membrane filter and analyzed within 24 h. Surface and ground waters were measured in the field for dissolved oxygen (DO), pH, conductivity and temperature (°C) using a YSI 556 multiprobe. A 60 ml water sample was field filtered with a 0.45 µm nylon syringe filter (Millipore) and analyzed within 48 h for NH_4^+ and NO_3^-. A second water sample was collected for DOC and preserved by acidification with HCl to pH < 2. The vanadium chloride method was used to spectroscopically determine NO_3^-–N (LOD = 0.01 mg L^{-1}; Doane and Howarth 2003). DOC was measured by ultraviolet enhanced persulfate digestion and infrared detection (LOD = 0.1 mg L^{-1}; EPA standard method 5310C; Phoenix 8000; Teledyne Tekmar, Mason, OH). Determination of NH_4^+–N was made spectroscopically with the Berthelot reaction, using a salicylate analog of indophenol blue (LOD = 0.01 mg L^{-1}; Forster 1995).

Statistical analysis

Homogeneity of variance was tested with Shapiro–Wilk's and, if necessary, data were log + 1 or hyperbolic arcsine transformed. Spearman and Pearson's correlation coefficients were used to assess relationships between various physico-chemical characteristics, N_2O fluxes, and dissolved N gases.

Stepwise regression and non-linear regression models were used to assess predictor variables that significantly correlated with N_2O fluxes and dissolved N gases. Univariate analysis using general linear models was used to test for differences in soil properties, fluxes and groundwater N between sites and topographic positions (site and depth for groundwater). Least significant difference (LSD) post hoc tests were used to analyze within site differences between positions. Paired t-tests were used to examine differences between years for environmental factors and N dissolved gases. All data were analyzed using SPSS 20 (SPSS 2001).

Results

Environmental properties in riparian zone

Soil texture was dominantly sandy at all sites. Average particle size among all three sites was comprised of 13 ± 3.9 % coarse sand (1– 0.5 mm), 29 ± 3.3 % medium sand (0.5– 0.25 mm), 40 ± 4.3 % fine sand (0.25–0.125 mm), 15 ± 1.6 % very fine sands (0.125– 0.06 mm) and 3 ± 0.3 % silt (<0.06 mm). Soils from CL had a significantly higher percentage of coarse sands ($P < 0.002$) compared to PT and NW, which were comprised predominantly of fine to very fine sands. Percent WFPS and extractable DOC concentrations varied spatially across riparian positions, averaging 8.2 ± 2.2 % WFPS and 315.5 ± 34.3 mg C kg^{-1} in OR, 9.5 ± 2.4 % and 253.3 ± 25.7 in IR, 44.8 ± 4.1 % and 330.5 ± 63.1 in BR and 56.6 ± 2.3 % and 164 ± 17.9 in RR sediments. Ammonium, %WFPS and extractable DOC were significantly different between sampling years with higher concentrations in 2011 compared to 2010 ($P < 0.002$, Table 1; Table S1). Extractable DOC and NH_4^+–N concentrations were significantly lower at CL compared to PT and NW, whereas pH values were significantly higher at CL. Average NH_4^+–N concentration was 14.4 and 5.7 mg kg^{-1} in 2011 and 2010, respectively. Bulk density (range = 0.7–1.2 g cm^{-3}) and pH (range = 4.77–8.09) varied spatially across positions with lowest values in OR positions and steadily increasing from the outside position (OR) to benthic sediments (BR). Nitrate–N concentrations ranged from 0.04 to 26.1 mg kg^{-1} and did not differ

temporally, but were significantly highest in IR and lowest in RR positions ($P < 0.001$).

Within surface waters, pH ranged from 7.5 to 8.5 and NO_3^-–N, DOC and DO concentrations ranged from 1.4 to 3.5, 1.6 to 7.7 and 6.6 to 9.4 mg L^{-1}, respectively (Table 2). Nitrate–N concentrations increased downstream and were significantly higher at PT ($P < 0.001$). DOC concentrations in surface waters were significantly lower in the last sampling event (mean = 2.6 mg L^{-1}, $P < 0.001$). Although there was a small range in pH, values incrementally decreased during the study period ($P < 0.001$, Table 2).

Groundwater depth relative to the surface soil was between 1.2 and 3.3 m with shallowest levels observed in July/August of 2011, following several months of spring flooding from the SJR (Table 2). Ammonium-N concentrations were below 0.5 mg L^{-1} for the duration of the study for all samples except for the NW shallow well (range 0.96–2.07 mg L^{-1}). Nitrate–N levels were highest in the NW groundwater wells (range 0.92–3.64 mg L^{-1}), whereas concentrations at the other two sites were substantially lower (range 0.01–0.91 mg L^{-1}, Table 2). DOC concentrations ranged from 1.0 to 5.1 mg L^{-1} and were significantly higher in shallow wells and at PT. Specific conductivity (range 504–6752 μS cm^{-1}), DO (0.17–0.66 mg L^{-1}) and temperature (18.4–19.8 °C) did not vary across sites, depths or sampling events.

N_2O fluxes

N_2O fluxes ranged from 0.03 to 54.4 mg N_2O m^{-2} d^{-1}, with the highest mean fluxes in the OR (6.5 ± 2.3 mg N_2O m^{-2} d^{-1}) and RR positions (4.4 ± 1.0 mg N_2O m^{-2} d^{-1}, Fig. 2) and lower flux rates in the IR (2.7 ± 0.7 mg N_2O m^{-2} d^{-1}) and BR positions (1.6 ± 0.2 mg N_2O m^{-2} d^{-1}). In 2011, fluxes at PT and NW were an order of magnitude greater than fluxes in 2010, whereas no significant difference between years was found at CL. N_2O fluxes at PT ($P < 0.004$) and NW ($P < 0.001$) were significantly different between sampling events with highest fluxes measured in 2011 (Fig. 2). N_2O fluxes from PT (mean = 5.85 ± 1.88 mg N_2O m^{-2} d^{-1}) and NW (mean = 3.62 ± 0.90 mg N_2O m^{-2} d^{-1}) were not significantly different from one another, however

Table 2 Variables measured in permanent bank wells and surface waters at the three study sites

Sites	Newman				Crows Landing				Patterson			
Date	Sept. 10	Oct. 10	Aug. 11	Sept. 11	Sept. 10	Oct. 10	Jul. 11	Aug. 11	Jul. 10	Sept. 10	Jul. 11	Sept. 11
N$_2$O–N (µg L^{-1})												
Wells	1.48 ± 0.66	4.13 ± 0.52	0.66 ± 0.21	1.23 ± 0.46	0.14 ± 0.06	0.07 ± 0.03	0.48 ± 0.11	0.65 ± 0.19	NA	NA	0.23 ± 0.02 NA	NA
Surface water	0.96 ± 0.11	1.35 ± 0.05	0.67 ± 0.01	1.44 ± 0.16	0.61 ± 0.01	0.88 ± 0.04	1.24 ± 0.04	0.91 ± 0.05	1.01 ± 0.06	1.30 ± 0.05	0.94 ± 0.01	1.24 ± 0.06
Excess N$_2$–N (mg L^{-1})												
Wells	3.87 ± 0.29	5.43 ± 0.25	3.8 ± 0.23	5.87 ± 0.40	2.96 ± 0.26	3.68 ± 0.25	6.96 ± 0.06	5.75 ± 0.55	8.40 ± 0.16	8.23 ± 1.18	5.38 ± 0.72	7.75 ± 0.97
Surface water	2.98 ± 0.02	6.17 ± 0.11	−0.79 ± 0.01	−0.31 ± 0.00	1.73 ± 0.16	4.72 ± 0.12	−0.15 ± 0.06	−0.24 ± 0.12	2.08 ± 0.32	3.26 ± 0.09	−0.46 ± 0.16	0.55 ± 0.00
DOC (mg L^{-1})												
Wells	1.93 ± 0.41	1.47 ± 0.1	3.10 ± 0.49	2.64 ± 0.46	3.33 ± 0.04	2.52 ± 0.39	1.94 ± 0.12	2.11 ± 0.43	2.81 ± 0.58	3.55 ± 0.46	3.35 ± 0.53	3.74 ± 0.57
Surface water	4.77 ± 0.26	3.37 ± 0.11	2.90 ± 0.01	1.58 ± 0.02	4.60 ± 0.06	5.88 ± 0.09	5.56 ± 0.02	3.86 ± 0.01	5.17 ± 0.12	6.29 ± 0.01	6.28 ± 0.01	2.42 ± 0.01
NH$_4^+$–N (mg L^{-1})												
Wells	0.51 ± 0.22	0.48 ± 0.21	1.05 ± 0.46	0.64 ± 0.27	0.05 ± 0.01	0.05 ± 0.01	0.03 ± 0.01	0.04 ± 0.01	0.22 ± 0.09	0.07 ± 0.01	0.01 ± 0.00	0.02 ± 0.00
Surface water	0.03 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.06 ± 0.00	0.02 ± 0.00	0.06 ± 0.02	0.08 ± 0.01	0.08 ± 0.00	0.02 ± 0.00
NO$_3^-$–N (mg L^{-1})												
Wells	0.79 ± 0.35	0.82 ± 0.36	0.02 ± 0.01	0.03 ± 0.00	0.48 ± 0.20	0.76 ± 0.33	0.29 ± 0.13	0.02 ± 0.00	0.53 ± 0.17	0.01 ± 0.00	0.02 ± 0.00	0.06 ± 0.03
Surface water	2.01 ± 0.04	2.02 ± 0.05	0.48 ± 0.01	1.4 ± 0.02	2.40 ± 0.05	1.73 ± 0.00	1.92 ± 0.04	1.68 ± 0.04	3.07 ± 0.02	3.50 ± 0.05	2.27 ± 0.01	2.27 ± 0.01
N$_2$O–N:NO$_3^-$–N × 100												
Wells	0.17 ± 0.01	0.30 ± 0.01	0.19 ± 0.04	0.13 ± 0.01	0.57 ± 0.26	0.34 ± 0.15	1.78 ± 0.96	19.9 ± 5.20	0.00 ± 0.00	0.00 ± 0.00	1.41 ± 0.18	0.00 ± 0.00
Surface water	0.03 ± 0.01	0.02 ± 0.01	1.00 ± 0.00	1.00 ± 0.02	0.03 ± 0.00	0.02 ± 0.00	1.00 ± 0.00	1.00 ± 0.00	0.05 ± 0.01	0.03 ± 0.00	1.00 ± 0.00	0.23 ± 0.00
N$_2$O:N$_2$ × 100												
Wells	0.04 ± 0.02	0.09 ± 0.01	0.02 ± 0.00	0.02 ± 0.01	0.01 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.00 ± 0.00
Surface water	0.05 ± 0.01	0.07 ± 0.01	0.14 ± 0.00	0.10 ± 0.01	0.03 ± 0.00	0.05 ± 0.00	0.06 ± 0.00	0.05 ± 0.00	0.03 ± 0.00	0.04 ± 0.00	0.05 ± 0.00	0.04 ± 0.00
GW depth/SW flow												
Wells	2.46 ± 0.05	2.65 ± 0.17	1.52 ± 0.04	1.72 ± 0.75	3.02 ± 0.13	3.07 ± 0.13	1.28 ± 0.12	2.19 ± 0.38	2.01 ± 0.02	2.63 ± 0.41	1.30 ± 0.40	2.49 ± 0.56
Surface water	9.70	21.2	61.4	23.7	15.9	21.6	40.8	58.3	16.3	23.5	36.3	35.2
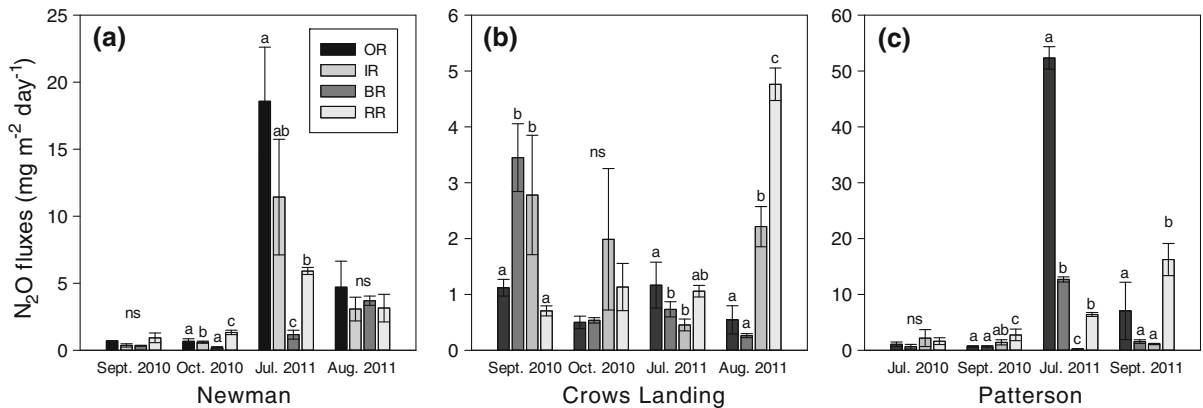
Fig. 2 N$_2$O fluxes at Newman (**a**), Crows Landing (**b**) and Patterson (**c**) in the outside riparian (OR), inside riparian (IR), river bank (BR) and benthic sediments (RR). *Values* represent mean of three replicates. *Bars* within groups labeled with the *same letter* are not significantly different as determined by LSD at α = 0.05

fluxes from both sites were significantly higher than CL ($P < 0.02$, mean = 1.34 ± 0.23 mg N$_2$O m^{-2} d^{-1}, Fig. 2).

Within sites, significant differences were found in 2010 at CL with highest fluxes in IR and BR whereas higher fluxes at NW and PT were measured in the RR position (Fig. 2). In the first sampling event of 2011, across all sites, a clear spatial trend was prominent with highest fluxes measured in OR with lower fluxes in IR and RR and lowest fluxes measured in BR (Fig. 2). N$_2$O fluxes from the second sampling event in 2011 were significantly different at CL ($P < 0.001$) and PT ($P < 0.03$) with fluxes from RR three times higher than any previous measurements (Fig. 2).

Across all positions, sites and sampling events, N$_2$O fluxes were positively correlated to %WFPS ($r = 0.24$, $P < 0.016$) and NH$_4^+$–N concentrations ($r = 0.34$, $P < 0.001$), while negatively correlated to pH ($r = -0.24$, $P < 0.004$). When data were pooled by IR and OR only, stepwise regression showed that %WFPS and pH explained 39 % of the variability ($P < 0.001$). Pooling data by topographic position also revealed a positive relationship between N$_2$O flux and NO$_3^-$–N in IR positions ($r = 0.22$, $P < 0.013$). The N$_2$O flux and NO$_3^-$–N relationship was strengthened when pooling by site for CL ($r = 0.42$, $P < 0.02$) and PT ($r = 0.74$, $P < 0.001$). N$_2$O fluxes in RR were significantly correlated to soil texture, demonstrating a positive correlation with the fine sand fraction ($r = 0.43$, $P < 0.002$). When data from the RR position at PT from Sept 2011 were removed, a positive correlation was found in RR with river flow ($r = 0.68$, $P < 0.001$) and a negative correlation was found with DO concentrations ($r = 0.64$, $P < 0.001$). Stepwise regression with the correlated factors showed that 78 % of the N$_2$O flux in RR could be explained by DO concentrations and river flow.

Dissolved N gases in groundwater wells and surface water

Dissolved N$_2$O–N in groundwater ranged from <0.01 to 5.97 μg L^{-1} (mean = 0.65 μg L^{-1}, Fig. 3). Concentrations were similar at PT and CL and significantly lower than concentrations at NW ($P < 0.001$, Table 2; Fig. 3). N$_2$O–N concentrations did not differ temporally or between shallow ($\sim$3 m) and deep wells ($\sim$30 m). Dissolved N$_2$O–N was strongly correlated with NO$_3^-$–N concentrations ($R^2 = 0.76$, $P < 0.001$, Fig. 4). Excess dissolved N$_2$–N in groundwater wells ranged from 1.64 to 9.96 mg L^{-1} (Fig. 3). Excess N$_2$ concentrations did not differ between depths but concentrations were significantly higher in the fourth sampling event compared to the first three events ($P < 0.009$). A negative relationship between dissolved N$_2$ with DO concentrations was significant ($r = -0.43$, $P < 0.001$), demonstrating a role for anoxic conditions in promoting denitrification. The N$_2$O–N/N$_2$–N ratio was low, ranging from <0.0001 to 0.0022 and significantly higher in shallow wells and at NW. The mean N$_2$O–N/NO$_3^-$–N ratio was 0.02 and ranged from <0.01 to 0.34. Ratios were significantly
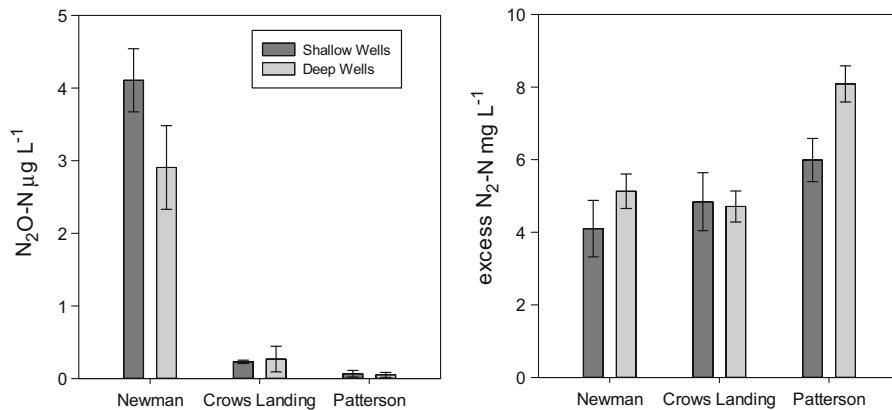
Fig. 3 Dissolved $N_2O–N$ and excess $N_2–N$ concentrations in permanent groundwater wells ($n = 8$)
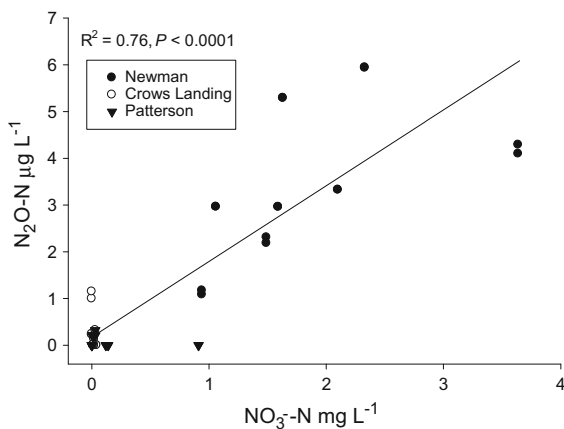
Fig. 4 Relationship between dissolved $N_2O–N$ and $NO_3^-–N$ concentrations in permanent groundwater wells

higher at CL ($P < 0.03$) and during the third sampling event (Table 2).

$N_2O–N$ was supersaturated in all SJR surface water samples, with a mean concentration of 1.05 µg L^{-1} (range 0.59–1.08 µg L^{-1}, Table 2). Excess dissolved N_2 concentrations in surface waters were lower than groundwater concentrations, ranging from <0.01 to 6.17 mg L^{-1} (mean = 1.73 mg L^{-1}) and significantly decreased from 2010 to 2011 ($P < 0.001$). No significant differences in surface water N gases were found between sites. The first sampling event in 2010 had significantly lower $N_2O–N$ concentrations than the other three sampling events ($P < 0.035$). $N_2O–N$ concentrations were significantly related to surface water $NH_4^+–N$ concentrations ($r = 0.47$, $P < 0.004$). Excess $N_2–N$ concentrations in 2011 were slightly

undersaturated with respect to atmospheric N_2 concentration, averaging -0.39 mg L^{-1}. Multiple regression showed that water temperature combined with river flow explained 88 % of N_2 variability ($P < 0.001$).

Discussion

N_2O fluxes

Results from this study demonstrate that the riparian zone of the San Joaquin River was a net source of N_2O in 2011. Peak fluxes were (54.4 mg N_2O m^{-2} d^{-1}) greater than those reported in forested systems (0.08– and 1.12 mg N_2O m^{-2} d^{-1}; Mander et al. 2008; Soosaar et al. 2011), mixed vegetation (-0.9–3.9 mg N_2O m^{-2} d^{-1}; Dhondt et al. 2004) and riparian wetlands (0–30 mg N_2O m^{-2} d^{-1}; Burgin and Groffman 2012). Fluxes were an order of magnitude greater in 2011 than 2010 at NW and PT. Between February and May 2011, all sites and topographic positions were flooded due to above-average Sierra Nevada snowmelt (CDEC 2011). River water flooded beyond the riparian zone outer boundary by as much as 300 m. N_2O fluxes have been found to peak shortly after or during flood events and decrease with time post-flooding presumably due to a decrease in NO_3^- concentrations (Elmi et al. 2005; Jacinthe et al. 2012). Hernandez and Mitsch (2006) found higher N_2O fluxes in riparian marshes a week after flooding due to the elevated water table. Due to difficulties in accessibility and inundation of our study sites, we were unable to

capture N_2O fluxes during the flooded months. The soils at all sites were still highly saturated during our first N_2O flux measurements of 2011. Multiple factors indicated that the effects of flooding were still evident during the first post-flood sampling, such as significantly higher %WFPS (mean = 13.66 ± 3.4 % in 2010 vs 26.98 ± 4.3 % in 2011), NH_4^+ and ~1 m shallower water table in 2011.

The substantially higher N_2O fluxes measured in the outside, inside and riparian soils at NW and PT after the flooding event is most likely a result of multiple N_2O producing pathways. As the water table drops and oxygen re-enters the soil, both aerobic and anaerobic microsites becomes available with favorable conditions for coupled nitrification and denitrification (Abbasi and Adams 2000). The high NH_4^+ concentrations become available for nitrification, a process that produces twice as much N_2O per unit N converted as compared to denitrification (Mosier 1998). A possible pathway that may have contributed to the high NH_4^+ in 2011 is dissimilatory NO_3^- reduction to NH_4^+ (DNRA). DNRA is favored in organic rich-low NO_3^- systems (Burgin and Hamilton 2007). This process has been reported in fresh water sediments but has mostly been considered a minor pathway for NO_3^- removal (Gardner et al. 2006; Erler et al. 2008). To the best of our knowledge, DNRA has not been investigated in the SJR and Zamora et al. (2012) suggested anaerobic mineralization is a key process for explaining high NH_4^+ concentrations in SJR bed sediments. This was supported by the significantly higher NH_4^+ in 2011 and strong correlation with extractable DOC ($r = 0.74$, $P < 0.001$). As this is the first investigation of N_2O dynamics in riparian zones along the SJR, the main objective was to establish if N_2O was present and quantify the fluxes. A key component of future studies should focus on quantifying the proportions of N_2O produced from these specific pathways and the environmental conditions favoring each pathway.

Fluxes of N_2O display a high degree of spatial variability due to heterogeneity in soil properties, especially for soils in riparian zones (Groffman et al. 1998; Hill et al. 2000; van den Heuvel et al. 2009). In this study, N_2O fluxes were variable among sites but showed a dominant spatial trend within sites: OR > RR > IR > BR. Assuming denitrification is occurring along the groundwater flowpath within the riparian zone, NO_3^- concentrations would decrease along the OR → IR → BR flowpath. Although some sampling events measured higher NO_3^- in the IR than OR position, NO_3^- concentrations in bank sediments were consistently lower than IR and OR concentrations. In addition, N_2O fluxes in OR and IR were inversely related to pH values. A study by Van den Heuvel et al. (2011), found that within riparian zones with low pH values, N_2O reduction was suppressed until completion of NO_3^- reduction. Both of these factors could lead to greater accumulation of N_2O in the OR and particularly in IR position as a result of higher NO_3^- concentrations.

Overall, N_2O fluxes were lowest in bank sediments. This is most likely due to significantly lower NO_3^- concentrations, and higher %WFPS, extractable DOC and water residence times that resulted in complete NO_3^- reduction to N_2. As the bank sediments receive the majority of their NO_3^- from up-gradient groundwater flow, much of the NO_3^- appears to be consumed within the riparian zone prior to reaching the bank position resulting in NO_3^- limitation to N_2O generating processes. These controlling factors would all contribute to greater consumption of N_2O to form N_2 as a product of denitrification.

The N_2O fluxes in benthic sediments were significantly influenced by soil texture and surface water factors. Given that surface water provided a constant source of NO_3^- through hyporheic exchange, differences in NO_3^- availability were not considered a primary factor. The strong positive relationship between river flow and N_2O concentrations found in this study suggest an influence of hydrological factors. During periods of higher river flow there is greater hyporheic exchange resulting in less time for surface water-benthic sediment interactions and therefore less time for denitrifying microbes to reduce N_2O to completion as N_2 gas (Muholland et al. 2008).

In contrast to NW and PT, N_2O fluxes from CL were not significantly higher in 2011 (Table 2). CL had a greater percentage of coarse sand and lower %WFPS compared to the other sites. Pinay et al. (2000) found a positive relationship between denitrification activity with soil texture when percent silt and clay were above 65. Similarly in this study, N_2O fluxes were positively related to the fine sand and silt fractions. Fine textured soils become anoxic at lower soil moisture content, have slower water movement, and have a higher capacity for nutrient retention (Gregorich et al. 1991). Therefore, the coarser sand

with a lower water holding capacity reduces the potential for denitrification activity resulting in lower N_2O production.

N_2O fluxes in the RR position at CL were four times higher in August 2011 than previous sampling events. The DOC during the first three sampling events ranged between 92 and 233 mg kg^{-1} whereas, in August 2011, maximum DOC concentration was 49.8 mg kg^{-1}. The alteration of extractable DOC is potentially due to removal of large trees and shrubs in the riparian zone by flood waters between the 2010 and 2011 sampling years. Several studies have shown that when abundant labile carbon is available, rates of denitrification increase and the $N_2O:N_2$ ratio decreases (Weier et al. 1993; Chung and Chung 2000; Senbayram et al. 2012; Morley et al. 2014). Hunt et al. (2007) measured N_2O production in coastal riparian soils and found a decrease in N_2O production when the C/N ratio was above 25. In this study the benthic sediments at CL displayed a strong negative relationship between N_2O and DOC ($R^2 = 0.91$, $P < 0.001$). This strong negative relationship suggests that decreases in microbially-labile carbon result in higher fluxes of N_2O due to incomplete denitrification to N_2 (Vallejo et al. 2006; Wondzell et al. 2009). As removal of riparian vegetation can significantly influence N_2O fluxes, further and direct research on the importance of microbially-labile carbon both in-stream and in riparian zones for mitigating N_2O is warranted.

Dissolved N_2 and N_2O in groundwater

Nitrate concentrations in groundwater wells (approximately 1–2 km away) up-gradient from PT at the Modesto Regional Water Treatment Plant averaged 6.71 ± 1.2 mg L^{-1} NO_3^-–N in 2010 (range 0.001–31.1 mg L^{-1}, MRWTP 2010) and wells surrounding NW and CL ranged from 1.2 to 13.2 and 0.11 to 6.5 mg L^{-1} for NO_3^-–N, respectively (GAMA 2010). Piecewise regression showed that excess N_2 was negatively related to NO_3^-–N above concentrations of 0.05 mg L^{-1} ($R^2 = -0.69$, $P < 0.001$). These data suggest that some of the NO_3^- in the groundwater was denitrified before reaching our down-gradient study sites (Hedin et al. 1998). It can also be argued that this negative relationship indicates that denitrification efficiency was inhibited by increasing NO_3^- concentrations. This is supported by the strong positive relationship between NO_3^- and N_2O,

indicating N_2O is a more prevalent end product at higher nitrate concentrations (Fig. 4, Weier et al. 1993; Rissanen et al. 2013). This was also observed in groundwater that was collected from paired groundwater wells from the opposite side of the river from our study sites. Samples were collected several times in 2011 from paired wells at all three sites (Table S2). The highest concentrations of NO_3^-–N and N_2O–N were found at CL, ranging from 10.7 to 16.9 mg L^{-1} and 35.7 to 40.8 μg L^{-1}, respectively. In addition, the N_2O–N:N_2–N ratio was an order of magnitude higher (range 0.01–0.03) than any other groundwater sampled. These results support many previous studies that have shown high concentrations of NO_3^- contribute to higher concentrations of N_2O (Weier et al. 1993; Skiba et al. 1998; Wang et al. 2014).

The IPCC defines EF5 as the N_2O yield from NO_3^- (kg N_2O–N per kg NO_3^-–N leached) associated with leaching and runoff (Forster et al. 2007). The current EF5 value of 0.0075 includes N_2O emissions from groundwater and surface drainage (EF5-g), rivers (EF5-r) and estuaries (EF5-e), with each component contributing 0.0025 kg N_2O–N per kg N (IPCC 2006). The average N_2O–N:NO_3^-–N ratio in this study surpasses this value with 0.004, 0.054 and 0.006 for NW, CL and PT, respectively. The groundwater measured at CL in August 2011 had the highest value of 0.34 (Table 2). Surface water ratios were low, ranging from 0.0002 to 0.001. However ratios above the IPCC value were found at CL and NW and other locations along the SJR in April, June and August of 2011 (Hinshaw and Dahlgren 2013). This is a major concern for global and regional N_2O inventories and further measurements are required to determine how the N_2O–N:NO_3^-–N ratio compares to IPCC estimates over the long term.

The contribution of groundwater N_2O to surface fluxes is dependent on multiple environmental factors such as soil moisture and texture that influence the production and consumption of N_2O as it diffuses upwards through the vadose zone (von der Heide et al. 2009; Weymann et al. 2009). N_2O fluxes from IR positions were inversely related to groundwater depth in shallow wells ($r = -0.49$, $P < 0.001$, Figure S1; Table 2). When the groundwater table was below 1.5 m, N_2O fluxes in IR positions were <2.5 mg N_2O m^{-2} d^{-1}. With the shallower groundwater tables in 2011, N_2O had a slower upward advection and molecular diffusion time between the

groundwater-soil interface. Thus, the high groundwater levels likely have a greater impact on soil surface N_2O fluxes by slowing upward diffusion (Deurer et al. 2008; von der Heide et al. 2009; Minamikawa et al. 2011). The estimated fluxes (Equation S1) from groundwater were less than 0.06 mg N_2O m^{-2} d^{-1} (data not shown), which is very low compared to soil surface fluxes. Thus, these results were inconsistent with our hypothesis. Rather, there is stronger evidence indicating soil surface characteristics and water table depth, and not dissolved N_2O, governed N_2O fluxes as demonstrated by the relationship with %WFPS and the correlation between N_2O and NO_3^- in IR positions.

Weymann et al. (2008) suggested that hotspots of N_2O emissions from groundwater may occur where groundwater is discharged into surface waters after NO_3^- has been partially attenuated by riparian transport (Hefting et al. 2003). Six incremental depths of porewater measured from benthic sediments in 2010, approximately 10 m from the river bank, showed high N_2O–N at 100 cm at PT (20.3 µg L^{-1}, Figure S2). This was presumed to be collected from incoming regional groundwater as the temperature was 1-2 degrees lower at 100 cm compared to the upper sediment layers (Zamora et al. 2012; Hinshaw and Dahlgren 2013). The flux estimate calculation (Equation S1) was applied to determine the contribution of dissolved N_2O from riverbed porewater to surface fluxes. Here, calculated N_2O fluxes from riverbed porewater and incoming groundwater ranged from <0.01 to 3.71 mg m^{-2} d^{-1} (Figure S3). This indicates that dissolved N_2O in groundwater is more likely to contribute to riverbed fluxes within the SJR rather than contributing to atmospheric fluxes from riparian soils. Groundwater recharge and discharge are highly spatially and temporally variable in the SJR Valley due to agricultural practices such as groundwater pumping and return flows by agricultural drainage (Phillips et al. 1991; KHE 2002). The knowledge gap in understanding groundwater hydrology and subsurface-surface water interactions requires further analysis to better understand and accurately estimate contributions of dissolved N_2O to atmospheric fluxes.

Dissolved N_2 and N_2O in surface water

Dissolved N_2O was detectable in all surface water samples. The lower concentration of N_2O in surface waters compared to groundwater was expected due to oxygen concentrations ranging from 6.9 to 9.5 mg L^{-1}. Although there was a positive relationship between N_2O and NH_4^+ during the study period, monthly monitoring of surface waters over a 13 month period did not reveal any relationship between N_2O and NH_4^+ that would support a dominant role for nitrification as a process for N_2O production (Hinshaw and Dahlgren 2013). However, water column nitrification cannot be ruled out as a significant process, especially since it produces twice as much N_2O per unit N converted as compared to denitrification (Mosier 1998).

The strong negative relationship between river flow and excess N_2 concentrations is most likely a result of shorter residence time and a decreased time for interaction between benthic sediment and water column NO_3^- (Alexander et al. 2009). N_2 concentrations were slightly under-saturated at times during the study period. A likely possibility is that the calculated N_2 equilibrium concentration does not accurately account for the strong diel temperature fluctuations (5–7 °C) that occur in surface waters during the summer-fall. Another possibility is N-fixation by *Eichhornia crassipes,* a common water hyacinth found in the SJR, which forms an association with *Azotobacter chroococcum*, a N_2 fixer (Purchase 1977). Long-term measurements of dissolved N_2:Ar in surface waters are needed to determine if N_2 fixation is a viable N_2 consuming process in the SJR.

Summary

While numerous studies have investigated riparian zone N_2O fluxes, the contribution of N_2O from riparian zones and groundwater from one of the most nitrogen-enriched and second largest river in California has been understudied (EPA 2010; Teh et al. 2011). The San Joaquin River has approximately 243 km^2 of riparian zones (Moise and Hendrickson 2002). Overall this study indicates that riparian zones are a significant source of N_2O, compared to other studies, in the agriculturally impacted San Joaquin River. Variations in N_2O fluxes followed a general spatial trend perpendicular from the river: outside riparian zone > inside riparian zone > bank sediments. Fluxes were lower inside the riparian zone and showed decreased NO_3^- concentration along the

groundwater flowpath from IR to BR positions. Nitrate, pH, %WFPS and NH_4^+ were identified as the main factors contributing to variations in N_2O fluxes within the riparian zone. Temporally, fluxes were higher in 2011 and appeared to be related to several months of flooding preceding the 2011 flux measurements.

In contrast, N_2O fluxes from benthic sediments were governed by surface water properties with river flow and DO demonstrating the strongest relationships. Nitrate concentrations from bank sediments were consistently lower than other positons suggesting these riparian zones may have played a role in reducing NO_3^- concentrations. However N_2O fluxes from benthic sediments were comparable to outside riparian zone fluxes. Different factors were attributed to regulating fluxes from benthic sediments suggesting that in-stream processes and surface water nitrate concentrations may play a significant role in N_2O fluxes. Dissolved N_2O in groundwater within the riparian zones was not found to be a significant contribution to atmospheric fluxes. NO_3^- concentrations were strongly related to dissolved N_2O–N and negatively related to excess N_2–N concentrations demonstrating higher NO_3^- concentrations decreased the efficiency of denitrification to reduce to completion.

The loss of organic carbon due to removal of vegetation by flooding at CL highlights the importance of sustaining abundant carbon in riparian zone soils of large river systems as well as small streams (Schipper et al. 1993; Wondzell et al. 2009). High organic carbon in benthic sediments can sustain high denitrification rates with reduction of water column nitrate through hyporheic exchange. Restoration of organic matter in agricultural soils and fertilization management have been found to be key practices for reducing N_2O fluxes (Cavigelli et al. 2012). As the future climate changes, management of in-stream processes and nitrate reduction is equally as important as riparian zone management.

There is a critical need to further investigate the relationship between groundwater and surface N_2O fluxes. Climate models predict dryer summers and higher flood risks for California (Karl et al. 2009; Ficklin et al. 2013). Characterizing N_2O dynamics during periods of long- and short-term flooding within riparian zones should be considered when estimating regional N_2O flux models. Increased flood frequency may result in more frequent aerobic and anaerobic

cycles resulting in increases in N_2O fluxes due to coupled nitrification–denitrification. Riparian zone management, with the goal of increasing denitrification and mitigating NO_3^- loads to large rivers, should include risk management of N_2O fluxes from groundwater and surface soils as well as benthic and surface water.

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