Evaluation of watershed-derived mass loads to prioritize TMDL decision-making

S. Gulati, A. A. Stubblefield, J. S. Hanlon, C. L. Spier, M. K. Camarillo and W. T. Stringfellow

S. Gulati (corresponding author) A. A. Stubblefield J. S. Hanlon C. L. Spier M. K. Camarillo W. T. Stringfellow: Ecological Engineering Research Program, University of the Pacific, 3601 Pacific Ave, Stockton, CA 95211, USA E-mail: sgulati@pacific.edu; W. T. Stringfellow: Earth Science Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA

Abstract

A total maximum daily load (TMDL) for oxygen demanding substances is being implemented in the San Joaquin River (SJR) in California (USA) due to frequently occurring low dissolved oxygen conditions. The SJR is a eutrophic river, heavily impacted by agriculture. A mass balance was developed to identify the sources of oxygen-demanding substances and nutrients to the river with the objective of providing a scientific basis for management actions needed to meet TMDL requirements. Data were collected for flow and water quality and mass loads calculated for sites within the main stem of the SJR, river inputs (tributaries), and diversions in the study area. Using a quadrant analysis, tributary flows and loads are ranked to identify targets for water quality improvement efforts. Additionally, all mass loads were summed (inputs minus diversions) and compared with observed loads at the downstream limit of the study area. The mass balance analysis identifies major contributors of mass loads and mass balance closure is assessed for each constituent. These analysis methods inform the TMDL process which includes a load allocation, and is useful for determining locations for implementation of improvement projects needed to improve the health of the river.

Key words | agricultural ecosystems, chemometrics, diffuse pollution, mass balance

INTRODUCTION

The San Joaquin River (SJR) estuary has experienced frequently occurring low dissolved oxygen (DO) conditions since the 1960s (Bain *et al.* 1968; US ACE 1988) which adversely affects warm and cold water fish habitats (Brown & Moyle 1993). Also, the estuary has been widened, deepened, and channelized for navigation, which has exacerbated low DO conditions. Previous studies have identified suspended algae and nutrients entering the SJR from upstream tributaries as major contributing factors to low DO conditions in the estuary (Lee & Jones-Lee 2003; Kratzer *et al.* 2004; Ohte *et al.* 2007).

As a result of its impaired water quality, the SJR was placed on the California 303(d) list and a total maximum daily load (TMDL) was calculated (Gowdy &

Grober 2005; Stringfellow *et al.* 2009). This process is consistent with the 1972 Clean Water Act and the DO TMDL developed included major point and non-point sources of pollution as well as reduced flow and alteration of the river for navigation (US EPA 2008). An important component of the TMDL process is to identify the sources of pollution (US EPA 2008). The purpose of the current study was to determine the sources of oxygen-demanding substances (ODS) – and their precursors (e.g. nutrients) – in order to develop data-driven and scientifically based management decisions for reducing these sources by selecting the best locations for improvements. The State of California uses an adaptive management strategy for TMDLs – consistent with US EPA (2002) – where monitoring and modeling both precede and follow improvements in order to assess their efficacy. The delineation of mass loads performed in this study – in addition to other components of the TMDL program – allows for bench-marking and assessment of such improvements. Providing a scientific basis for improvements engages stakeholders, a major goal of the TMDL process.

The study area comprises a 96-km portion of the SJR upstream of the estuary where extensive water quality data were collected at locations within the main stem of the SJR, major river inputs (tributaries), drains, and major diversions. Surface water runoff, major point sources and non-point sources enter the river via the major tributaries and drains, and, consequently, their contributions are contained in the collected water quality data. The lower study boundary was the Vernalis station, where the river transitions to an estuary. Vernalis is used for compliance monitoring by multiple agencies and extensive data are collected there. January 1, 2007 to December 31, 2007 was selected for analysis because studies had been conducted in the region that investigated sources and transformation mechanisms for ODS and ODS precursors and a wealth of monitoring data were available for this year (Stringfellow 2008; Stringfellow *et al.* 2008).

In this study, we present a combined analysis method enabled by extensive water quality data. First, a mass balance analysis was performed to determine the sources of ODS and ODS precursors (e.g. nutrients). Mass loads were calculated by numeric integration with various average representations of flow and concentration data from continuous and grab sampling, respectively. This averaging approach was used because of the variable flow and concentrations within the SJR and its tributaries and the lack of a consistent relationship between flow and concentration, due in part to the regulated nature of the SJR (Gulati *et al.* 2014). All mass loads upstream of the Vernalis monitoring station (tributary inputs minus diversion outputs) and groundwater estimates were summed and compared with the measured mass loads observed at the Vernalis compliance station; closure is expected for conserved parameters but not for non-conserved water quality constituents. Secondly, a quadrant analysis, similar to that developed by Stringfellow (2008), was performed to determine the best targets for TMDL management efforts. Each tributary site is categorized into one of four quadrants based on their total flow volume and mass load contributions. Good target sites are those with high mass load contributions but with small flow volumes.

METHODS

Site description

The SJR watershed comprises the southern two-thirds of the Central Valley of California and is bound by the Coast Range to the west and the Sierra Nevada Mountains to the east (Figure 1). The area has a semi-arid Mediterranean climate and receives 13–41 cm of rainfall annually, most of which falls between October and March, resulting in a distinct dry season. Land use in the San Joaquin Valley is dominated by irrigated agriculture, which has greatly altered the land surface, including the flow path of the SJR and its tributaries. While some streambeds located outside of agricultural areas have no flow during the dry season, many tributaries receive flow almost exclusively during the dry season and these flows are comprised almost entirely of irrigation drainage.

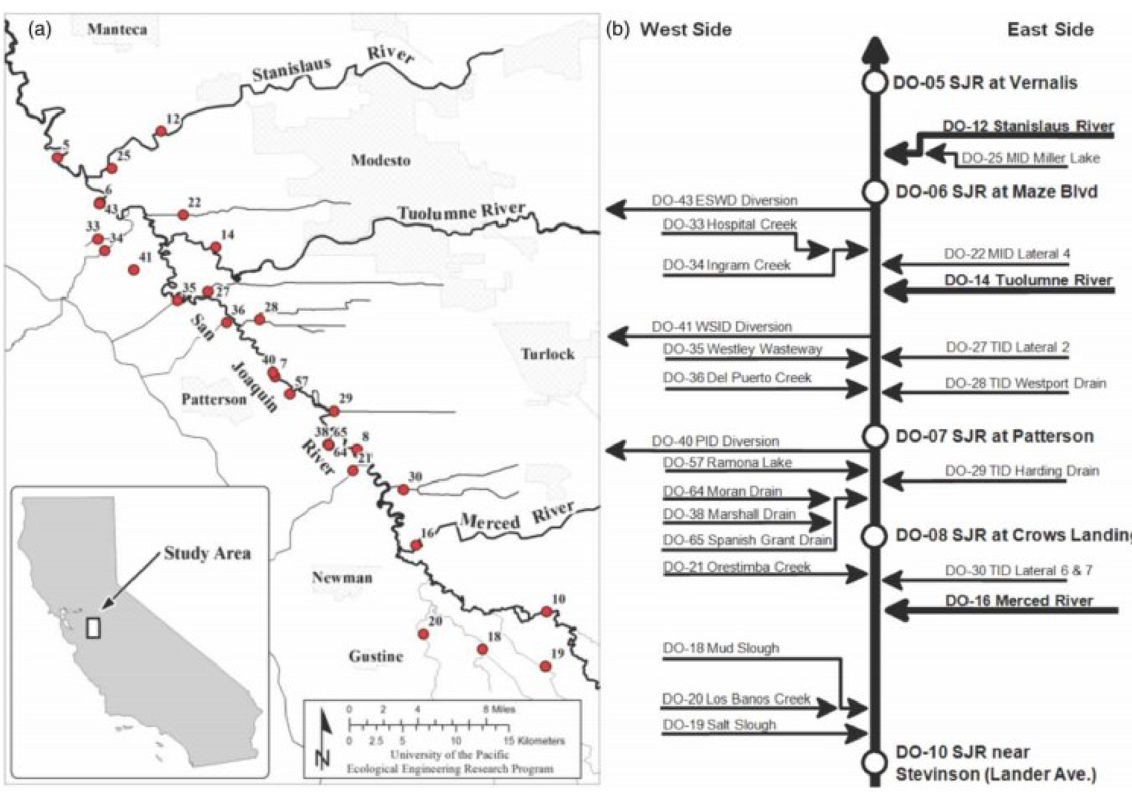

Figure 1 | (a) The SJR and all primary tributaries and diversions. (b) The relative location of surface water inputs and diversions which were used in the mass balance.

The study area comprises a 96-km segment of the SJR beginning upstream at the Lander Avenue monitoring station near Stevinson, CA and ending at the Vernalis monitoring station (Figure 1). Vernalis was identified as the lower study boundary because it is the legal limit of the Sacramento-SJR

Delta and it defines the extent of tidal influence in the SJR. As an upstream boundary, the Lander Avenue station represents the first reasonable access to the SJR with reliable year-round flow and a recognizable stream bed. The largest three tributaries to the SJR are the Merced, Tuolumne, and Stanislaus Rivers, which originate in the Sierra Nevada and are impounded in the foothills for agricultural and urban use before draining to the SJR. The Orestimba, Del Puerto, Ingram, and Hospital Creeks originate in the Coast Range and follow historical creek beds to the valley floor where they have been channelized for use in agricultural drainage conveyance. Mud Slough, Salt Slough, and Los Banos Creek channel both agricultural runoff and wetland drainage from the State, National, and private wetlands. There are many manmade inputs to and outputs from the river, including six agricultural drains discharging runoff into the SJR on the east side of the river, Turlock (TID) Lateral 6 & 7, TID Harding Drain, TID Westport Drain, TID Lateral 2, TID Lateral 4, and Modesto (MID) Miller Lake, and five agricultural drains on the west side of the river, Spanish Grant Drain, Marshall Road Drain, Moran Drain, Ramona Lake, and Westley Wasteway. Harding Drain also conveys wastewater treatment plant effluent and stormwater runoff from the City of Turlock. On the west side of the SJR, there are also three pumping stations used by irrigation districts to divert water from the SJR (Patterson (PID), West Stanislaus (WSID), and El Solyo Water District (ESWD)).

Continuous flow data

Continuous flow data for sites were obtained either from the California Data Exchange Center (CDEC), directly from station loggers recorded at 15-min intervals, or from the irrigation districts reported as hourly, daily, and monthly averages of pump meter readings. Flow measurements were collected near the confluence of tributaries except at the Merced, Tuolumne, and Stanislaus Rivers, where the flow measuring stations were located more than 10 miles upstream of the confluence. Flow inputs to the rivers downstream of the monitoring stations could cause the calculated loads to the SJR to be biased low; however, Kratzer *et al.* (1987) determined that flows do not change significantly between the flow monitoring stations and the confluence with the SJR.

Grab sample collection

Depth-integrated grab samples were collected at mid-channel, in close proximity to flow monitoring stations except at the sites of the Merced, Tuolumne, and Stanislaus Rivers, where grab samples were collected near the confluence with the SJR. Main stem sites, rivers, and sloughs were typically sampled at weekly to biweekly intervals during the irrigation season (April–September) and at biweekly to monthly intervals during the remainder of the year. Monthly sampling during the non-irrigation season was not always possible as many of the smaller drains and creeks run dry during the non-irrigation season.

Analytical methods

Specific conductance (SpC) was measured *in situ* using a YSI 6600 sonde and YSI 650 MDS handset (Yellow Springs, OH, USA). Total dissolved solids (TDS) were calculated using a TDS:SpC ratio of 0.64 (mg L^{-1} cm μmho^{-1}). This TDS:SpC ratio is the average value reported for waterbodies in the SJR basin (Kratzer *et al.* 1987), and is consistent with the approximations used by others (Snoeyink & Jenkins 1980; Chapra 1997). Unfiltered samples were analyzed for biochemical oxygen demand (BOD) by SM 5210 B (APHA 2005), with a modification for a 10-day test to be consistent with previous studies (Lee & Jones-Lee 2003). Nitrate-nitrogen was quantified on filtered samples using a membrane diffusion/conductivity method (Carlson 1978, 1986). Total phosphorus (total-P) was quantified using an ascorbic acid method adapted from SM 4500-P E (APHA 2005), after digestion in accordance with Yu *et al.* (1994).

Mass balance analysis

Mass loads were calculated using the following equation:

$$\text{Mass load (kg)} = \sum_{i=1}^{n} C_i \bar{Q}_i \Delta t \qquad (1)$$

where n is the number of grab samples, C_i is the concentration of ith grab sample (kg L^{-1}), Δt_i is half the time between the $(i-1)$th and the $(i+1)$th grab samples or the duration of the calculation interval (s), and is the mean flow rate for the calculation interval (L s^{-1}). This mass load method, which we term the mean-load method, was selected because there is poor correlation between flow and concentration for the sites due, in part, to the regulated nature of the SJR, the availability of complete flow data sets from continuous sampling, and the variability in grab sampling frequency of concentration between sites (Gulati *et al.* 2014).

Concentration data were not available for diversions. Assuming complete mixing across the river section upstream of the diversion, the concentration in the diversion and that just upstream are equal. Hence, the diverted mass loads is the fraction of the upstream mass load related by the ratio of the diverted volume to the river volume, given by the following equation:

$$\text{Mass load diversion (kg)} = \frac{V_d}{V_r} L_r \qquad (2)$$

where V_d is the volume of water that passed through the diversion over the calculation interval (L), V_r is the volume of water that passed through the river just upstream of the diversion over the calculation interval (L), and L_r is the total mass load that passed through the river just upstream of the diversion over the calculation interval (kg). The total mass load L_r is calculated by adding all upstream tributary loads and subtracting all upstream diversion loads.

The estimated mass loads at Vernalis were determined by adding the 22 tributary mass loads upstream of Vernalis and subtracting the three mass loads originating from the diversions located along the study reach of the SJR (Figure 1). The SJR at Lander Avenue sample site, which is the upstream study boundary, was considered a tributary (input) in the mass balance analysis.

Precipitation and evapotranspiration in the mass balance for flow

The volume gain/loss due to precipitation (pp) and evapotranspiration (ET) was calculated using the following equation:

$$\mathrm{Volume}_{\mathrm{pp/ET}}(L) = 4.06 \times 10^4 * \left(\sum \mathrm{pp} - 0.92 * \sum \mathrm{ET}_{\mathrm{pan}}\right) \mathrm{A}_{\mathrm{SJR}} - \mathrm{V}_{\mathrm{RV}} \qquad (3)$$

where $\sum \mathrm{PP}$ is the precipitation over the year (cm), $\sum \mathrm{ET}_{\mathrm{pan}}$ is the pan evaporation over the year (cm), 0.92 is a conversion factor for pan evaporation to ET for surface water (Doorenbos & Pruitt 1977, Kratzer *et al.* 1987), is the surface area of the SJR from Lander Avenue to Vernalis (acres), 4.06×10^4 is a conversion factor (L/cm-acres), and V_{RV} is the volume of water lost to riparian vegetation water use (L). Hourly incremental pp data were obtained from the California Irrigation Management Information System (CIMIS) station in Modesto. Daily pan evaporation data were obtained from the Hidden Dam (Hensley) monitoring station located in Madera County. Estimated surface area of the SJR between the Lander Avenue and Vernalis flow stations is 1,634 acres as obtained from a California State Water Resources Control Board report on the regulation of agricultural drainage (Kratzer *et al.* 1987). Riparian vegetation water use data for the water years 1977–1985 were obtained from Kratzer *et al.* (1987) and were used for lack of more recent information. It was assumed that the net volume loss/gain due to pp and ET only affected the flow volume balance and did not affect the mass balance as rainwater and condensate has minimal ion content.

Groundwater contributions

The groundwater contributions to the balances for TDS, total-P, and nitrate-N were estimated using measured concentration values from Zamora *et al.* (2013) for bank wells sampled during 2007. The measured concentrations were 1,622 mg/L TDS, 0.29 mg/L phosphate-P, and 1.94 mg/L nitrate-N. BOD was not measured by Zamora *et al.* (2013). Groundwater flow was estimated from the volume balance.

RESULTS AND DISCUSSION

TDS, total-P, nitrate-N, and BOD mass loads were calculated for the 26 sample sites (Figure 1(b)) using Equation (1) for tributaries and Equation (2) for diversions (Table 1). The net sum of surface water inputs (inputs minus diversions) and the observed mass load at Vernalis are also presented in Table 1. Pie charts were used to illustrate the proportional contribution of various tributary sources of the mass load inputs to the SJR. The results for BOD are given in Figure 2(a) as an example. The load designated as 'other' represents sources other than surface water inputs and is the remaining difference between the net sum input mass loads (inputs minus diversions) and the mass load observed at the Vernalis monitoring station. For some constituents, the net input mass load is greater than the mass load at Vernalis as a result of transformation processes within the main stem. Thus, the percentage of the computed surface water mass as compared with the mass at Vernalis is greater than 100% for these cases. While mass balance closure is expected for the conserved parameters, flow and TDS, it is not expected for total-P, nitrate-N, and BOD. Nitrate-N and total-P are used for primary productivity. Nitrate-N can transform into other nitrogen species, including transformation via denitrification and subsequent off-gassing of the nitrogen gas. River sediments can act as both sources and sinks for nutrients, especially phosphorus. River BOD decreases as organic carbon is oxidized and increased as the result of primary productivity.

Table 1 | Total volume and mass loads for constituents (TDS, total-P, nitrate-N, BOD) by sample site for 2007 (January 1, 2007 to December 31, 2007). The total volume of water was plotted against mass load to calculate quadrants. In this analysis, sites classified in quadrant 2 are considered the most likely to present practical targets for TMDL implementation activities

			Total annual load (Mg)				Quadrant		
Site name	**Site no. (Figure 1)**	**Total volume (10^6 L)**	**TDS**	**Total-P**	**Nitrate-N**	**BOD**	**Total-P**	**Nitrate-N**	**BOD**
Del Puerto Creek	36	15,549	12,001	6	74	89	III	III	III
ESWD Diversion	43	−19,745	−7,861	−4	−54	−58			
Hospital Creek	33	2,949	1,565	1	9	40	III	III	III
Ingram Creek	34	5,103	3,639	2	27	53	III	III	III
Los Banos Creek	20	20,633	22,036	12	11	272	III	III	II
Marshall Road Drain	38	2,508	1,763	1	15	38	III	III	III
Merced River	16	328,566	29,130	12	80	372	IV	I	I
MID Lateral 4	22	7,381	376	0.2	4	15	III	III	III
MID Miller Lake	25	10,363	2,028	3	29	64	III	III	III
Moran Drain	64	2,330	1,375	0.4	13	13	III	III	III
Mud Slough	18	86,131	134,349	23	293	554	I	I	I
Orestimba Creek	21	7,412	3,747	1	22	31	III	III	III
PID Diversion	40	−56,215	−31,232	−16	−173	−201			
Ramona Lake Drain	57	5,225	5,216	2	12	95	III	III	III
Salt Slough	19	138,794	130,312	42	187	502	I	I	I
SJR at Lander Avenue	10	32,240	20,663	9	56	315	III	III	II
Spanish Grant Drain	65	6,387	4,805	2	47	63	III	III	III
Stanislaus River	12	604,746	32,473	38	131	618	I	IV	I
Tuolumne River	14	329,474	38,858	34	469	526	I	I	I
TID Lateral 2	27	4,192	478	0.1	9	6	III	III	III
TID Westport Drain	28	25,383	10,476	4	286	64	III	II	III
TID Harding Drain	29	32,525	16,126	75	353	123	II	II	III
TID Lateral 6 & 7	30	10,203	4,362	6	179	27	III	II	III
Westley Wasteway	35	1,706	686	0.5	2	11	III	III	III
WSID Diversion	41	−60,117	−33,185	−16	−205	−215			
Total Surface Water		1,543,723	404,185	237	2,677	3,417			
ET/pp		−42,029							
Groundwater*		184,762	229,684	54	358	n/a			
SJR at Vernalis	5	1,686,456	641,841	318	2,598	5,489			

*Groundwater mass load contributions were estimated using the observed water quality data from Zamora *et al.* (2013).

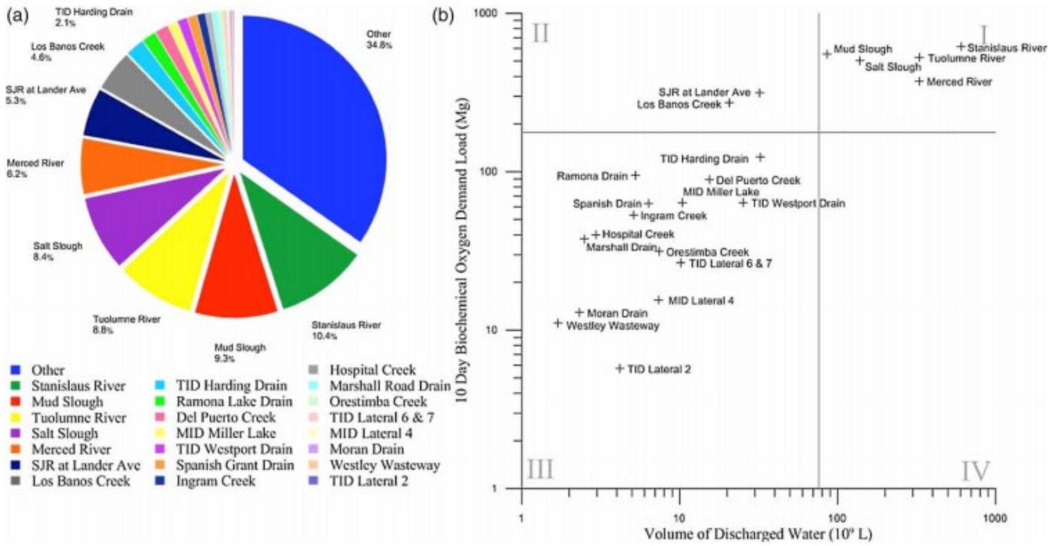

Figure 2 | (a) Pie chart represents the proportional origins of BOD from surface water inputs in the SJR from January 1, 2007 to December 31, 2007. BOD load designated as 'other' represents input load that was not accounted for by surface water loads and was likely due mostly to in-stream primary production. (b) Quadrant plot of discharged volume versus 10 day BOD load for all SJR tributaries over the year 2007. Quadrants are divided by average load and average volume.

Approximately 91.5% of the 1.7 trillion liters of water observed at Vernalis was accounted for by surface water inputs and outputs (Table 1). Based on 17.9 cm of pp, 258.9 cm of pan evaporation, and an estimated 27.5 billion liters transferred to riparian vegetation (Kratzer *et al.* 1987), it was estimated that 42 billion liters (Equation (3)), or 2.5% of total SJR volume, was lost due to the cumulative effect of evaporation, pp, and riparian vegetation water use. The remaining volume unaccounted for by surface water flows (11.0% of total inflow) was attributed to groundwater, resulting in an estimated inflow of 61 L-s^{-1} per river km annually. The estimated groundwater flow is consistent with previous estimates of 64 and 76 L-s^{-1} per river km (Zamora *et al.* 2013) and 56 and 118 L-s^{-1} per river km (Phillips *et al.* 1991), which were calculated using mass balance approaches.

During 2007, 641.8 million kg of TDS was observed in the SJR at Vernalis. Approximately two-thirds (63.0%) of this TDS load at Vernalis was accounted for by surface water inputs and 46.7% attributed to groundwater inputs (Table 1), resulting in 109.7% of the TDS at Vernalis. Having mass balance closure error within 10% may be reasonable given that a 96-km section of river was under evaluation. Error in the TDS mass balance is likely due to errors in flow and TDS measurements – especially those for groundwater that is a significant source of salinity.

A total of 318.4 million kg of total-P was measured at Vernalis, 74.7% of which originated from surface water loads and 16.8% from groundwater (Table 1). The remaining mass is assumed to originate from storage in river sediments. Nitrate-N accounted for 77.8% of the 3.3 million kg of total load measured in the SJR at the Vernalis flow station (data not shown). Surface water and groundwater loads accounted for 103.0% and 13.8%, respectively, of the nitrate-N load measured at Vernalis (Table 1). The deficit between the load at Vernalis and the loads from surface water and groundwater is assumed to be due to nitrogen transformation due to uptake via algal biomass production within the main stem of the SJR and possible transformations to other nitrogen species. Nearly two-thirds (62.2%) of the 5.5 million kg of BOD measured at Vernalis comes from surface water (Table 1). The remaining unaccounted for BOD load is likely due to algal growth within the main stem of the river, which is typically significant (Leland 2003; Jassby 2005). Nutrients from the tributaries and drains stimulate algal growth, and this growth is accelerated by the slow flow rate of the river, its shallow depth, and the abundance of sunlight during the long growing season (Lee & Jones-Lee 2003).

A quadrant analysis was performed where the total volume of water was plotted against mass load for each tributary with quadrant divisions defined at the average mass load and average volume. The results for BOD are given in Figure 2(b) as an example. Quadrant I (upper right) contains tributaries with high flows and high mass loads. While these tributaries are large load contributors, these tributaries are less attractive targets for watershed management because their large flows make them difficult to treat and implement best management practices and their constituent concentrations are often already lower than other tributaries. Quadrant II (upper left) contains tributaries with low flows and high loads. These tributaries are attractive targets for water quality improvement due to their smaller flows and higher impacts on river water quality. Quadrant III (lower left) contains tributaries with low flows and low loads, constituting a majority of the tributaries. These tributaries are easier to target for water quality improvement projects, but their improvement may have less impact on the total load in the river compared with other tributaries. Finally, quadrant IV (lower right) contains high flow and low load tributaries. These tributaries are the least attractive for watershed management improvement efforts.

The quadrant plot can be used to identify target sites based on a single constituent. As previously mentioned, the sites in quadrant II are ideal targets for remediation; for the BOD quadrant analysis (Figure 2(b)), SJR at Lander and Los Banos Creek would be selected. If financial resources permit, management action should be considered for sites positioned nearest the horizontal boundary of quadrant III such as TID Harding Drain, Ramona Drain, and Del Puerto Creek in the BOD example. Sites in quadrant I nearest the vertical boundary with quadrant II can also be considered so long as the flows are not too large. For BOD, Mud Slough could be targeted for TMDL management. Additional targets can be selected by proceeding sequentially down in load within quadrant III until the load impact is not large enough to merit the resources.

Presenting the quadrant results in a tabular format can be used to identify priority target sites for water quality improvement across multiple constituents. The quadrant results for each tributary and each constituent are summarized in Table 1. Since DO impairment is the emphasis in this study, the quadrant positions for total-P, nitrate-N and BOD are evaluated. All three constituents are considered because productivity in the SJR has been shown to be light-limited, rather than nutrient-limited, in the summer months (Leland 2003; Jassby 2005), which is not uncommon for eutrophic rivers (Hilton *et al.* 2006). Viewing the quadrant results in a tabular format enables simultaneous evaluation of all critical constituents by site; target sites are those with constituents residing in quadrants II and quadrant III with highest ranking to sites with more than one parameter in quadrant II. TID Harding Drain has two constituents in quadrant II and one in quadrant III and would be a good first target for management actions taken to reduce the corresponding loads. Additionally, Los Banos Creek, SJR at Lander, TID Westport Drain, and TID Lateral 6 & 7, which have one constituent in quadrant II and two in quadrant III, could be attractive additional targets for improvement efforts.

CONCLUSIONS

A mass balance analysis was conducted on the SJR for four water quality constituents using continuous monitoring and frequent grab sample data. Total mass loads from surface water contributions were compared with observed loads at the downstream limit of the study area for each constituent. Major contributors of mass loads were identified, mass balance closure assessed for each constituent, and sources or sinks identified when closure was not attained. A quadrant analysis is used to classify tributaries by flow volume and mass ranks. Sites with low flows and high loads were prioritized for TMDL management actions. The mass balance approach informs the TMDL process by identifying sources of impairment based on extensive data, presenting a fair and defensible approach intended to engage stakeholders.

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