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SOURCES AND TRANSPORT OF PHOSPHORUS TO RIVERS IN CALIFORNIA AND ADJACENT STATES, U.S., AS DETERMINED BY SPARROW MODELING[1]

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ABSTRACT: The SPARROW (SPAtially Referenced Regression on Watershed attributes) model was used to simulate annual phosphorus loads and concentrations in unmonitored stream reaches in California, U.S., and portions of Nevada and Oregon. The model was calibrated using de-trended streamflow and phosphorus concentration data at 80 locations. The model explained 91% of the variability in loads and 51% of the variability in yields for a base year of 2002. Point sources, geological background, and cultivated land were significant sources. Variables used to explain delivery of phosphorus from land to water were precipitation and soil clay content. Aquatic loss of phosphorus was significant in streams of all sizes, with the greatest decay predicted in small- and intermediate-sized streams. Geological sources, including volcanic rocks and shales, were the principal control on concentrations and loads in many regions. Some localized formations such as the Monterey shale of southern California are important sources of phosphorus and may contribute to elevated stream concentrations. Many of the larger point source facilities were located in downstream areas, near the ocean, and do not affect inland streams except for a few locations. Large areas of cultivated land result in phosphorus load increases, but do not necessarily increase the loads above those of geological background in some cases because of local hydrology, which limits the potential of phosphorus transport from land to streams.

(KEY TERMS: nutrients; phosphorus; geology; transport and fate; simulation; watersheds; SPARROW.)

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INTRODUCTION

Phosphorus is a naturally occurring element that occurs in the earth's crust within rocks and soils, and in all living organisms. The average crustal abundance of phosphorus is 0.1% (Rudnick, 2003; Canfield *et al.*, 2005). Phosphorus is one of 16 elements necessary for plant growth, and is a primary nutrient along with nitrogen and potassium (Mullins, 2009). The management of phosphorus use in watersheds, and particularly agricultural watersheds, is recognized as especially important because of the global demand for phosphorus fertilizers (Cordell *et al.*, 2009; Carpenter and Bennett, 2011), and problems, such as eutrophication, caused by runoff or erosion of soils from agricultural fields (Vollenweider, 1968). The global biogeochemical cycle of phosphorus includes inputs to soils through chemical weathering of phosphorus-containing minerals, cycling through terrestrial and aquatic ecosystems, runoff to the oceans and associated biogeochemical processes, and sedimentation. Tectonic processes such as volcanism and uplift move phosphorus to continental systems

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under geologic time frames (Compton *et al.*, 2000). Unlike nitrogen, there is essentially no atmospheric component of the global phosphorus cycle, except by dust. The terrestrial and aquatic biogeochemical cycles are complicated by interactions between living material and charged mineral surfaces in soils or sediments, such as iron or manganese oxides, which sorb phosphorus and limit its bioavailability (Compton *et al.*, 2000) and transport to aquifers.

The problems associated with phosphorus use have prompted studies or tools to assess specific risks. These tools use soil phosphorus levels, application methods, tillage, soil erodibility, and other factors to determine and mitigate the risks (Lemunyon and Gilbert, 1993; Eghball and Gilley, 2001). Although those types of tools have value, they do not necessarily address how much phosphorus may be transported on the watershed or catchment level. Management considerations designed to lower phosphorus concentrations or yields in specific river systems must take into account the broader context of processes, including geological sources, affecting transport in order to develop realistic water quality goals. Phosphorus is one of many different constituents on the 303(d) list of impaired water bodies mandated under the Clean Water Act for protection of the beneficial uses of water. In 2010, there were 192 listings for phosphorus of impaired water bodies on the California 303(d) list (http://www.waterboards.ca.gov/water_issues/programs/tmdl/integrated2010.shtml). The listings include 42 different streams or reservoirs located throughout the state.

In this study, the SPARROW (SPAtially Referenced Regression on Watershed attributes) model was used to provide a regional understanding of phosphorus sources and transport in most of California and portions of adjacent Oregon and Nevada. SPARROW is a hybrid statistical and mechanistic model for estimating the movement of the mass of a particular constituent through the landscape under long-term steady-state conditions (Schwarz *et al.*, 2006; Preston *et al.*, 2009). This model utilizes watershed characteristics including sources of the modeled constituent, land use or land cover, climate, and stream properties to explain the spatial variation in measured mean annual stream load. The SPARROW model provides interpretations relevant to an "average" year in a region, and does not capture the seasonality of stream load, nor can it capture the loadings that would occur during storm events. Streamflow and water quality data are de-trended, as explained in the methods section to capture long-term average conditions. A modification to the SPARROW model is being tested that would incorporate transient conditions, that is using nonaveraged or de-trended data, and be able to distinguish seasonal loads. SPARROW models are useful for a management context because of the knowledge gained on how constituents are sourced and transported in the unmonitored catchments. Several SPARROW models of phosphorus from other large watersheds have been previously published (Brown *et al.*, 2011; Garcia *et al.*, 2011; Moore *et al.*, 2011; Wise and Johnson, 2011).

STUDY AREA AND METHODS

Location and Geology

The study area included most of the state of California and portions of adjacent Oregon and Nevada (Figure 1). The study area is made up of 17 six-digit hydrological unit code regions (HUC6). A listing of these HUCs, and their areas, is shown in Table 1. The boundaries of the six-digit HUCs are shown in Figure 1. There are several large rivers of management or ecological importance in the study area. The largest river, the Sacramento River (Figure 1), is the major source of freshwater to the Delta (Figures 1 and 2) of the Sacramento and San Joaquin Rivers. Water from the Sacramento River is used for agriculture and is a source of drinking water (CADWR, 2009a, b). A large portion of the entire study area drains to the Delta, making source identification for nutrients an important management tool. The Delta, along with the rest of the San Francisco Bay system, is the largest estuary on the North American west coast, and also very important to California water use and the state's economy (http://www.water.ca.gov/swp/delta.cfm). The San Joaquin River has considerably less discharge relative to the Sacramento River, but is also a major source of nutrients to the Delta. Other large rivers include the Klamath, Russian, Eel, Salinas, Merced, Stanislaus, Tuolumne, and numerous others that drain to the Pacific Ocean. Selected rivers are shown in Figure 1 and their relevance to the model and to phosphorus loads transported to coastal regions is discussed later in this manuscript. Discharge on most of the major rivers of the study area result from a combination of natural and managed flow. There are a number of reservoirs present throughout the study area that supply water for agriculture, urban, and environmental uses, and provide flood protection. Most of the larger reservoirs are situated in undeveloped or relatively undeveloped areas, and there are also many smaller ones located in mixed land use areas.

There are three "Level-Three" ecological regions as defined by the U.S. Environmental Protection Agency

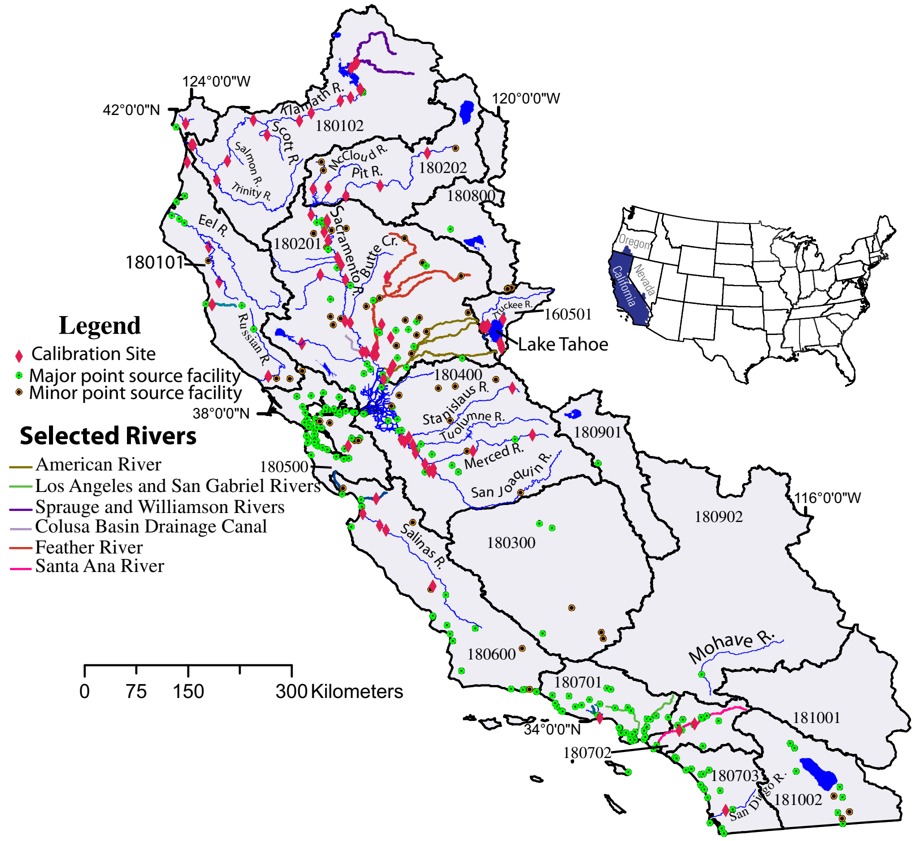

FIGURE 1. Map of Study Area Showing Selected Rivers, Calibration Sites, Point Source Facility Locations, and Six-Digit Hydrologic Unit Code (HUC6) Boundaries.

(USEPA) (Figure 2). These regions were delineated by the USEPA for the purpose of developing suggested numerical nutrient criteria for surface water (http://www.epa.gov/wed/pages/ecoregions.htm). The western-forested mountains region is mostly rural land with mainly mixed conifer forests. There is some development and logging, but the streams in that region have the lowest effects from human impacts. In contrast, the Central Valley is highly impacted with intensive irrigated agriculture and water diversions, urban development, and wastewater treatment. The Xeric West contains a mix of rural land, intensive urban development with large cities, such as Los Angeles, and some irrigated agriculture. A full land use/land cover map of the study area is shown in Figure S1. Land use/land cover is for 2006, Ludington *et al.* (2007) (http://www.mrlc.gov/nlcd06_data.php). Parts of the Xeric West have rivers that drain to the ocean, but there is also internal drainage in large areas where rivers have no outlet to the ocean. The recommended criteria for nutrients by the USEPA are for either total nitrogen or total phosphorus (TP). Therefore, SPARROW models can be directly compared to these recommendations. The recommended concentration criteria for TP in the Central Valley is 0.047 mg/l, that for the western forested mountains is 0.01 mg/l and that for the Xeric West is 0.022 mg/l of phosphorus as P (USEPA, 2000). These are recommended criteria and do not currently have regulatory authority.

Precipitation in this study area is unevenly distributed. A map of the 30-year mean annual precipitation is shown in Figure S2. Precipitation is very low in the southern portion of the Central Valley of California and increases northward. Much of the Central Valley is in agricultural production and irrigation is required throughout. The desert areas of the southeastern portion have the lowest annual precipitation, while the northwest coastal portion generally has the highest. There are portions of the northern study area with high precipitation, which generally follow elevation trends. There is also a region of the northeastern portion with low precipitation.

The geology of the study area is highly varied (Figure S3). The Central Valley is composed of a thick sequence of Quaternary sediments sourced from the adjacent highlands. Rocks to the east of the Central Valley, are a mix of igneous (granodiorite and quartz monzanite), volcanic (andesites and others), and metamorphic assemblages. Rocks to the west of the Central

TABLE 1. Full Names for Six-Digit Hydrologic Unit Code (HUC6) Watersheds in the Study Area.

HUC6 Number	HUC6 Name	Area, km^2	Number of Calibration Sites
160501	Truckee	5,025	9
180101	California North Coastal	23,905	6
180102	Klamath and Trinity River	40,525	15
180200	Pitt and McCloud River	19,851	5
180201	Sacramento River	52,082	23
180300	Tulare-Buena Vista Lakes	42,513	0
180400	San Joaquin River	40,955	12
180500	San Francisco Bay	11,145	1
180600	Central California Coastal	29,371	5
180701	Los Angeles-Ventura	11,791	1
180702	Newport Bay-Santa Ana	7,006	2
180703	San Diego	9,877	1
180800	North Lahontan	11,771	0
180901	Crowley, Mono, Owens Lake	11,331	0
180902	Northern Mojave	61,859	0
181001	Southern Mojave	22,884	0
181002	Salton Sea	18,189	0

Valley are mostly of marine origin, with some mélanges and serpentines. Marine sedimentary rocks occur throughout much of the coastal regions. The northern portion of the study area has extensive volcanic rocks, and the northern central portion has extensive igneous and metamorphic assemblages including rocks of ophiolite origin. The southeast portion of the study area is largely desert with a mix of Quaternary sediments and ranges of igneous rocks typical of the Basin and Range Province. Quartz diorite rocks occur in the southwest portion of the study area.

Mathematical Formulation

The SPARROW model is based a nonlinear least-squares multiple regression on elements of a hydrologic framework that solves a mathematical expression of constituent load. Detailed explanations of the mathematical formulation are available elsewhere (Schwarz *et al.*, 2006; Alexander *et al.*, 2008). Briefly, the load at the outlet of a catchment, L_i, is expressed as:

$$Li = A_i L_{i-1} + A_i' \sum_{n=1}^{N} \alpha_n S_{ni} \exp\left(\sum_{m=1}^{M} \delta_{mn} \theta_m Z_{mi}\right) \quad (1)$$

The load leaving an individual catchment, L_i, is a function of the incoming load (L_{i-1}), aquatic decay (A_i), phosphorus sources within that catchment ($\alpha_n S_{ni}$), and land to water delivery $\left(\exp\left(\sum_{m=1}^{M} \delta_{mn}\theta_m \; Z_{mi}\right)\right)$. The aquatic decay term accounts for a variety of physical or biogeochemical processes resulting in loss of phosphorus from the stream. The source terms are those that are determined to be statistically significant for the model during the calibration process. Source terms may be mass related, such as phosphorus in wastewater discharges, or the amount of fertilizer applied in a catchment, or can be spatially relevant, such as the area of a particular land use. The land-to-water delivery term represents processes that can move phosphorus from land to a stream. Possible terms might include precipitation, soil texture, base-flow index, etc. Coefficients, θ_m, are calculated by the model to adjust the amount of a source of phosphorus, within a catchment, that reaches the stream before any decay occurs. The aquatic decay term is specified for either streams or reservoirs. It is a first-order decay function for instream decay, where the fraction of mass transported is a continuous function of the mean reach water travel time, mean water depth, and the estimated coefficient. For reservoirs, aquatic decay is a first-order mass transfer rate dependent on the inverse of areal hydraulic loading, in units of year per meter and a model-estimated coefficient.

Data Compilation

SPARROW models are built upon a base year for which data on sources and other characteristics must be available. The base year for this model was 2002. There must also be a sufficient amount of calibration sites throughout the watershed where water chemistry and discharge have been collected. De-trended annual loads are calculated for each of the calibration sites. Both streamflow and water chemistry data are de-trended around the base year in order to remove the effect of variations caused by changing environmental conditions. The period of time of available data for either streamflow or water chemistry varies at the calibration sites. By removing the trends, the SPARROW model can be calibrated according to an "average" condition for each of the watersheds. The model coefficients are estimated on the basis of the calibration site records and predictions can then be made on the entire study area, which is mostly composed of unmonitored stream reaches. The chemistry and discharge data for calibration must span the base year. The stream network is the basic building block of the SPARROW model and all data are referenced to individual catchments. This SPARROW model was developed for TP, which includes both dissolved and particulate forms. Data for TP in stream water were

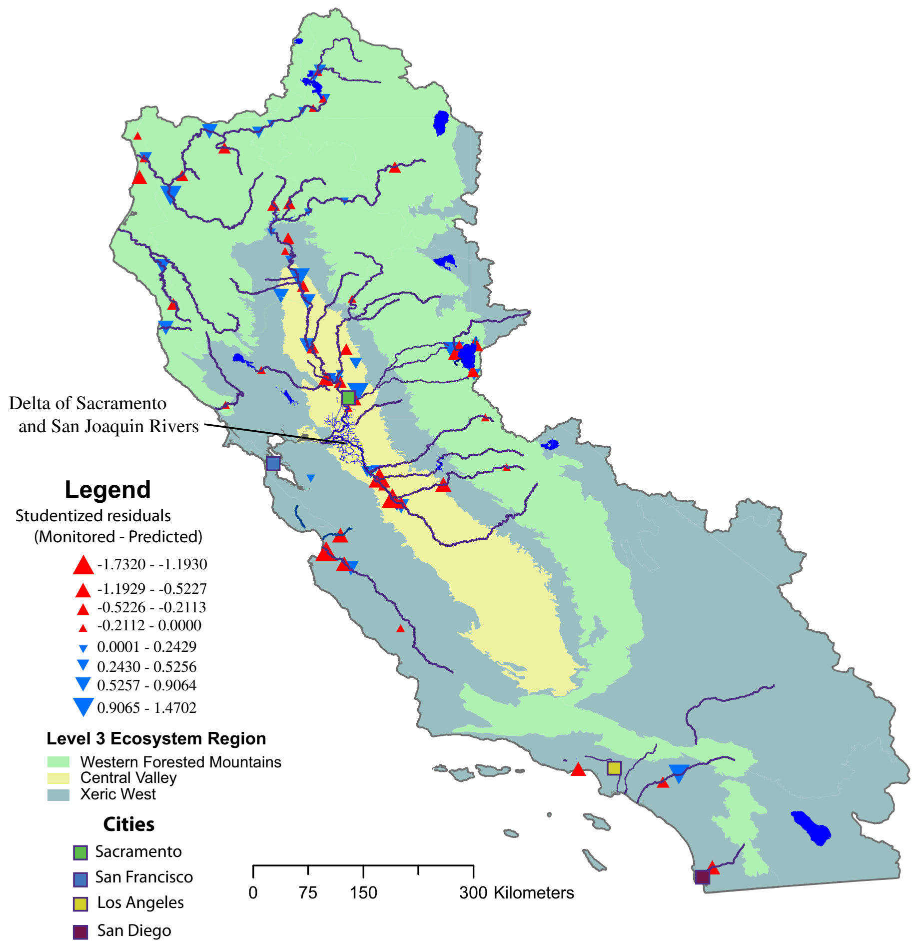

FIGURE 2. Map of Studentized Residuals for the SPARROW Model Phosphorus Calibration, Locations of U.S. Environmental Protection Agency Level-3 Ecosystem Regions, and Locations of Selected Cities.

obtained from federal, state, university, and other sources. A total of 80 sites (Figure 1) were used for calibration (Table S1 and S2). The distribution of these sites by HUC6 is shown in Table 1. Some HUC6 regions were well represented with calibration sites, but other locations, especially the arid regions such as Mojave, Salton Sea, and others had few calibration sites mainly because of the scarcity of gauging stations and associated water quality records. Streamflow data were mainly obtained from the U.S. Geological Survey (USGS) except for a few sites.

Before the SPARROW model could be calibrated, it was necessary to have estimates of annual TP stream loads for each of the 80 sites. These were estimated using the USGS Fluxmaster model (Schwarz *et al.*, 2006). The Fluxmaster model is similar to other regression methods for estimating loads, such as that developed by Cohn (2005) in that it uses a bias-corrected log-linear regression model with maximum likelihood estimation that relates the concentration to time, discharge, and seasonal terms (Schwarz *et al.*, 2006; Saad *et al.*, 2011). The Fluxmaster model requires a continuous record of mean daily discharge for the modeled period, and a sufficient number of water quality samples, collected over the range of flow conditions, to develop a suitable relation. A total of 20 water quality samples are usually considered a minimum, but the model can be run with fewer. In this study, the fewest number of samples at a particular site was 16, the maximum was 1,176, and the median was 102. More information about matching water quality data with streamflow data is given by Saad *et al.* (2011). The process for the Fluxmaster calibration and de-trending of hydrologic data is described in more detail in the Supporting Information.

Data for the SPARROW model must be organized according to a spatial hydrologic network. The 1 : 100,000 scale NHDPlus version 2 hydrologic dataset (McKay *et al.*, 2012) was used. NHDPlus is described as an integrated suite of application-ready geospatial data products, incorporating many of the features of the National Hydrography Dataset (NHD), the National Elevation Dataset, and the

National Watershed Boundary Dataset (WBD) (McKay *et al.*, 2012). Further information about the NHDPlus system is given by Brakebill *et al.* (2011). A total of 144,405 individual catchments were used for the model calibration and predictions. Each catchment has a unique identifier with classifications for a flow line, direction of flow, and connectivity to subsequent flow lines. Spatial data associated with each of the catchments must be available for SPARROW simulations. Catchments used for calibration will have a value for the annual load as determined by the Fluxmaster calculation, and catchments with point sources will have the annual discharge of TP. Data on phosphorus sources, and all other hydrologic data used in the model, must be present for each catchment. These data sources are described below. Although NHDPlus version 2 incorporates major diversions of rivers, it was necessary to add more diversions because of the importance of irrigation and other water uses in California. The locations of these diversions and the fraction of water diverted were obtained from various state, federal, and local agencies. The fractional amount transported after a diversion is used in the data input to the model to account for the mass balance of water.

Point source data were obtained mostly from Maupin and Ivahnenko (2011). The data included the discharge and the associated annual load of TP. Wastewater facilities were defined as "major" when the average discharge was greater than 3,785 m^3/day. Facilities with lower discharge were classified as minor. The locations of these facilities are shown in Figure 1. Many of the larger facilities are located near the ocean because of their proximity to coastal cities, so those loads only minimally affect the inland rivers, but may have some effect on the near shore ocean environment. A total of 261 facilities were used in the calibration, and about 66% of those were domestic wastewater treatment plants. It was always desirable to acquire actual chemical data on the amount of phosphorus in the discharge, but in some cases, as for wastewater, phosphorus had to be estimated using a procedure described by McMahon *et al.* (2007). Similar to the calculations made for stream loads, an annual amount at the point of discharge was utilized to account for that source of phosphorus to the streams.

Potential TP sources included wastewater discharges, land-use categories (urban, agricultural, forested, etc.), fertilizer applied to crops, agricultural livestock (manure from livestock production or from confined and unconfined production), and geological background. Information on phosphorus applied to crops came from county level estimates (Ruddy *et al.*, 2006). These were expressed in the model as kg/yr for each catchment where fertilizer was applied. Similarly, phosphorus from various sources of manure, also obtained from Ruddy *et al.* (2006), was expressed as kg/yr. Geological sources of phosphorus were expressed as an indirect measure as described by Terziotti *et al.* (2009). Bed-sediment samples collected at headwater streams in relatively undisturbed areas were aggregated by using geochemical map units and ecoregion classifications. The mapped values are in parts per million, which was then scaled by catchment area (ppm km^2) to serve as a surrogate in the model for the mass of phosphorus contributed by geological sources. The national land cover database (Homer *et al.*, 2004) was used for amounts of various land use categories, expressed as km^2.

After significant source terms were identified, land to water variables were considered for the delivery of TP to streams. Land to water variables considered in this model included mean annual precipitation (Oregon State University, 2007), soil K factor, soil permeability, soil organic matter, soil clay content and other soil features, soil pH (U.S. Department of Agriculture, 1994), average slope in the catchment, temperature, and presence of tile drains (Wieczorek and LaMotte, 2010). The soil erodibility factor (K factor) is a quantitative description of the inherent erodibility of a soil; it is a measure of the susceptibility of soil particles to detachment and transport by rainfall and runoff. For any soil, the erodibility factor is the rate of erosion per unit erosion index from a standard plot. Aquatic decay terms tested include instream loss, which is the product of travel time and inverse of mean water depth with units of m/day, and reservoir loss, which is the inverse of areal hydraulic loading. The aquatic loss in streams was modeled according to a first-order decay process as a continuous function of time of travel as described by Schwarz *et al.* (2006). Instream decay was tested for streams of various levels of discharge. Instream decay rates are estimated on the basis of travel times within the stream segments and evaluated on the basis of statistical significance of the explained spatial variation in stream load.

Output of the SPARROW model includes information on TP sources and mass within catchments, both incremental and total. An incremental load or flux of TP within a catchment is that which originates within a single catchment before any decay, transport out of the catchment, or loss has occurred. Total load or flux in a catchment is defined in this manuscript as the sum of processes including mass transferred to a catchment from adjacent ones, the amount that originated in the catchment, and all losses accounted by the decay terms. Yields of TP (mass per area) are described in a similar manner using the area of each individual catchment. Catchments along the flow line of individual rivers can be isolated from the model results. This allows for an understanding of loads in an individual river and the sources of those loads.

RESULTS

Model Calibration and Estimation

The first step in building the SPARROW model was establishing a concentration/discharge model for the calibration sites. Phosphorus concentrations varied at the calibration sites within and across the Level III ecological regions (Figure S4). Residuals from the output of the load model, Fluxmaster, were examined and the Nash-Sutcliffe efficiency index (Nash and Sutcliffe, 1970) was used to determine if any bias was present in the load calculations. The Nash-Sutcliffe index suggested a slight negative bias indicating that the modeled load tended to underestimate the actual.

Calibration of the SPARROW model requires testing the statistical significance of phosphorus sources, land-to-water delivery variables, and aquatic decay variables. Statistically significant variables and the data sources identified are shown in Table 2. The statistical significance of each source coefficient was determined using a one-sided *t*-test with a significance level of 0.10. A one-sided test was used, as sources have to be positive. Sources with significance levels greater than 0.1 were excluded from the model. The first variable tested was point sources (locations shown in Figure 1). The significance level (*p*-value) for point sources was 0.04 (Table 3). Geological background was then added and found to be highly significant ($p = 0.001$) (Table 3). Geological sources of phosphorus are shown in Figure 3.

It was hypothesized that agriculture would be an important source of phosphorus. Cultivated land as a land-use category was significant ($p = 0.008$). The locations of cultivated land are shown in the land use/land cover map in Figure S1. The amount of chemical fertilizer as phosphorus and the amount of manure applied were also tested, but these were not significant.

Source terms were tested for possible problems caused by multicollinearity. Independence of source variables was assessed by calculating the variance inflation factor and the eigenspread. Multicollinearity was also evaluated by calculating the eigenspread of the predictor variables as described previously (Schwarz *et al.*, 2006). Multicollinearity was not found to be a problem.

Other land uses or land covers were tested but were not significant for the model. These included forested land, urban or developed land, grasslands and pasture, and wetlands.

TABLE 2. Phosphorus Source Variables and Land-to-Water Delivery Variables Used in Developing the SPARROW Model for California and Portions of Oregon and Nevada.

Phosphorus Source Variable	Mass Unit	Spatial Dataset Tested
Point source	kg/yr	P in NPDES-permitted discharge of municipal, domestic, and industrial wastewater (McMahon *et al.*, 2007)
Geological sources	ppm km^2	P content of bed sediment in headwater streams based on regionalizing National Geochemical Survey data (Terziotti *et al.*, 2009), multiplied by catchment area
Cultivated land	km^2	Area of cultivated crops (Category 82) as classified by the 2001, National Land Cover Dataset (Homer *et al.*, 2004)
Land-to-Water Variable	**Unit of Measure**	**Spatial Dataset Tested**
Precipitation	mm	Annual mean precipitation, 1971-2000, PRISM, Oregon State University, 2007
Clay content	%	Clay in soil, STATSGO (U.S. Department of Agriculture, 1994)

Note: NPDES, National Pollutant Discharge Elimination System.

Land-to-water delivery variables are used to model how phosphorus moves from the landscape to a stream. The statistical significance of each delivery coefficient, whether positive or negative was determined using a two-sided *t*-test and a significance level (*p*-value) of 0.05. Delivery variables tested that had a significance level (*p*-value) greater than 0.05 were excluded from the model. Possible delivery variables include climate terms such as temperature or precipitation, soil characteristics such as percent sand or clay, base-flow index, slope of land surface, soil pH, soil organic matter, soil erodibility, etc. The delivery factors found to be significant included mean annual precipitation and average clay content of the soil (Table 3). Including sand and clay percent together indicated a multicollinearity problem, and since clay resulted in a model with a more favorable *p*-value, it was used for subsequent model prediction. The distribution of the percent clay in the catchments is shown in Figure S5. Groundwater discharge to streams, as indicated by the base-flow index, was not significant. Groundwater can be a source of phosphorus to streams (Domagalski *et al.*, 2008; Holman *et al.*, 2008) but this was not significant over the study area.

Aquatic decay is based on the stream reach length and time of travel. Stream types range from

TABLE 3. Results of Nonlinear Least Squares Estimation and Bootstrap Analysis for the SPARROW Phosphorus Model Developed for California and Portions of Oregon and Nevada.

Nonlinear Least Squares Calibration			Results of Bootstrap Analysis				
Variable	**Model Coefficient Units**	**Model Coefficient**	**Lower 90% Confidence Interval**	**Upper 90% Confidence Interval**	**Standard Error of Coefficient**	***p*-Value***	**Nonparametric Bootstrap Estimate of Coefficient (mean)**
Sources of phosphorus							
Point sources	Dimensionless	1.46	–0.52	2.92	0.82	0.04	1.36
Geological sources	kg/ppm km^2	0.036	0.012	0.049	0.01	0.001	0.039
Cultivated land	kg/km^2/yr	259.4	89.4	395.8	106.0	0.008	267.3
Land-to-water delivery							
Precipitation	log (mm)	0.70	0.34	1.05	0.25	0.006	0.71
Clay	Dimensionless	0.05	0.023	0.08	0.016	0.001	0.05
Aquatic loss							
Instream loss ($Q < 1.4$ m^3/s) (m/day)	per day	1.45	–0.86	1.96	0.42	0.0005	1.71
Instream loss ($Q > 1.4$ m^3/s and <14.1 m^3/s) (m/day)	per day	1.24	0.43	1.73	0.36	0.0005	1.34
Instream loss ($Q > 14.1$ m^3/s) (m/day)	per day	0.27	0.11	0.45	0.11	0.006	0.26
Model Root Mean Square Error: 0.65 Model R^2: 0.91 Model Yield R^2: 0.51							

*p-Values are one-sided for source and aquatic loss terms, and two-sided for land-to-water delivery terms.

intermittent with either seasonal or longer time periods between discharges to large perennial rivers. The average annual and de-trended streamflow was 2.9 m^3/s and the median was 0.04 m^3/s. The 90th percentile of streamflow was 1.6 m^3/s. The maximum streamflow was 700 m^3/s. Clearly, relatively small streams with a few large rivers dominate the study area. There are also many intermittent streams, especially in the Xeric West portion of the study area. Different stream classes, with respect to size, were tested for their significance for aquatic decay. Three perennial stream classes were found to be significant, while intermittent streams were not found to be significant. Small streams, less than 1.4 m^3/s and medium-sized streams (greater than 1.4 m^3/s and less than 14.1 m^3/s, $p = 0.0005$), were highly significant for aquatic loss, with similar coefficients, 1.45-1.24 day^{-1}. Large streams were also significant ($p = 0.006$) but with a smaller coefficient, 0.27 day^{-1}. Reservoirs were not significant for the aquatic loss of phosphorus ($p > 0.1$). It might be expected that reservoirs would be significant since sediment is trapped in reservoirs. Many of the reservoirs in California are located in upland areas in regions where most of the phosphorus inputs are from background sources and not anthropogenic sources. In those cases, phosphorus loads from the reservoir might be in balance with inputs and therefore aquatic decay is insignificant. Previous SPARROW phosphorus models have shown mixed results regarding whether reservoirs are significant for aquatic loss. Models developed in the midwestern or eastern United States (U.S.) have shown that reservoirs are significant, such as in the southeastern U.S. (Garcia *et al.*, 2011), within the Missouri River Basin (Brown *et al.*, 2011), the Great Lakes (Robertson and Saad, 2011), and the South central U.S. (Rebich *et al.*, 2011). In contrast, Wise and Johnson (2011) did not find any significance of reservoirs for phosphorus loss in the Pacific Northwest, U.S. A more recent study (Milstead *et al.*, 2013) demonstrated that nutrient dynamics in reservoirs could be more effectively studied by coupling predicted SPARROW loads to reservoirs with a linear Vollenweider type regression.

Model coefficients and model summary statistics are shown in Table 3. The model coefficient of determination, R^2, was 0.91 indicating that the model accounted reasonably well for the spatial variability in monitored loads. The coefficient of determination for phosphorus yields was 0.51. This coefficient was based on the log-transformed data. As explained by Schwarz *et al.* (2006), the model coefficient of determination for SPARROW models, R^2, tend to be large (greater than 0.6). This is because much of the

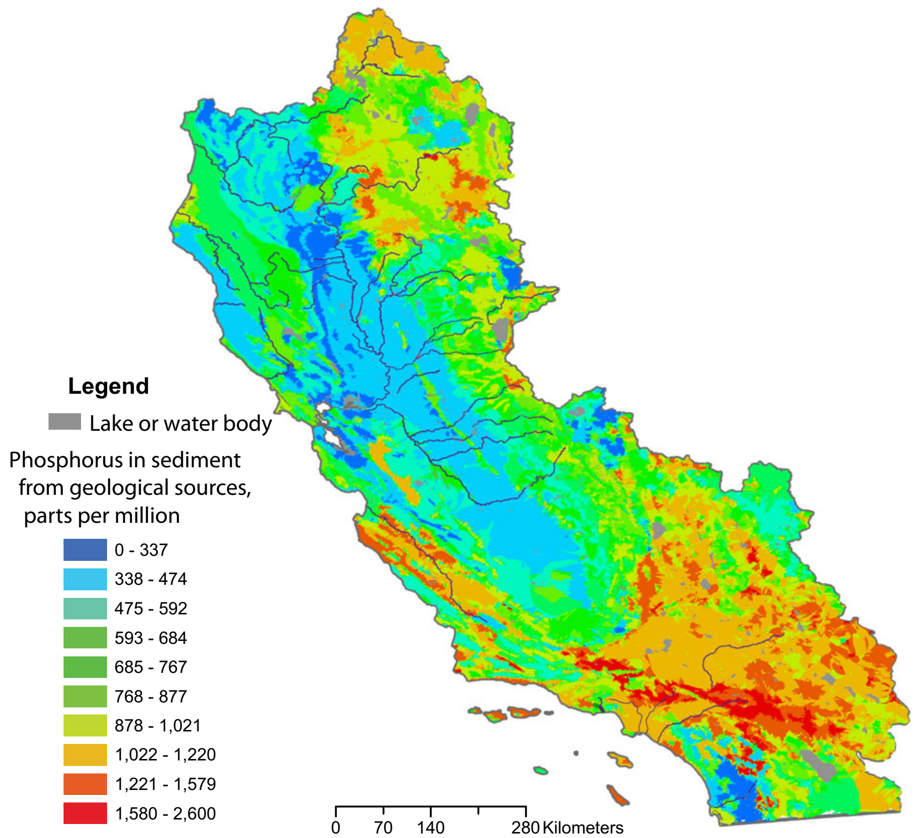

FIGURE 3. Map Showing Concentrations of Sedimentary Phosphorus in Surficial Soils or Stream Beds from Geological Sources.

variation in the dependent variable is associated with the size (drainage area) of the basin upstream from the monitored reach, and drainage area is typically highly correlated with contaminant source variables (Schwarz *et al.*, 2006). A high value of the coefficient of determination does not necessarily indicate the strength of the model within smaller basins. The goodness of model fit for small basins might be better described by the coefficient of determination of the logarithm of contaminant yield (mass per unit area) (Schwarz *et al.*, 2006). The root mean square error (RMSE) of the model was 0.65. This is similar to the RMSE of other SPARROW TP models, which ranged from 0.345 to 0.755 (Preston *et al.*, 2011). Studentized residuals from the model are shown in map form (Figure 2). The distribution of calibration sites with over- or underpredictions is somewhat randomly distributed throughout the northern portion of the study area, but there appears to be a bias toward overprediction in the southern portion of the study area. This might be attributed to fewer calibration sites in that part of the study area. Plots of observed and predicted loads, residuals and predicted loads, residuals and predicted yield, and a probability plot of residuals are shown in Figure S6. In general, the overall relationship between observed and predicted loads, shown in Figure S6A, suggests that no significant bias was detected throughout the study area.

The robustness of the calculated model coefficients (defined as the ability of the calibrated model coefficients to remain stable with random variations in the input data) was examined using nonparametric resampled bootstrapping with 200 iterations. This is based on repeated reestimation of the model applying a different set of randomly selected (with replacement), nonnegative integer weights, each set summing to the number of model observations (Schwarz *et al.*, 2006). Bootstrapping was used to estimate the mean of calculated coefficients for the 200 estimates. The means of the bootstrap estimates of the 200 iterations were generally between 0 to 7.5% of the least-squares estimates (Table 3). There was one exception. This was for the aquatic loss term for the small streams where there was a 15% difference.

Loads and Yields

Loads are defined as mass per year, while yields are mass per year normalized by catchment area. A map of TP loads exported from catchments is shown in Figure 4 and the loads attributed to cultivated land and geological background in Figures 5 and 6. Phosphorus loads leaving catchments are calculated by taking the incoming load into a catchment from the adjoining catchments, adding the load contributed by the catchment and subtracting the amount of loss from aquatic decay. Incremental loads, which are loads originating in individual catchments (no transport from adjacent catchments or aquatic decay), for the six-digit hydrologic units that make up the study area are shown in Table 4. Maps of incremental load for TP, incremental from geological sources, and incremental from cultivated land are shown in Figures S7, S8, and S9. The table and plots of incremental loads represent the TP sourced within a catchment. The incremental loads, therefore, are only representative of the individual catchments and can be thought of as the starting condition before downstream transport or any loss occurs. The difference between the incremental and total load maps shows how downstream transport is attenuated by aquatic decay. The incremental sources of phosphorus over the entire study area are attributed to geological background (39%), point sources (23%), and cultivated land (38%).

The largest continuous regional area of high phosphorus load from cultivated land is the Central Valley (Figure 5). The lower portion of the Central Valley (HUC 180300, Tulare-Buena Vista Lake) has mostly closed drainage because of water management, and essentially none of the load leaves the HUC. The HUC representing the Sacramento River (180201) and that for the San Joaquin (180400)

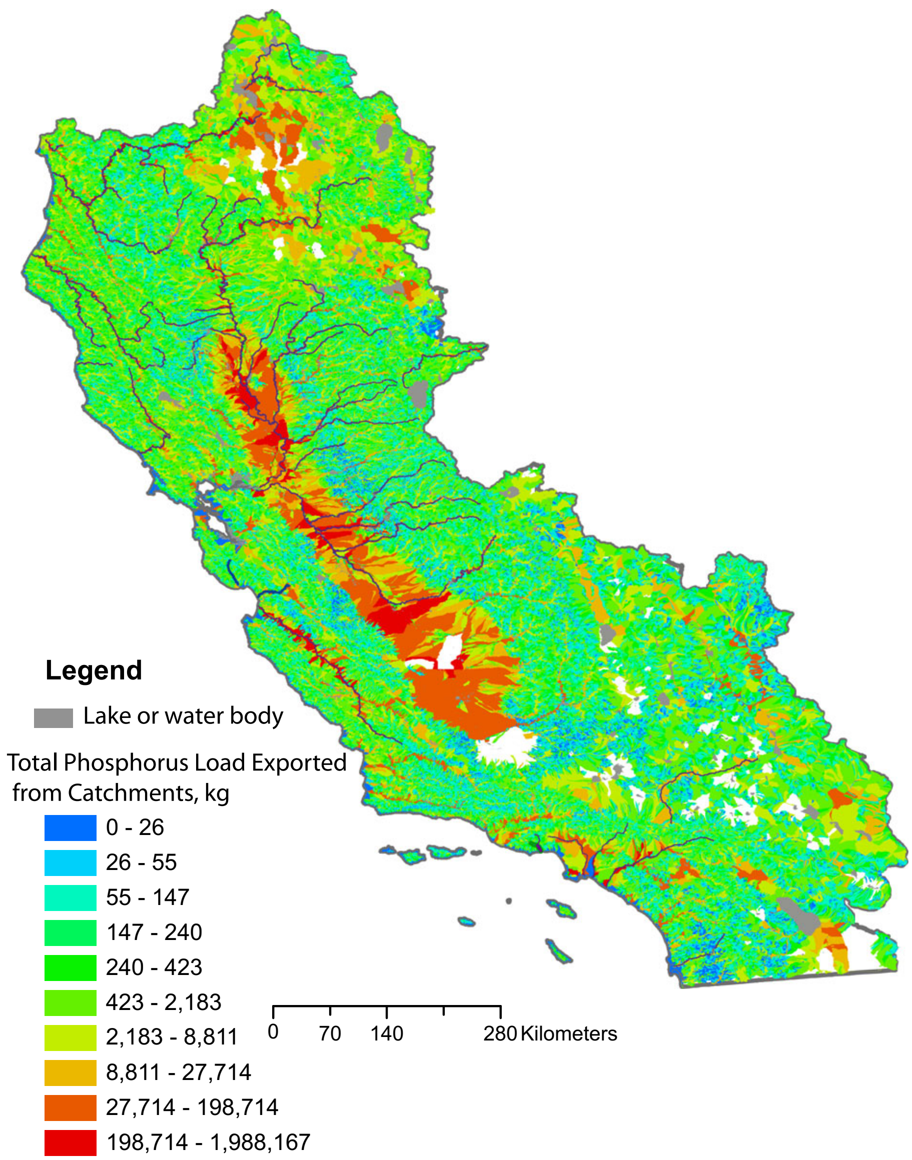

FIGURE 4. Map Showing Total Phosphorus Load Exported from Catchments.

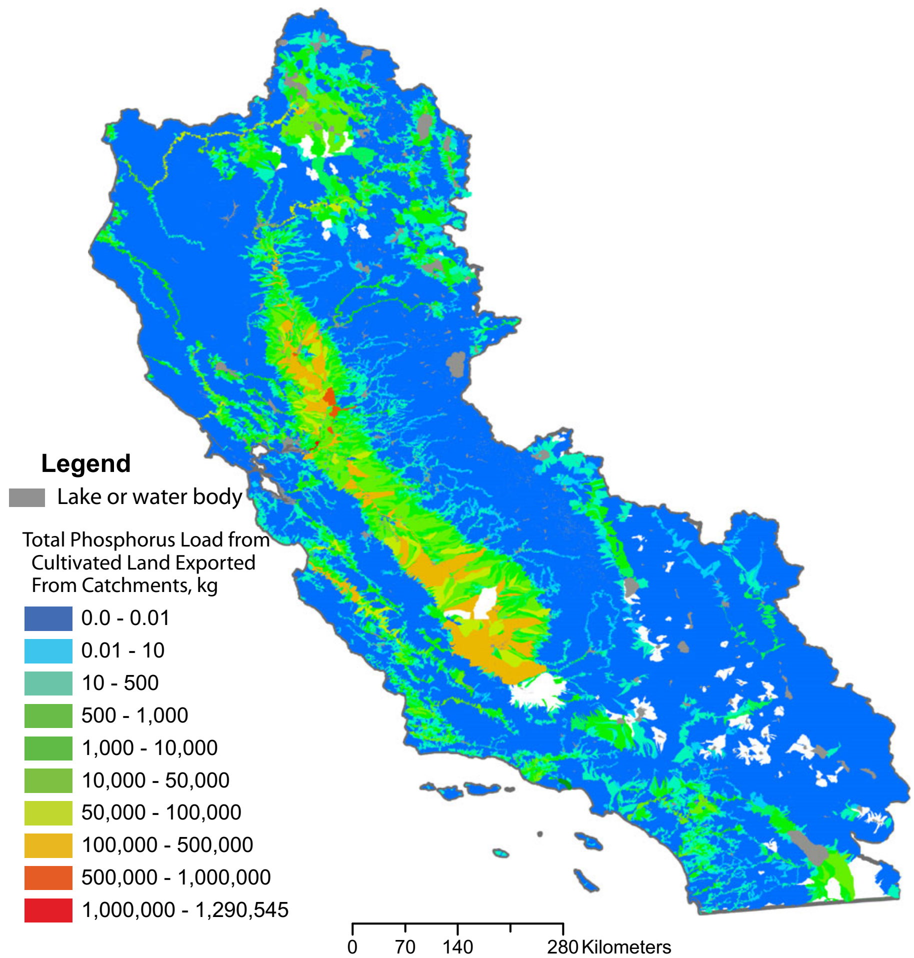

FIGURE 5. Map Showing Total Phosphorus Load from Cultivated Land Exported from Catchments.

demonstrate the importance of cultivated land for the sourcing of phosphorus to streams. Those two watersheds have the highest estimated incremental load and each have about 63 or 64% of the incremental load from cultivated land. The incremental TP load of the Tulare-Buena Vista Lakes HUC is about 75% from cultivated land. Incremental inputs from cultivated land are also locally important within the Central California Coast and the upper portion of the Klamath-Trinity region. Incremental load of phosphorus in the Central California Coast (HUC 180600) and Klamath and Trinity River (180102) is from mixed sources and geologic background is important. One river within the Central Valley Coast with extensive agriculture in the watershed is the Salinas River. Some hydrologic units have point sources that are important for incremental phosphorus loading. These are mostly in coastal regions and include the Los Angeles-Ventura (180701), Newport Bay-Santa Ana (180702), San Diego (180703), and San Francisco (180500). Since these point source locations are near the ocean, most of that incremental load is discharged to the coast or estuaries. There are large regions in the study area with closed drainage besides the Tulare-Buena Visa Lakes region. Two of these are the northern and southern Mojave Desert and another HUC (180901, Crowley, Mono, Owens Lake) to the north. These are sparsely populated areas as indicated by the low amount of incremental load from point sources and most of the load is from geological background. The Salton Sea HUC (181002) also has closed drainage and there is significant agriculture in that region because of the availability of irrigation water. Incremental load is high in some regions, such as the Mojave, but there is essentially no phosphorus transported from this region, because of closed drainage. The California North Coastal area (HUC 180101) is drained by several large rivers and has 80% of the incremental phosphorus load is from geologic background. The Tahoe region (HUC 160501, Truckee) is especially important from a management perspective. The lake is deep with very low primary productivity and high clarity. Streams enter Lake Tahoe from the south, east, and west, and the

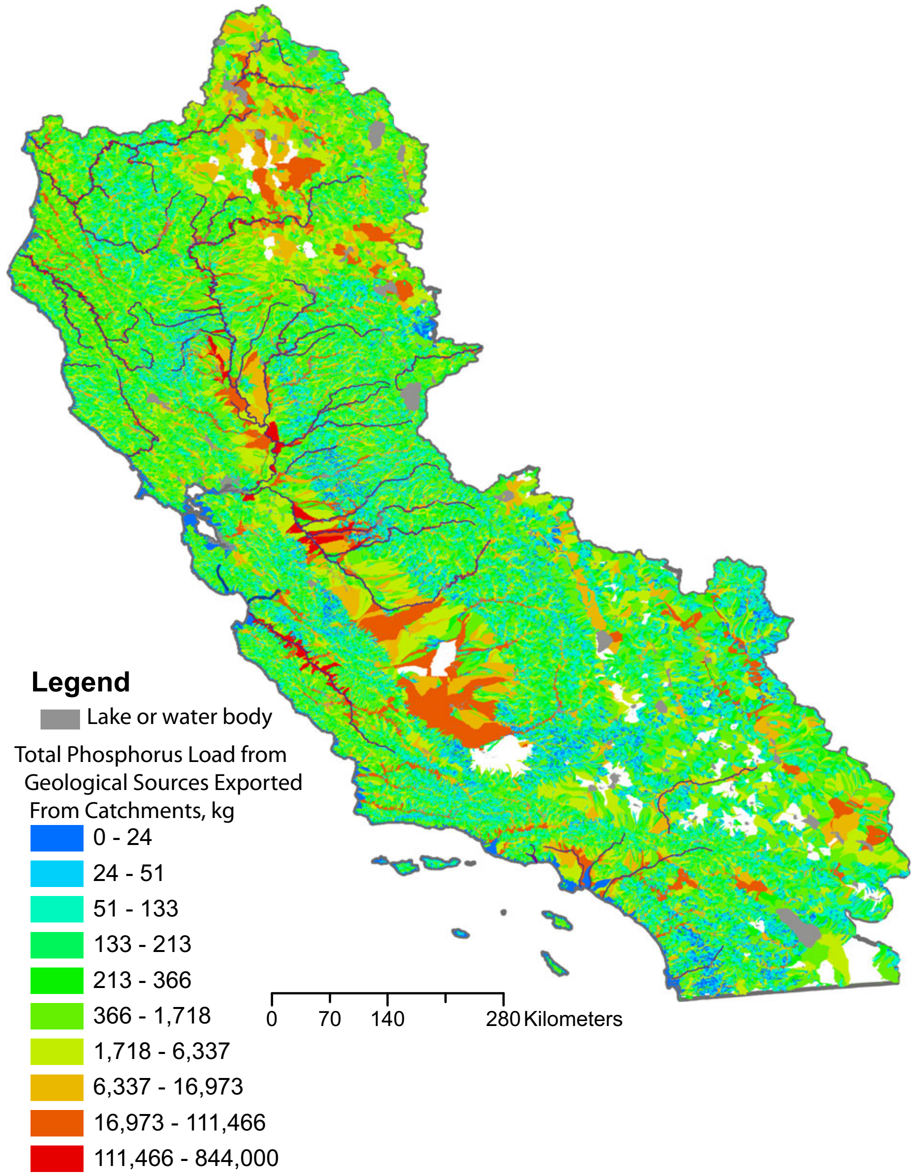

FIGURE 6. Map Showing Total Phosphorus Load from Geological Sources Exported from Catchments.

Truckee River has its origin at the outlet on the northwest portion of the lake. Precipitation amounts are somewhat lower in this region of the study area and as a result, the phosphorus incremental load is relatively low.

Surficial geology greatly affects the levels of background phosphorus in this study area and sourcing of phosphorus to streams. In portions of the northern study area, there is high background phosphorus attributable to the presence of basaltic rocks mostly of andesite composition (Surficial geology is shown in Figure S3). In contrast, certain rock types result in lower amounts of background phosphorus contributed to streams. Along the reach of the Klamath River, geological sources of phosphorus decrease due to a transition from the volcanic rocks to a suite of igneous and metamorphic rocks, which, includes argilites, quartz diorite, greenschist, blueschist, peridotite, mafic volcanics, slates, and sandstones within the Trinity Mountains (see Figure S3 for location). As the Klamath River flows toward the ocean, there is one more region of intermediate background phosphorus, as the rock type changes from mostly igneous to marine sediments, before the river discharges to the coast. The Central Valley is a region of relatively low geological sources of phosphorus (Figure 3). The Central Valley is mapped as a thick sequence of Quaternary alluvium. In contrast, drainages to the east of the Central Valley tend to be higher. Most of the geological sources of phosphorus upgradient from the

TABLE 4. Estimated Incremental Loads and Yields and Source Shares of Total Nitrogen in Six-Digit Hydrologic Unit Code (HUC6) Watersheds.

Six Digit Hydrologic Unit Code (HUC6) Watershed	Estimated Incremental Load, kg/yr	Share from Geologic Background, %	Share from Point Sources, %	Share from Cultivated Land, %	Median Catchment Yield, kg/km^2/yr
180201-Sacramento River	9,294,371	27.0	10.0	63.0	51
180400-San Joaquin River	4,503,446	27.7	8.1	64.2	64
180701-Los Angeles-Ventura	3,981,300	14.2	83.4	2.4	52
180300-Tulare-Buena Vista Lakes	3,506,708	25.2	0.3	74.5	42
180600-Central California Coastal	2,553,197	58.5	11.3	30.2	56
180102-Klamath and Trinity River	2,456,911	69.1	1.5	29.4	36
180101-California North Coastal	2,290,880	80.1	6.2	13.7	77
180500-San Francisco Bay	2,127,205	22.5	67.5	10.0	50
180200-Pit and McCloud River	1,549,334	73.1	0.4	26.5	72
180702-Newport Bay-Santa Ana	1,456,127	17.7	77.8	4.5	41
180703-San Diego	1,029,275	23.1	70.7	6.2	22
180902-Northern Mojave	851,808	93.5	1.9	4.6	13
180800-North Lahontan	729,029	77.0	1.7	21.3	53
181002-Salton Sea	490,868	45.5	23.7	30.8	13
181001-Southern Mojave	281,933	99.5	0.0	0.5	13
160501-Truckee	196,609	98.0	0.0	2.0	43
180901-Crowley, Mono, Owens Lake	185,654	94.3	0.0	5.7	17

Central Valley are from igneous rocks of the Sierra Nevada. A map of TP load exported from catchments from geological sources is shown in Figure 6. In spite of low geological sources of phosphorus throughout the Central Valley, some portions of the Central Valley actually have elevated loads of TP from geological sources leaving catchments. Much of that can be attributed to geological sources transported from upgradient areas from the major tributaries from the surrounding mountains as discussed later in this report.

The coastal areas of central to southern California are also regions of elevated geological background levels of phosphorus. The rocks in this region are mostly marine sediments, and some volcanic rocks. Some of the streams draining these regions will tend to have elevated levels of phosphorus derived from natural geological background. Portions of the southern California coast also have elevated phosphorus contributions from geological sources that are discussed later in this report. The desert region of southern California is also Quaternary alluvium and background levels of phosphorus tend to be elevated. However, because of the low rainfall, transport of TP from those areas is low and the drainage is internal. There are very localized regions with glacial deposits, such as near Lake Tahoe. These are potential sources to streams and the lake.

Yields of phosphorus exported from catchments for the study area are shown on Figure 7. Maps of incremental yields are shown in Figures S10, S11, and S12. Similar to the calculation for load, yields of phosphorus exported from catchments are calculated for the connected catchments and include aquatic decay along the flow paths. The Central Valley of California, coastal regions, and parts of the northern study area have some of the highest yields. Median incremental yields, by HUC are shown in Table 4. Yields from the desert area are lowest because of the closed drainage. Local geology affects yields. For example, there is a contrast in the incremental yields for the southern portion of the Central Valley, the San Joaquin Valley. Incremental yields on the western portion of that region are generally higher than those directly to the east (Figure S10). This shows the effect of one of the delivery variable terms in the model. The western portion of the San Joaquin Valley has more soils with elevated clay content, while the soils of the eastern San Joaquin Valley are generally composed of sand. This is due to different surficial geology on either side of the Valley. Clay soils, typical of the western San Joaquin Valley, tend to increase the yield of phosphorus. Incremental yields in the southern portion of the Central Valley tend to be lower relative to the northern portion, the Sacramento Valley. There is lower rainfall in the southern

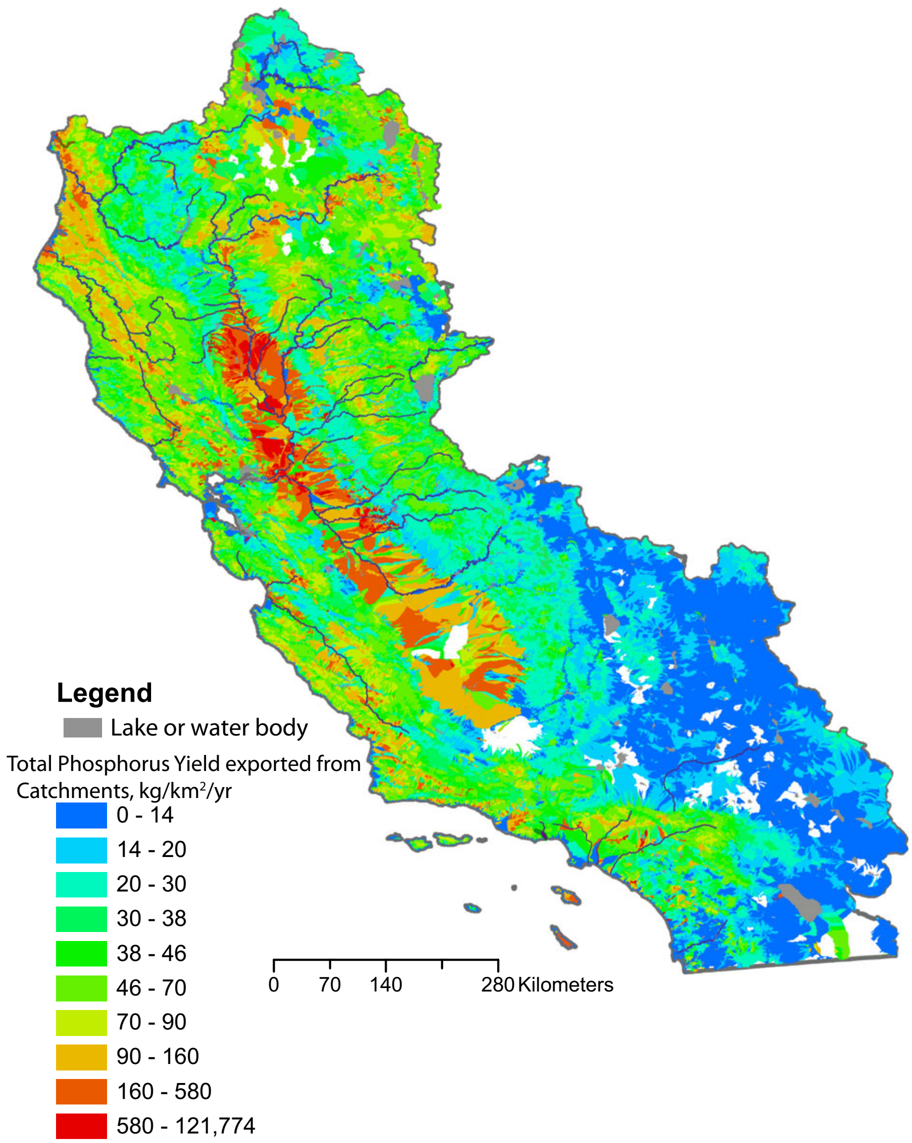

FIGURE 7. Map Showing Total Yield of Phosphorus Exported from Catchments.

portion of the valley, and streamflows are lower. As mentioned, the eastern portion of the San Joaquin Valley has more land with sandy soils, which tends to limit the amount of surface runoff to streams but increases groundwater recharge. The Sacramento Valley has a higher distribution of clay soils relative to the San Joaquin Valley. As a result, incremental and exported yields tend to be uniformly elevated on both sides of the Sacramento River (Figure 7). For the two six-digit HUCs that make up the Sacramento River watershed (180200 and 180201), exported yields are 16.8 kg/km^2/yr for the Sacramento River as it leaves HUC 180200 (northern portion) and 30 kg/km^2/yr for the southern HUC (180201) where the Sacramento River flows into the Delta. The higher yield for the southern HUC is due to a combination of sources including cultivated land and point sources. The exported yield from the lower San Joaquin River (HUC 180400) is 42 kg/km^2/yr, as the river flows into the Delta, also a result of the combination of sources from tributary rivers. Incremental and exported yields in the northern coastal region are elevated because that area has some of the highest precipitation in the study area. Precipitation is a highly significant delivery term for the model. The phosphorus along this portion of the California coast is almost entirely from geological sources as there is very little cultivated land and low population. For example, just upstream of the coastal wastewater treatment plants on the Eel River, the exported yield of phosphorus is 23 kg/km^2/yr. Point sources are present but are mostly located near the coast and increase the yields directly at the mouths of the rivers. Just below the wastewater treatment facilities, the exported yield of the Eel River is 27 kg/km^2/yr. In portions of the northern study area, there are regions with lower phosphorus yields. This corresponds to lower background levels of phosphorus. For example, the Klamath River crosses some of these areas of low geological background (Trinity Mountains, Figure S3), and as a result, the exported yield near the mouth of the river is only 10 kg/km^2/yr. The Trinity River watershed is mostly within this region of low geological background, and has a relatively low upstream yield at the point of discharge into the Klamath River at 13 kg/km^2/yr. Some coastal rivers, such as the Salinas have elevated incremental yields from a combination of sources. The Salinas watershed is also highly agricultural. In addition, there is a high background level of phosphorus, which increases the load and yield. Another example of a river with high yields is the Pit River. The Pit River is a major tributary to the upper Sacramento River and discharges directly into Shasta Lake, a large reservoir that discharges to the Sacramento River. There is a high background level of phosphorus and cultivated land in that watershed.

Case Studies of Selected Watersheds

The SPARROW model can be used to show the cumulative mass of phosphorus along the course of the river and the amount of phosphorus from each source. This is particularly useful for formulating nutrient management plans, as it will help to demonstrate how reasonable or effective load reductions can or cannot be accomplished. We chose several river systems in different parts of the study area to demonstrate how processes such as the types of geologic background, hydrology, precipitation, and soil types interact to influence the sources of TP along river reaches and the locations contributing to TP loads. For each river system discussed below, the river flow line is that of the entire system, from headwater to mouth. Eight rivers were chosen for this comparison. These include the Klamath, Eel, Pit, Sacramento, San Joaquin, Salinas, Russian, and Malibu Creek (Figure 1). These rivers range from small watersheds, such as Malibu Creek, to the largest in the study area, the Sacramento River. The rivers or creeks also range from being in mostly undeveloped areas, such as the Eel, to highly developed or hydrologically modified such as the San Joaquin.

Two selected rivers in the northern portion of the study area are the Klamath and Pit Rivers. The Klamath River has its source from Upper Klamath Lake, which is a shallow hypereutrophic lake (Colman *et al.*, 2004). There are no point sources above Upper Klamath Lake, and the sources of phosphorus are natural background and cultivated land. There are also wetlands in the region although many of them have been drained for agriculture. Two of the larger rivers that discharge to Upper Klamath Lake, the Sprague and Williamson Rivers, have natural background geological sources accounting for 78% of the incoming TP to the lake and cultivated land accounting for the remaining 22%. The main geologic sources of TP to Upper Klamath Lake are andesite and other basaltic rocks. Phosphorus loads from specific sources in the Klamath River below Upper Klamath Lake are shown in Figure 8A. Just below Upper Klamath Lake the percentage of TP load from point sources is 25%, the percentage of TP load attributed to cultivated land is about 28%, and the percentage of TP load attributed to geologic background is about 47%. There are no additional sources of wastewater TP along the remainder of the Klamath River, so the contribution of TP from that source decreases and becomes negligible as the river flows to the ocean. There is some cultivated land just below the lake, and the percentage of TP from agriculture is highest until about 330 km from the mouth at which location, geologic background is the main source of TP. Geological sources of TP in Klamath River below Upper Klamath Lake are very different from those of the rivers upstream of the lake. Some of the very lowest areas of background TP for the entire study area are located along that reach (Figure 3). The reach of the Klamath River from about 280 km from the mouth to about 80 km from the mouth does not show a very large increase in TP load except for a few locations. A tributary, near 200 km from the mouth results in an increase in TP load. That reach of river has some of the lowest geological sources of TP to the river. The geology is dominated by a mix of igneous and metamorphic rocks including ophiolites and mafic rocks, which contribute only minimally to the TP load. The load of TP has a significant increase near 80 km from the mouth because of discharge from the Trinity River. The Trinity River also flows through a region of low geologic P background, which includes argillite, slate, and blueschist assemblages. A final increase in TP load occurs near the mouth of the river as the river flows into an area of Pliocene to Holocene alluvium that contributes TP to the river. The estimated amount of phosphorus discharged to the ocean from the Klamath River is 622 tonnes (one tonne = 1,000 kg) of which 88% can be attributed to geological background, 1.5% from point sources, and 10.5% from cultivated land.

The Pit River is located south of the Klamath and is a major tributary to the Sacramento River (Figure 1). Today, the Pit River forms one of three major arms to the largest reservoir in California (Shasta Lake) with the other two being the Sacramento and

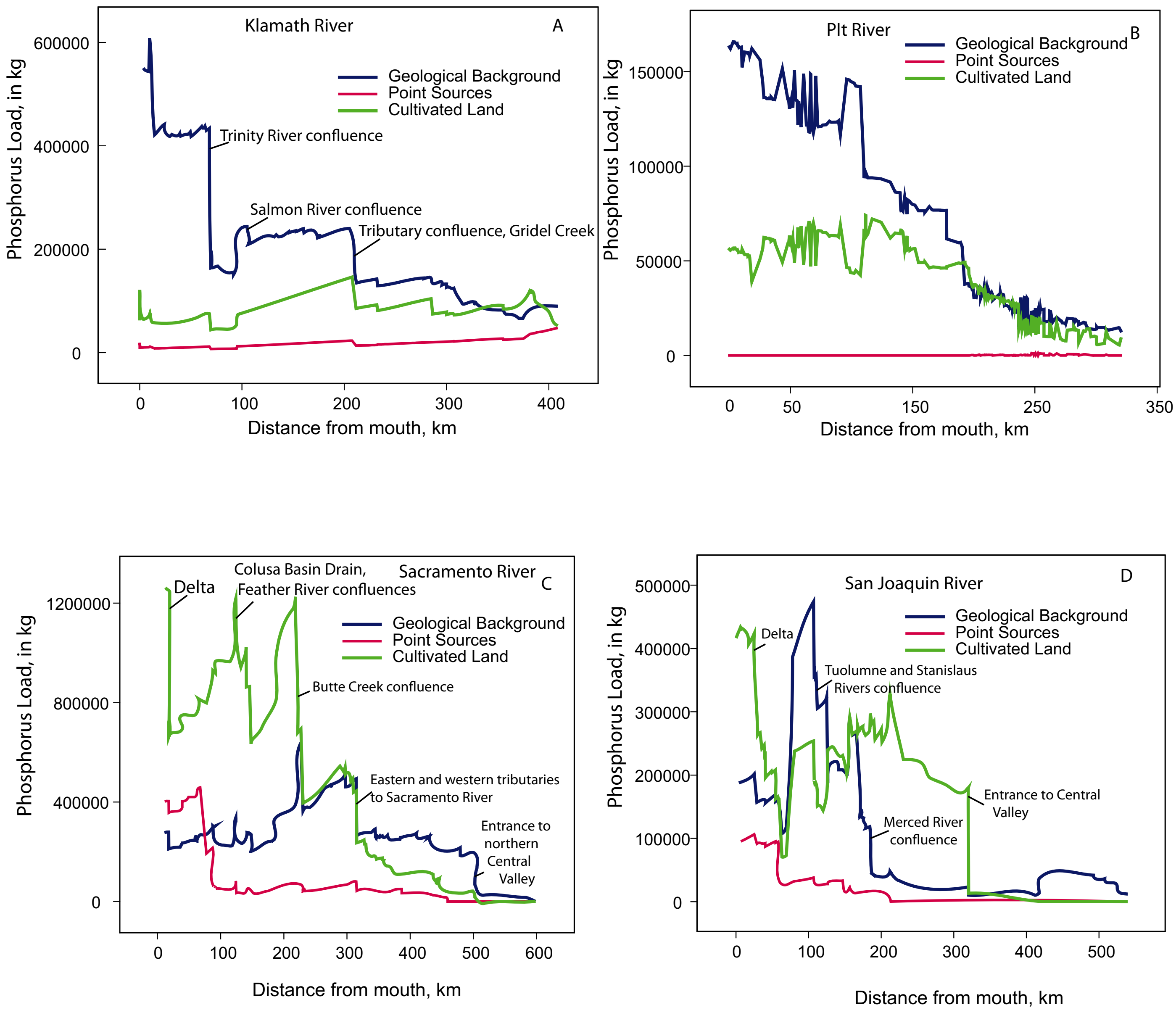

FIGURE 8. Graphs Showing Sources of Phosphorus Load at Four Selected Rivers by Source.

the McCloud Rivers. Discharge of the Pit River into Shasta Lake accounts for about 59% of the total average annual inflow to the lake (Rettig and Bortleson, 1983). The Pit River is on the 303(d) list of impaired water bodies for nutrients, temperature, and organic enrichment. The geology of the Pit River watershed is mostly Cenozoic volcanic rocks of andesite or basaltic composition. The watershed is sparsely populated and there is very little input of TP from wastewater. There is some agriculture in the upper part of the watershed. That part of the watershed also has extensive clay soils which is expected as basaltic rocks generally weather to clays (Eggleton *et al.*, 1987). However, precipitation is low in the upper portion of the Pit River. Irrigation runoff might be more significant than rainfall for TP transport. Phosphorus loads generally increase downstream with some variability (Figure 8B). The amount of phosphorus from cultivated land increases to about 50% of the total load about 200 km from the entry to Shasta Lake, and steadily decreases to about 25% of the total load as the river discharges to the lake. The estimated TP load from the Pit River into Shasta Lake is 222 tonnes. The upper Sacramento River discharges 42 tonnes of TP into Lake Shasta of which 93% is from geological background. The McCloud River discharges 28 tonnes of TP to Shasta Lake, almost all of which is from geological sources. The Pit River therefore discharges 76% of TP into the upper part of Shasta Lake from these three rivers. Approximately

25% of that total load from the three rivers is from cultivated land in the upper portion of the Pit River watershed.

Loads assigned from specific sources for the Sacramento and San Joaquin River systems are shown in Figures 8C and 8D. The total load of phosphorus entering the Delta is 1,944 tonnes from the Sacramento River watershed and 732 tonnes from the San Joaquin. For the Sacramento River, 14.4% of the phosphorus load entering the Delta is from geological sources, 64.9% from agriculture, and 20.7% from point sources. For the San Joaquin River, 27.6% is from geological sources, 57.9% from agriculture, and 14.5% from point sources. For both rivers, the contribution of phosphorus in the headwaters is mostly from geological sources. As the water moves into the Central Valley, sources change, and cultivated land becomes the dominant source. For the Sacramento River system, cultivated land is the dominant source of phosphorus throughout most of the Central Valley until the river passes the city of Sacramento and a wastewater facility discharges to the river. The wastewater treatment facility in the lower Sacramento Valley is the largest source of point source phosphorus in this region of the study area. The load assigned to cultivated land increases in the northern Sacramento Valley and then loads of TP from background and cultivated land show a decrease because of water diversion. Loads from cultivated land increase at about 225 km from the mouth due to the discharge from Butte Creek (eastern side of Sacramento Valley, Figure 1). Much of the Sacramento River, within the Central Valley, has levees that limit the direct discharge of agricultural or other runoff into the river. As a result, increases in TP loads, or changes in the sources of TP loads occur only at tributary sites. There is a decrease in TP load between the Butte Creek and Feather River confluences. That decrease is due to a large water diversion. The increase in TP load at 125 km from the mouth of the river from cultivated land is due to discharge from the Colusa Basin Drain, a major source from the western side of the Valley and the Feather River to the east. There is an increase in point source TP near 100 km from the mouth, due to discharge from a large wastewater facility near the city of Sacramento.

Phosphorus from specific sources in the San Joaquin River system is more complicated and shows the effect of land use, hydrology, and whether or not local sources of TP from cultivated land are important. Similar to the Sacramento River, the upstream or headwater source is exclusively from geological background. As mentioned, the geological source of phosphorus throughout much of the Central Valley is relatively low. There is a sudden increase in TP from cultivated land at about 325 km from the mouth as the river enters the Central Valley. A large increase in TP from geological sources occurs within the Central Valley at about 200 km from the mouth. It is unlikely that the background TP at that location was sourced locally, but more likely was sourced from the Merced River which discharges into the San Joaquin River at that location. The loads of phosphorus from cultivated land and background are more or less equal at that location. At about 125 km from the mouth, geological sources of TP become the major source and this can be attributed to the discharge of the Tuolumne River into the San Joaquin River. Therefore, unlike the Sacramento River system where increases of TP from cultivated land along the river flow line can be attributed to localized sources, TP loads in the San Joaquin River in the lower part of the San Joaquin Valley are dominated by inputs from adjacent highlands transported by the three large eastside tributaries, the Merced, Tuolumne, and Stanislaus Rivers. Downstream of these three tributaries, TP from cultivated land increases again about 75 km from the mouth. The large decrease in load at about 75 km from the mouth can be attributed to water diversion. Approximately 73% of the river flow is diverted westward to a large pumping facility, where it is used subsequently for irrigation. That large diversion accounts for the large loss in phosphorus mass at that location. Soil type and stream hydrology are important in the lack of contribution from local sources of TP within the San Joaquin Valley. Soils east of the San Joaquin River are mostly sandy except for some locations and agricultural runoff is limited as there is infiltration into the soil. Soils to the west of the San Joaquin River are clay and although clay is significant in TP transport, streamflows along that portion of the San Joaquin River are much lower relative to the east side tributaries. Those lower streamflows result in a low amount of TP entering the San Joaquin River from the western side of the San Joaquin Valley. There are local sources of TP to the San Joaquin River from the western San Joaquin Valley, but those are relatively low compared to the loads from the Merced, Tuolumne, and Stanislaus Rivers. Those three rivers account for much of the flow of the San Joaquin River before the river discharges to the Delta. As a result of the high flows from those tributaries, geological phosphorus from upland sources dominates the lower reach of the San Joaquin River between those rivers despite the large amount of land in agricultural production. The load of TP increases again about 50 km from the mouth. That is due to TP from cultivated land in the Delta of the Sacramento and San Joaquin Rivers.

Three coastal rivers of similar size watersheds are the Eel, Russian, and Salinas (Figure 1). Both the

Eel and Russian are in the California North Coastal HUC (180101) and the Salinas is in the Central California Coastal HUC (180600). These three rivers can be considered in the context of a gradient of development, hydrologic, and climate factors that affect TP transport. Geohydrological factors that affect streamflow and groundwater recharge in these three basins are similar. Aquifers occur in Pleistocene to Holocene alluvium with variable amounts of sand, silt, and clay. These aquifers have extensive connection with the rivers and are largely recharged by these rivers (Vengosh *et al.*, 2002; Constantz *et al.*, 2003). Each river is likely to have gaining and losing reaches, which can change seasonally. These watersheds vary in the amount of precipitation received with the Eel having the highest amount, the Russian intermediate, and the Salinas the lowest. The Salinas and Russian River watersheds have a mix of agricultural, urban, and undeveloped land. Agriculture is most intensive in the Salinas watershed with a number of specialty crops such as strawberries, and various row crops. There is evidence of localized contamination of the Salinas River aquifer system by nitrate from fertilizer and sulfate from gypsum soil amendments (Vengosh *et al.*, 2002). The Russian River watershed has grape and wine production, some developed land, and some undeveloped land. Plots of the phosphorus load along the reach of each river by source are shown in Figure S13. The Eel River has almost all of the phosphorus sourced from geological background, with a contribution from point sources near the coast, and some cultivated land in the lower part of the watershed. The estimated amount discharged into the Pacific Ocean is 282 tonnes of which 70% can be attributed to geological background, 6.5% to point sources, and 14.5% to cultivated land. Along the Eel River flow path, two tributaries, the Middle Fork Eel, and the South Fork Eel increase the phosphorus load as they discharge into the main river. There is a decrease in load between those two tributary inputs, which is likely due to a losing reach of the river. For the Russian River system, phosphorus is sourced from both geologic background and cultivated land, with very little inputs from point sources (see Figure S13B). Along the entire reach of the river, the contribution from both sources appears to rise or fall in a similar manner. The estimated discharge of phosphorus from the Russian River to the Pacific Ocean is 133 tonnes of which 49% is from geological background, 49% is from cultivated land, and 2% is from point sources. The estimated discharge of phosphorus from the Salinas River to the Pacific Ocean is 391 tonnes of which 62% is from geological background, 0.2% is from point sources, and 37.8% is from cultivated land. The loads of phosphorus from either the Russian or Salinas River appear to rise or fall in tandem along their reaches, which is likely due to the fact that the rivers are connected closely to the underlying bed and in equilibrium with those sources. Collectively these three rivers discharge 806 tonnes to the ocean of which about 30% can be attributed to cultivated land.

The Malibu Creek watershed occupies 284 km^2 in southern California, and is in a mixed land use area with varying degrees of developed land. Loads of phosphorus by source for Malibu Creek and one of its tributaries, Las Virgenes Creek, are shown in the Figure S14. Phosphorus content of streambed sediments in catchments and geological formations within the Malibu Creek watershed are shown in Figures S15 and S16. Some streams in the watershed, including Las Virgenes, Malibu Creek, and Medea Creek, are listed as impaired under section 303(d) of the Clean Water Act and, as a result, a management plan is in place to attempt to bring the streams into compliance with numerical objectives (http://www.epa.gov/region9/water/tmdl/malibu/final_nutrients.pdf). Impairments include nutrient enrichment. Management plans for impaired water bodies under the Clean Water Act are called total maximum daily load (TMDL) plans. The TMDL document states that potential sources include wastewater effluent, septic system effluent, urban and agriculture runoff, golf course runoff, and groundwater discharge. The numerical concentration target for the creeks in this watershed is 0.1 mg/l of TP as P. As mentioned previously, the Miocene Monterey Formation outcrops in portions of southern California including the northern portion of the Malibu Creek watershed. Detailed geology of Los Angeles County was obtained from Yerkes and Campbell (2005). Malibu Creek, Las Virgenes, and other small creeks flow through a mixed lithology of marine sedimentary and volcanic rocks. Rocks of the Monterey Formation accumulated significant amounts of phosphorus due to its origin in a restricted basin (Filippelli *et al.*, 1994). However, the Monterey Formation is not the only geological source of phosphorus to the streams in this watershed. Volcanic rocks are also part of the lithology. At least one relatively rare volcanic formation, the Canejo Volcanics, is present (Figure S15). The Canejo Volcanics are inter-bedded with limestone (Stanton and Alderson, 2013). Limestone contains variable amounts of phosphorus and might contribute to the load of TP in this watershed. The sediments that are within the Canejo Volcanics and the Monterey Formation have the greatest amount of sedimentary phosphorus within the Malibu Creek catchments.

Line plots of the phosphorus loads from specific sources along the entire reach of Malibu Creek are shown in Figure S14A. The Potrero Valley Creek flows directly into Malibu Creek and another unnamed tributary discharges at the same location. The TP load at that point on upstream Malibu Creek is 5.8 tonnes of which 1 tonne is from cultivated land, with the remainder attributed to geological sources. There are no point sources in this portion of the watershed. This part of the watershed is composed most of Canejo Volcanics with some outcrops of Monterey Formation in the northern portion of the subwatershed. The TP load of Malibu Creek increases slightly until the point where Medea Creek discharges into Malibu Creek. The TP load increases to over 9 tonnes at that point and about 90% is attributed to geological background. The channel of Medea Creek crosses Monterey and Canejo Volcanics rocks. The TP load increases again where Las Virgenes Creek discharges into Malibu Creek and the total load is 13.4 tonnes of which geological sources account for 92% of the total load. Las Virgenes Creek contributes about 3.2 tonnes of TP to the load of Malibu Creek at that point. The TP load sources from Las Virgenes Creek are 96% attributed to geological sources (See Figure S14B), with the remainder attributed to cultivated land. The channel of Las Virgenes Creek passes through two different sandstone formations as well as the Monterey Formation. The wastewater treatment facility is about 3 km from the ocean and about 1 km downstream of where Las Virgenes Creek discharges into Malibu Creek. The modeled total load of TP at the point where the wastewater facility discharges into Malibu Creek is 34.7 tonnes of which 63% is contributed by the wastewater facility, 34% by geological sources, and the remainder from cultivated land. If all of the TP load from the Potrero Valley Creek was transported conservatively from the point where it discharges into Malibu Creek, to the location where Malibu Creek discharges into the ocean, it would have provided about 49% of the TP load attributed to geological background. In contrast, Las Virgenes Creek would have contributed about 16% of the load contributed by geological sources. At the location where the wastewater facility discharges into Malibu Creek, about 63% of the TP load is contributed by the wastewater facility.

Annual Flow-Weighted Total Phosphorus Concentrations

The model output also can be used to estimate stream concentrations (Figure 9). The concentrations are modeled annually averaged flow-weighted concentrations and will not necessarily match exactly to those measured at calibration stations. Nevertheless, they can provide useful information with regard to the level of expected concentrations. This is particularly useful to show how the various potential sources contribute to local concentrations and how concentrations compare to numerical targets, such as the USEPA ecoregion specific criteria for nutrients.

DISCUSSION

Geological material was found to be an important source of TP throughout this study area. In general, geological sources of TP can be explained by considering surficial geology (Figure S3). Phosphorus from geological materials is recognized as a source to streams when anthropogenic inputs are limited, but is generally recognized to be small (Withers and Jarvie, 2008). In the absence of anthropogenic processes, weathering from geologic sources is the principal contributor of new phosphorus to terrestrial and aquatic ecosystems since, unlike nitrogen, there is no atmospheric component (Mishra *et al.*, 2013). Phosphorus is a common element in igneous rocks (Hem, 1985). The average crustal abundance of phosphorus in continental rocks is 0.1% by weight (Canfield *et al.*, 2005). The average phosphorus content of basalts and andesites is 0.10-0.12 weight percent as P and for granodiorites (intrusive igneous rocks) is 0.09% (Hyndman, 1972). The average phosphorus content (expressed as P) of silicic igneous rocks is 0.07% (Huang, 1962). Although the average phosphorus contents of andesites and granodiorites are nearly the same, Susfalk (2000) found that extractable phosphorus in granite-derived soils from the eastern Sierra Nevada was up to three orders of magnitude greater than andesite-derived soils which would be especially common in the northeastern part of the study area.

There are geologic deposits that can be significant sources of phosphorus to streams in the study area. Although limited in geographical area, one of these is the Miocene Monterey Formation and similar formations of southern to central California. The Monterey Formation is composed of siliceous pelagic and hemi-pelagic rocks in the western half of California (Pisciotto and Garrison, 1981). Outcrops of the Monterey occur along the coastal region of California from near San Francisco to southern California. There are also outcroppings of the Monterey in the southern portion of the Central Valley. The Monterey contains extensive siliceous deposits, dominated by diatoms and radiolarians, some of which are high in phosphorus (Pisciotto and Garrison, 1981; Behl, 1999). Phosphorus concentrations in portions of the Monterey Formation exceed 1% by weight (Filippelli *et al.*, 1994). Monterey Formation rocks are composed

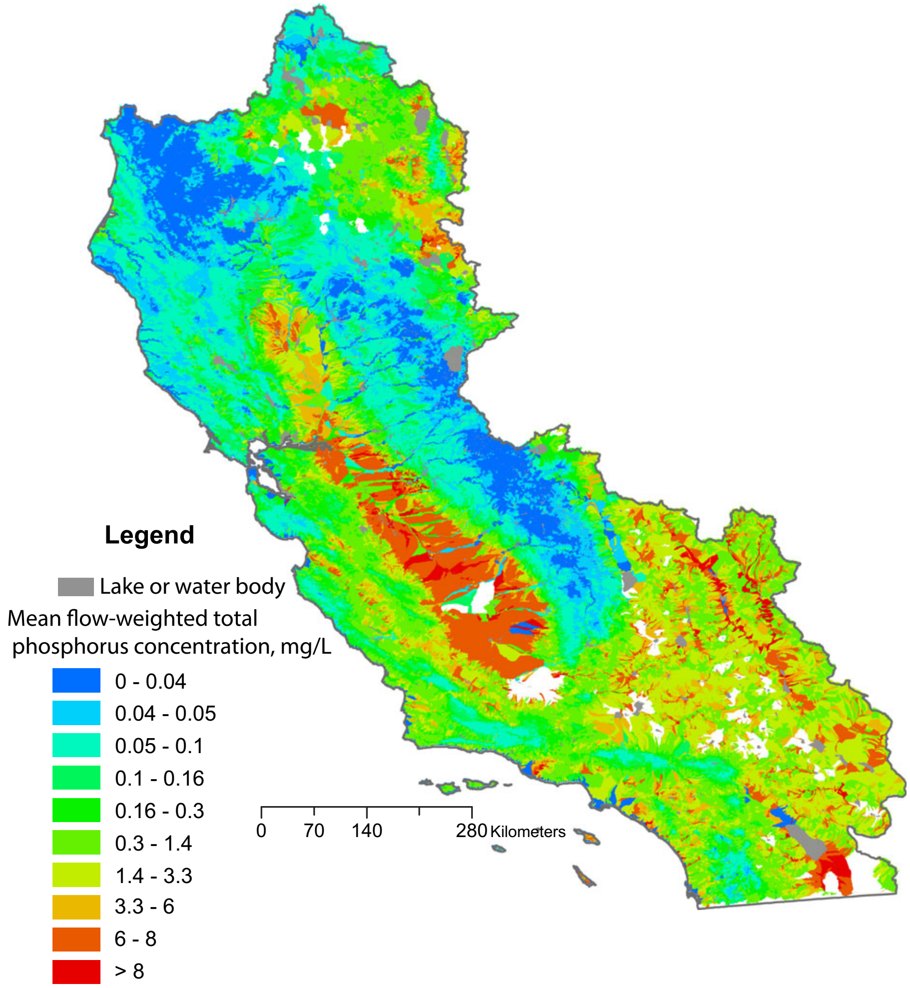

FIGURE 9. Mean Flow-Weighted Concentrations of Total Phosphorus, in mg/l.

of three different lithologies: siliceous rocks, phosphatic rocks, and calcareous rocks (Filippelli *et al.*, 1994). Authigenic carbonate fluorapatite occurs in these deposits and represents a locally important source of phosphorus to streams.

The modeled flow-weighted stream concentrations (Figure 9) have similarities to the land-use, and geology maps, also shown in Figures S1 and S3. For example, stream concentrations tend to be elevated in the northeast portion of the study area where geological contributions to phosphorus from volcanic rocks and agriculture contribute to the stream concentrations and loads. Stream concentrations tend to be low in the Trinity Mountain Region (Figures 9, S3) as the geological background indicated low sourcing to streams, very little agriculture, and few point sources. The Trinity Mountain region is a low source of geological phosphorus because of the rock types. Streams in that region have annual median phosphorus concentrations between 0.02 and 0.05 mg/l. The modeled concentrations for streams of the Malibu Creek watershed all exceeded the regulatory goal of 0.1 mg/l. Potrero Valley Creek, for example, had a median modeled TP concentration near 1 mg/l. Malibu Creek had a median modeled concentration also near 1 mg/l and Medea Creek has a median modeled concentration of 1.1 mg/l. Las Virgenes Creek had a median-modeled concentration of 0.8 mg/l. As indicated by the SPARROW modeling, these elevated concentrations are mostly the result of water-rock interactions with the Monterey Formation and Canejo Volcanics, with a small contribution from phosphorus use on cultivated land. Concentrations of phosphorus that are attributed to geological sources must be taken into account for any effective management plans to reduce phosphorus loading in receiving waters. In contrast, the Eel River, previously discussed, had a median-modeled concentration of 0.04 mg/l. The contrast between the modeled TP concentrations of streams of the Malibu Creek watershed and those of the Eel demonstrate the importance that significant geological sources of

P can have. The Russian River, which is in a similar geological region as the Eel, also has cultivated and developed land, and, as a result, the median-modeled TP concentration was 0.1 mg/l. The Salinas River, which has already been described as being in a region of elevated geological background sources along with input from cultivated land has a median-modeled TP concentration of 0.65 mg/l. Collectively, the streams of HUC 160501, which include Lake Tahoe, and also include the urbanized area of Reno, Nevada, have a median-modeled TP concentration of 0.06 mg/l, with the streams draining into Lake Tahoe having lower concentrations, mostly between 0.02 and 0.05 mg/l. The Lake Tahoe region has a management plan in place to limit water quality degradation. One management strategy is the elimination of any sources of wastewater to streams, which drain into the lake, by moving wastewater out of the region. Therefore, wastewater sources to the lake are nonexistent. Geologic sources of phosphorus in the Lake Tahoe region include granodiorites, volcanic rocks, and some glacial deposits. The region does have less precipitation because the watershed is on the eastern side of the Sierra Nevada divide, which limits the amount of streamflow into the lake. The Truckee River is the major river draining the lake and flows into a desert area.

Geological sources of phosphorus resulted in the lowest model coefficient, 0.037 kg/ppm/km^2, which is expected, given the low crustal abundance of phosphorus in rocks and that erosion must occur to generate phosphorus sourcing.

The highest model coefficient for sources was for cultivated land, 259.5 kg/km^2/yr. This estimate is reasonable, given that fertilizer is placed on the land surface and can easily be eroded with rain or excess irrigation water runoff. Loads of phosphorus from cultivated land have been reported on. For example, citrus and vegetable crop production in Florida results in export amounts of phosphorus between 42 and 2,169 kg/km^2 (He *et al.*, 2006). Export values for small agricultural watersheds in Georgia were between 8 and 408 kg/km^2 (Langdale *et al.*, 1985). Cultivated land was found to be a major source in several areas including the Central Valley, the Salinas Valley, and locally in other areas. It is not known why farm fertilizer was not a significant source variable for this SPARROW model. However, cultivation of agricultural crops includes the application of fertilizer or manure, and animal operations are present in the Central Valley and elsewhere including confined and unconfined operations. The inclusion of cultivated land in the model takes into account potential sources of phosphorus from both fertilizer application and the presence of animal operations. Fertilizer was found to be a significant source in most, but not all other SPARROW phosphorus models. For example, fertilizer was found to be a significant source of phosphorus by Rebich *et al.* (2011), Robertson and Saad (2011), Brown *et al.* (2011), and Wise and Johnson (2011). However, Garcia *et al.* (2011), used cultivated land as a source, similar to this report.

Although urban land is widely distributed throughout the study area, it was not a significant source. This might possibly be attributed to the fact that many of the largest urban centers, are on the coast and the streams drain directly to the ocean or an estuary.

Wastewater was a significant source of TP even though many of the facilities were downstream of calibration sites, especially many of the larger wastewater treatment plants near the Pacific Ocean, which serve the metropolitan areas of San Francisco and Los Angeles. The model coefficient for point sources was expected to be close to 1 since the treatment facilities discharge phosphorus directly to a stream, and there is presumably no loss because of that. The coefficient, 1.46, is higher than 1, which indicates an underestimation of TP discharged from these sources.

Both land-to-water delivery terms, clay content, and precipitation, were positive indicating that precipitation and clay increase the delivery of phosphorus to streams. A negative coefficient for land-to-water delivery variable would indicate a loss. Precipitation was expected to be significant since stormwater runoff can generate field erosion. Clay was also expected to be a significant variable as small particles can be easily mobilized by stormwater runoff. Rainfall may result in mobilization of soil particles, and is one primary way that phosphorus is transported to the stream network. Although phosphorus can be measured in groundwater in portions of the study area and may be elevated under agricultural fields, much of the phosphorus is bound to iron or manganese oxides in the unsaturated zone or shallow aquifers, which contain enough dissolved oxygen to maintain oxidizing conditions (Domagalski and Johnson, 2011). In addition, the availability of streams in the study area to contribute to base flow is limited because of pumpage and lowering of water tables (Faunt *et al.*, 2009). Although groundwater discharge may be a locally important source of phosphorous, groundwater transport of phosphorus is not a significant source within this study area.

Fine-grained soil or sediment is more likely to be mobilized by flowing water, and this makes clay a significant land-to-water delivery factor. Soil erodibility was tested and was found to be significant, but not as much as clay content, so that factor was not used in the final model. None of the other tested factors were found to be significant.

SUMMARY

The SPARROW model was used to simulate phosphorus loads, yields, and concentrations in California streams and portions of adjacent Nevada and Oregon. Model output showed how geological sources and anthropogenic processes (cultivated land and point sources) contributed to the load and concentrations of phosphorus in streams and the sources that contributed to loads, yields, and concentrations. This regional study will provide useful information on nutrient management plans by providing a basis for reasonable water quality goals or targets.

A limitation of the model is that it is based on average conditions for a single year, in this case 2002. Results can only be expressed on annual loads, thereby eliminating any analysis of seasonal changes in loads and concentrations. The model only considers average conditions throughout a study area and the effects of large precipitation events on the transfer of phosphorus from land to water cannot be simulated. Nevertheless, the output provides useful information with regard to major sources of phosphorus and distinguishing how concentrations can be attributed to geological background or anthropogenic processes. The hydrological network used, NHD Plus, provides excellent spatial resolution for tracking concentrations, loads, and sources. Tracking phosphorus sources along these catchment flow lines produces a useful tool for effective water quality management strategies.

SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article:

Further details of the SPARROW mathematical approach are given, along with several maps of ancillary information and model output. Plots of model residuals are also given. A table of annual loads calculated from the calibration sites is also provided, along with a table showing sources of water chemistry and river discharge data.

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