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TITLE: Assessing the Influence of Salinization on Aquatic Life in Santa Ana Region Wadeable Streams

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SOUTHERN CALIFORNIA COASTAL WATER RESEARCH PROJECT

Technical Report 1324

Assessing the Influence of Salinization on Aquatic Life in Santa Ana Region Wadeable Streams

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EXECUTIVE SUMMARY

Salinization is a growing threat to aquatic life in streams in the Santa Ana region by disrupting organisms' physiological processes and increasing sensitivity to other contaminants. Plans to increase wastewater recycling, as well as continued reliance on water diverted from the Colorado River, are likely to increase ionic concentrations in streams with urban or agricultural land use.

Because stream salinity can vary due to natural factors, such as geology and climate, we developed models to predict natural background levels of ionic parameters. Because these models are dynamic, they can reflect changes in natural levels associated with variations in season and annual precipitation. Application of the models to streams in the Santa Ana watershed show considerable spatial variation, with the lowest salinity levels typically being observed in the high elevation headwaters of the Santa Ana, San Bernardino, San Jacinto, and San Gabriel mountains. Deviations from modeled expectations can be used to identify streams where salinization has occurred. We found evidence of widespread salinization areas with urban or agricultural land use, such as the lower elevations of coastal Orange County and the Inland Empire.

Biological response models based on biointegrity indices (specifically the California Stream Condition Index [CSCI] for benthic invertebrates and the Algal Stream Condition Indices [ASCIs]) showed that elevated ionic concentrations were associated with poor biological conditions. These models can support the identification of thresholds for ionic parameters that provide a high level of probability of protecting stream biointegrity. We identified reach-specific thresholds for all studied parameters (except Magnesium). These thresholds could be adjusted to account for season, as well as for drought or years with high levels of precipitation. These thresholds can be used to assess stressors on sites, prioritize sites for restoration or additional investigation, or in causal assessments.

In certain circumstances, field-based integrated measures of ionic strength (e.g., specific conductivity or total dissolved solids) can serve as a stand-in for lab-based measurements of individual ionic parameters. When used as surrogates, integrated measures sometimes afforded a higher level of protection, compared to when individual ionic parameters were measured. Because field-based measurements are relatively easy to measure, community-based monitoring groups may be able to identify streams likely to exceed basin plan objectives for individual ions without the need for high-cost laboratory analysis.

Conclusions

- Salinization potentially affects up to half the length of streams in the Santa Ana watershed, and the problem is likely to get worse in light of changes in climate and water use continue.
- Salinization can negatively impact aquatic life. Numeric thresholds for salinization indicators based on levels of biological response have been identified. These thresholds may be used by monitoring or management programs to identify streams at risk, prioritize sites for protection, and improve causal assessments.
- Integrated parameters (such as specific conductivity and total dissolved solids) may be used as surrogates for ionic parameters (such as chloride or sulfate concentration) to assess sites when the latter are unavailable. These surrogates may be particularly cost-effective for community-based monitoring programs.

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INTRODUCTION

Salinization, or the increased concentrations of ionic constituents in freshwaters, is a growing problem worldwide (Cañedo-Argüelles et al. 2019, Melles et al. 2023). Increased salinity of freshwater can disturb the physiology of aquatic organisms and harm their ability to metabolize pollutants (e.g., Velasco et al. 2019, Walker et al. 2020), leading to altered biological communities and degraded ecosystem function (Olson and Cormier 2019). Consequently, managers may require targets for ionic parameters in order to protect aquatic life in waterbodies they manage.

Several anthropogenic activities are associated with increased salinity of freshwaters. In cold regions, road salt application is a major contributor of stream salinization (Hintz and Relyea 2019), as well as mining, particularly in the southern Appalachian mountains (Timpano et al. 2015). In semi-arid regions, like southern California and adjacent areas, important factors include irrigation with imported, high-salinity Colorado River water, aquifer depletion, or groundwater contamination (Lee et al. 1993, Cardona et al. 2004, Olson 2019). Climate change is likely to increase the severity and extent of stream salinization due to changes in precipitation and increases in evapotranspiration (Olson 2019, Albano et al. 2022, Bolotin et al. 2023).

Establishing targets for naturally occurring constituents, such as ions, requires an understanding of natural background levels, which may vary considerably from one waterbody to another (Hawkins et al. 2010, Ode et al. 2016, Cormier et al. 2018, Olson and Cormier 2019). Natural factors that influence ionic concentrations in streams include climate (especially precipitation and evapotranspiration), geology (such as marine sediments), and topography (e.g., snow influence associated with high elevations) (Olson and Cormier 2019, Bolotin et al. 2023).

Water quality targets should be informed not only by an understanding of natural variability, but also by the biological response as parameters increase beyond natural levels (Hawkins et al. 2010, Cormier et al. 2018). Biological integrity indices provide a convenient and effective tool for assessing biological responses to stress (Karr 1991, Rosenberg and Resh 1993, Mazor et al. 2019). Indices based on benthic macroinvertebrate or algal assemblages have been used to identify targets for hydrologic alteration (e.g., Armanini et al. 2011, Mazor et al. 2018) and nutrients (e.g., Heiskary and Bouchard 2015, Poikane et al. 2022, Mazor et al. 2022) in California and elsewhere. Biological response models are a fundamental line of evidence recommended by the EPA for establishing water quality criteria (U.S. Environmental Protection Agency 2000, Cormier et al. 2018). Thus, response models that assess changes in California's biointegrity indices (e.g., the California Stream Condition Index [CSCI] for benthic macroinvertebrates, [Mazor et al. 2016], and the Algal Stream Condition Indices [ASCIs, Theroux et al. 2020]) based on alterations from natural levels of ionic parameters would help managers identify thresholds that protect aquatic life.

In this study, we identify thresholds following the approach shown in Figure 1. First, we developed models that predict natural background levels of ionic parameters in streams following the approach of Olson and Cormier (2019). These models allow us to quantify the level of ionic alteration by comparing observed levels to levels expected by the models (calculated as a ratio of observed-to-expected, or O/E). Second, we calibrated models to assess the biological response to ionic alteration. These models calculated the probability of low biointegrity index scores as O/E increases. Third, these models were used to identify thresholds associated with probabilities representing a range of risk tolerances. Finally, we compared thresholds derived for ionic parameters (e.g., chloride) to those derived for field-measured integrated measures (e.g., specific conductivity) to see if these parameters could provide equivalent protection to parameters requiring laboratory measurement.

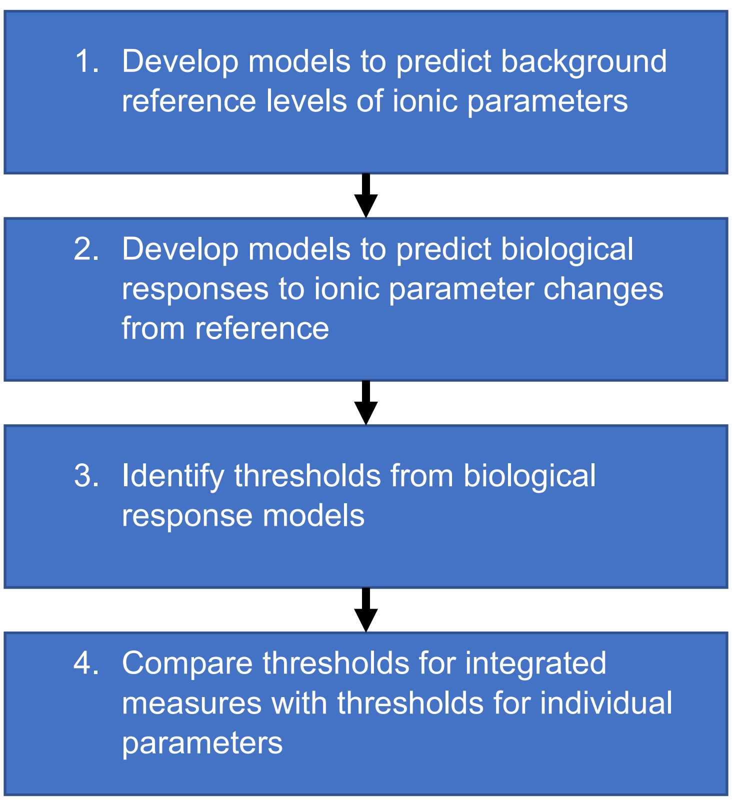


Figure 1. A flow chart of the overall approach for the evaluation of biological responses to alteration of ionic concentrations in wadeable streams in California.

PART 1: ASSESS REFERENCE LEVELS OF IONS IN CALIFORNIA

Introduction

Degraded water quality has the potential to negatively affect the biological integrity of streams and other waterbodies (Karr 1991, Rosenberg and Resh 1993, Cañedo-Argüelles et al. 2019, Velasco et al. 2019). To gain a better understanding of how the alteration of water chemistry affects aquatic species, natural background levels need to be estimated to determine how far current stream conditions have shifted from natural levels. The variability of water chemistry suggests that watershed topographic, geological, and climatic variables need to be considered when predicting natural background water quality (Hawkins et al. 2010, Cormier et al. 2018, Olson and Cormier 2019). Once the degree of change from natural conditions is quantified, ecological responses to the alteration can be assessed, and protective thresholds that minimize the likelihood of ecological response may be identified—an approach that has been used for a wide range of stressors, such as nutrients and hydromodification, as well as elevated ionic concentrations (Poff et al. 2010, Vander Laan and Hawkins 2014, Heiskary and Bouchard 2015, Cormier et al. 2018, Mazor et al. 2022).

Salinization, or the increased concentrations of ionic parameters, is a widespread and growing concern with the potential to affect aquatic organisms (Cañedo-Argüelles et al. 2013, 2019, Kaushal et al. 2018, Velasco et al. 2019, Mazumder et al. 2021). For example, salinization of freshwater streams is known to alter hormone responses, energy metabolism, and other physiological processes in fish (Velasco et al. 2019, Walker et al. 2020). Within the Santa Ana Basin, a number of aquatic vertebrates are known to be sensitive to salinization, such as the Santa Ana sucker, arroyo chub, speckled dace, arroyo toad, and the southwestern pond turtle (Moyle 2002, Meador and Carlisle 2007, U.S. Fish and Wildlife Service 2014, Agha et al. 2019). Sensitive invertebrates, such as mayflies, are frequently extirpated from sites that have increased salinity (Kefford 2019). These losses of sensitive invertebrates can be reflected in bioassessment indices based on the composition of benthic macroinvertebrate communities, such as the California Stream Condition Index (CSCI; Mazor et al. 2016).

Salinization could become more pervasive and severe in California due to the direct and indirect impacts of climate change (Olson 2019, Bolotin et al. 2023). Direct impacts include increased evapotranspiration (Albano et al. 2022), loss of snowmelt related to increased temperatures (Hammond et al. 2018), and changes in timing of precipitation (Willis et al. 2021). Indirect impacts include more diversion of surface or groundwater, as well as increased water reuse, leading to the discharge of more concentrated effluent (Hendricks et al. 1982, Toze 2006, Bhide et al. 2021).

Climate is a major driver of natural variation in surface water quality (Hawkins et al. 2010, Olson 2019, Olson and Cormier 2019). In general, high precipitation and snowmelt has a “dilution” effect that lowers concentrations of ionic parameters, whereas high air temperatures contribute to accelerated evaporation and increased concentrations of solutes in stream systems (Olson 2019, Bolotin et al. 2023). Geologic factors are also major drivers of natural variation in surface water quality (Olson 2019, Olson and Cormier 2019). Areas with large amounts of limestone, for example, may be expected to have greater natural calcium concentrations than an area surrounded by granite. Peters (1984) found that annual precipitation and rock type were the most important factors affecting the yield of ions in the basins studied. Thus, predicting natural levels of ionic parameters requires an understanding of static factors, such as watershed geology, and dynamic factors, like antecedent climate conditions. In California, which exhibits extreme climatic and geological diversity, this variation can be considerable (Willis et al. 2021, Bolotin et al. 2023).

The basin plan for the Santa Ana River has inland surface water quality objectives for certain ionic parameters, such as chloride and sulfate (Regional Water Quality Control Board-Santa Ana 2019). The objectives in the basin plan date back to the 1971 Interim Water Quality Control Plan for the Santa Ana region (Santa Ana Regional Water Quality Control Board and California State Water Resources Control Board 1971), which was based on data collection efforts by the California Department of Fish and Wildlife, the California Department of Public Health, the California Department of Water Resources, and the Santa Ana Watershed Project Authority, among other agencies. These data were initially used to characterize baseline conditions, and these baseline conditions were described in early versions of the basin plan as non-degradation targets (Regional Water Quality Control Board-Santa Ana 2019). The numeric objectives for ionic parameters vary from reach to reach based, in part, on geological differences that contribute to natural variation in water quality. For example, Day Canyon Creek has a chloride objective of 4 mg/L, whereas the mainstem Santa Ana below Seven Oaks Dam (Reach 5) has an objective of 20 mg/L. Although the potential impacts of increased ionic concentration on aquatic life is well documented (e.g., Cañedo-Argüelles et al. 2013, Kaushal et al. 2018, Walker et al. 2020), the narrative statements for these parameters focus instead on other beneficial uses, such as human health, agricultural, and industrial uses.

We modeled natural temporal and spatial variation to predict variation in major ion concentrations and integrated measures for streams throughout California, allowing management stakeholders to better understand California's natural water quality parameters and assist management agencies with their conservation and restoration efforts. We modeled five ionic parameters (i.e., calcium, chloride, magnesium, sodium, and sulfate) and four integrated parameters (i.e., alkalinity, hardness, total dissolved solids, and specific conductivity) using natural environment factors that influence natural variation in water quality. The modeled estimates of these parameters allowed us to determine the amount of alteration from natural levels by comparing them to current measured concentrations throughout California. These comparisons and natural estimates can be used to establish water quality thresholds for aquatic life and to restore stream health. We then evaluated the predictive metrics to determine what environmental factors drive natural background levels. This research will improve management practices by enhancing the ability of managers to account for natural variation in ionic parameters when setting or evaluating objectives, identifying suitable habitat for sensitive species, or prioritizing sites for water quality improvements.

Methods

This flow chart summarizes steps for the development of models to predict background levels of ionic parameters or integrated measures (Figure 2).

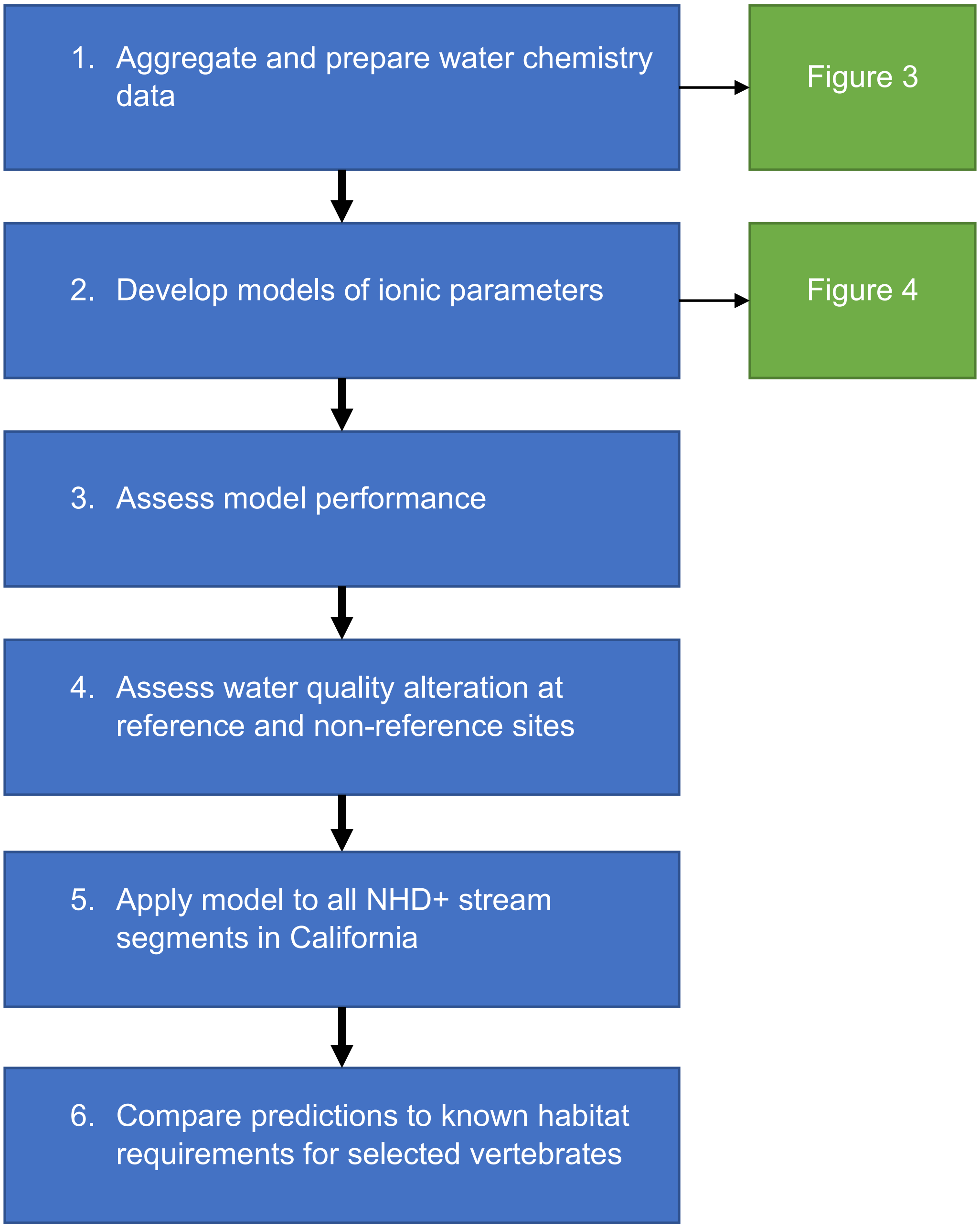


Figure 2. A flow chart of steps in the development of models to predict background levels of ionic parameters or integrated measures.

Aggregate and prepare water chemistry data

In order to prepare a water chemistry data set for analysis, we first acquired water chemistry data from national and statewide water quality monitoring programs, and then assigned each site to unique catchments in the National Hydrography Dataset Plus (NHD+; McKay et al. 2014). We combined sampling events that were repeated within an NHD+ catchment and month by averaging values. Finally, we obtained geospatial data that could be used as model predictors or as reference screens by joining catchments with the StreamCat dataset (Hill et al. 2016), a database of landscape metrics calculated for every stream segment in the NHD+. We augmented StreamCat by calculating dynamic climatic predictors by summarizing antecedent conditions before each sampling event (Figure 3).

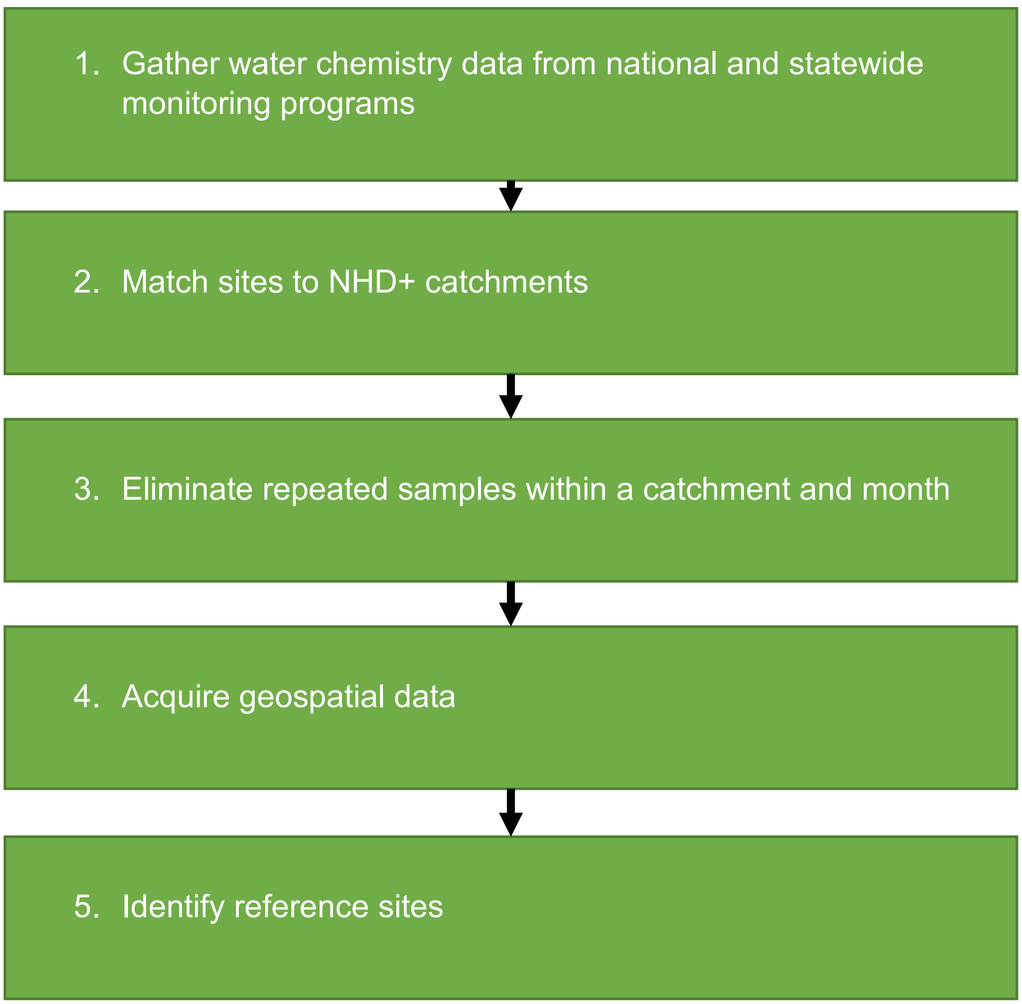


Figure 3. A flow chart summarizing the data preparation process.

Data gathering

We modeled how California's natural water quality varies among individual stream segments over time, using water quality data from the Contiguous United States obtained from bioassessment databases.

These databases included the California Environmental Data Exchange Network (CEDEN, https://ceden.waterboards.ca.gov/), the National Rivers and Streams Assessment (NRSA, https://www.epa.gov/national-aquatic-resource-surveys/nrsa), and the National Water-Quality Assessment Project (NAQWA, https://www.usgs.gov/mission-areas/water-resources/science/national-water-quality-assessment-nawqa), as well as data gathered in Olson and Cormier (2019). We used data from the contiguous United States to aid in the development of our water quality models for a better representation of the range of environments across spatially heterogeneous California.

From these sources, we extracted measurements of nine water quality parameters:

- Individual ionic parameters:
  - Calcium (mg/L)
  - Chloride (mg/L)
  - Magnesium (mg/L)
  - Sulfate (mg/L)
  - Sodium (mg/L)
- Integrated measures
  - Alkalinity as $CaCO_3$ (mg/L)
  - Hardness as $CaCO_3$ (mg/L)
  - Total dissolved solids (mg/L)
  - Specific conductivity (µS/cm)

None of the aggregated data was excluded based on quality assurance (QA) information. QA codes were available for data from the CEDEN database. Over 99.5% of all data points either had no QA flags or were flagged for violations unlikely to substantially affect measurements (e.g., holding time violations, dilutions performed during measurement, etc.). Of those with the potential to greatly affect measurements, the most common violation was unacceptable drift checks (affecting 8 specific conductivity measurements). No more than one or two samples for each analyte were affected by other violations with the potential to affect measurements (e.g., poor matrix spike recovery, blank contamination, or high variability among lab replicates).

Matching sites to NHD+ catchments

In order to associate sampling locations with geospatial data used as predictors in our water quality models, we matched each site to a catchment in the NHD+ (McKay et al. 2014). Sites were matched by overlaying our sample locations with NHD+ catchments to determine the catchment's unique identifier (i.e., FEATUREID). Sites could then be matched with the corresponding unique identifier in the StreamCat dataset (i.e., COMID) to obtain additional geospatial data. Sites that were unable to be matched to a catchment were excluded from further analysis.

Although sites may not have been evenly distributed within a catchment, we assumed that all samples were equally representative of water quality conditions within each stream segment. All segments that had at least one matching site were used in analysis.

Eliminating repeated samples within a catchment and month

We took steps to eliminate sample bias and duplication. We removed duplicate site observations sampled during the same month and in the same stream catchment. The retained sample was selected at random to prevent a bias caused by over-representing sites that were repeatedly sampled. Sites with values below the method detection limit were replaced with a value of zero.

Acquiring geospatial data

Once matched to a catchment, we extracted geospatial data from the StreamCat dataset (Hill et al. 2016). We acquired two kinds of geospatial data from StreamCat: 1) metrics that characterize natural gradients that could influence ionic concentrations (predictors) and 2) metrics that characterize human disturbance (human activities). Natural gradient metrics were used as predictors in our models, and human disturbance metrics were used to identify minimally disturbed reference sites. All StreamCat variables evaluated in this study are presented in Table 1. Additionally, we determined the Omernik Level 3 ecoregion (Omernik and Griffith 2014) of each site based on its location. StreamCat defines a catchment as an area that drains directly to an NHD+ stream segment and defines a watershed as a set of connected catchments that flow to a focal point (Hill et al. 2016).

Table 1. StreamCat variables used in model development. All variables were evaluated both at the watershed and catchment scales. "Predictor variables" characterize natural gradients and were used as candidate predictors in random forest models, whereas "Reference screens" characterize human activity and were used to identify reference sites.

Type	Description	Variable name	Unit	Use
Climate	Evapotranspiration from PRISM	1- and 2-month values, and 3-,6-, and 12-month averages	˚C	Predictor
Climate	Precipitation from PRISM	1- and 2-month values, and 3-,6-, and 12-month averages	mm	Predictor
Climate	Mean Temperature from PRISM	1- and 2-month values, and 3-,6-, and 12-month averages	˚C	Predictor
Climate	Maximum Temperature from PRISM	1- and 2-month values, and 3-,6-, and 12-month averages	˚C	Predictor
Climate	30-year normal mean precipitation in watershed	PrecipWs	mm	Predictor
Geology	Mean soil erodibility of soils within watershed on agricultural land	AgKffactWs	Unitless	Predictor
Geology	Mean % aluminum oxide within watershed	Al2O3Ws	%	Predictor
Geology	Mean percent Calcium Oxide within watershed	CaOWs	%	Predictor

Type	Description	Variable name	Unit	Use
Geology	Mean percent clay content within watershed	ClayWs	%	Predictor
Geology	Mean lithological uniaxial compressive strength within watershed	CompStrgthWs	Mpa	Predictor
Geology	Mean lithological ferric oxide in watershed	Fe2O3Ws	%	Predictor
Geology	Mean lithological hydraulic conductivity in watershed	HydrlCondWs	um/s	Predictor
Geology	Mean lithological potassium oxide in watershed	K2OWs	%	Predictor
Geology	Mean soil erodibility within watershed	KffactWs	Unitless	Predictor
Geology	Mean magnesium oxide in watershed	MgOWs	%	Predictor
Geology	Mean sodium oxide in watershed	Na2OWs	%	Predictor
Geology	Mean nitrogen in watershed	NWs	%	Predictor
Geology	Mean organic matter in watershed	OmWs	%/weight	Predictor
Geology	Mean phosphorous oxide in watershed	P2O5Ws	%	Predictor

Type	Description	Variable name	Unit	Use
Geology	Alkaline intrusive volcanic rock in watershed	PctAlkIntruVolWs	%	Predictor
Geology	Alluvium and fine textured coastal sediment in watershed	PctAlluvCoastWs	%	Predictor
Geology	Carbonate residual material in watershed	PctCarbResidWs	%	Predictor
Geology	Coarse coastal zone sediment in watershed	PctCoastCrsWs	%	Predictor
Geology	Colluvial sediment in watershed	PctColluvSedWs	%	Predictor
Geology	Coarse eolian sediment in watershed	PctEolCrsWs	%	Predictor
Geology	Fine eolian sediment in watershed	PctEolFineWs	%	Predictor
Geology	extrusive volcanic rock in watershed	PctExtruVolWs	%	Predictor
Geology	Coarse textured glacial outwash and glacial lake sediment in watershed	PctGlacLakeCrsWs	%	Predictor
Geology	Fine textured glacial lake sediment in watershed	PctGlacLakeFineWs	%	Predictor
Geology	Glacial till, clayey in watershed	PctGlacTilClayWs	%	Predictor

Type	Description	Variable name	Unit	Use
Geology	Coarse textured glacial till in watershed	PctGlacTilCrsWs	%	Predictor
Geology	Loamy glacial till in watershed	PctGlacTilLoamWs	%	Predictor
Geology	Peat and much hydric soils in watershed	PctHydricWs	%	Predictor
Geology	non-carbonate residual material in watershed	PctNonCarbResidWs	%	Predictor
Geology	Saline like sediment in watershed	PctSalLakeWs	%	Predictor
Geology	Silicic residual material in watershed	PctSilicicWs	%	Predictor
Geology	Mean permeability of soils in watershed	PermWs	cm/hr	Predictor
Geology	Mean depth to bedrock in watershed	RckDepWs	cm	Predictor
Geology	Sand content in watershed	SandWs	%	Predictor
Geology	Silicon dioxide content in watershed	SiO2Ws	%	Predictor
Geology	Sulfur content in watershed	SWs	%	Predictor
Hydrology	Ground water discharge into streams in watershed ratio	BFIWs	%	Predictor

Type	Description	Variable name	Unit	Use
Hydrology	Mean seasonal water table depth in watershed	WtDepWs	cm	Predictor
Landcover	Barren land cover in watershed	PctBl2016Ws	%	Predictor
Landcover	Evergreen forest landcover in watershed	PctConif2016Ws	%	Predictor
Landcover	Deciduous forest land cover in watershed	PctDecid2016Ws	%	Predictor
Landcover	Grassland/herbaceous landcover in watershed	PctGrs2016Ws	%	Predictor
Landcover	Herbaceous wetland cover in watershed	PctHbWet2016Ws	%	Predictor
Landcover	Ice/snow land cover in watershed	PctIce2016Ws	%	Predictor
Landcover	Mixed deciduous/evergreen forest cover in watershed	PctMxFst2016Ws	%	Predictor
Landcover	Open water land over in watershed	PctOw2016Ws	%	Predictor
Landcover	Shrub/scrub land cover in watershed	PctShrb2016Ws	%	Predictor
Landcover	Watershed area that is water	PctWaterWs	%	Predictor
Landcover	Woody wetland land cover in watershed	PctWdWet2016Ws	%	Predictor

Type	Description	Variable name	Unit	Use
Topography	Mean watershed elevation	ElevWs	m	Predictor
Topography	Mean composite topographic index in watershed	WetIndexWs	Unitless	Predictor
Human activity	Density of canals, ditches, or pipelines within watershed	CanalDensWs	km/km2	Reference screen
Human activity	Density of georeferenced dams within watershed	DamDensWs	#/km2	Reference screen
Human activity	Total possible volume of all reservoirs in watershed	DamNIDStorWs	m3/km2	Reference screen
Human activity	Normal volume of all reservoirs in watershed	DamNrmStorWs	m3/km2	Reference screen
Human activity	Density of mines in watershed	MineDensWs	#/km2	Reference screen
Human activity	Crop land use in watershed	PctCrop2016Ws	%	Reference screen
Human activity	Hay land use in watershed	PctHay2016Ws	%	Reference screen
Human activity	Mean impervious surfaces in watershed	PctImp2011Ws	%	Reference screen
Human activity	Developed, high-intensity land use in watershed	PctUrbHi2016Ws	%	Reference screen

Type	Description	Variable name	Unit	Use
Human activity	Developed, low-intensity land use in watershed	PctUrbLo2016Ws	%	Reference screen
Human activity	Developed, medium-intensity land use in watershed	PctUrbMd2016Ws	%	Reference screen
Human activity	Developed, open space land use in watershed	PctUrbOp2016Ws	%	Reference screen
Human activity	Density of road-stream intersections multiplied by NHD+ slope in watershed	RdCrsSlpWtdWs	(Crossings*slope / km2)	Reference screen
Human activity	Density of road-stream intersections in watershed	RdCrsWs	crossings/km2	Reference screen
Human activity	Density of roads in watershed	RdDensWs	km/km2	Reference screen

Identify reference sites

We used StreamCat data to identify reference sites minimally affected by human activity, following the procedure in Ode et al. (2016). Any site that failed one or more of the thresholds in Table 2 was not considered reference. Once screened, sites with exceptionally high ionic parameter values were further evaluated in Google Earth. This screen often provided evidence of human impact or natural (but unusual) sources of ions (e.g., hot springs or evaporite deposits) not detected in the initial reference screening. Disturbances included tidal influence, cattle grazing, industrial complexes, and excessive erosion in an area. If evidence of a disturbance was found, the site was no longer considered reference and was removed.

Table 2. Criteria used to identify reference sites from StreamCat data, adapted from Ode et al. (2016)

Reference screen	Threshold
Agricultural landcover in watershed or catchment	<3%
Urban land cover in watershed or catchment	<3%
Developed open space (i.e., Code 21) in the watershed or catchment	<5%
Dam density in the watershed or catchment	<2/km^2
Road density	<2 km/km^2
Road crossings in the watershed	<10/km^2
Road crossings in the catchment	<5/km^2

Develop models of ionic parameters

To develop random forest models to predict reference levels of ionic parameters, we followed the steps shown in Figure 4. First, we split reference sites into training (80%) and testing (20%) data sets. Training sites were used to calibrate models, whereas the testing data sets were withheld to evaluate model performance characteristics with independent data. The subsets were stratified by the eighty-five Level 3 Ecoregions (Omernik and Griffith 2014), ensuring that major ecoregions were equally represented in the calibration and validation data sets.

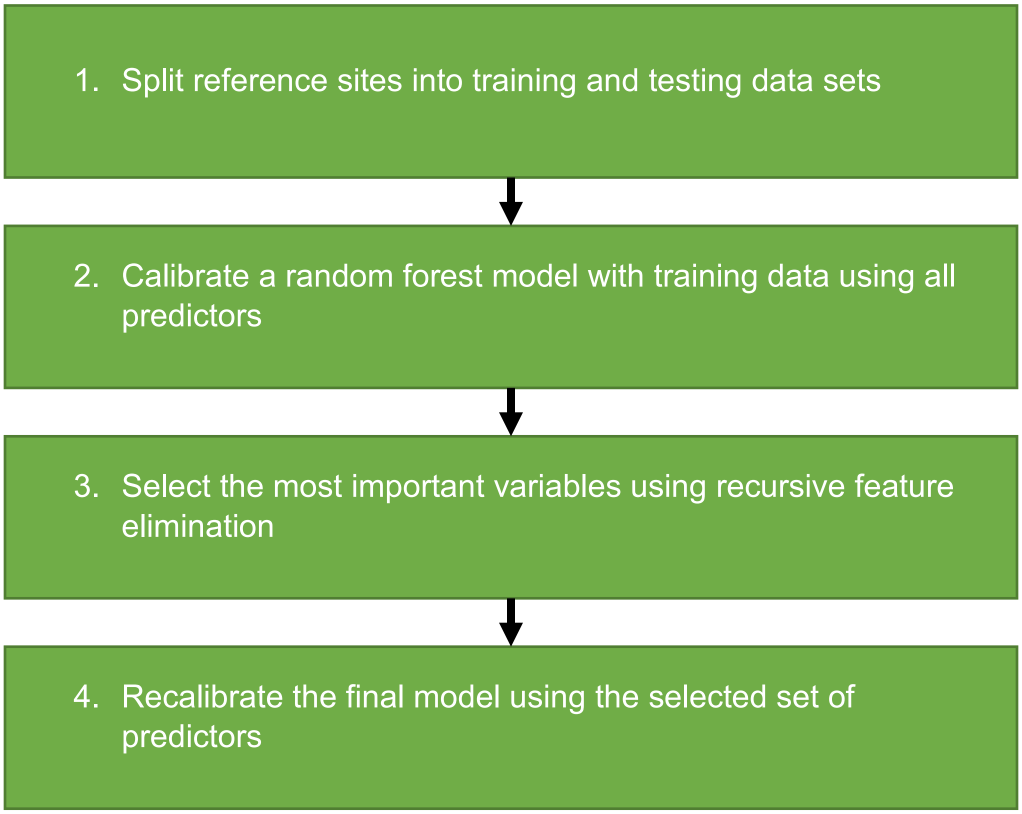


Figure 4. Steps in the development of random forest models of reference levels of ionic parameters.

Once we divided the reference data into training and testing subsets, we used the training data to build random forest models for each parameter. We used the randomForest function from the randomForest package in R for all random forest models (Liaw and Wiener 2002, R Core Team 2022). Each model was initially run with all predictors present (predictors in Table 1). We used recursive feature elimination (RFE) in the caret package in R (Kuhn 2020) to select the simplest subset of predictors that yielded a model with comparable accuracy to the all-predictor model. RFE is a backwards stepwise process that removes the least important predictors until model accuracy (measured as percent variance explained) declines. Five variables were dropped at each step. An evaluation of the stability of variable selection using this method was completed by Fox et al. (2017) determining that the "out-of-bag" (OOB) performance remained steady until minimum variables remained.

Assess model performance

We assessed model performance by looking at the accuracy and precision of our modeled results. To determine the accuracy and precision values, we used pseudo-R^2, root mean squared error (RMSE), and out-of-bag predictions for each random-forest model. Predicted values from the random forest models were compared to observed values in the calibration and validation reference data sets. Out-of-bag (OOB) predictions, generated when random forest created a subset of trees withholding the sites in question, were used to assess calibration performance. This validation approach allowed us to use the OOB predictions to measure model performance independent of the sample data used to train the model. Linear regressions comparing observed to expected values were calculated. Model precision was estimated with the regression's R^2 value; larger values indicated better precision. Model accuracy was assessed using the slope and intercept of the regression; intercepts close to zero indicated higher accuracy, and slopes close to 1 indicated that model performance is consistently accurate across a range of conditions. These model performance parameters were summarized for the entire contiguous United States. Model performance was also assessed for California sites alone following this procedure.

Model performance was also evaluated for spatial bias by plotting model residuals on a map, depicting any geographic patterns in the model errors. The residuals were calculated by subtracting the predicted values from the sites' observed values. If the areas with insufficient predictive power were all located in similar geographic regions, that indicates potential geographic bias in our model. If the sites with insufficient predictive power were equally spread throughout geographic locations, our model had less likelihood of geographical bias.

Assess water quality alteration at reference and non-reference sites

We used the models to generate predictions for all stream segments in California with observations of ionic parameters, and quantified differences as percent change (100 * observed divided by expected). We plotted these measures of change to identify regions of California where alteration was more pervasive or severe.

Apply models to all NHD+ segments in California

In order to obtain natural background estimates for California streams, we applied our models to all stream segments in California. The model application, and map generation of expected natural levels, were possible because StreamCat data is available for almost every NHD+ segment in California. These predictions are available from https://sccwrp.shinyapps.io/RB8_Threshold.

To evaluate inter- and intra-annual variability, we calculated averages for each analyte for each season in wet, dry, and normal years. First, we acquired monthly precipitation data from the weather station at the John Wayne Airport in Santa Ana (NOAA Weather Station USW00093184; https://www.ncdc.noaa.gov/cdo-web/datasets/GHCND/stations/GHCND:USW00093184/detail). Then, we calculated total precipitation for each calendar year from 2001 to 2019 was calculated. Based on the annual total precipitation, we divided the years into wet, normal, and dry thirds based on cutoff values of 6.9 and 10.0 inches of rainfall per year. Finally, we then compared the average values by subtracting dry years from wet years (i.e., inter-annual variation) and dry seasons from wet seasons (i.e., intra-annual variation); the dry season was defined as April through September, and the wet season as October through May. We mapped these differences to determine if there were spatial patterns to this variation.

To see if the John Wayne Airport weather data was typical of other portions of the watershed, we queried data from Ontario International Airport (NOAA Weather Station USW00003102), Lake Elsinore (USC00042805), Newport Harbor (USC00046175), and Big Bear Lake (USC00040741). Overall, patterns were highly consistent among the different weather stations, particularly during extremely wet (e.g., 2010) or dry (e.g., 2007) years. However, the one high elevation station (i.e., Big Bear Lake) diverged from the other stations during more moderate conditions (Table 3). Therefore, although the model predictions are no less accurate in higher elevations, the mean summaries we calculated may be less precise than in low elevation areas.

Table 3. Annual precipitation in inches at 5 weather stations in the Santa Ana watershed. Cells are colored on a gradient of red (drier) to blue (wetter) to indicate the total precipitation that occurred that year, ranked within each station.

Year	Big Bear Lake	Elsinore	Newport Harbor	Ontario Intl Airport	John Wayne Airport
2001	12.2	11.63	13.34	14.13	13.19
2002	10.35	4.65	5.05	6.19	5.12
2003	22.63	12.14	8.89	10.59	8.55
2004	12.7	15.34	8.48	13.71	15.21
2005	34.87	26.18	12.28	21.21	16.4
2006	13.96	6.86	4.08	10.33	7.28
2007	8.19	0.33	1.37	6.56	4.27
2008	19.72	5.1	5.59	12.24	10.51
2009	15.7	8.39	2.9	8.61	5.76
2010	43.57	26.83	11.01	21.7	24.6
2011	18.2	10.81	4.81	10.25	7.85
2012	11.62	6.94	4.91	8.26	6.89
2013	10.79	3.36	2.44	3.71	3.02

Year	Big Bear Lake	Elsinore	Newport Harbor	Ontario Intl Airport	John Wayne Airport
2014	18.49	8.15	3.65	9.38	6.42
2015	11.86	5.61	5.02	8.68	6.5
2016	21.95	9.65	6.49	10.47	9.95
2017	12.06	12.25	12.02	10.85	9.7
2018	18.12	7.29	7.4	8.11	8.32
2019	33.78	19	13.33	18.34	18.84

Comparison predicted values to known habitat requirements for selected vertebrate species

We identified three aquatic vertebrate species found in the Santa Ana watershed with known tolerances to chloride, specific conductivity, and sulfate. Meador and Carlisle (2007) reported weighted averages of observed water quality values where North American fish species were observed (Table 4). We used these values to determine the frequency (that is, percent of months between 2001 and 2019) with which each reach in the Santa Ana watershed would have suitable water quality for each species. We compared these maps to historical and present-day HUC12-scale distributions of each taxon reported in the PISCES database (Santos et al. 2014; https://pisces.ucdavis.edu/).

Table 4. Tolerance values of three fish species found in the Santa Ana watershed for three ionic parameters. Tolerance values are weighted averages reported in Meador and Carlisle (2007).

Species name	Common name	Chloride (mg/L)	Sulfate (mg/L)	Specific conductivity (µS/cm)
Catostomus santaanae	Santa Ana sucker	82	89	1046
Gila orcutti	Arroyo chub	71	81	1039
Rhinichthys osculus	Speckled dace	28	75	483

Results

Aggregation of water quality data

Aggregation of national and statewide monitoring databases yield data from 8,588 potential reference stream segments, 11% of which were in California (Table 5). Reference data sets were largest for specific conductivity (which had over 9,000 reference sites for modeling), followed by chloride (over 2,000 reference sites). Data sets were smallest for TDS and hardness (each of which had under 500 reference sites; Table 6). We withheld a random subset of 20% of the sites at both the national (Figure 5) and California (Figure 6) scales for model validation following Olson and Cormier (2019).

Table 5. Data sources and number of sites available for model development. NAQWA: National Water-Quality Assessment Project. NRSA: National Rivers and Streams Assessment. CEDEN: California Environmental Data Exchange Network.

Program	Extent	# unique stream segments	# reference sites nationwide	# reference sites in California
NAQWA	Nationwide	112	1378	0
NRSA	Nationwide	4166	457	23
CEDEN	California	2433	976	976
Olsen and Cormier (2019)	Nationwide	1877	6864	0

Table 6. Number of sites available for modeling and analysis for each parameter.

Parameter	Total sites – California	Total sites – Nationwide	Reference sites – California	Reference sites – Nationwide
Cl	9643	15,426	611	2238
SO4	4478	6834	502	1704
Na	8244	12,786	232	1496
Ca	8562	13,506	258	1558
Mg	8558	13,504	258	1558
TDS	8873	9069	247	429
Hardness	8271	5375	415	493
Alkalinity	2053	3337	546	1106
Specific conductivity	10,880	28,470	944	9575

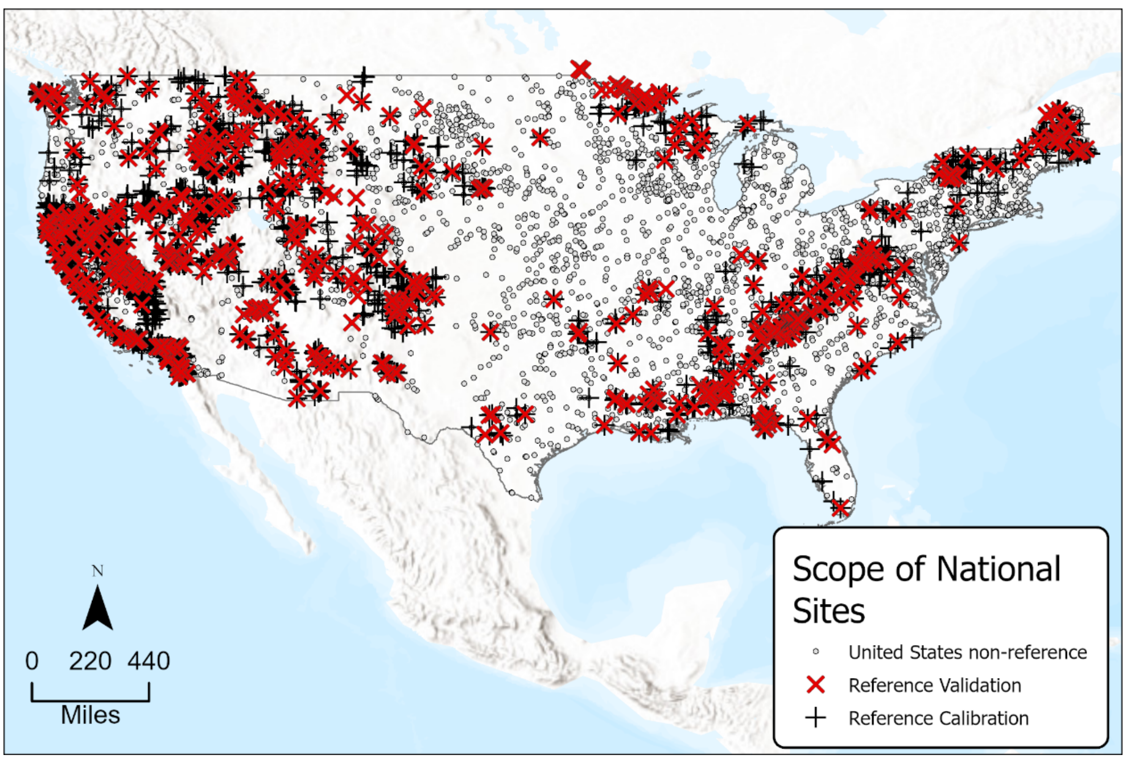


Figure 5. Nationwide sites used in model development or evaluation.

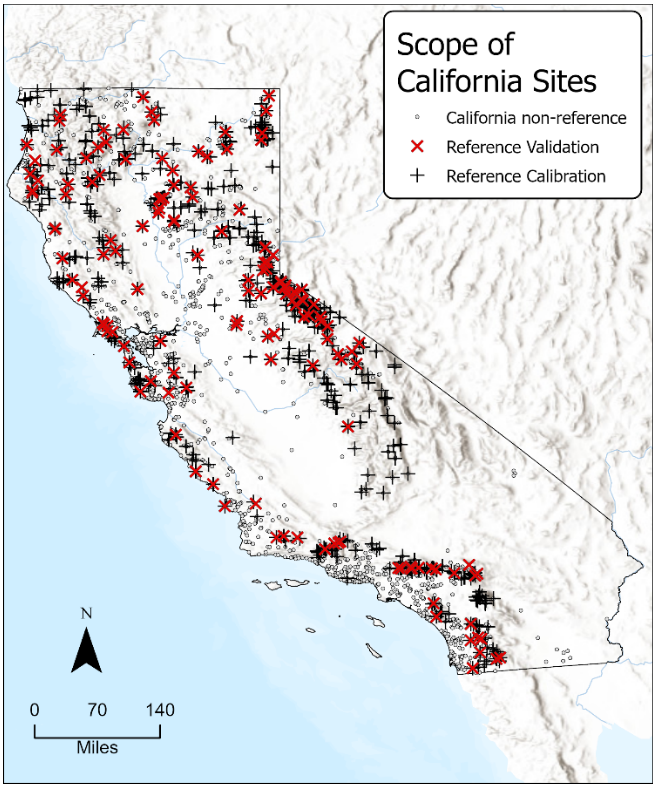


Figure 6. Sites from California used in model development or evaluation.

Model performance

In general, geologic factors were less important than climatic factors or watershed morphology in predicting reference levels of ionic parameters. Several factors were selected for 9 models: three measures of antecedent precipitation, a measure of antecedent temperature, the amount of sulfur-bearing geology in the watershed, and the baseflow index (a prediction of dry weather streamflow based on watershed area and long-term precipitation; Wolock 2003). Among climatic predictors, those reflecting antecedent conditions over the previous 12 months were more important than those reflecting more short-term antecedent conditions, as well as those based on long-term average conditions. The relative importance of selected variables in the final models is shown in Figure 7.

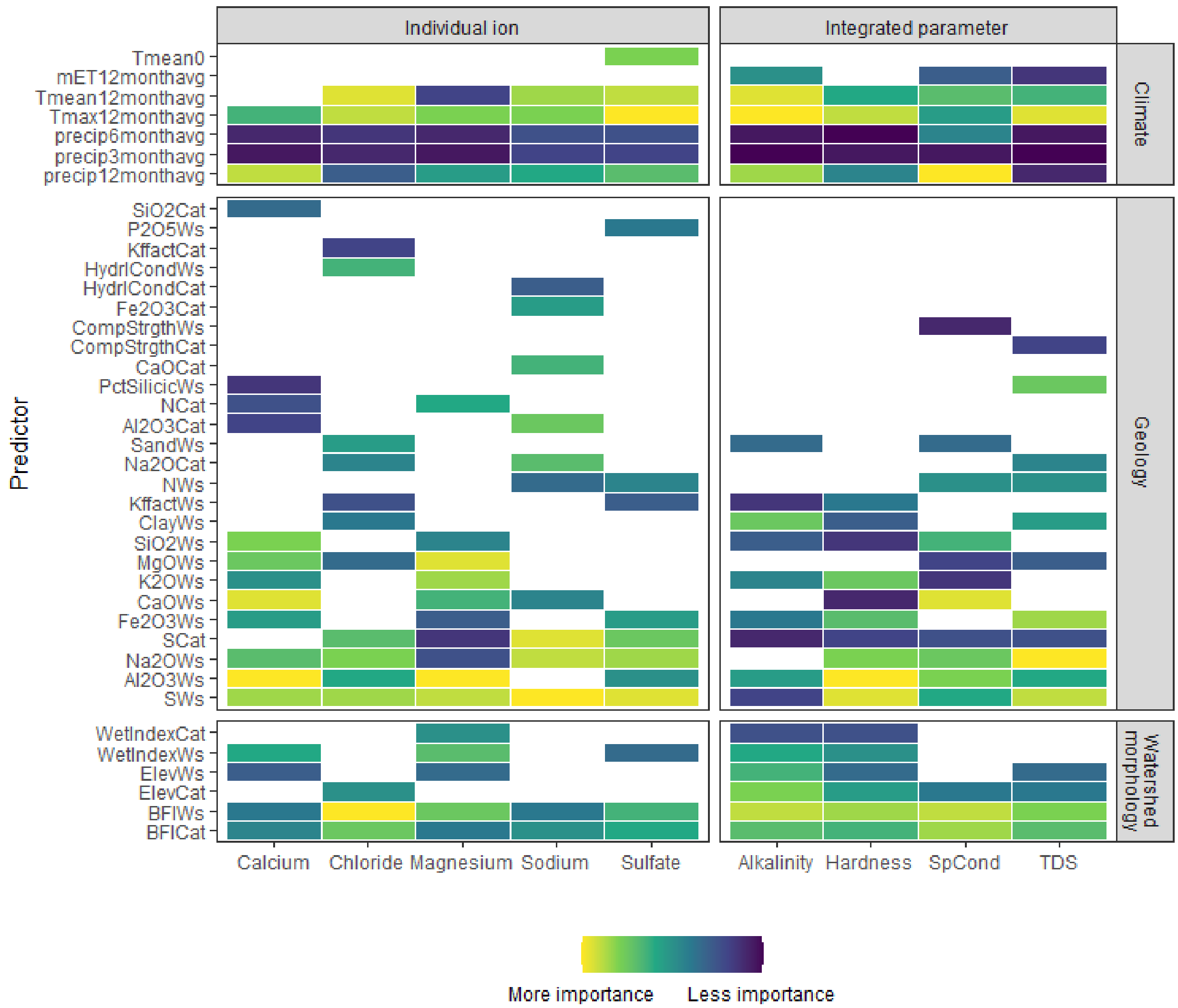


Figure 7. Importance of selected predictors in each of the nine models of reference levels of ionic parameters. Blank cells indicate that the predictor was not selected for that model. Abbreviations are in Table 1.

All models had relatively good predictive power, as indicated by high pseudo-R^2. The worst performance was for the Sodium model, which had a pseudo-R^2 of 0.63.The models performed very well when validated at the California scale, with Pearson correlation coefficients (r^2) values between observed to predicted values at validation sites ≥0.7 for all analytes, with the exception of the alkalinity model at validation sites (Table 7). The slope values close to 1 and intercept values close to 0 showed that the model predictions were accurate, precise, and consistent.

Table 7. Model performance statistics across all analytes at the nationwide and California (CA) scale. Cal: Calibration (training) data set. Val: Validation (testing) data set. N ref: Number of reference sites in the Cal or Val data sets. OE r^2: Squared Pearson correlation cofficient between observed and expected (i.e., predicted by model) values. OE Slope: Slope of a regression between observed and expected values. OE Slope SE: Standard error of the slope of a regression between observed and expected values. OE Intercept: Intercept of a regression between observed and expected values. OE Intercept SE: Standard error of the intercept from a regression between observed and expected values.

Parameter	Set	Scale	N ref	OE r^2	OE Slope	OE Slope SE	OE Intercept	OE Intercept SE
Mg	Cal	CA	209	0.98	1.06	0.01	-0.9	0.25
Mg	Val	CA	49	0.95	1.01	0.03	-0.6	0.91
Mg	Cal	Nationwide	1247	0.81	1.55	0.01	-0.45	0.17
Mg	Val	Nationwide	311	0.88	0.98	0.02	-0.08	0.25
Ca	Cal	CA	211	0.97	1.06	0.01	-1.85	0.57
Ca	Val	CA	48	0.94	1.02	0.04	-1.63	2
Ca	Cal	Nationwide	1247	0.75	1.03	0.02	-0.75	0.45
Ca	Val	Nationwide	311	0.88	0.99	0.02	-0.61	0.6
Na	Cal	CA	188	0.97	1.07	0.01	-1.38	0.31
Na	Val	CA	44	0.92	1.09	0.05	-1.09	1.26
Na	Cal	Nationwide	1198	0.63	1.05	0.02	-0.45	0.25
Na	Val	Nationwide	298	0.66	1.05	0.04	-0.32	0.51
Cl	Cal	CA	497	0.98	1.11	0.01	-0.93	0.12
Cl	Val	CA	114	0.80	1.14	0.05	-1.11	0.7
Cl	Cal	Nationwide	1791	0.83	1.09	0.01	-0.48	0.1
Cl	Val	Nationwide	447	0.76	1.05	0.03	-0.4	0.2
SO4	Cal	CA	403	0.95	1.14	0.01	-4.39	0.88
SO4	Val	CA	99	0.73	1.48	0.09	-10.75	5.14

Parameter	Set	Scale	N ref	OE r^2	OE Slope	OE Slope SE	OE Intercept	OE Intercept SE
SO4	Cal	Nationwide	1365	0.70	1.07	0.02	-0.74	0.66
SO4	Val	Nationwide	339	0.75	1.41	0.05	-3.81	1.43
TDS	Cal	CA	201	0.95	1.08	0.02	-23.22	5.76
TDS	Val	CA	46	0.78	1.08	0.09	-2.85	26.37
TDS	Cal	Nationwide	345	0.80	1.01	0.03	-0.9	6.66
TDS	Val	Nationwide	84	0.85	1.1	0.05	-9	11.6
Sp.Cond	Cal	CA	745	0.97	1.08	0.01	-21.41	2.66
Sp.Cond	Val	CA	119	0.78	1.01	0.04	-3.43	0.04
Sp.Cond	Cal	Nationwide	7661	0.82	1.03	0.01	-6.22	1.54
Sp.Cond	Val	Nationwide	1914	0.81	1.03	0.01	-4.35	3.33
Hardness	Cal	CA	334	0.98	1.04	0.01	-6.36	1.61
Hardness	Val	CA	81	0.73	1.09	0.07	0.12	14.02
Hardness	Cal	Nationwide	396	0.86	1	0.02	-1.7	3.28
Hardness	Val	Nationwide	97	0.76	1.09	0.06	-1.65	11.01
Alkalinity	Cal	CA	438	0.96	1.13	0.01	-14.38	1.37
Alkalinity	Val	CA	108	0.73	1.21	0.07	-18.32	8.84
Alkalinity	Cal	Nationwide	631	0.73	1.08	0.03	-7.16	2.59
Alkalinity	Val	Nationwide	221	0.65	1.13	0.06	-14.12	5.49

Application of the models to sites in the Santa Ana basin showed that most parameters showed lower concentrations in the high-elevation headwaters of the San Gabriel, San Bernardino, and San Jacinto, as well as in larger waterbodies in lower elevations (e.g., the mainstem of the Santa Ana River; Figure 8, Figure 9). In contrast, smaller tributaries in lower elevations (e.g., the Chino Hills) had higher concentrations of several analytes.

An exploration of unexpectedly high Chloride predictions

Results for Chloride show an unusual pattern with very high expected values in portions of Riverside County, specifically, streams northeast of Hemet (e.g., Poppet Creek and Mellor Creek), and streams near Woodcrest (e.g., Goldenstar Canyon and Mockingbird Canyon; Figure 8). Predictions for these streams are about 100 mg/L, whereas most other streams in the Santa Ana watershed are predicted to have concentrations below 65 mg/L. Predictions are sharply lower at adjacent tributaries and downstream reaches—a pattern not seen with other analytes (Figure 8).

We were unable to evaluate the accuracy of these predictions. None of the streams with high predictions near Hemet have been sampled, and thus we have no data to evaluate the accuracy of these predictions in that region. For streams near Woodcrest, data from two sites were available (i.e., 801M16861 in Goldenstar Canyon, and 801M16957 in Mockingbird Canyon). Both sites had high values reported (i.e., 460 mg/L at Goldenstar and 290 at Mockingbird). However, both sites drain developed watersheds that receive both agricultural and urban runoff, and thus the high values may not be from strictly natural sources.

We were unable to identify factors that produced these high predictions at these streams. Factors that contribute to high predictions, such as low precipitation and high temperatures, and certain soil conditions are present in these regions, although they are also present at other regions with lower predictions. We do not believe these high predictions are errors produced during data processing (either during the manipulation of predictor data that was passed on to the model, or during the synthesis of model predictors that were used to generate the map in Figure 8).

Further investigation is needed to determine whether high predictions of Chloride in portions of the Santa Ana watershed are accurate, and what factors are driving these patterns. These investigations may include additional review of training data for outliers, as well as collecting new samples from Poppet or Mellor Creek, where reference or near-reference conditions are likely to occur.

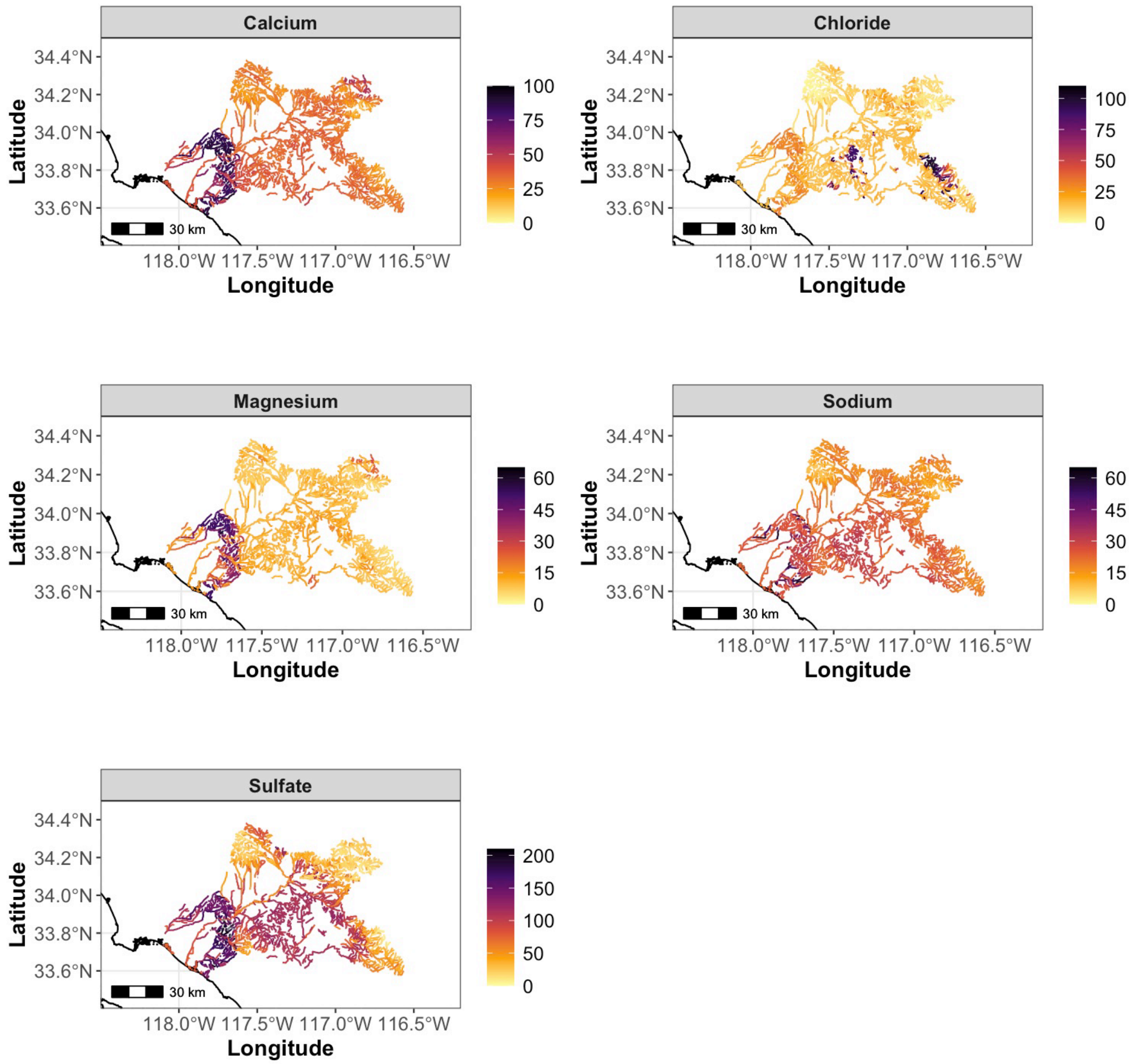


Figure 8. Average predicted concentrations for the five ionic parameters in the Santa Ana Region.

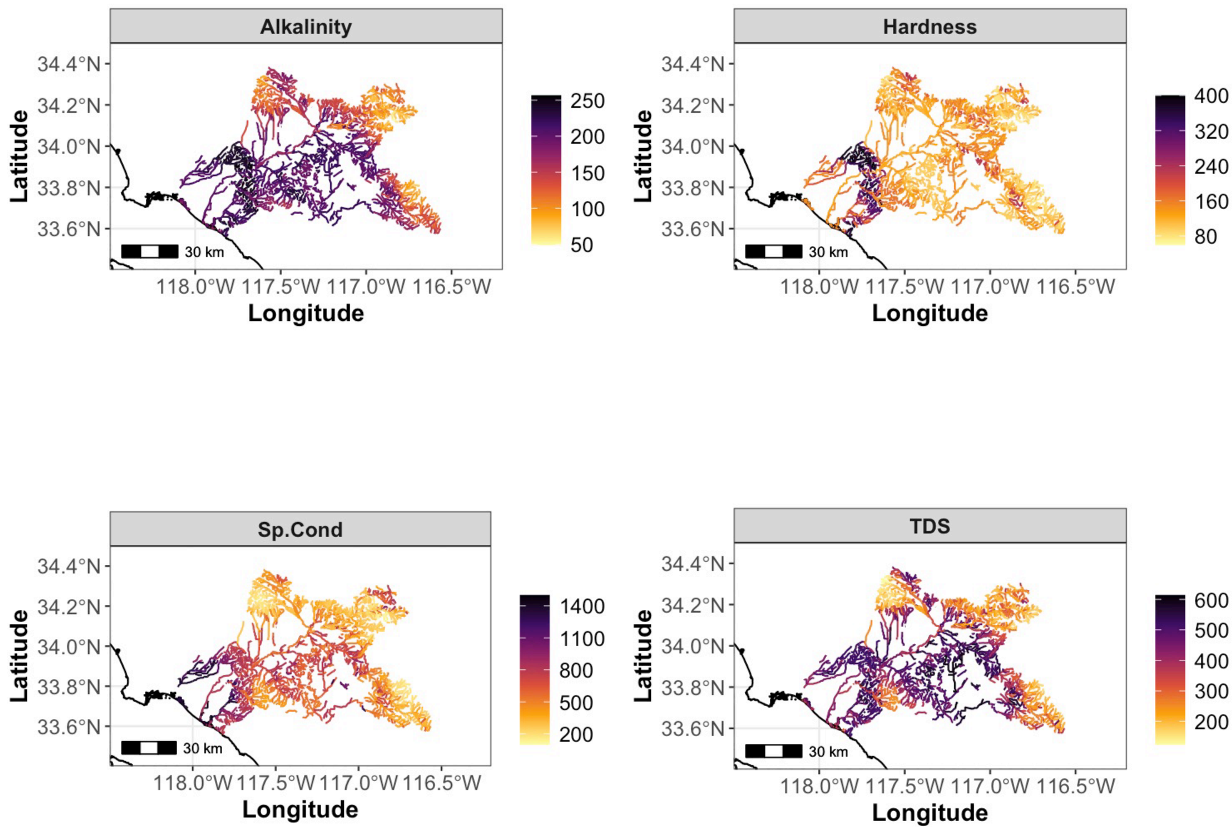


Figure 9. Average predicted concentrations for the four integrated parameters in the Santa Ana Region.

Assessment of water quality alteration in California

Extent of alteration of ionic parameters varied from a low of 35% of sites for TDS, to a high of 65% for sulfate (Table 8). Severe alteration (i.e., observed values greater than 300% of expected levels) was most extensive for chloride and magnesium. For most parameters severe alteration was most common in the South Coast, the Bay Area, and parts of the Central Valley (Figure 10).

Table 8. Percent of non-reference sites with elevated levels of ionic parameters, relative to reference levels calculated for the month of sampling.

Analyte	No increase	Up to 150%	Up to 300%	More than 300%
Alkalinity	53	31	14	2
Calcium	43	19	20	18
Chloride	52	12	11	26
Hardness	48	21	17	15
Magnesium	45	17	14	23
Sodium	55	17	15	13
Specific conductivity	55	22	15	7
Sulfate	65	10	11	14
TDS	35	16	27	22

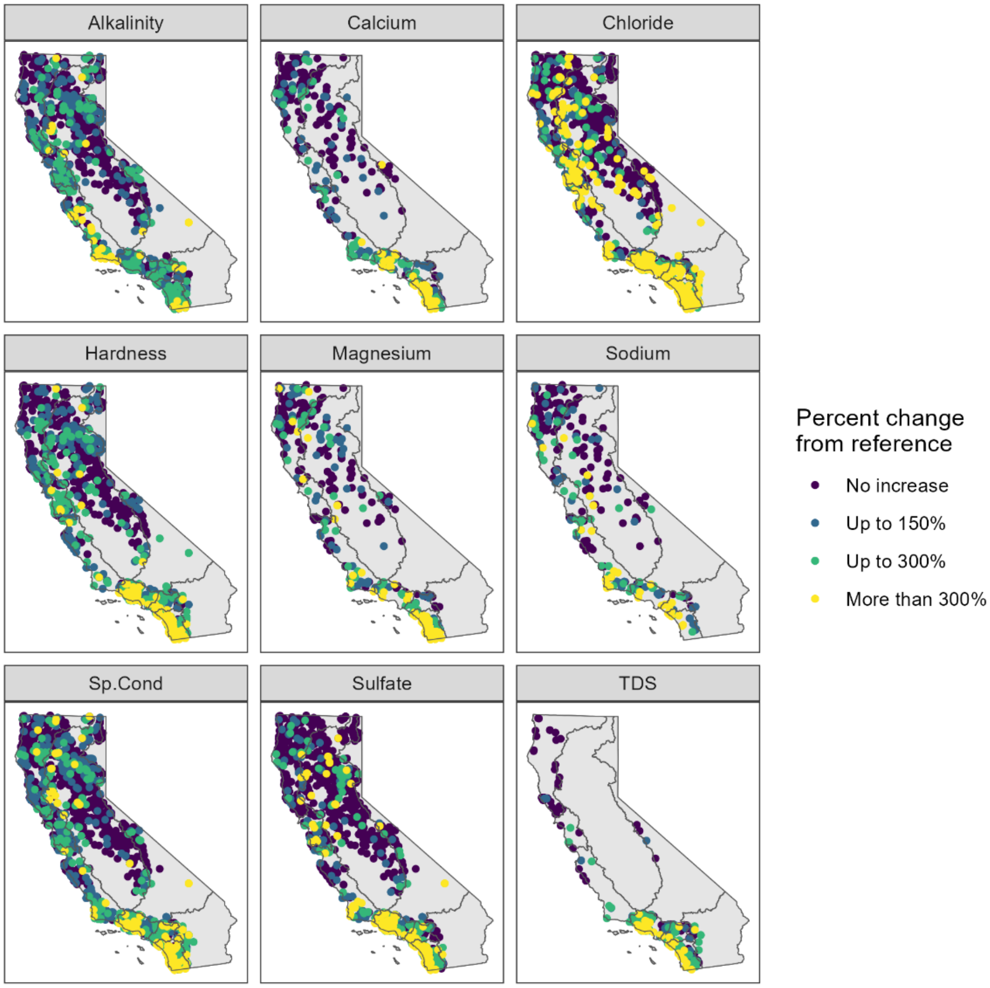


Figure 10. Alteration of water chemistry estimated as the difference between observed and predicted levels of ionic parameters.

Intra- and inter-annual variability in background levels of ionic parameters

Predictions of natural background levels of ionic parameters varied by season and climatic condition for all the analytes. Levels were usually higher in the wet season (i.e., October through March) than the dry season (Figure 11), likely reflecting the elevated concentrations that occur during flushing flows associated with winter storms. However, concentrations were lower during years with high rainfall (Figure 12), likely reflecting the dilutionary effect of increased flows during summer baseflows.

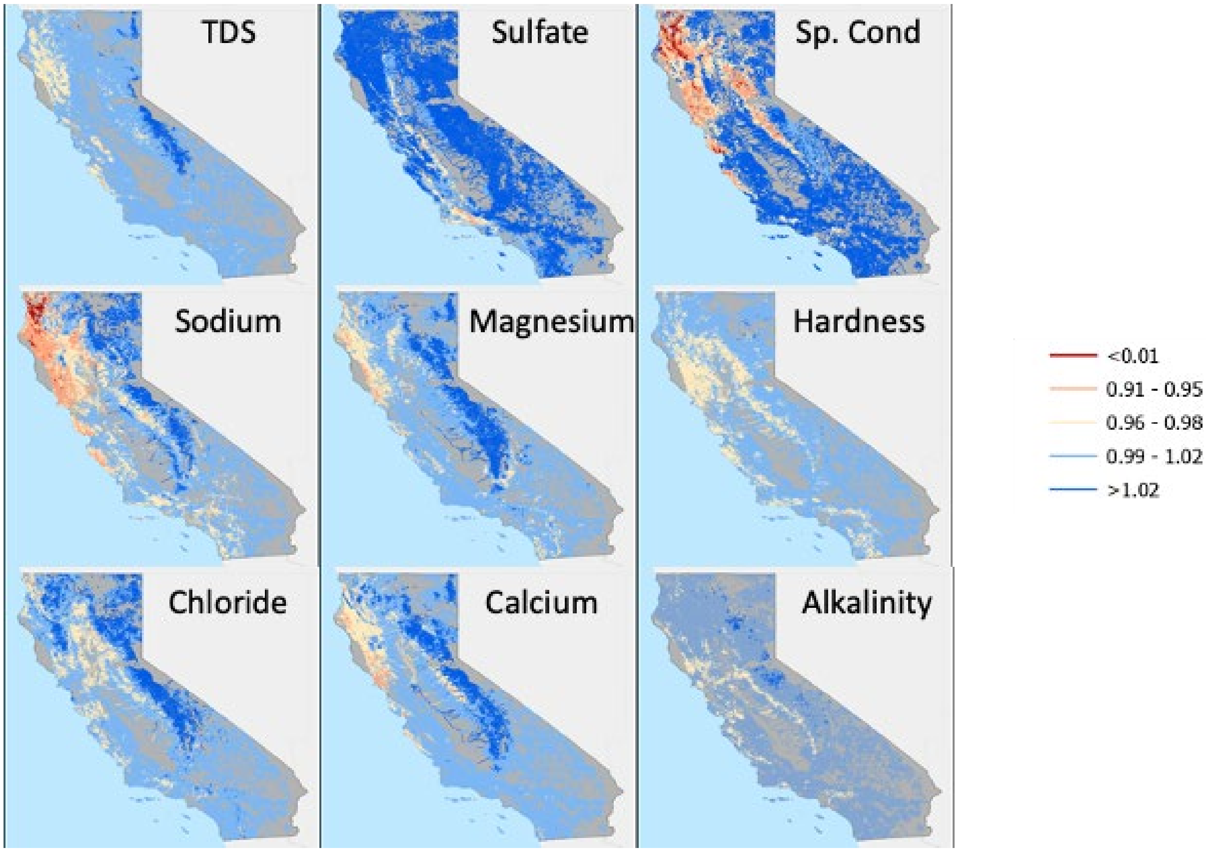


Figure 11. Intra-annual differences in predicted natural background levels of ionic parameters, calculated as the ratio of mean predict values in the wet season (i.e., October through March) over the mean predicted values in the dry season (i.e., April through September.

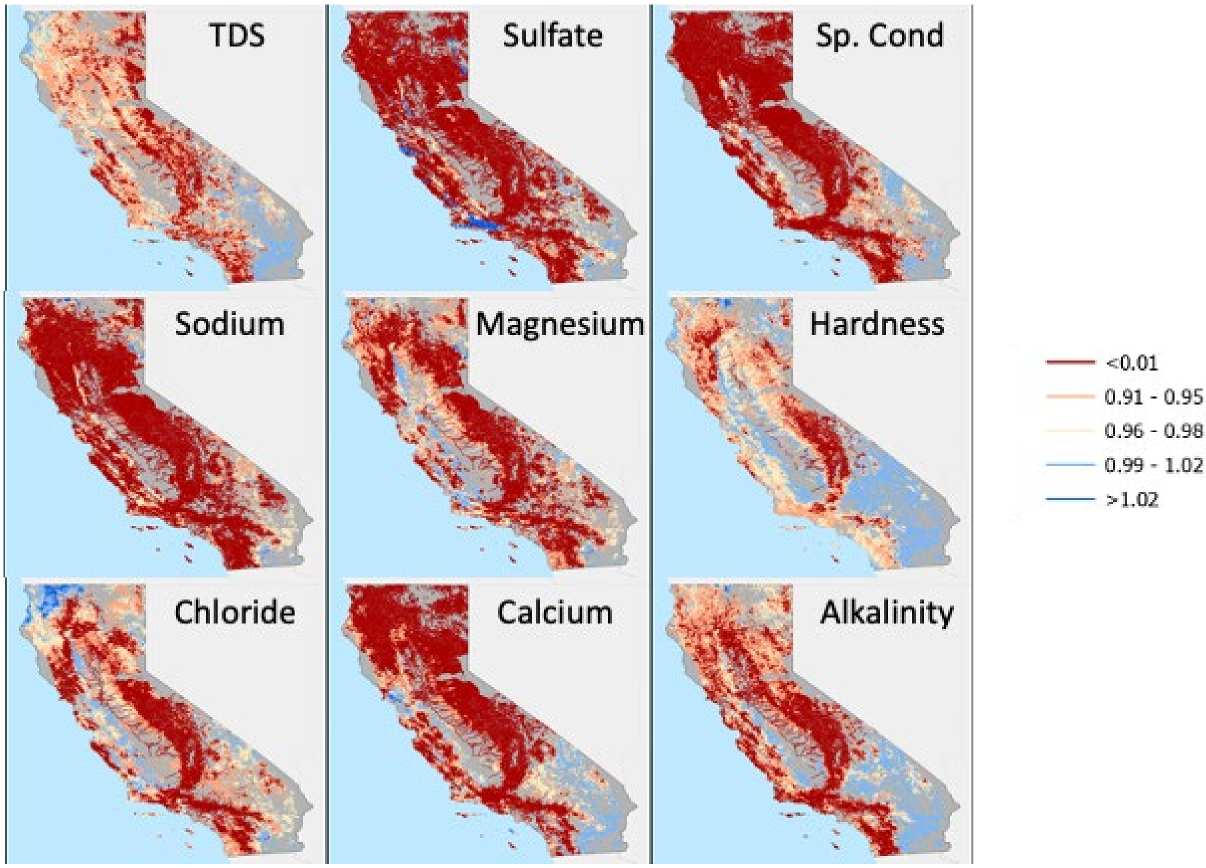


Figure 12. Inter-annual differences in predicted natural background levels of ionic parameters, calculated as ratio of the mean predicted values in wet years over the mean predicted values in wet years.

In general, the greatest variability in predicted levels across months and years occurred in headwater areas, as evident in maps of standard deviations of predicted values in the Santa Ana watershed (Figure 13, Figure 14). Exceptions to this pattern include TDS and specific conductivity, which was generally most variable in the driest parts of the study area, such as the San Jacinto watershed.

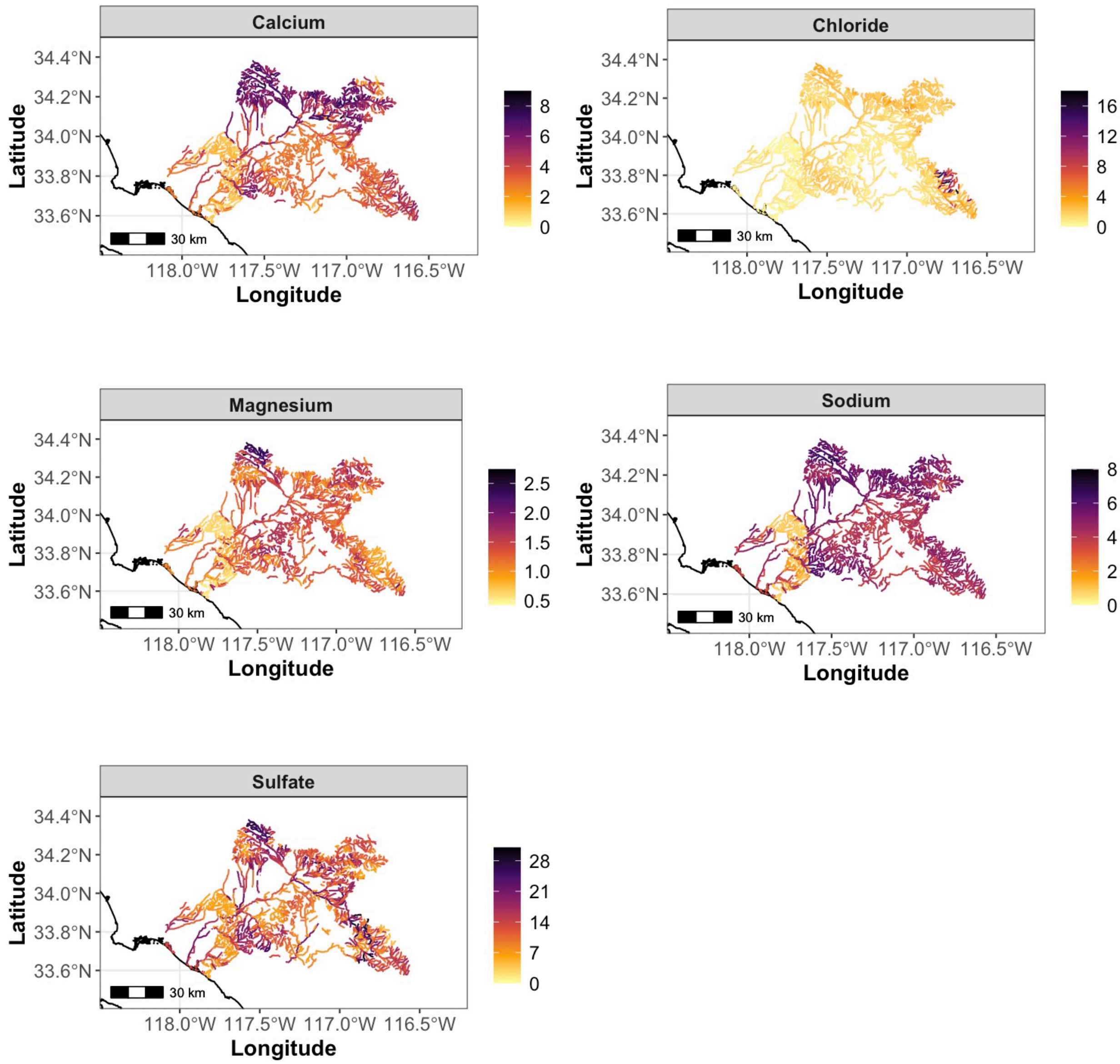


Figure 13. Standard deviation of predicted concentrations for the five ionic parameters in the Santa Ana Region.

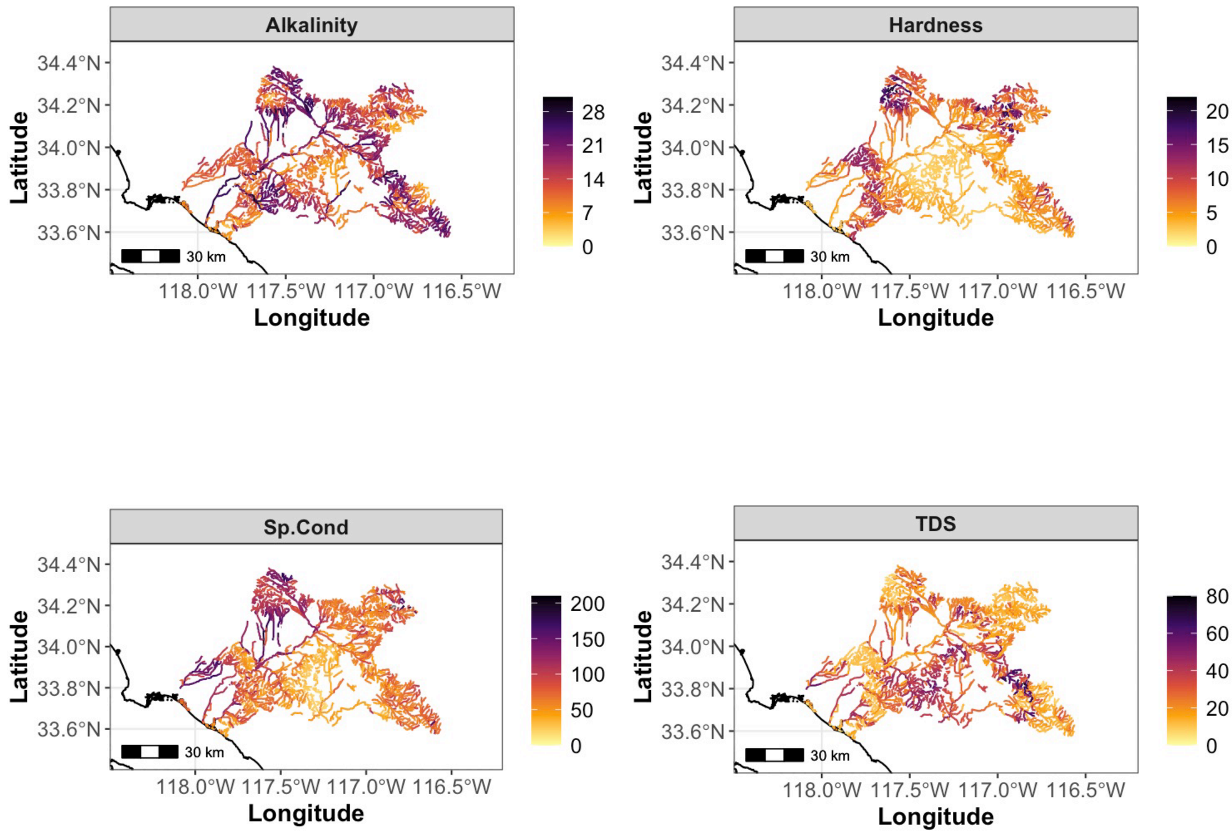


Figure 14. Standard deviation predicted concentrations for the four integrated parameters in the Santa Ana Region.

Comparison with habitat requirements for selected vertebrate species

In general, headwaters frequently had suitable water quality for the Santa Ana sucker, the arroyo chub, and the speckled dace (Figure 15 to Figure 17). In addition to the headwaters, main stem Santa Ana, San Antonio Creek, Deer Creek, Santiago Creek, San Timoteo Creek, San Diego creek headwaters, and parts of the San Jacinto River were identified as suitable for most of the months analyzed. These locations largely corroborate known occurrences of these taxa in species management documents (https://pisces.ucdavis.edu), except for the San Jacinto River, which is hydrologically disconnected from the rest of the watershed and may not have ever supported these species despite providing suitable water quality conditions. Our models appear to have overestimated the suitability of smaller tributaries and headwaters because of their exclusive focus on ionic parameters. Other factors that affect habitat suitability, such as flow duration, are ignored by these models. The small headwater streams erroneously identified as suitable habitat frequently exhibit ephemeral or intermittent flows, which may be insufficient to support most fish taxa.

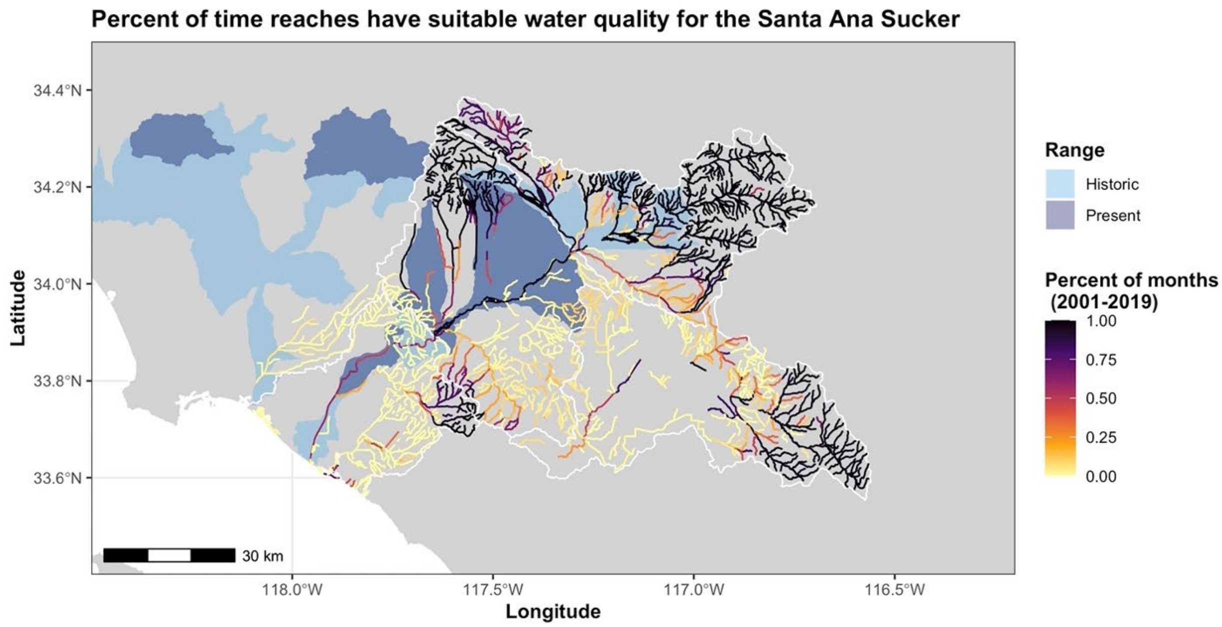


Figure 15. Streams with suitable water quality for the Santa Ana sucker *(Catostomus santaanae)*, compared to historical and present-day distribution.

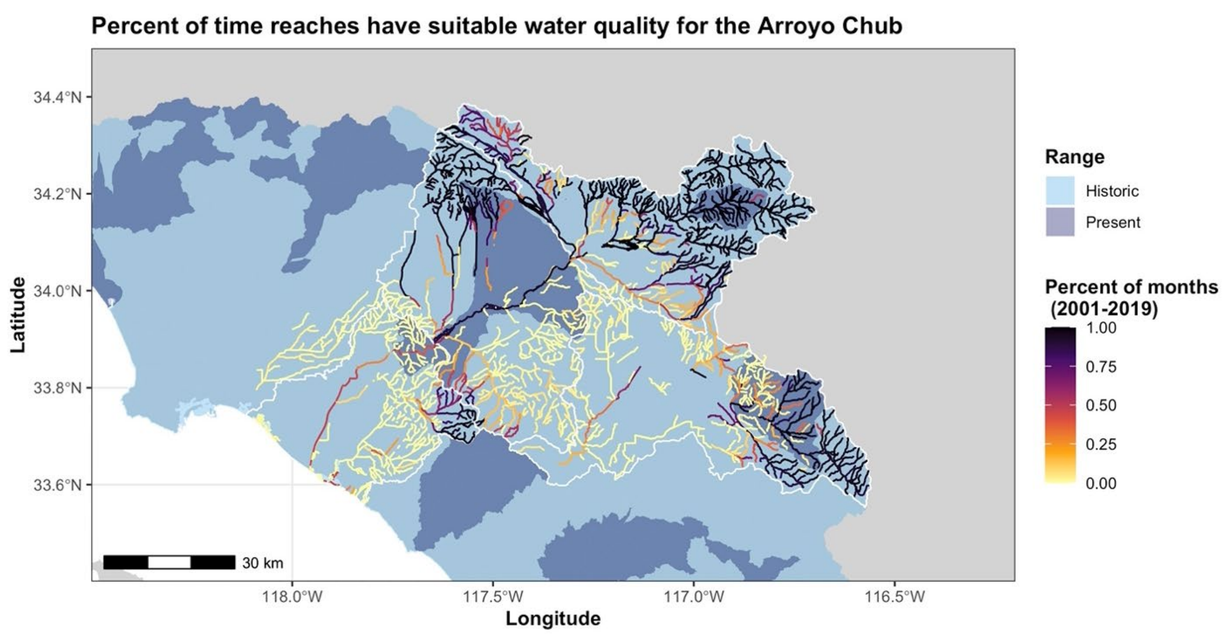


Figure 16. Streams with suitable water quality for the arroyo chub (*Gila orcutti*), compared to historical and present-day distribution.

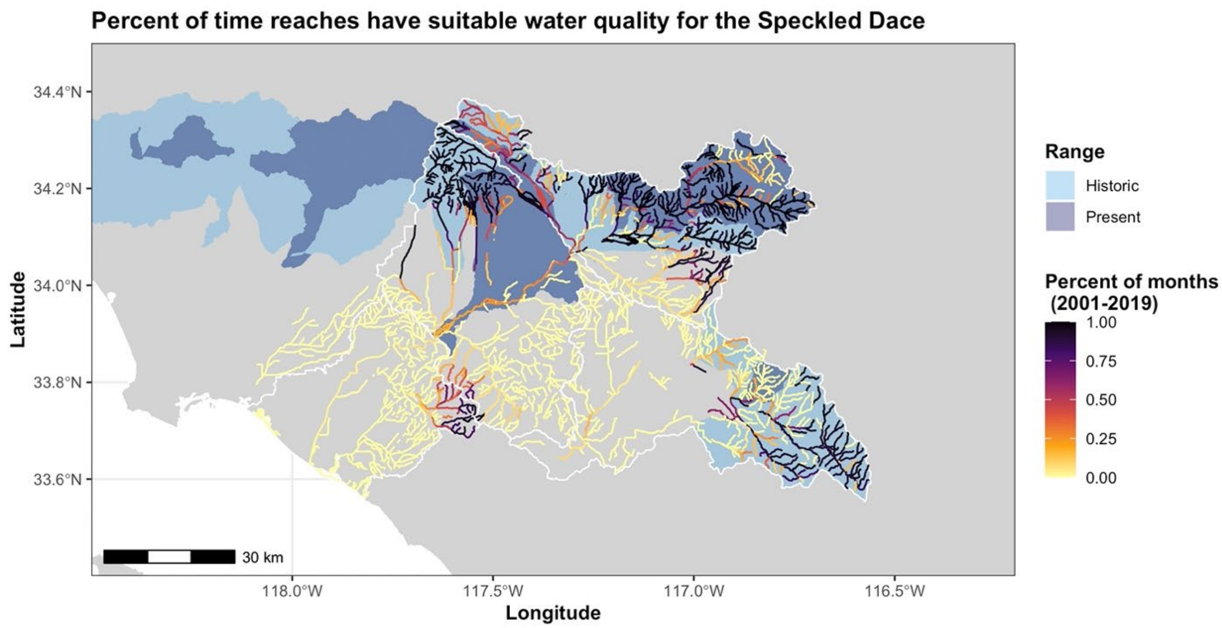


Figure 17. Streams with suitable water quality for the speckled dace *(Rhinichthys osculus)*, compared to historical and present-day distribution.

Discussion

This study demonstrates that national data sets can be used to develop models with high levels of performance suitable for state or regional applications. Our models performed well, explaining more than 70 percent of the variation in each water quality parameter across California. Since we created multiple models, including almost all major ions and integrated measures, we could look at water quality in greater detail than previous studies. This study builds off of Olson and Cormier (2019), who provided a national view of how specific conductivity reacts with differing temporal and spatial scales. In addition to expanding their effort to address a range of ionic parameters beyond specific conductivity, we took steps to bolster the confidence of watershed managers in California in applying these models. First, we increased the number of sites in California used for model training, and second, we assessed model performance within California, rather than at the national scale.

Our models' spatial and temporal sensitivity will aid in adjusting aquatic life and water quality thresholds for current climate patterns and will allow future water quality responses to climatic shifts to be estimated. Our model predictions have the potential to help us understand the effects of future climates on California streams. For example, these models can be used to estimate the future shifts in natural background water quality in California streams due to climate change, similar to work done by Olson and Cormier (2019). In addition to estimating future climatic shifts, our model predictions may help researchers study the effects of aquatic stress, metabolic rates, and oxygen demand by providing natural background levels to calculate the amount of divergence and its impact on aquatic species.

Salinization could be affected by climate change through several pathways, a few of which are likely to be more pronounced in the Santa Ana watershed and other parts of California. Under some scenarios, wet years may become more frequent, with high intensity rain events associated with atmospheric rivers becoming more common (Shields and Kiehl 2016). During these years, concentrations will likely be lower than normal (Figure 12). However, dry years may be more common and warmer overall (Swain et al. 2018, Albano et al. 2022), which could drive more saline conditions. Snowmelt, which has a small influence on streamflow in the highest elevations of the Santa Ana watershed, is likely to have an even smaller effect in the future (Hammond et al. 2018, Bolotin et al. 2023), leading to increased concentrations in headwater areas. Climate change may also exacerbate river salinization through sea-level rise (Benson et al. 2019, McIver II 2022), although this mechanism is unlikely to affect many stream-miles in the Santa Ana Watershed.

The seasonal prediction capabilities of our models provide land managers and researchers with a way of identifying streams suffering from freshwater salinization syndrome (FSS). Kaushal et al. (2018) argue that freshwater salinization syndrome has many far-reaching effects regarding ground and surface water, the quality of drinking water, and ecosystem functions. Given the seasonal predictions our models can make, we suggest water quality monitoring should occur multiple times a year and consider the sampling year's precipitation levels. These patterns will help researchers and managers target areas that need the greatest conservation and restoration efforts to decrease the occurrence of freshwater salinization syndrome and the metabolic stress on native aquatic organisms.

PART 2: EVALUATE BIOLOGICAL RESPONSE TO ELEVATED IONIC CONCENTRATIONS

Introduction

Water quality targets should be informed not only by an understanding of natural variability, but also by the biological response as parameters increase beyond natural levels (Hawkins et al. 2010, Cormier et al. 2018). Biological response models are one of the key pieces of evidence recommended by the U.S. Environmental Protection Agency that regulators should evaluate when establishing water quality criteria (Davis and Simon 1995, U.S. Environmental Protection Agency 2000, Cormier et al. 2018). These response models require two elements: A measure of stress, and a measure of ecological condition. The former is provided by the modeled reference expectations of ionic parameters developed in Part 1 of this study: ratios of observed-to-expected values greater than 1 indicate that a stream has been affected by salinization. Measures of ecological condition may be provided by indices of biotic integrity, which provide a broad-based measure of aquatic ecosystem health (Karr 1991). California has several biointegrity indices that are suited to building biological response models. The California Stream Condition Index (CSCI; Mazor et al. 2016) is based on benthic macroinvertebrates, and the Algal Stream Condition Indices (ASCIs; Theroux et al. 2020) are based on benthic diatoms (ASCI_D) or a hybrid of diatom and soft-bodied algal assemblages (ASCI_H). These indices have already been used to model ecosystem responses to flow alteration (Mazor et al. 2018) and eutrophication (Mazor et al. 2022). Thus, response models that assess changes in California's biointegrity indices based on alterations from natural levels of ionic parameters would help managers identify thresholds that protect aquatic life.

Benthic macroinvertebrates have well-known responses to stream salinization (Wallace and Biastoch 2016, Kefford 2019, Orr et al. 2022). Kefford (2019) hypothesized that the sensitivity of mayflies is related to the increased energy burden of maintaining internal osmolar concentrations, disruption of pH regulation processes, and direct toxic effects. Several studies have also documented a synergistic effect where salinization heightens the toxicity of other pollutants (Velasco et al. 2019, Walker et al. 2020).

Salinity has also been known to be a primary driver of benthic diatom assemblage composition (van Dam et al. 1994, Porter-Goff et al. 2013, Noune et al. 2023), although non-diatom algal taxa are less well studied (Theroux et al. 2020). Noune et al. (2023) demonstrated that increased salinity is associated with a higher frequency of deformities of diatom valves, leading to a loss of sensitive species. Salinization not only affects the composition of benthic algal communities, it may also reduce stream productivity and photosynthesis rates, potentially exacerbating impacts from eutrophication (Herbst and Blinn 1998) and lead to major changes in food web structure (East et al. 2017). Additionally, salt exposure can lead to the proliferation of toxin-producing cyanobacteria in eutrophic systems (Osburn et al. 2023). Physiological stress and energetic burdens of maintaining internal osmolar concentrations are thought to be the primary drivers reducing populations of sensitive algal taxa in salinized environments (Herbst and Blinn 1998).

We followed previous approaches in developing biointegrity response models for the purposes of threshold identification (e.g., Heiskary and Bouchard 2015, Mazor et al. 2018, 2022, Poikane et al. 2022). First, we compared biointegrity scores to a range of reference-based thresholds to classify streams as meeting or not meeting biointegrity goals. At the same time, we calculated the ratio of observed-to-expected levels of ionic parameters to characterize levels of salinization stress. Then, we calibrated logistic regression models to calculate the probability of meeting biointegrity goals as stress increases. We then identified levels of stress associated with a range of probabilities (80% to 99%). Finally, we converted these levels of stress to thresholds by multiplying them by segment- and month-specific reference levels of the ionic parameter. Once these thresholds were identified, we calculated the percentage of sites exceeding each threshold in the Santa Ana watershed. In addition, we compared these thresholds to basin plan objectives for selected segments.

Methods

Conceptual approach

To evaluate assessment threshold concentrations that are likely to maintain good biological integrity, we first assembled a data set to characterize biointegrity and ionic stressors. Biointegrity was characterized with three bioassessment indices: the California Stream Condition Index (CSCI; Mazor et al. 2016) for benthic macroinvertebrates, and two Algal Stream Condition Indices (ASCIs; Theroux et al. 2020) for diatoms (ASCI_D) and two combined assemblages (diatoms and soft-bodied algae; ASCI_H). We characterized ionic stressor gradients for five ions (chloride, sulfate, sodium, calcium, and magnesium) and four integrated measures (TDS, hardness, alkalinity, and specific conductivity) by calculating the ratio of observed concentrations over the expected, predicted concentrations (Part 1). We chose a stressor gradient that accounted for natural variation and acknowledged that some increases in concentrations have bigger impacts in some streams than others. We classified sites as attaining or not attaining a biointegrity goal, and then modeled the likelihood of attainment based on an ionic indicator using logistic regression, one indicator at a time. Numeric values of each ionic indicator associated with a high probability of attaining a range of biointegrity goals were then identified. We evaluated several approaches for selecting biointegrity goals, and calculated thresholds for each of these goals. To evaluate these thresholds, we compared them to basin plan objectives for selected segments and parameters. Finally, we used the resulting thresholds to assess the extent of streams potentially affected by salinization in the Santa Ana watershed (Figure 18).

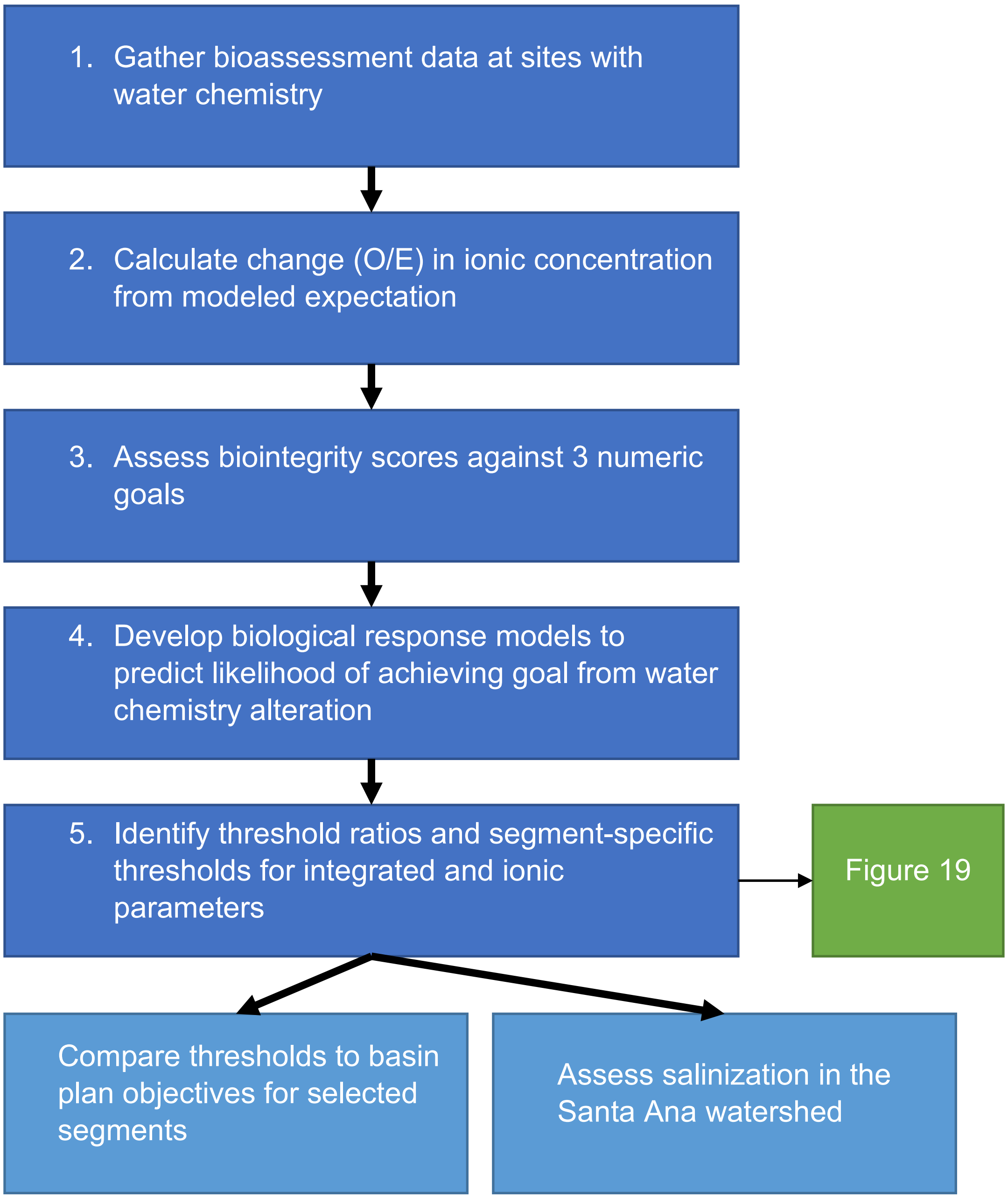


Figure 18. A flow chart of steps in the development of models to evaluate biological response to elevated ionic concentrations.

Gather bioassessment data at sites with water chemistry

Building from the set of sites with observed ionic parameters in California, we identified the subset of these sites where bioassessment data had been collected between 2001 and 2019 (that is, the dates for which model predictions from Part 1 were available). Biological data was extracted from the California Environmental Data Exchange Network (CEDEN, https://ceden.waterboards.ca.gov/) and the Storm Monitoring Coalition (SMC, https://smc.sccwrp.org/), and were used to calculate CSCI or ASCI scores. Using the predictions from models created in Part 1, reference conditions for each ionic parameter (calculated for each month from 2001 to 2019) were paired with observed water chemistry data at each bioassessment location. This aggregation resulted in a data set of nearly 3000 samples with at least one bioassessment index score and one observed ionic parameter (Table 9). These 3000 samples were collected at over 2000 sites, representing more than 1800 unique stream segments.

Table 9. Number of samples, sites and stream-segments (COMIDs) used to develop biological response models.

Analyte	Santa Ana COMIDs	California COMIDs	Santa Ana Sites	California Sites	Santa Ana Samples	California Samples
CSCI	185	1706	259	1970	338	2676
ASCI_D	94	1250	121	1410	143	1825
ASCI_H	93	1218	120	1377	142	1787
Calcium	18	396	18	430	18	463
Chloride	79	1277	97	1428	112	1803
Sodium	18	243	18	245	18	258
Magnesium	18	320	18	335	18	368
Sulfate	78	1235	95	1381	106	1656
Alkalinity	109	1386	139	1587	180	2179
Hardness	72	1124	87	1263	94	1499
Sp.Cond	183	1714	258	1986	335	2732
TDS	42	285	46	342	49	374

Calculate change (O/E) in ionic concentration from modeled expectation

We characterized ionic stressor gradients for every ionic parameter by calculating the ratio of observed concentrations over the expected reference concentrations (derived in Part 1). We chose this formulation (O/E) over other possible formulations (e.g., O-E or (O-E)/E) because it provided a simple and consistent way to characterize alterations of different parameters that have different scales, or even different units (e.g., mg/L vs µS/cm).

Assess biointegrity scores against 3 numeric goals

Samples were classified as being in either good/intact biological condition or poor/altered condition. Several biointegrity goals were used to identify intact or altered condition in order to relate those states back to ionic thresholds. We evaluated scores corresponding to the 30th, 10th, and 1st percentiles at reference sites (Ref30, Ref10, and Ref01, respectively; Mazor et al. 2016, Theroux et al. 2020). The 10th percentile of the CSCI has been used to identify impaired waterbodies in recent versions of the Integrated Report (e.g., California State Water Resources Control Board 2022). Every sample was classified as meeting or not meeting each of these goals. Numeric values associated with biointegrity goals are presented in Table 10.

Table 10. Numeric values associated with biointegrity goals.

Reference percentiles	CSCI	ASCI_D	ASCI_H
30th	0.92	0.94	0.94
10th	0.79	0.86	0.86
1st	0.63	0.75	0.75

Develop biological response models to predict likelihood of achieving goal from water chemistry alteration

We developed logistic regressions to calculate the probability of meeting biointegrity thresholds at increasing levels of ionic stress (characterized as ratios between observed and expected (O/E) concentrations of ionic parameters). Logistic regression models were created with the probability of good biological condition as the response variable and the observed/expected ratio as the predictor variable. The glm function in R, with a binomial error distribution and a logit link function was used for all logistic regressions (R Core Team 2022). Models were developed for every ionic parameter (chloride, sulfate, sodium, calcium, magnesium, TDS, hardness, alkalinity, and specific conductivity), bioassessment index (CSCI, ASIC_D, ASCI_H), and biointegrity goal (1st, 10th, and 30th percentile; 81 models).

The accuracy of the models was assessed as the percent of calibration or validation samples with biointegrity status consistent with model predictions (i.e., attaining biointegrity goals when the model predicted 50% or greater probability of attaining them, and not attaining them when the probability was lower). For each model, the data was split into calibration (80%) and validation (20%) subsets. These subsets were done independently of each other, as well as of the calibration-validation split used in Part 1; therefore, a site may be used to calibrate one model, and to validate another model. Unlike the data used in Part 1, these data included non-reference sites where stress from salinization was expected to have occurred.

Identify thresholds for integrated and ionic parameters

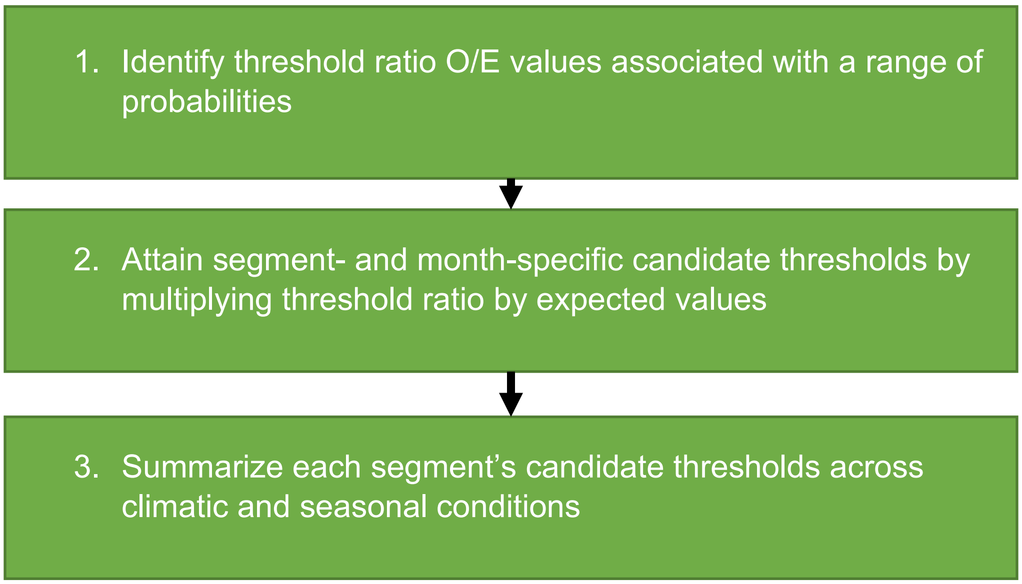


Figure 19. Steps in identifying thresholds for integrated and ionic parameters.

Identify threshold ratio O/E values associated with a range of probabilities

Significant logistic regression models ($p < 0.05$) for each combination of ionic parameter, bioassessment index, and biointegrity goal were then used to identify O/E ratios that were predictive of a ≥0.8, ≥0.9, or ≥0.95 probabilities of good intact biological condition occurring (Figure 19). First, we established a range of values to evaluate for each O/E ratio for each ion (from 1 to a maximum of 15 times expected background levels for alkalinity, 20 hardness, 20 TDS, 75 chloride, 25 calcium, 40 magnesium, 30 sodium, 40 sulfate, or 15 specific conductivity). These ranges were determined by preliminary visual inspection of the data; specifically, we plotted the predicted probabilities associated with the O/E ratios in the calibration data set and attempted to identify the range where probabilities decreased most rapidly. We then ran the models for 1,000 values along this range, as well as 95% confidence limits (as 1.96 times the standard error). These increasing O/E values represent a gradient of increasing stress from salinization.

For each O/E value, we predicted the probability of achieving biointegrity goals; predictions and confidence limits were expressed in terms of the linear predictors before transforming into probabilities through an inverse-link function. To account for background levels of stress that may degrade biointegrity when the ion concentration was at natural levels, model outputs were divided by the calculated probability when the O/E was set to one. For example, if the probability of good CSCI when chloride was at natural background levels was equal to 0.8, we calculated the relative probability at higher levels of chloride by dividing the model predictions by 0.8 (transformations were actually calculated on model outputs and confidence intervals expressed in the scale of the linear predictors, which were then transformed into probabilities using an inverse link function). These relativized probabilities represent the likelihood of attaining the biointegrity goal, given background levels of other types of disturbance. Thus, if in the previous example, a model predicted a probability of 0.6 when Chloride was elevated by a certain degree, the relative probability was calculated as 0.75 (i.e., 0.6/0.8).

Attain segment- and month-specific candidate thresholds

The previous step in the analysis results in a ***threshold ratio*** O/E that could apply to all stream segments, which have a range of expected values (E) that vary depending on the month and year. We converted this threshold ratio into a range of ***segment- and month-specific threshold concentrations*** by multiplying the ratio by the segment- and month-specific expected values. For example, if a model identified a threshold ratio of 2, and a stream segment had an expected value of 100 for a given month, then the threshold concentration would be 200 for that month. These thresholds were calculated for all 2,845 segments in the Santa Ana watershed for every month between 2001 and 2019, resulting in 228 thresholds per segment for each of the 9 analytes, 3 indices, 3 biointegrity goals, and 3 probabilities (over 150 million thresholds total for the Santa Ana watershed).

Summarize each segment's candidate thresholds across climatic and seasonal conditions

The large number of thresholds calculated for each stream segment underscores the need to summarize across climatic and seasonal conditions. We summarized ionic thresholds across climatic conditions (wet, dry, and normal years) and sampling period (whether the sample was measured in months between April and September or not), as well as an overall average for each specific reach. Climatic conditions were calculated by categorizing the years 2001-2019 into thirds based on annual precipitation. Annual precipitation was obtained from the weather station at the John Wayne Airport in Santa Ana (NOAA Weather Station USW00093184; https://www.ncdc.noaa.gov/cdo-web/datasets/GHCND/stations/GHCND:USW00093184/detail). As noted above, this weather station is a good indicator of overall conditions in the lower elevations of the Santa Ana watershed, whereas higher elevations may show different patterns outside of extremely wet or extremely dry years. We report these ionic thresholds at concentrations corresponding to 80%, 90%, and 95% relative probabilities, allowing policy makers to choose their tolerance for the risk of failing to meet biointegrity goals.

Compare thresholds to basin plan objectives for selected segments

In a selected number of segments, we compared the expected conditions of each segment to the ionic thresholds expected to protect indices at Ref10 and the Santa Ana Basin Plan Objectives (Regional Water Quality Control Board-Santa Ana 2019). We evaluated 10 segments: Strawberry Creek and San Jacinto River, North Fork; Big Bear Lake Tributaries: Rathbone (Rathbun) Creek; Barton Creek; San Antonio Creek; Chino Creek Reach 1a: Santa Ana River confluence to downstream of confluence with Mill Creek (Prado Area); Chino Creek 1b: Confluence of Mill Creek (Prado Area) to beginning of concrete-lined channel south of Los Serranos Road; San Jacinto River Reach 3: Canyon Lake to Nuevo Road; San Jacinto River Reach 6: Poppet Creek to Cranston Bridge; Santa Ana River Reach 3: Prado Dam to Mission Blvd in Riverside; and Santa Ana River Reach 6: Seven Oaks Dam to Headwaters. Segments were chosen where Basin Plan objectives existed, as well as to include segments across multiple elevations.

Assess salinization in the Santa Ana watershed

In order to assess the extent of salinization in the Santa Ana watershed, we compared mean observed values of each ionic parameter against the mean segment-specific thresholds identified above. We then calculated the percentage of sites exceeding the threshold for each parameter.

Results

Relationship between ionic stressors and biointegrity indices

Biointegrity index scores exhibited a negative, but noisy, relationship with ionic stressors (Figure 20). Although high index scores were sometimes observed at sites with high ionic stress, these observations were rare. At low levels of ionic alteration (e.g., O/E < 1), a wide range of bioassessment index scores were observed. This “wedge-shaped relationship” is commonly found with biological stress-response models (e.g., Mazor et al. 2018, 2022) because sites may be affected by stressors not included in the model, such as other ionic parameters, as well as stressors unrelated to salinization (e.g., eutrophication, or habitat alteration). That is, sites where a certain ionic parameter is unaltered might have poor biology due to other stressors.

Spearman correlations between biointegrity index scores and ionic stressors were always negative, ranging from -0.68 (between ASCI_H and Sodium) and -0.18 (CSCI and Alkalinity; Table 11).

Table 11. Spearman correlation coefficients between ionic stressors (expressed as Observed/Expected ratios) and index scores.

Analyte	CSCI	ASCI_D	ASCI_H
Alkalinity	-0.18	-0.24	-0.20
Calcium	-0.20	-0.49	-0.51
Chloride	-0.41	-0.49	-0.45
Hardness	-0.29	-0.40	-0.36
Magnesium	-0.21	-0.54	-0.55
Sodium	-0.28	-0.55	-0.68
Sp.Cond	-0.23	-0.35	-0.30
Sulfate	-0.23	-0.40	-0.34
TDS	-0.52	-0.48	-0.42

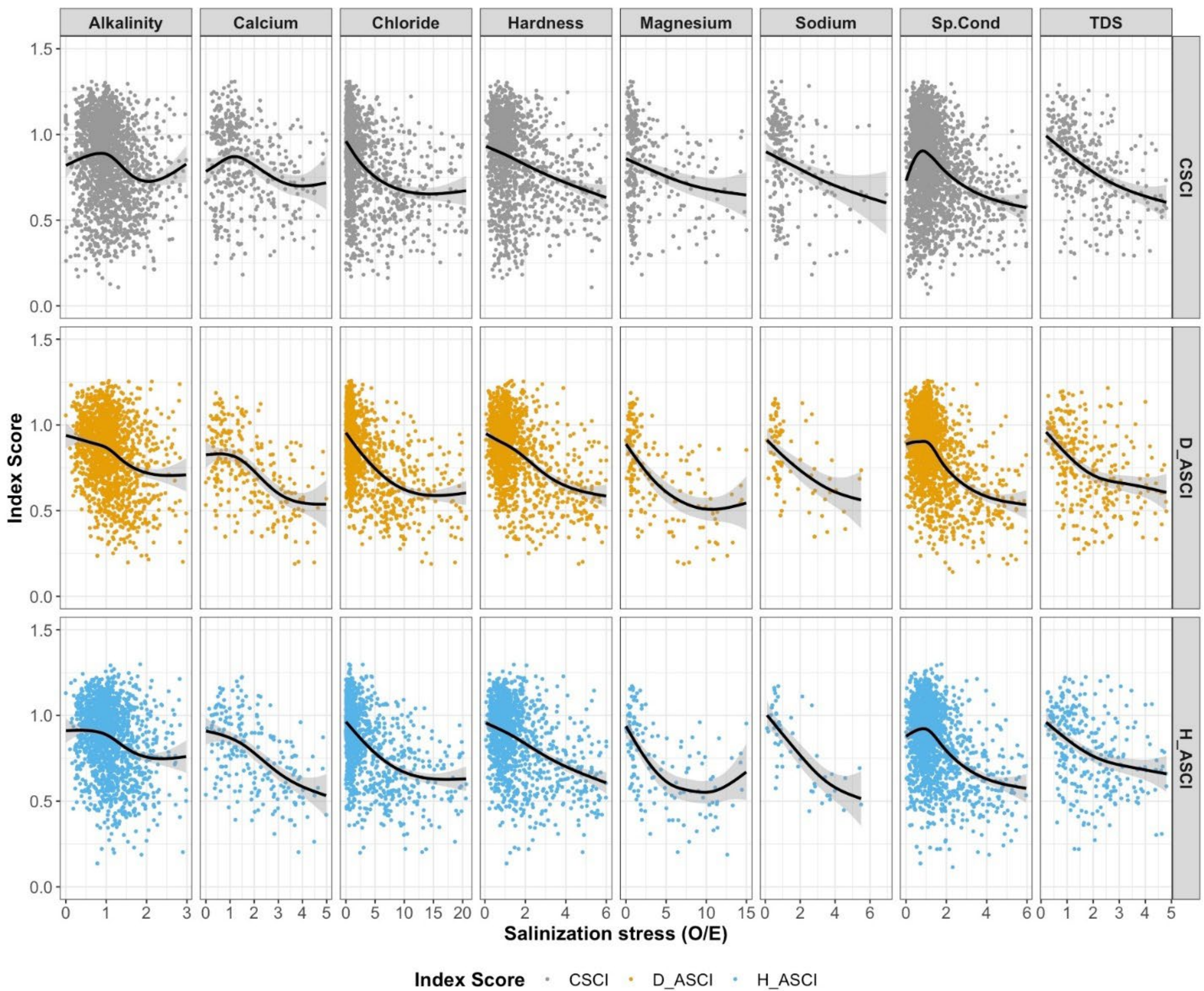


Figure 20. Biointegrity scores in relation to ionic stressor ratios (observed/expected concentrations). Black lines represent a fit from a generalized additive model; gray ribbons represent the 95% confidence interval around the fit. The x-axes have been truncated to highlight areas where the model shows the greatest response to ionic gradients.

Biological response model performance

Logistic regression models were usually successful in predicting the likelihood of attaining a biointegrity goal (Table 12, Figure 21, Figure 22, Table S1). Of the 81 models, 71 of the models had statistically significant coefficients ($p < 0.05$). Magnesium models were unable to predict a Ref01 goal for CSCI, ASCI_D or ASCI_H, a Ref10 goal for CSCI or ASCI_D, and a Ref30 goal for CSCI (Table S1). Sodium models performed poorly at predicting a Ref01 goal for the ASCI_D and ASCI_H, a Ref10 goal for ASCI_H, and Ref30 goal for ASCI_H. Among the models with statistically significant coefficients, accuracy ranged from 61% to 74% at calibration sites.

Table 12. Performance of biological response models to predict probability of meeting biointegrity goals at increasing levels of ionic stress. Only models for the "Ref10" biointegrity goal are shown (results for Ref01 and Ref30 goals in Table S1). Cal: Calibration. Val: Validation. P-values are represented as * <0.05, ** <0.01, * <0.001. Note: the total number of calibration and validation samples in this table is less than the number of samples in Table 9 because a sample needed to have both chemistry results and bioassessment index scores to be used in modeling.**

		# Samples		Accuracy rate (%)		Coefficient		Intercept		
Analyte	**Index**	**Cal**	**Val**	**Cal**	**Val**	**estimate**	**std error**	**estimate**	**std error**	**P**
Alkalinity	CSCI	1706	427	63	63	-0.445	0.081	1.018	0.105	***
Alkalinity	ASCI_D	1335	334	61	63	-0.676	0.106	0.879	0.129	***
Alkalinity	ASCI_H	1327	332	62	60	-0.643	0.103	1.047	0.130	***
Calcium	CSCI	364	91	61	62	-0.290	0.069	0.651	0.162	***
Calcium	ASCI_D	228	58	67	67	-0.726	0.147	0.371	0.252	***
Calcium	ASCI_H	193	49	69	67	-0.389	0.106	0.234	0.273	***
Chloride	CSCI	1414	354	70	71	-0.108	0.012	0.974	0.069	***
Chloride	ASCI_D	1260	315	70	71	-0.164	0.017	0.664	0.073	***
Chloride	ASCI_H	1219	305	68	69	-0.089	0.012	0.674	0.071	***
Hardness	CSCI	1176	294	69	68	-0.373	0.041	1.150	0.094	***
Hardness	ASCI_D	1136	285	67	63	-0.666	0.064	1.125	0.106	***
Hardness	ASCI_H	1097	275	69	65	-0.585	0.056	1.234	0.106	***
Magnesium	CSCI	288	73	54	49	0.000	0.001	0.183	0.119	0.904
Magnesium	ASCI_D	152	39	66	69	0.000	0.001	-0.690	0.173	0.776
Magnesium	ASCI_H	117	30	72	73	-0.222	0.065	0.227	0.284	**
Sodium	CSCI	215	54	66	59	-0.398	0.107	0.836	0.206	***
Sodium	ASCI_D	83	21	66	76	-1.005	0.368	0.806	0.406	**
Sodium	ASCI_H	48	12	79	83	-0.144	0.116	0.267	0.386	0.213
Sp.Cond	CSCI	2152	539	66	71	-0.461	0.045	1.041	0.075	***

		# Samples		Accuracy rate (%)		Coefficient		Intercept		
Analyte	**Index**	**Cal**	**Val**	**Cal**	**Val**	**estimate**	**std error**	**estimate**	**std error**	**P**
Sp.Cond	ASCI_D	1480	371	65	70	-0.554	0.060	0.868	0.093	***
Sp.Cond	ASCI_H	1437	360	67	66	-0.456	0.053	0.953	0.091	***
Sulfate	CSCI	1303	326	69	68	-0.291	0.029	1.046	0.077	***
Sulfate	ASCI_D	1115	279	65	66	-0.224	0.031	0.421	0.076	***
Sulfate	ASCI_H	1076	269	65	64	-0.173	0.027	0.543	0.077	***
TDS	CSCI	291	73	71	74	-0.637	0.099	1.380	0.239	***
TDS	ASCI_D	263	66	74	68	-0.660	0.127	0.609	0.256	***
TDS	ASCI_H	263	66	70	73	-0.457	0.093	0.585	0.227	***

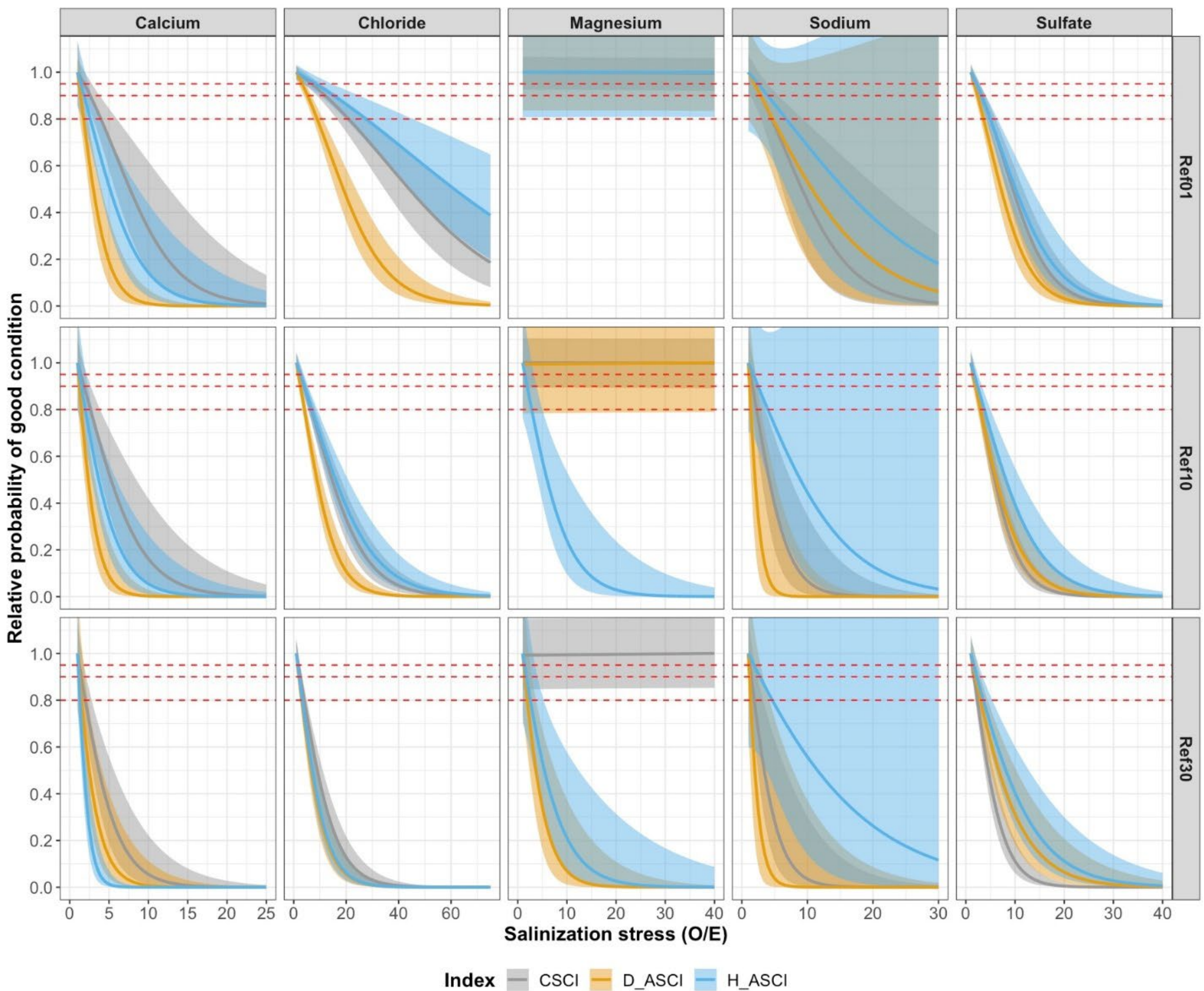


Figure 21. Relative probabilities of meeting biointegrity goals at increasing levels of ionic stress (defined as the ratio of observed to expected levels of ionic concentration, O/E). Dotted lines represent 80%, 90% and 95% relative probability.

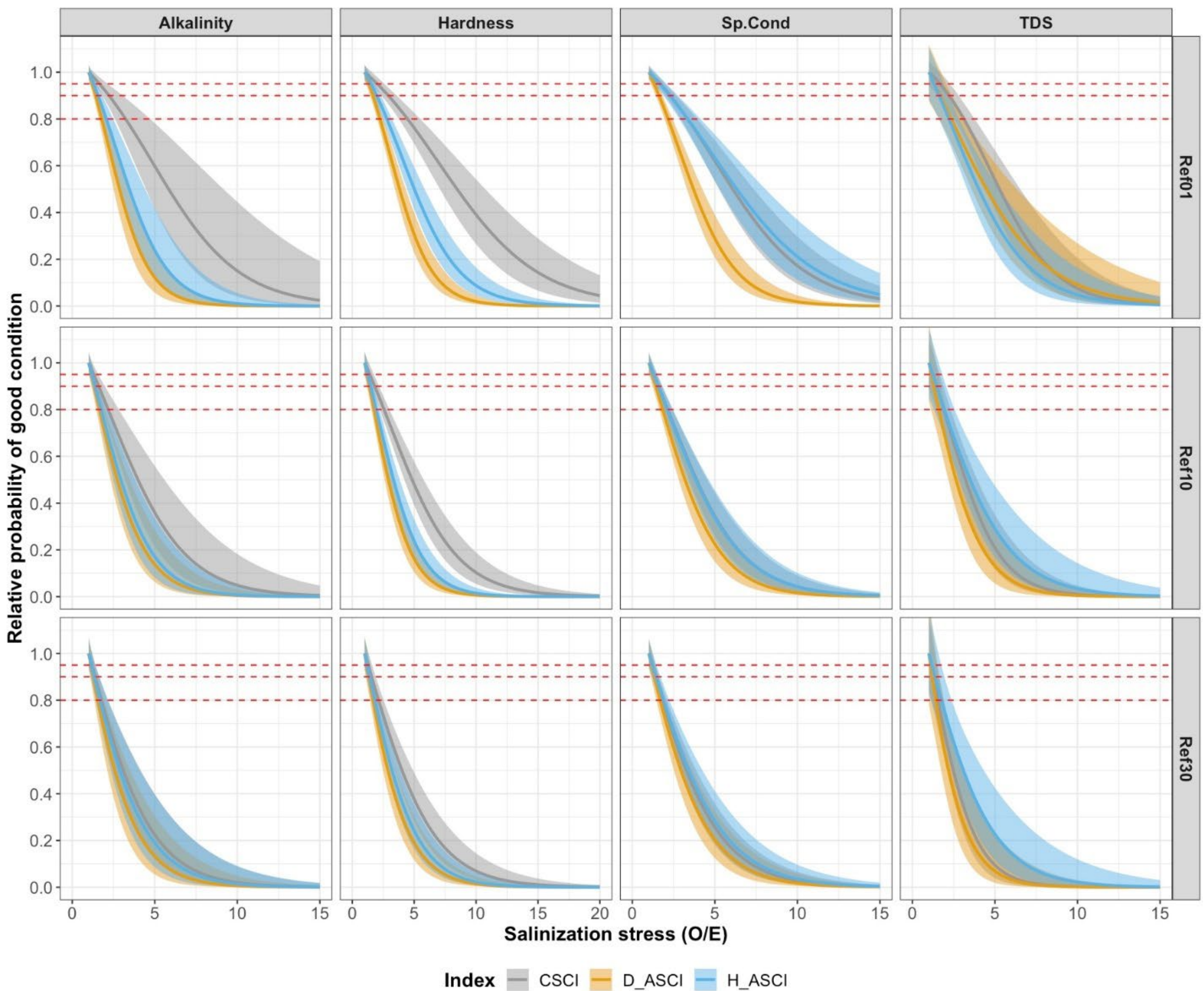


Figure 22. Relative probabilities of meeting biointegrity goals at increasing levels of integrated ionic stress. Dotted lines represent 80%, 90% and 95% relative probability.

The ASCI_D was more sensitive than other indices, resulting in lower observed-to-expected thresholds than the other indices (Table 13). In general, integrated parameters were more sensitive (i.e., had lower thresholds) than ionic parameters (Figure 23). Chloride was the least sensitive parameter overall, with thresholds generally well above those for other parameters, across all indices.

Table 13. Predicted observed/expected ionic thresholds corresponding to 80%, 90%, and 95% relative probabilities of meeting biointegrity goals. Only models for the "Ref10" biointegrity goal are shown (results for Ref01 and Ref30 goals in (Table S 2). The most sensitive index for each analyte is indicated with an asterisk (*). NI: Threshold not identified due to poor performance of the biological response model.

Analyte	Index	80% probability	90% probability	95% probability
Alkalinity	CSCI	2.18	1.60	1.29
Alkalinity	ASCI_D*	1.64	1.32	1.15
Alkalinity	ASCI_H	1.74	1.38	1.18
Calcium	CSCI	2.63	1.82	1.41
Calcium	ASCI_D*	1.48	1.22	1.10
Calcium	ASCI_H	1.96	1.48	1.22
Chloride	CSCI	6.63	3.89	2.48
Chloride	ASCI_D*	4.04	2.56	1.74
Chloride	ASCI_H	6.93	3.96	2.48
Hardness	CSCI	2.56	1.80	1.40
Hardness	ASCI_D*	1.74	1.36	1.19
Hardness	ASCI_H	1.93	1.48	1.23
Magnesium	CSCI	NI	NI	NI
Magnesium	ASCI_D	NI	NI	NI
Magnesium	ASCI_H*	2.80	1.90	1.43
Sodium	CSCI	2.22	1.61	1.29
Sodium	ASCI_D*	1.35	1.17	1.09
Sodium	ASCI_H	3.96	2.45	1.73
Sp.Cond	CSCI	2.14	1.57	1.29
Sp.Cond	ASCI_D*	1.83	1.42	1.21
Sp.Cond	ASCI_H	2.11	1.56	1.28
Sulfate	CSCI	2.95	2.02	1.51
Sulfate	ASCI_D*	2.95	1.98	1.47
Sulfate	ASCI_H	3.73	2.37	1.66
TDS	CSCI	1.90	1.46	1.22
TDS	ASCI_D*	1.59	1.29	1.14
TDS	ASCI_H	1.92	1.46	1.22

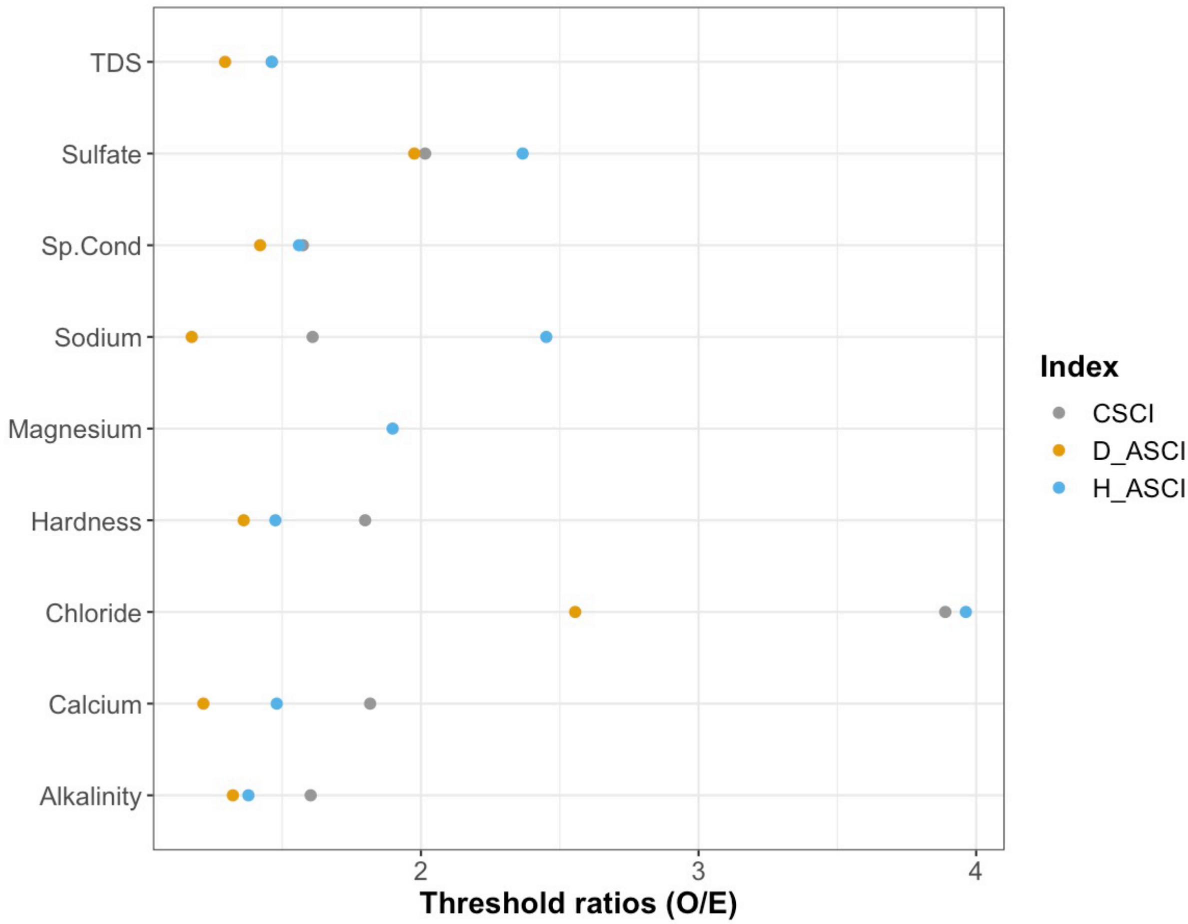


Figure 23. Threshold ratios (observed-to-expected values) for each parameter, calculated as a 90% probability of achieving an index score above the 10th percentile of reference.

Identification of ionic thresholds in the Santa Ana watershed

Consistent with predictions of natural levels of ionic concentrations, thresholds for most parameters were lowest in the high elevation tributaries in the San Gabriel, San Bernardino, and San Jacinto mountains as well as the mainstem Santa Ana river, and were highest in smaller low-elevation tributaries (Figure 24, Figure 25). When thresholds were compared across climatic conditions, thresholds tended to be higher in dry years (Figure 26); however, spatial variation in thresholds was far greater than seasonal or climatic variation.

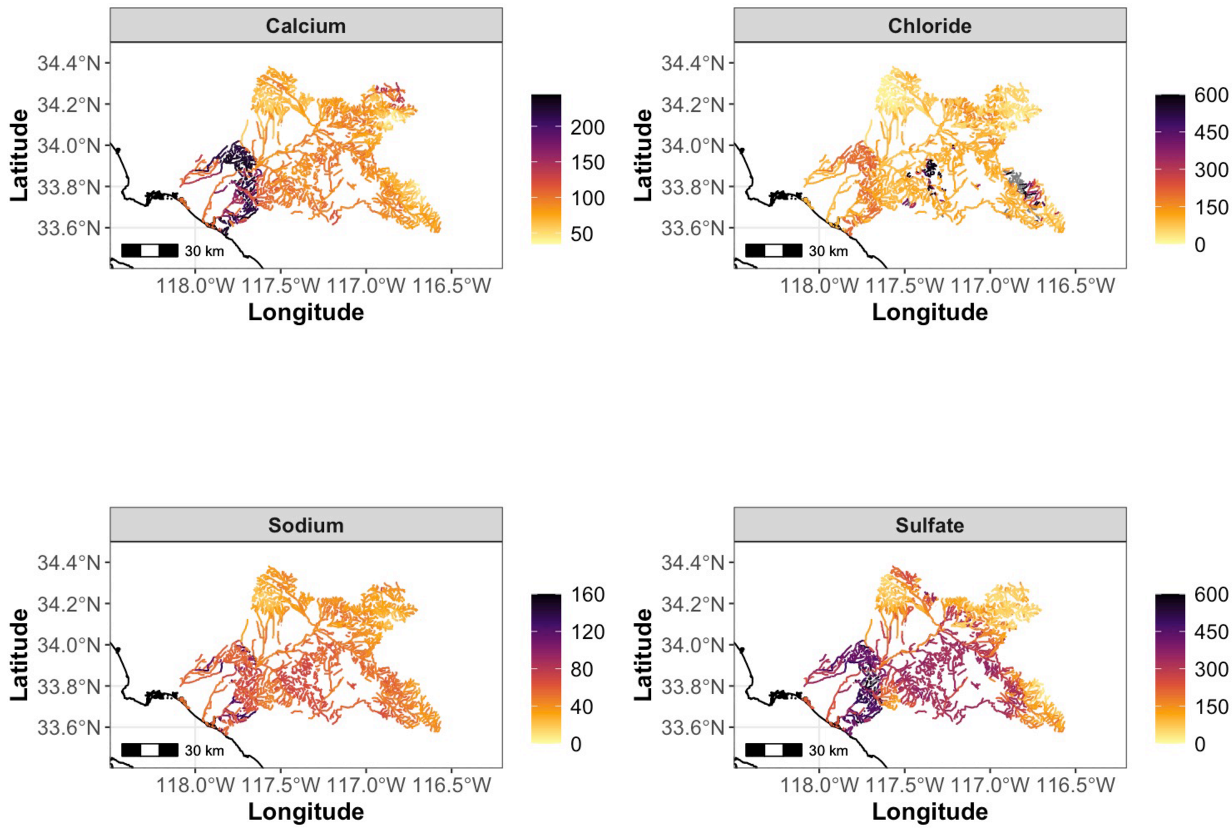


Figure 24. Average ionic thresholds based on 80% probability of achieving a CSCI Ref10 biointegrity goal.

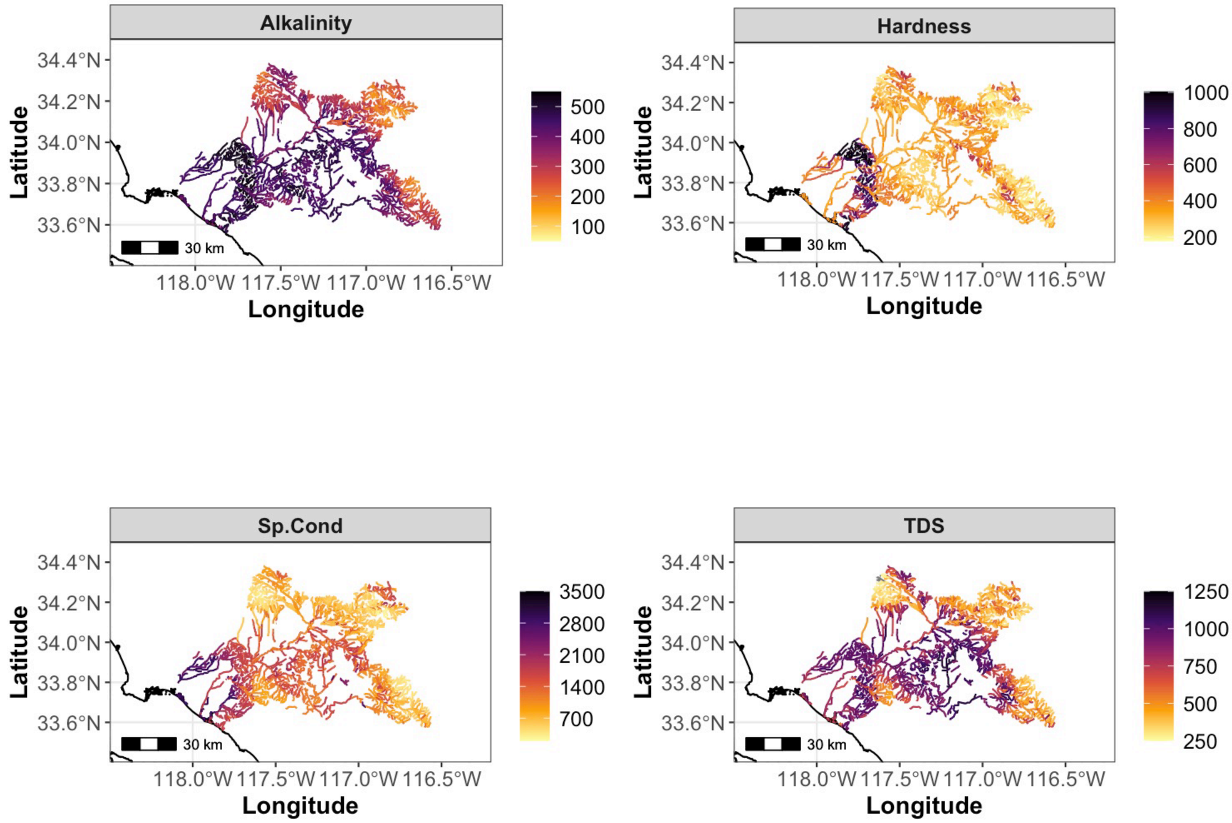


Figure 25. Average integrated ion thresholds based on 80% probability of achieving a CSCI Ref10 biointegrity goal.

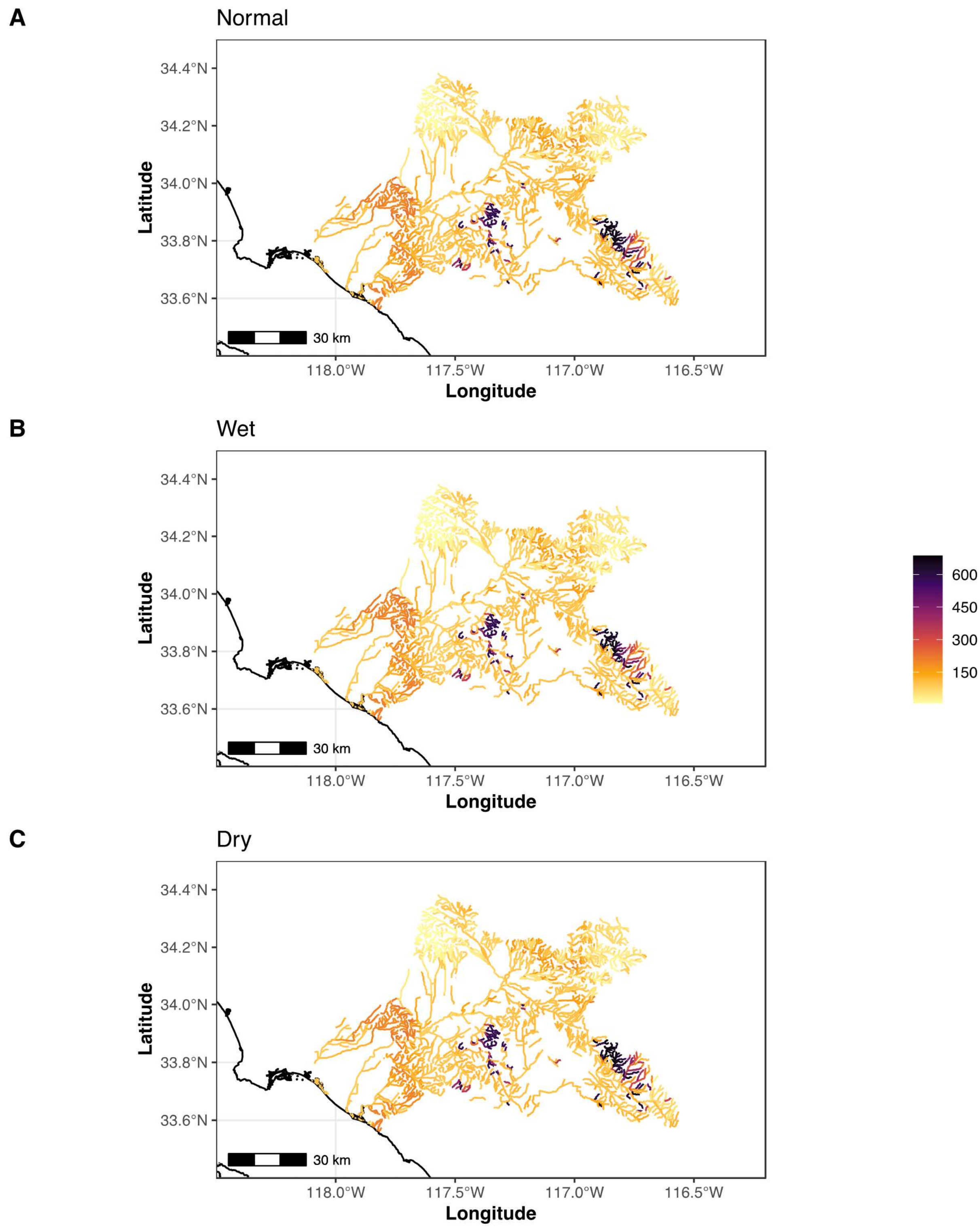
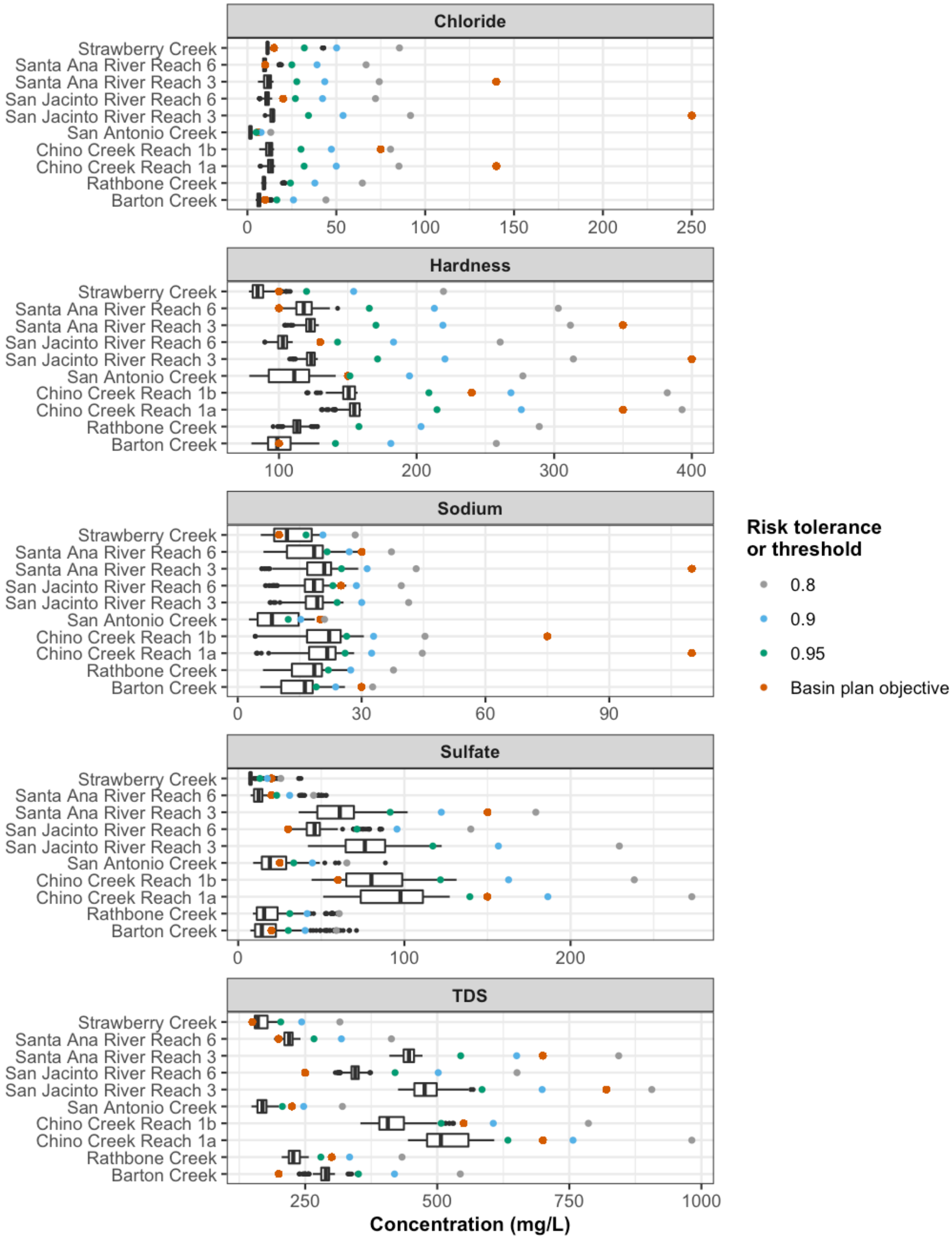


Figure 26. Chloride thresholds based on 80% probability of achieving a CSCI Ref10 biointegrity goal in (A) normal, (B) wet, and (C) dry years.

Comparison of thresholds to basin plan objectives for selected segments

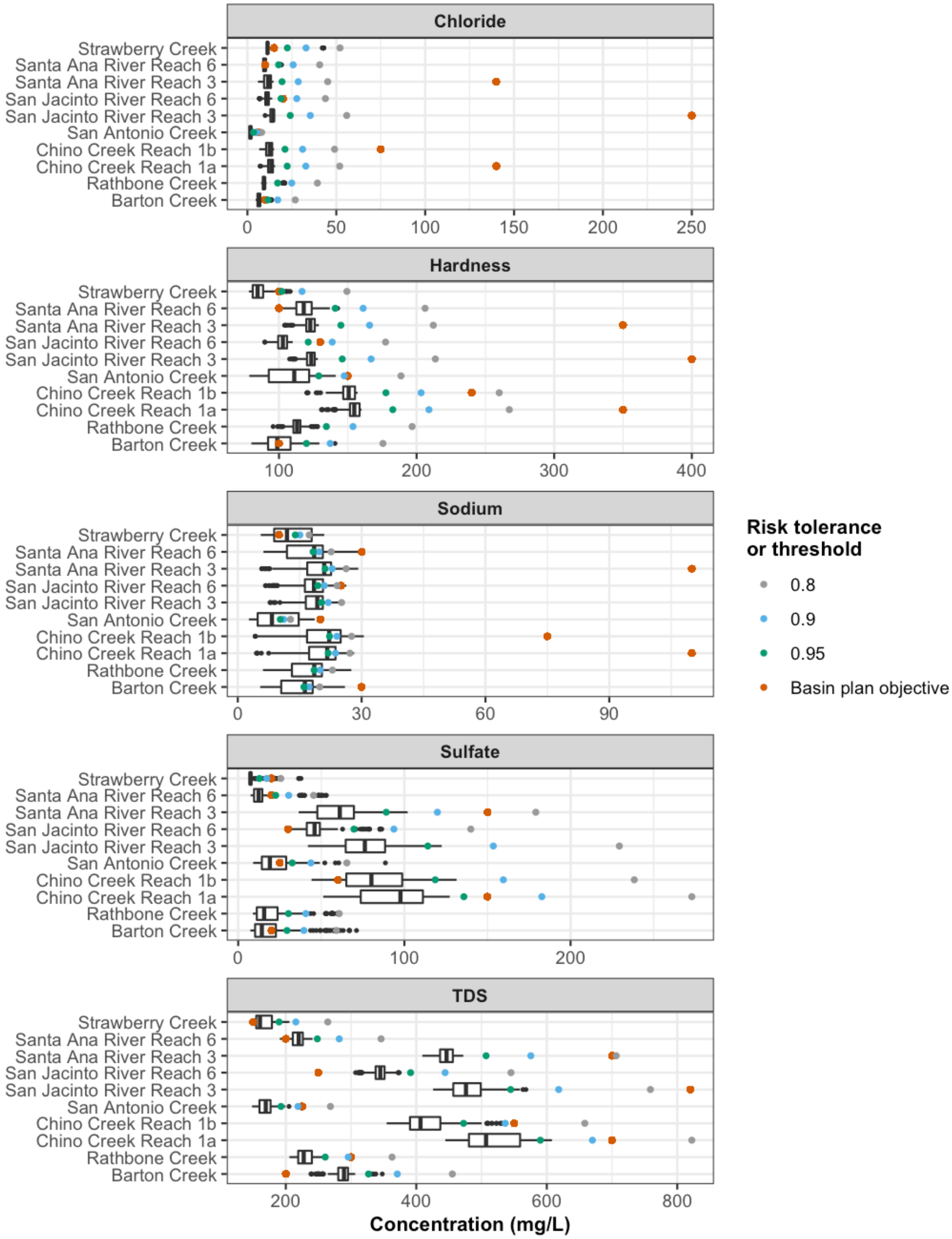
In many cases, basin plan objectives were close to thresholds identified from biological response models (Figure 27). For example, the basin plan objective for TDS in San Jacinto River Reach 3 (820 mg/L) was within the range of 80% thresholds identified for this reach (i.e., 724 to 905 mg/L, depending on the biointegrity index). However, there was evidence that aquatic life in some stream segments may not be adequately protected by basin plan objectives. For example, the Santa Ana River Reach 3 has a chloride objective of 140 mg/L, while biological response models predict a greater than 20% chance of a poor CSCI score when chloride exceeds ~75 mg/L (depending on the specific stream segment). Thus, the basin plan objective may not protect biointegrity in this reach. However, we also found reaches where basin plan objectives were not just lower than response model thresholds, they were lower than the predicted natural range of ionic parameters (e.g., TDS in San Jacinto River Reach 6). Because the segments in this analysis were selected at random, we cannot be sure which situations are more prevalent in the Santa Ana watershed. A more comprehensive analysis of all segments in the Santa Ana watershed is required to determine if basin plan objectives are protecting biointegrity in most streams, and if they are set lower than natural background levels.

A. CSCI



Chloride
Hardness
Sodium
Sulfate
TDS
Strawberry Creek
Santa Ana River Reach 6
Santa Ana River Reach 3
San Jacinto River Reach 6
San Jacinto River Reach 3
San Antonio Creek
Chino Creek Reach 1b
Chino Creek Reach 1a
Rathbone Creek
Barton Creek
0
50
100
150
200
250
100
200
300
400
0
30
60
90
0
100
200
250
500
750
1000
Concentration (mg/L)
Risk tolerance or threshold
0.8
0.9
0.95
Basin plan objective

B. D_ASCI


Chloride
Hardness
Sodium
Sulfate
TDS
Strawberry Creek
Santa Ana River Reach 6
Santa Ana River Reach 3
San Jacinto River Reach 6
San Jacinto River Reach 3
San Antonio Creek
Chino Creek Reach 1b
Chino Creek Reach 1a
Rathbone Creek
Barton Creek
0 50 100 150 200 250
100 200 300 400
0 30 60 90
0 100 200
200 400 600 800
Concentration (mg/L)
Risk tolerance or threshold
0.8
0.9
0.95
Basin plan objective

C. H_ASCI

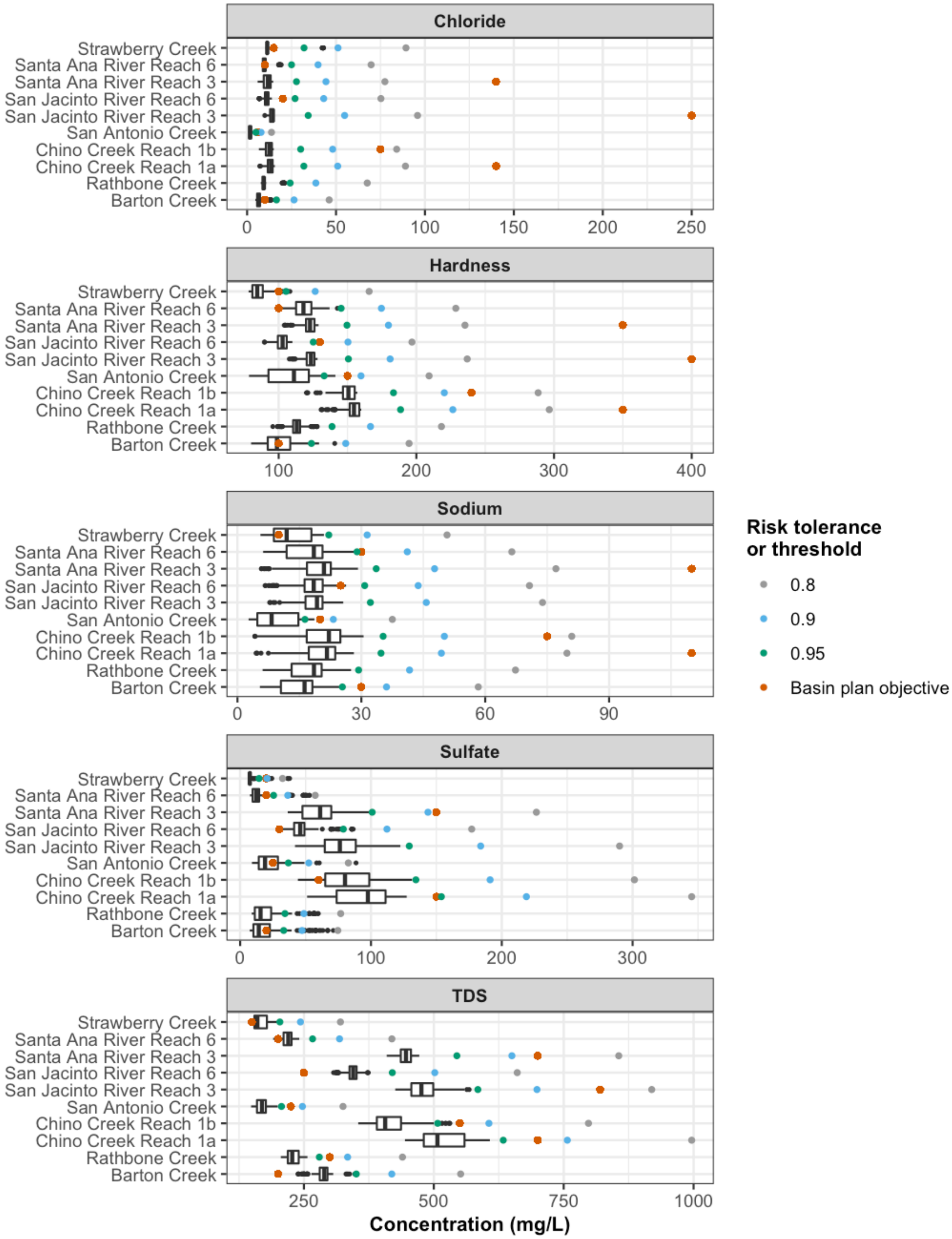


Figure 27. Comparison of expected concentrations in 9 segments to the thresholds protecting a Ref10 biointegrity goal and the Santa Ana Basin Plan Objectives for each index – A) CSCI, B) ASCI_D, and C) ASCI_H. Boxes represent the median expected concentrations and 1.5 standard deviation tails. Colored points represent the risk tolerances of protecting each index with a Ref10 goal – gray (80% probability), blue (90% probability), and green (95% probability). Red points represent the current Basin Plan Objectives.

Assessment of salinization in the Santa Ana watershed

Overall, most sites in the study met even the most stringent thresholds (i.e., 0.95 probability thresholds) for most parameters. Exceedances were most common for TDS, sodium, hardness, and chloride than for other parameters (Table 14, Figure 28). In particular, severe exceedances (i.e., exceedances of the least stringent threshold) were most common for sodium and chloride. Applying the most sensitive thresholds (i.e., thresholds based on ASCI_D scores attaining the 30th percentile of reference with a probability greater than 0.95), between a quarter to half of all streams within the Santa Ana watershed were at risk of salinization impacts to aquatic life. Exceedances were more common in urban portions of Orange County and the Inland Empire than in the upper watersheds (Figure 29, Figure 30), despite the fact that the numeric values of the thresholds were highest in low-elevation areas (Figure 24 to Figure 26). For analytes with high data density, clusters of sites exceeding the thresholds could be identified. For example, chloride exceedances were most evident along Coyote Creek, the mainstem of the Santa Ana River, San Diego Creek, and San Timoteo Canyon (Figure 29).

Table 14. The percentage of sites where the average observed ion concentration does not exceed the average threshold for each index, biointegrity goal, and probability of achieving the goal. NI: Threshold not identified due to poor performance of the biological response model.

Analyte	Index	Bio-integrity goal	n	% passing 0.95 thresholds	% passing 0.90 thresholds	% passing 0.80 thresholds	% failing all thresholds
Alkalinity	CSCI	Ref1	139	93	98	100	0
Alkalinity	CSCI	Ref10	139	80	92	98	2
Alkalinity	CSCI	Ref30	139	74	83	96	4
Alkalinity	ASCI_D	Ref1	139	77	86	96	4
Alkalinity	ASCI_D	Ref10	139	72	82	93	7
Alkalinity	ASCI_D	Ref30	139	68	78	90	10
Alkalinity	ASCI_H	Ref1	139	80	91	98	2
Alkalinity	ASCI_H	Ref10	139	74	84	95	5
Alkalinity	ASCI_H	Ref30	139	72	82	94	6
Calcium	CSCI	Ref1	20	80	90	100	0
Calcium	CSCI	Ref10	20	75	80	90	10
Calcium	CSCI	Ref30	20	65	75	85	15
Calcium	ASCI_D	Ref1	20	65	75	80	20
Calcium	ASCI_D	Ref10	20	60	65	75	25
Calcium	ASCI_D	Ref30	20	60	65	75	25
Calcium	ASCI_H	Ref1	20	75	80	90	10
Calcium	ASCI_H	Ref10	20	65	75	80	20
Calcium	ASCI_H	Ref30	20	60	65	70	30
Chloride	CSCI	Ref1	99	79	91	99	1
Chloride	CSCI	Ref10	99	65	69	79	21

Analyte	Index	Bio-integrity goal	n	% passing 0.95 thresholds	% passing 0.90 thresholds	% passing 0.80 thresholds	% failing all thresholds
Chloride	CSCI	Ref30	99	61	65	69	31
Chloride	ASCI_D	Ref1	99	66	70	83	17
Chloride	ASCI_D	Ref10	99	61	65	69	31
Chloride	ASCI_D	Ref30	99	58	63	66	34
Chloride	ASCI_H	Ref1	99	82	94	100	0
Chloride	ASCI_H	Ref10	99	65	69	79	21
Chloride	ASCI_H	Ref30	99	59	64	66	34
Hardness	CSCI	Ref1	87	82	93	97	3
Hardness	CSCI	Ref10	87	68	80	91	9
Hardness	CSCI	Ref30	87	57	74	83	17
Hardness	ASCI_D	Ref1	87	61	75	85	15
Hardness	ASCI_D	Ref10	87	51	63	78	22
Hardness	ASCI_D	Ref30	87	48	61	75	25
Hardness	ASCI_H	Ref1	87	72	82	92	8
Hardness	ASCI_H	Ref10	87	57	72	82	18
Hardness	ASCI_H	Ref30	87	51	68	80	20
Magnesium	CSCI	Ref1	20	100	100	100	0
Magnesium	CSCI	Ref10	NI	100	100	100	0
Magnesium	CSCI	Ref30	NI	100	100	100	0
Magnesium	ASCI_D	Ref1	NI	100	100	100	0
Magnesium	ASCI_D	Ref10	NI	100	100	100	0
Magnesium	ASCI_D	Ref30	20	65	65	90	10
Magnesium	ASCI_H	Ref1	NI	100	100	100	0
Magnesium	ASCI_H	Ref10	20	65	90	95	5

Analyte	Index	Bio-integrity goal	n	% passing 0.95 thresholds	% passing 0.90 thresholds	% passing 0.80 thresholds	% failing all thresholds
Magnesium	ASCI_H	Ref30	20	65	85	90	10
Sodium	CSCI	Ref1	20	70	75	80	20
Sodium	CSCI	Ref10	20	60	70	70	30
Sodium	CSCI	Ref30	20	55	65	70	30
Sodium	ASCI_D	Ref1	NI	70	75	85	15
Sodium	ASCI_D	Ref10	20	55	55	60	40
Sodium	ASCI_D	Ref30	20	55	55	60	40
Sodium	ASCI_H	Ref1	NI	75	75	95	5
Sodium	ASCI_H	Ref10	NI	70	70	75	25
Sodium	ASCI_H	Ref30	NI	70	75	85	15
Sp.Cond	CSCI	Ref1	260	85	95	97	3
Sp.Cond	CSCI	Ref10	260	74	82	93	7
Sp.Cond	CSCI	Ref30	260	70	77	88	12
Sp.Cond	ASCI_D	Ref1	260	75	83	94	6
Sp.Cond	ASCI_D	Ref10	260	70	77	88	12
Sp.Cond	ASCI_D	Ref30	260	67	75	85	15
Sp.Cond	ASCI_H	Ref1	260	84	94	97	3
Sp.Cond	ASCI_H	Ref10	260	73	81	93	7
Sp.Cond	ASCI_H	Ref30	260	70	77	89	11
Sulfate	CSCI	Ref1	NI	87	93	97	3
Sulfate	CSCI	Ref10	97	75	84	93	7
Sulfate	CSCI	Ref30	97	73	78	87	13
Sulfate	ASCI_D	Ref1	97	79	87	93	7
Sulfate	ASCI_D	Ref10	97	75	82	93	7

Analyte	Index	Bio-integrity goal	n	% passing 0.95 thresholds	% passing 0.90 thresholds	% passing 0.80 thresholds	% failing all thresholds
Sulfate	ASCI_D	Ref30	97	75	82	93	7
Sulfate	ASCI_H	Ref1	97	86	93	97	3
Sulfate	ASCI_H	Ref10	97	78	88	93	7
Sulfate	ASCI_H	Ref30	97	77	87	93	7
TDS	CSCI	Ref1	46	74	80	96	4
TDS	CSCI	Ref10	46	67	74	78	22
TDS	CSCI	Ref30	46	63	67	74	26
TDS	ASCI_D	Ref1	46	67	74	83	17
TDS	ASCI_D	Ref10	46	63	67	74	26
TDS	ASCI_D	Ref30	46	61	67	67	33
TDS	ASCI_H	Ref1	46	67	74	80	20
TDS	ASCI_H	Ref10	46	67	74	78	22
TDS	ASCI_H	Ref30	46	67	67	74	26

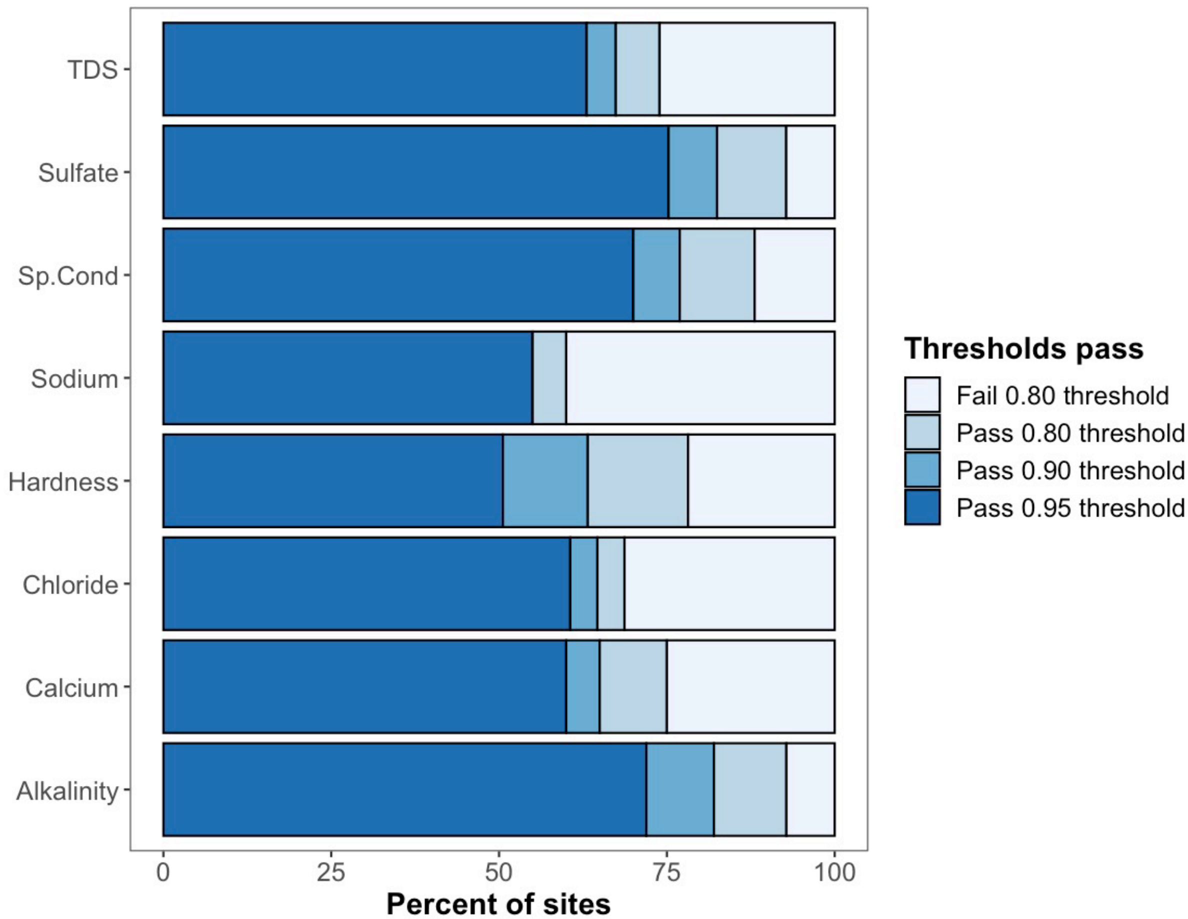


Figure 28. Percent of sites meeting thresholds for each analyte. Results for the ASCI_D response model with the "Ref10" biointegrity goal are shown.

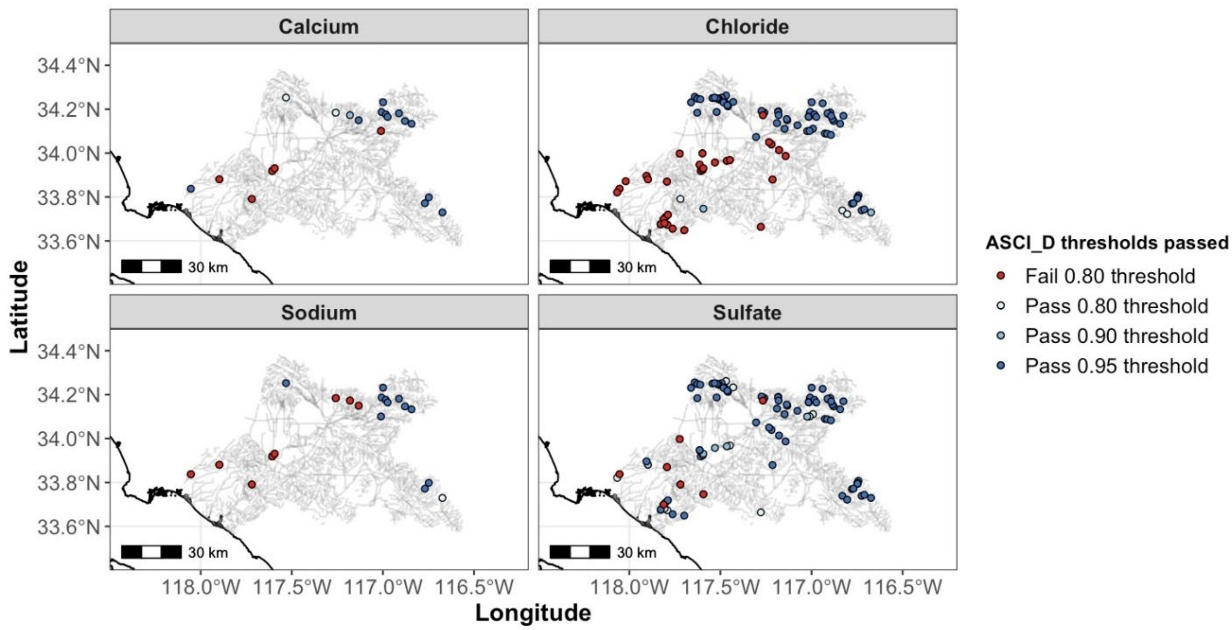


Figure 29. Location of sites where the average observed ion concentration exceeded the average threshold based on 80%, 90%, and 95% probability of achieving an ASCI_D Ref10 biointegrity goal.

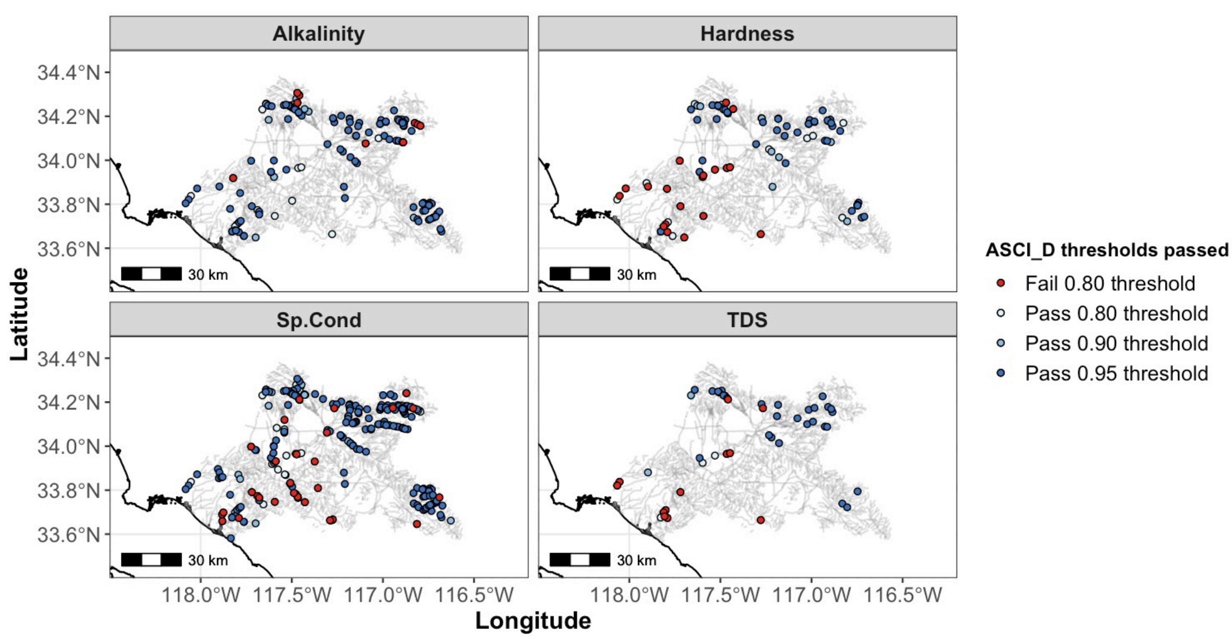


Figure 30. Location of sites where the average observed integrated ion concentration exceeded the average threshold based on 80%, 90%, and 95% probability of achieving an ASCI_D Ref10 biointegrity goal.

Identifying thresholds

To assist Waterboard staff with interpreting models and identifying potential thresholds, we created a dashboard to explore options for threshold selection and to visualize results: https://sccwrp.shinyapps.io/RB8_Threshold. Code and links for data download for the dashboard is available at https://github.com/SCCWRP/RB8_ShinyDashboard.

Users select which parameter they are interested in, and then indicate other factors related to threshold selection (Figure 31):

- Biointegrity index (ASCI_D, ASCI_H, or CSCI)
- Biointegrity goal (Ref30, Ref10, and Ref01)
- Probability of attaining the biointegrity goal if the threshold is met (0.8, 0.9, and 0.95)
- Climatic condition (wet, normal, dry, or overall)
- Season (April through September, October through March, or all months)

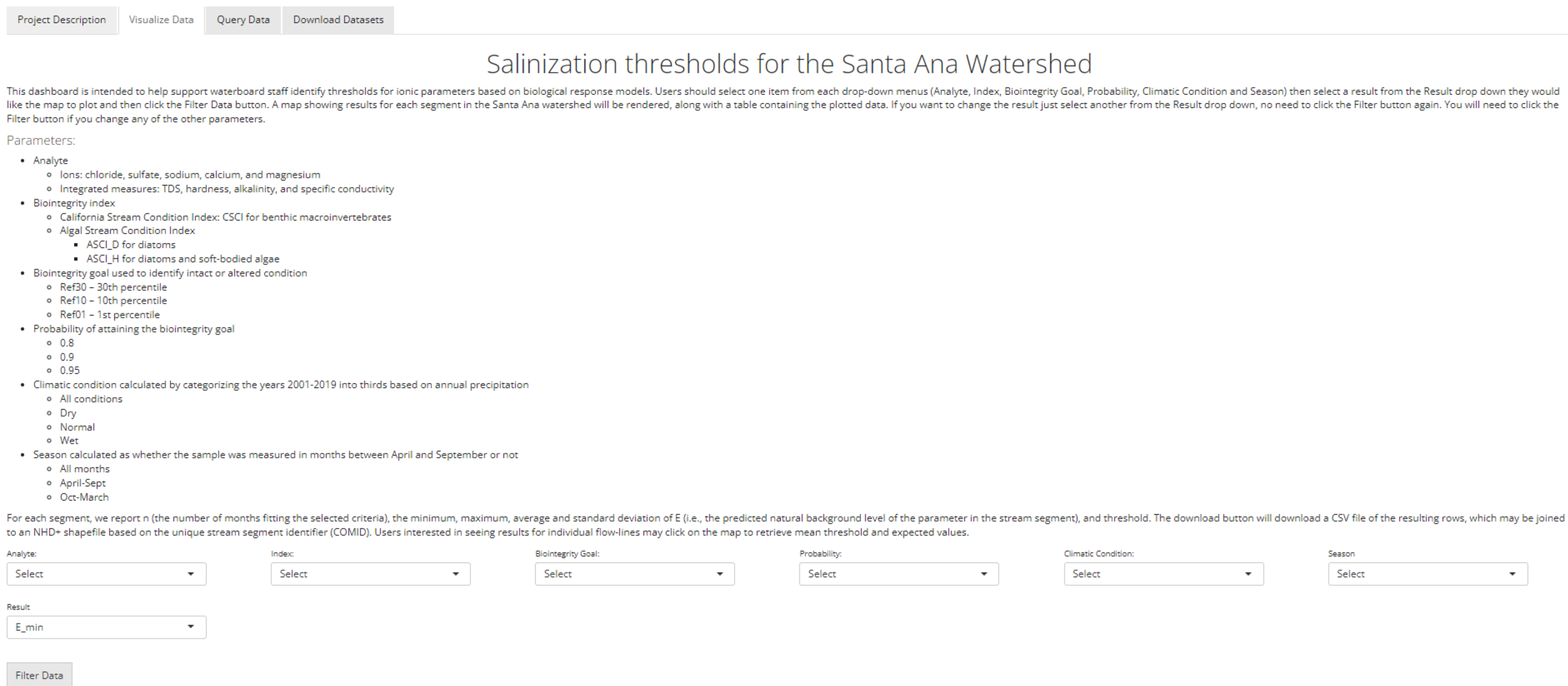
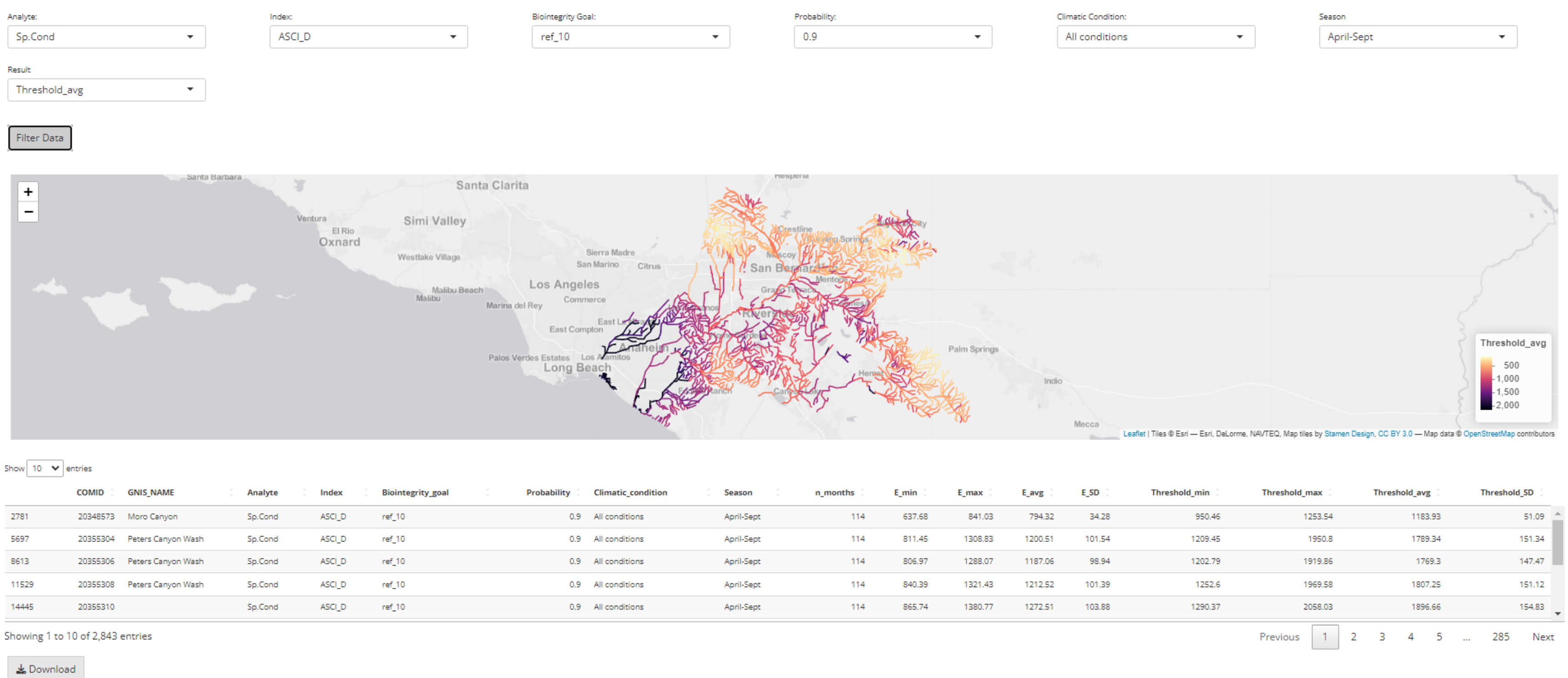


Figure 31. Screenshot of the user interface on the salinization threshold dashboard.

Based on these selections, the dashboard will identify the appropriate thresholds, based on the minimum, mean, and maximum values for all selected months and years meeting the desired climatic conditions (n indicates the number of months used to calculate these statistics). In addition, minimum, mean, and maximum expected value from the reference models in Part 1. Average threshold values are then plotted in a map (Figure 32). Users may download a CSV file with the resulting records to join with an NHD+ flowline shapefile and create their own maps in GIS software.



	COMID	GNIS_NAME	Analyte	Index	Biointegrity_goal	Probability	Climatic_condition	Season	n_months	E_min	E_max	E_avg	E_SD	Threshold_min	Threshold_max	Threshold_avg	Threshold_SD
2781	20348573	Moro Canyon	Sp.Cond	ASCI_D	ref_10	0.9	All conditions	April-Sept	114	637.68	841.03	794.32	34.28	950.46	1253.54	1183.93	51.09
5697	20355304	Peters Canyon Wash	Sp.Cond	ASCI_D	ref_10	0.9	All conditions	April-Sept	114	811.45	1308.83	1200.51	101.54	1209.45	1950.8	1789.34	151.34
8613	20355306	Peters Canyon Wash	Sp.Cond	ASCI_D	ref_10	0.9	All conditions	April-Sept	114	806.97	1288.07	1187.06	98.94	1202.79	1919.86	1769.3	147.47
11529	20355308	Peters Canyon Wash	Sp.Cond	ASCI_D	ref_10	0.9	All conditions	April-Sept	114	840.39	1321.43	1212.52	101.39	1252.6	1969.58	1807.25	151.12
14445	20355310		Sp.Cond	ASCI_D	ref_10	0.9	All conditions	April-Sept	114	865.74	1380.77	1272.51	103.88	1290.37	2058.03	1896.66	154.83

Figure 32. Example output of the salinization threshold dashboard.

Users interested in seeing results for individual flow-lines may click on the map to retrieve mean threshold and expected values (Figure 33).

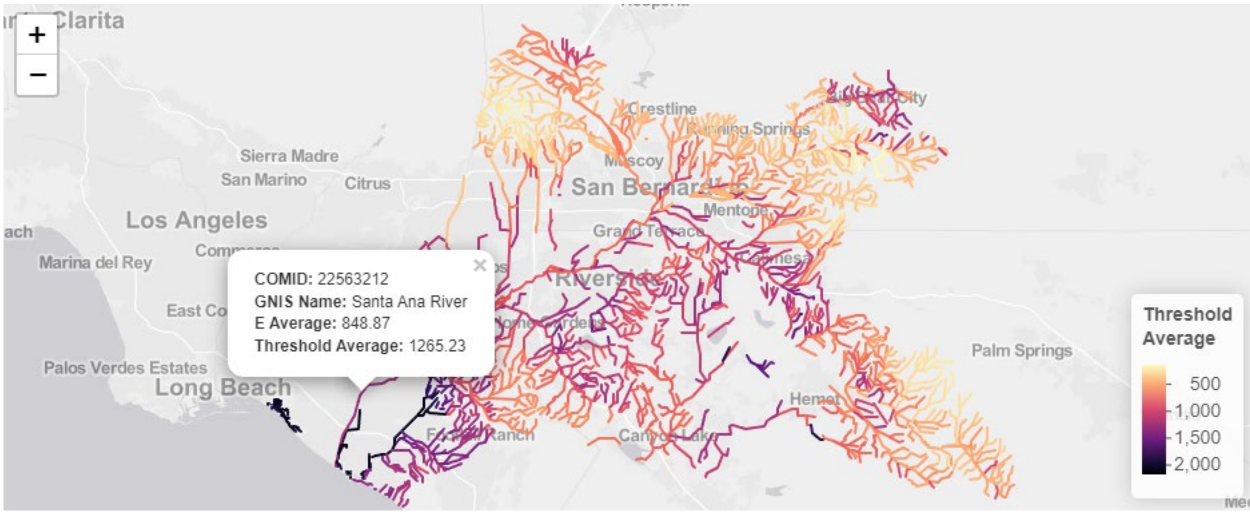


Figure 33. Screenshot of the salinization threshold dashboard showing how to find thresholds for individual segments.

Discussion

The strength of the biological response models reinforces the rational basis for managing stream salinization where aquatic life uses need to be supported, consistent with other studies on the risks of salinization (Cañedo-Argüelles et al. 2013, Hintz and Relyea 2019, Melles et al. 2023). Previous studies in southern California have found that elevated ionic concentrations are one of the most widespread stressors contributing to poor biological conditions in streams (Mazor 2015).

The thresholds identified from the models could be used to identify streams where salinization is likely posing a risk (Cormier et al. 2018). In addition, these thresholds could be used for causal assessments at sites in poor biological condition, or for setting management goals. These thresholds complement the numeric objectives in the Santa Ana basin plan (Regional Water Quality Control Board-Santa Ana 2019) by enabling analysis of a wider range of parameters than are included in the plan, and by providing additional confidence about potential impacts to aquatic life.

Although all indices responded to salinization stress gradients, the diatom index (ASCI_D) was more sensitive than the invertebrate index (CSCI) or the index that included soft-bodied algal taxa (ASCI_H). There have been few direct comparisons of the salinity tolerances of invertebrates to algal assemblages, but most are consistent with our finding of greater sensitivity of algae to water quality conditions than invertebrates (Hering et al. 2006, Mazor et al. 2006). Unlike the CSCI, the ASCI_D and ASCI_H both include metrics directly related to the salinity tolerance of diatom taxa (Theroux et al. 2020), which might account for the ASCIs' sensitivity to salinization. Many soft algal taxa (especially cyanobacteria and charophytes) are known to be highly tolerant of saline conditions (Hart et al. 1990, 1991), although no soft-algal metrics in the ASCI_H directly relate to salinity tolerance. A recent study has shown that increased salinity can lead to the proliferation of toxin-producing cyanobacteria in nutrient-enriched environments (Osburn et al. 2023).

Given that most sites in the Santa Ana watershed meet the thresholds identified in this study, managers should focus on protecting present-day water quality conditions from potential increases in salinization that could result from climate change, water recycling, or changes in water use. For sites where thresholds are exceeded, causal assessments (e.g., Norton et al. 2014, Gillett et al. 2023) would be necessary to determine if salinization alone is likely affecting aquatic life, or if a more broad-based rehabilitation plan is needed. For clusters of sites with many exceedances (i.e., Coyote Creek, Santa Ana mainstem, San Diego Creek, and San Timoteo Canyon), likely sources should be identified. Once sources are identified, appropriate mitigation strategies may be devised. For example, groundwater recharge can be an effective means to protect lower elevation streams from saltwater intrusion (Barlow and Reichard 2010). For most streams, source control (e.g., reduction of saline discharges) and increased dilution (e.g., reduction of diversions) are most effective (Cañedo-Argüelles 2020). Most research on reversing freshwater salinization focuses on reducing road salts, which is not a major mechanism of salinization in Southern California. In a review of several management strategies, Cañedo-Argüelles (2020) notes that restoration of environmental flows can reduce salinity in over-exploited rivers, such as the Murray Darling River in Australia (Paul et al. 2018).

This study supports the continued, broad-based monitoring of multiple ionic parameters. We found that no single parameter stood out as having more pervasive or severe exceedances of thresholds. For monitoring programs in the Santa Ana watershed lacking resources to assess all the parameters in this study, focusing on low-cost integrated parameters, such as specific conductivity and TDS, may be appropriate (see Part 3: Comparison of thresholds for integrated versus ionic parameters).

PART 3: COMPARISON OF THRESHOLDS FOR INTEGRATED VERSUS IONIC PARAMETERS

Introduction

Water quality monitoring programs may not always have the resources for comprehensive assessments of ionic parameters. Some may have access to standard field equipment, including water quality probes, yet not have access to or funding for analytical laboratories needed to assess concentrations of individual ions in water samples. Beyond the initial costs of purchasing probes, field-based measurements can be collected at essentially no cost beyond the expense of visiting a site. In contrast, programs would need to cover the costs of measuring each analyte in every sample. Although costs vary from lab to lab, the Santa Ana Regional Board's current bioassessment program pays an additional $25 per analyte for chloride, sulfate, magnesium, sodium, and calcium in each sample collected; in contrast, specific conductivity data is collected at no additional charge at every site where bioassessment is conducted. Even well-funded monitoring programs may not have access to an analytical lab or equipment capable of producing data. These constraints are particularly important for community-based or citizen-science monitoring efforts (San Llorente Capdevila et al. 2020). Therefore, smaller monitoring programs may want to know if field-based integrated measures of ionic strength (e.g., specific conductivity or total dissolved solids) can serve as a stand-in for lab-based measurements of individual ionic parameters.

When used as surrogates, integrated measures might afford a comparable level of protection, compared to when individual ionic parameters were measured, or serve as a screening tool to identify sites where lab analyses are warranted. We explored the utility of integrated measures (i.e., specific conductivity and total dissolved solids) as stand-ins for measurements of individual parameters (i.e., calcium, chloride, sodium, and sulfate).

Methods

Conceptual approach

To evaluate whether integrated measures can be used as a surrogate for measuring specific ions, we developed random forest models to estimate ionic concentrations (calcium, chloride, sodium, and sulfate) from integrated measures (TDS and specific conductivity). Next, we developed biological models based on the estimated ionic parameters from the random forest predictions. We then compared logistic curves based on estimated parameters to those based on direct observations. These comparisons allowed us to answer whether it is any less protective to use an integrated measure instead of an ionic parameter to assess risk from elevated concentrations (Figure 34).

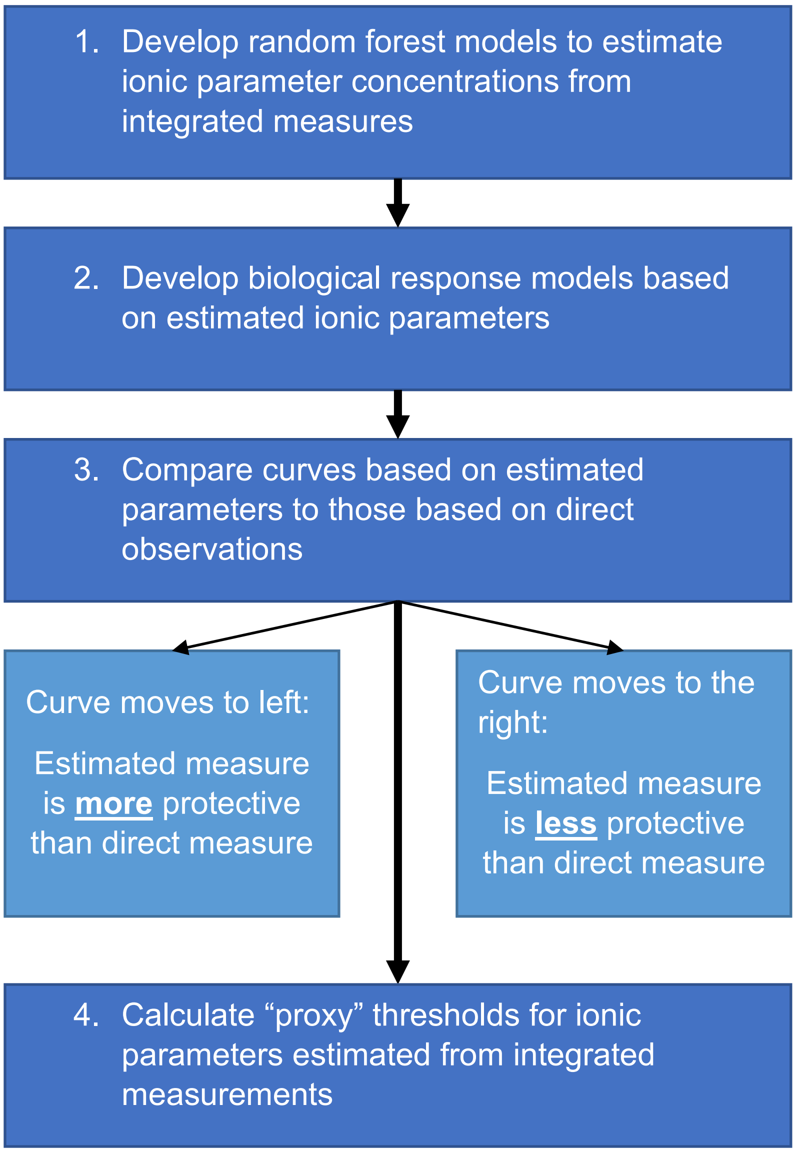


Figure 34. A flow chart of steps in the development of models to evaluate whether integrated measures can be used as a surrogate for measuring specific ions.

Develop random forest models to predict ionic parameter concentrations from integrated measures

We developed random forest models to predict ionic concentrations from integrated measures. The randomForest function from the randomForest package in R was used for all random forest models (Liaw and Wiener 2002, R Core Team 2022). Models were developed for four ionic parameters (calcium, chloride, sodium, sulfate) and two integrated measures (specific conductivity and TDS). We did not develop models to estimate magnesium from integrated measures due to poor predictive performance in biological response models (see Part 2: Evaluate biological response to elevated ionic concentrations). All random forest models were developed with observed concentrations that also had biological data (CSCI and ASCI scores).

Develop biological response models based on estimated ionic parameters

We developed logistic regressions to calculate the probability of meeting biointegrity thresholds at increasing levels of salinization based on the ionic parameter values estimated from random forest models. Logistic regression models were created with the probability of good biological condition as the response variable and the ionic concentration estimated from the integrated measure divided by the reference prediction (the expected concentrations derived from Part 1) as the predictor variable (O/E). Similar to the models developed in Part 2, the glm function in R, with a binomial error distribution and a logit link function, was used for all logistic regressions (R Core Team 2022). A separate set of models was developed for each ionic parameter (calcium, chloride, sodium, sulfate), bioassessment index (CSCI, ASIC_D, ASCI_H), and biointegrity goal (1st, 10th, and 30th percentile; 36 models), depending on whether the ionic parameters were estimated from TDS or specific conductivity (72 models total). These models were trained with the same data sets used in Part 2, representing streams from all over California (integrated parameters in Table 9). Model outputs are available from https://sccwrp.shinyapps.io/RB8_Threshold/.

Compare curves based on estimated parameters to those based on direct observations

Logistic regressions developed for ionic parameters estimated from integrated measures were then compared to models developed from direct observations. To do this, biological models developed in Part 2 were compared to the biological models developed based on estimated ionic parameters from integrated measures. Comparisons were made between the three types of models for each ionic parameter –observed concentrations, concentrations estimated from specific conductivity, and concentrations estimated from TDS. All three model types were compared for each ionic parameter (calcium, chloride, sodium, sulfate), bioassessment index

(CSCI, ASIC_D, ASCI_H), and biointegrity goal (1st, 10th, and 30th percentile; 36 models). The position of the curves was compared, where if curves moved to the left, then the integrated measure is more protective than direct measure when used as a proxy. If curves moved to the right, then the estimated measure is less protective than direct measure.

Calculate "proxy" thresholds for ionic parameters estimated from integrated measurements

Significant logistic regression models ($p < 0.05$) for each combination of model type, estimated ionic parameter, bioassessment index, and biointegrity goal were then used to identify concentrations that were predictive of a ≥0.8, ≥0.9, or ≥0.95 probabilities of good biological condition occurring. Following methods outlined in Part 2, we established a range of values to evaluate for each observed/expected ratio for each ion (from 1 to a maximum of 75 mg/L chloride, 25 mg/L calcium, 30 mg/L sodium, and 40 mg/L sulfate), and ran the models for 1000 values along this range, as well as 95% confidence limits (as 1.96 times the standard error); predictions and confidence limits were expressed in terms of the linear predictors before transforming into probabilities through an inverse-link function. Each threshold was expressed as a ratio (O/E threshold).

Results

Develop random forest models to estimate ionic parameter concentrations from integrated measures

Random forest models were successful in estimating ionic concentrations from integrated measures (Table 15, Figure 35). Of the 8 models, the weakest relationships were between chloride and specific conductivity ($r^2 = 0.496$) and chloride and TDS ($r^2 = 0.445$). For all analytes, random forest models tended to underestimate ionic concentrations (Figure 35).

Table 15. Performance of random forest models to predict ionic concentrations from integrated measures.

Ion	Integrated	Calibration sites in California	Calibration sites in the Santa Ana watershed	Pseudo R^2
Calcium	Sp.Cond	443	18	0.776
Calcium	TDS	129	3	0.631
Chloride	Sp.Cond	1679	112	0.496
Chloride	TDS	274	49	0.445
Sodium	Sp.Cond	240	18	0.807
Sodium	TDS	33	3	0.712
Sulfate	Sp.Cond	1542	106	0.670
Sulfate	TDS	310	49	0.824

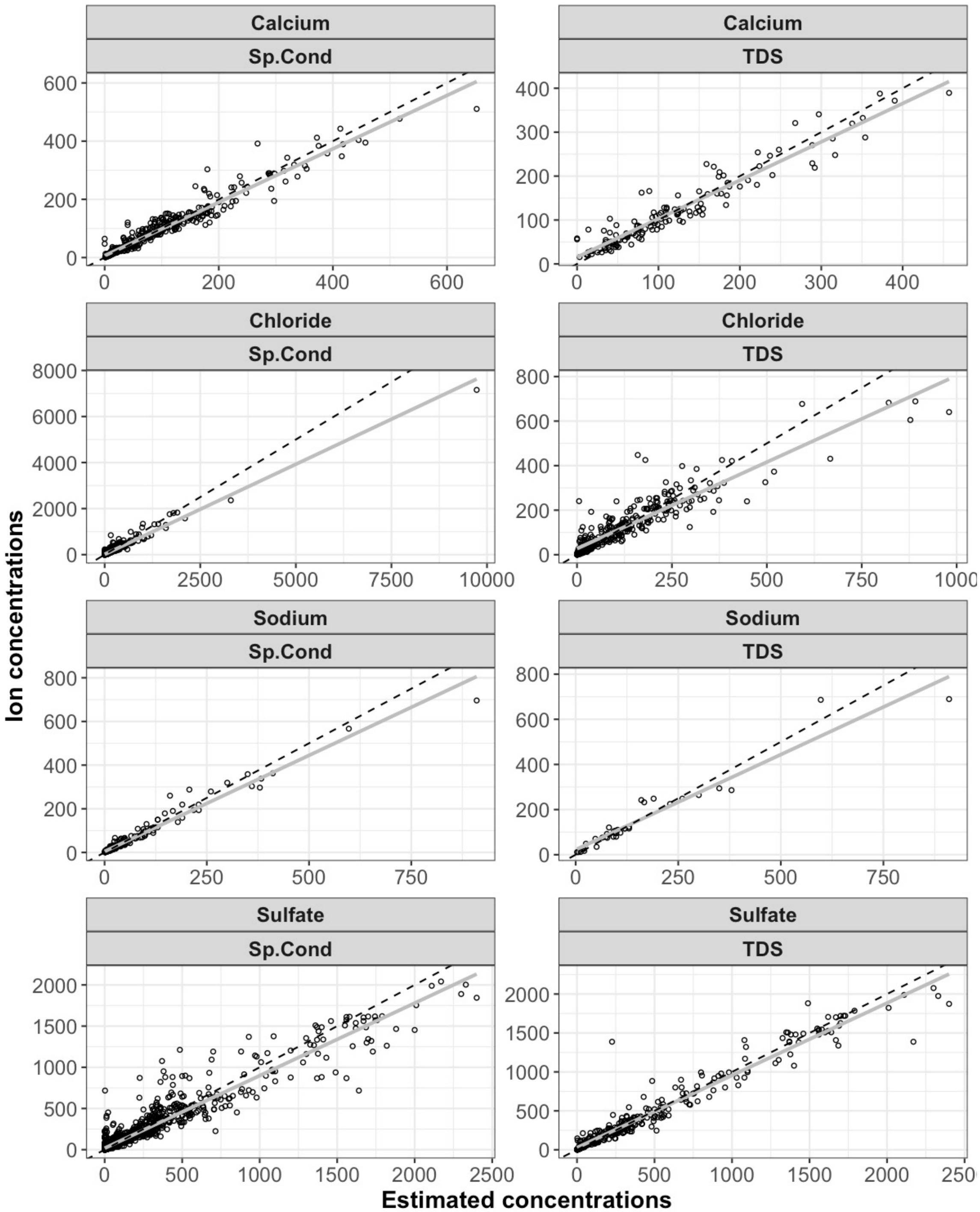


Figure 35. Relationships between observed ion concentrations (calcium, chloride, sodium, and sulfate) and estimated ion concentrations from integrated measures (specific conductivity and TDS). Panels in the left column show relationships between ion concentrations and predicted concentrations from specific conductivity. Panels on the right show relationships with TDS. Gray lines are linear regression lines between observed and estimated concentrations, and black dashed lines are 1:1 lines.

Develop biological response models based on estimated ionic parameters

Logistic regressions developed for ionic parameters estimated from integrated measures were usually successful in predicting the likelihood of attaining a biointegrity goal (Table 16; Figure 36). Of the 24 models estimating ionic concentration, 18 of the models had statistically significant coefficients ($p < 0.05$). Models estimating sodium concentrations from TDS were unable to predict a Ref10 goal for CSCI, ASCI_D, or ASCI_H.

Table 16. Performance of biological response models to predict probability of meeting biointegrity goals at increasing levels of ionic stress for each model type (observed ion concentrations, ion concentrations estimated from specific conductivity, and ion concentrations estimated from TDS). Only models for the "Ref10" biointegrity goal are shown. P-values for the coefficient are represented as * <0.05, ** <0.01, * <0.001. Model results for model type "Observed" are the same models shown in Table 10.**

			Coefficient		Intercept		
Analyte	**Model type**	**Index**	**estimate**	**Std error**	**estimate**	**Std error**	**P**
Calcium	Observed	CSCI	-0.290	0.069	0.651	0.162	***
Calcium	Sp. Cond	CSCI	-0.299	0.070	0.790	0.176	***
Calcium	TDS	CSCI	-0.660	0.225	1.247	0.524	**
Calcium	Observed	ASCI_D	-0.726	0.147	0.371	0.252	***
Calcium	Sp. Cond	ASCI_D	-0.631	0.139	0.335	0.279	***
Calcium	TDS	ASCI_D	-0.558	0.318	-0.461	0.686	0.079
Calcium	Observed	ASCI_H	-0.389	0.106	0.234	0.273	***
Calcium	Sp. Cond	ASCI_H	-0.829	0.154	1.010	0.329	***
Calcium	TDS	ASCI_H	-0.595	0.238	0.533	0.540	*
Chloride	Observed	CSCI	-0.108	0.012	0.974	0.069	***
Chloride	Sp. Cond	CSCI	-0.092	0.010	1.022	0.074	***
Chloride	TDS	CSCI	-0.178	0.031	1.227	0.245	***
Chloride	Observed	ASCI_D	-0.164	0.017	0.664	0.073	***
Chloride	Sp. Cond	ASCI_D	-0.097	0.012	0.556	0.075	***
Chloride	TDS	ASCI_D	-0.150	0.035	0.090	0.252	***
Chloride	Observed	ASCI_H	-0.089	0.012	0.674	0.071	***
Chloride	Sp. Cond	ASCI_H	-0.029	0.007	0.487	0.068	***
Chloride	TDS	ASCI_H	-0.114	0.030	0.328	0.241	***
Sodium	Observed	CSCI	-0.398	0.107	0.836	0.206	***
Sodium	Sp. Cond	CSCI	-0.304	0.090	0.872	0.209	**
Sodium	TDS	CSCI	-1.083	0.588	2.947	1.806	0.066

			Coefficient		Intercept		
Analyte	**Model type**	**Index**	**estimate**	**Std error**	**estimate**	**Std error**	**P**
Sodium	Observed	ASCI_D	-1.005	0.368	0.806	0.406	*
Sodium	Sp. Cond	ASCI_D	-1.109	0.421	1.252	0.487	*
Sodium	TDS	ASCI_D	0.000	5150	-25	53643	1.000
Sodium	Observed	ASCI_H	-0.144	0.116	0.267	0.386	0.213
Sodium	Sp. Cond	ASCI_H	-0.180	0.116	0.225	0.397	0.123
Sodium	TDS	ASCI_H	0.176	0.110	-3.744	1.438	0.109
Sulfate	Observed	CSCI	-0.291	0.029	1.046	0.077	***
Sulfate	Sp. Cond	CSCI	-0.065	0.015	0.775	0.070	***
Sulfate	TDS	CSCI	-0.407	0.061	1.268	0.210	***
Sulfate	Observed	ASCI_D	-0.224	0.031	0.421	0.076	***
Sulfate	Sp. Cond	ASCI_D	-0.031	0.013	0.136	0.069	*
Sulfate	TDS	ASCI_D	-0.431	0.084	0.369	0.232	***
Sulfate	Observed	ASCI_H	-0.173	0.027	0.543	0.077	***
Sulfate	Sp. Cond	ASCI_H	-0.005	0.007	0.250	0.065	0.487
Sulfate	TDS	ASCI_H	-0.311	0.061	0.404	0.213	***

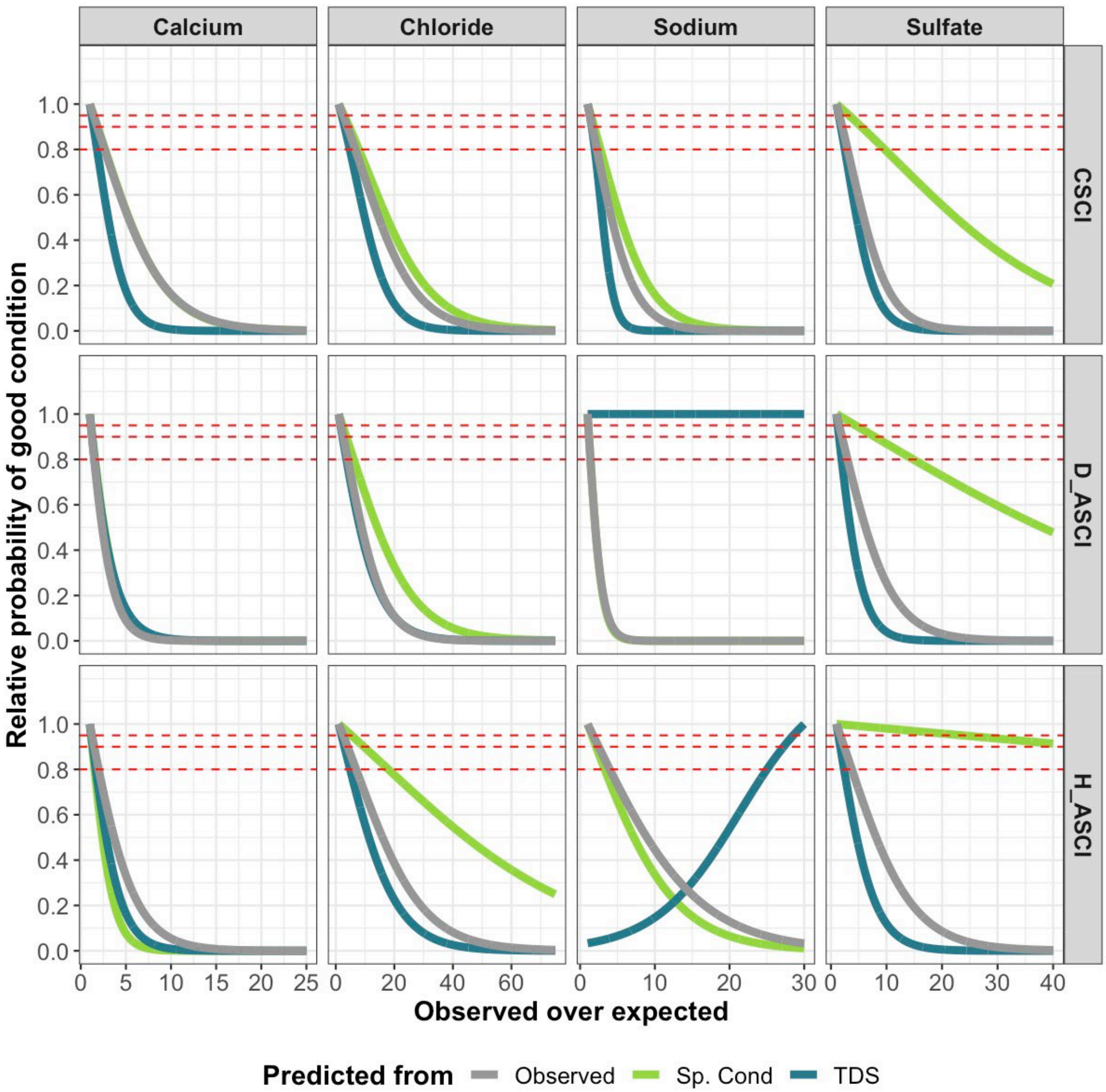


Figure 36. Relative probabilities of meeting biointegrity goals at increasing levels of ionic stress for each model type (observed ion concentrations, ion concentrations estimated from specific conductivity, and ion concentrations estimated from TDS). Only models for the "Ref10" biointegrity goal are shown. Dotted lines represent 80%, 90%, and 95% relative probability.

Compare curves based on estimated parameters to those based on direct observations

In general, TDS was a better surrogate for individual ions than specific conductivity. Most of the curves for TDS in Figure 36 are close to or to the left of (i.e., more sensitive) than the curves for direct measurements. As an exception, the relationships between sodium and TDS were relatively poor (likely due to insufficient data and poor performance of the random forest model, Table 15, Table 16), leading to non-significant relationships with the ASCIs. In contrast, parameters estimated from specific conductivity were often substantially less sensitive than the direct measures, with sodium again being a notable exception. Thus, TDS is a suitable surrogate for three ionic parameters (i.e., calcium, chloride, and sulfate), while specific conductivity is a suitable surrogate for two parameters (i.e., calcium and sodium).

Calculate "proxy" thresholds for ionic parameters estimated from integrated measurements

Thresholds identified from the biological response models based on estimated ionic concentrations are shown in Table 17. These thresholds provide ways to interpret measurements of integrated parameters in terms of whether specific ions are likely exceeding levels that pose risks to aquatic life.

Table 17. Thresholds corresponding to 80%, 90%, and 95% relative probabilities of meeting biointegrity goals for each model type (observed ion concentrations [Ob], ion concentrations estimated from specific conductivity [Sp.C], and ion concentrations estimated from TDS [TDS]). Only models for the "Ref10" biointegrity goal are shown. Green squares and * indicate estimated thresholds that are more protective than the direct measure. NI: Threshold not identified due to poor performance of the biological response model.

		80% probability			90% probability			95% probability		
Analyte	**Index**	**Ob**	**Sp.C**	**TDS**	**Ob**	**Sp.C**	**TDS**	**Ob**	**Sp.C**	**TDS**
Calcium	CSCI	2.634	2.682	1.793*	1.817	1.841	1.408*	1.408	1.432	1.192*
Calcium	ASCI_D	1.480	1.553	1.505	1.216	1.264	1.240	1.096	1.120	1.120
Calcium	ASCI_H	1.961	1.505*	1.649*	1.480	1.240*	1.312*	1.216	1.120*	1.144*
Chloride	CSCI	6.630	7.815	4.778*	3.889	4.556	3.000*	2.481	2.852	2.037*
Chloride	ASCI_D	4.037	6.111	3.593*	2.556	3.593	2.259*	1.741	2.259	1.593*
Chloride	ASCI_H	6.926	17.963	4.852*	3.963	9.593	2.926*	2.481	5.296	1.963*
Sodium	CSCI	2.219	2.713	1.958*	1.610	1.871	1.552*	1.290	1.435	1.290
Sodium	ASCI_D	1.348	1.377	NI	1.174	1.174	NI	1.087	1.087	NI
Sodium	ASCI_H	3.961	3.293*	NI	2.451	2.132*	NI	1.726	1.552*	NI
Sulfate	CSCI	2.952	9.667	2.483*	2.015	5.450	1.781*	1.508	3.264	1.390*
Sulfate	ASCI_D	2.952	14.820	1.898*	1.976	7.871	1.429*	1.468	4.435	1.195*
Sulfate	ASCI_H	3.733	NI	2.327*	2.366	NI	1.664*	1.664	23.643	1.312*

Discussion

This study demonstrates that low-cost field measurements of ionic strength can stand in for direct measures of ionic parameters. Exceeding the thresholds shown in Table 17 can serve as a screening and prioritization tool, to determine if follow-up measurements are needed. Due to the ways they are derived, the “proxy” thresholds shown in Table 17 should be interpreted differently from integrated parameter thresholds in Table 13. Proxy thresholds can identify streams at risk from certain ionic parameters, whereas the thresholds in Table 13 identify streams where overall ionic strength creates a risk.

In general, TDS was a more sensitive surrogate for individual ions than specific conductivity. This difference could be due to the fact that specific conductivity is influenced not just by ionic concentrations, but also by temperature. Although TDS was not demonstrated to be an effective surrogate for sodium measurements, we believe this is likely due to data limitations; with additional data collection, we are likely to identify thresholds for sodium estimated from TDS measurements as well.

CONCLUSIONS AND RECOMMENDATIONS

This study demonstrates that salinization has the potential to threaten aquatic life in the Santa Ana basin. We demonstrated that elevated ionic concentrations are pervasive, and at levels likely to degrade biological condition. The thresholds identified in this study can help managers identify streams where salinization poses a risk and set goals for improving degraded streams. We have presented options to help managers set thresholds customized for each stream segment in the Santa Ana watershed and for different seasonal or climatic conditions where thresholds may be needed.

We identified thresholds reflecting a range of probabilities of meeting biointegrity goals. Managers can identify thresholds consistent with their needs and tolerance for risk. Thresholds set at high probabilities (e.g., 99%) result in high stringency thresholds that may be effective for screening sites; however, high stringency thresholds may detect problems where none has occurred. Conversely, low stringency thresholds set at lower probabilities (e.g., 80%) run the opposite risk, where degraded streams are undetected. Whether high- or low-stringency thresholds are used, it will likely be necessary for managers to conduct follow-up assessments to confirm that biological degradation has occurred.

Overall, season and climate affected thresholds much less than location, suggesting that long-term, static thresholds may be appropriate if they account for site-specific factors that influence background levels of ionic concentrations. It is likely that seasonal effects are more important in snow-influenced landscapes, where spring snowmelt contributes to large influxes of very low salinity water (Bolotin et al. 2023). Within the Santa Ana watershed, very few stream miles likely experience substantial snowmelt influence.

Climate change will have complex effects on stream hydrology and biogeochemistry, including effects on stream salinity. Climatic factors, such as antecedent temperature and precipitation, were among the most important variables in predicting natural levels of ionic parameters. Under climate change in California, air temperatures are likely to increase, and precipitation will become more variable, leading to greater fluctuations in stream flow (Olson 2019). The likely outcome is that streams will experience higher levels of salinization (Bolotin et al. 2023). The models in this study were calibrated with 20 years of data, covering a wide range of climatic variability and providing them with a level of robustness to future changes in hydrology and natural stream salinity. However, periodic recalibration with newer data (particularly with long term data collected at a common set of sites) would ensure the appropriateness of their use under changing climatic conditions.

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SUPPLEMENTAL MATERIAL

Table S1. Performance of biological response models to predict probability of meeting biointegrity goals at increasing levels of ionic stress. P-values are represented as * <0.05, ** <0.01, * <0.001. NI: Threshold not identified due to poor performance of the biological response model.**

					Coefficient		Intercept		
Bio-integrity Goal	**Analyte**	**Index**	**Train n**	**Test n**	**estimate**	**Std error**	**estimate**	**Std error**	**P**
Ref1	Alkalinity	CSCI	1706	427	-0.384	0.081	1.869	0.117	***
Ref1	Alkalinity	ASCI_D	1335	334	-0.831	0.106	1.828	0.139	***
Ref1	Alkalinity	ASCI_H	1327	332	-0.661	0.098	1.788	0.135	***
Ref1	Calcium	CSCI	364	91	-0.260	0.062	1.559	0.182	***
Ref1	Calcium	ASCI_D	228	58	-0.598	0.116	0.889	0.240	***
Ref1	Calcium	ASCI_H	193	49	-0.314	0.087	0.817	0.251	***
Ref1	Chloride	CSCI	1414	354	-0.044	0.007	1.559	0.076	***
Ref1	Chloride	ASCI_D	1260	315	-0.095	0.011	1.344	0.079	***
Ref1	Chloride	ASCI_H	1219	305	-0.028	0.006	1.247	0.074	***
Ref1	Hardness	CSCI	1176	294	-0.253	0.033	1.776	0.102	***
Ref1	Hardness	ASCI_D	1136	285	-0.601	0.052	1.841	0.112	***
Ref1	Hardness	ASCI_H	1097	275	-0.435	0.043	1.751	0.108	***
Ref1	Magnesium	CSCI	288	73	-0.001	0.001	1.018	0.134	NI
Ref1	Magnesium	ASCI_D	152	39	0.000	0.001	-0.075	0.164	NI
Ref1	Magnesium	ASCI_H	117	30	0.000	0.001	-0.152	0.188	NI
Ref1	Sodium	CSCI	215	54	-0.199	0.063	1.333	0.200	**
Ref1	Sodium	ASCI_D	83	21	-0.125	0.076	0.424	0.281	NI
Ref1	Sodium	ASCI_H	48	12	-0.089	0.072	0.614	0.367	NI

					Coefficient		Intercept		
Bio-integrity Goal	**Analyte**	**Index**	**Train n**	**Test n**	**estimate**	**Std error**	**estimate**	**Std error**	**P**
Ref1	Sp.Cond	CSCI	2152	539	-0.367	0.040	1.864	0.083	***
Ref1	Sp.Cond	ASCI_D	1480	371	-0.598	0.056	1.704	0.100	***
Ref1	Sp.Cond	ASCI_H	1437	360	-0.320	0.043	1.569	0.092	***
Ref1	Sulfate	CSCI	1303	326	-0.223	0.024	1.770	0.089	***
Ref1	Sulfate	ASCI_D	1115	279	-0.249	0.029	1.223	0.084	***
Ref1	Sulfate	ASCI_H	1076	269	-0.179	0.026	1.311	0.087	***
Ref1	TDS	CSCI	291	73	-0.506	0.077	2.408	0.263	***
Ref1	TDS	ASCI_D	263	66	-0.364	0.077	0.804	0.214	***
Ref1	TDS	ASCI_H	263	66	-0.453	0.084	1.113	0.229	***
Ref10	Alkalinity	CSCI	1706	427	-0.445	0.081	1.018	0.105	***
Ref10	Alkalinity	ASCI_D	1335	334	-0.676	0.106	0.879	0.129	***
Ref10	Alkalinity	ASCI_H	1327	332	-0.643	0.103	1.047	0.130	***
Ref10	Calcium	CSCI	364	91	-0.290	0.069	0.651	0.162	***
Ref10	Calcium	ASCI_D	228	58	-0.726	0.147	0.371	0.252	***
Ref10	Calcium	ASCI_H	193	49	-0.389	0.106	0.234	0.273	***
Ref10	Chloride	CSCI	1414	354	-0.108	0.012	0.974	0.069	***
Ref10	Chloride	ASCI_D	1260	315	-0.164	0.017	0.664	0.073	***
Ref10	Chloride	ASCI_H	1219	305	-0.089	0.012	0.674	0.071	***
Ref10	Hardness	CSCI	1176	294	-0.373	0.041	1.150	0.094	***
Ref10	Hardness	ASCI_D	1136	285	-0.666	0.064	1.125	0.106	***
Ref10	Hardness	ASCI_H	1097	275	-0.585	0.056	1.234	0.106	***
Ref10	Magnesium	CSCI	288	73	0.000	0.001	0.183	0.119	NI
Ref10	Magnesium	ASCI_D	152	39	0.000	0.001	-0.690	0.173	NI
Ref10	Magnesium	ASCI_H	117	30	-0.222	0.065	0.227	0.284	**
Ref10	Sodium	CSCI	215	54	-0.398	0.107	0.836	0.206	***

					Coefficient		Intercept		
Bio-integrity Goal	**Analyte**	**Index**	**Train n**	**Test n**	**estimate**	**Std error**	**estimate**	**Std error**	**P**
Ref10	Sodium	ASCI_D	83	21	-1.005	0.368	0.806	0.406	**
Ref10	Sodium	ASCI_H	48	12	-0.144	0.116	0.267	0.386	NI
Ref10	Sp.Cond	CSCI	2152	539	-0.461	0.045	1.041	0.075	***
Ref10	Sp.Cond	ASCI_D	1480	371	-0.554	0.060	0.868	0.093	***
Ref10	Sp.Cond	ASCI_H	1437	360	-0.456	0.053	0.953	0.091	***
Ref10	Sulfate	CSCI	1303	326	-0.291	0.029	1.046	0.077	***
Ref10	Sulfate	ASCI_D	1115	279	-0.224	0.031	0.421	0.076	***
Ref10	Sulfate	ASCI_H	1076	269	-0.173	0.027	0.543	0.077	***
Ref10	TDS	CSCI	291	73	-0.637	0.099	1.380	0.239	***
Ref10	TDS	ASCI_D	263	66	-0.660	0.127	0.609	0.256	***
Ref10	TDS	ASCI_H	263	66	-0.457	0.093	0.585	0.227	***
Ref30	Alkalinity	CSCI	1706	427	-0.500	0.086	0.340	0.106	***
Ref30	Alkalinity	ASCI_D	1335	334	-0.612	0.116	0.116	0.135	***
Ref30	Alkalinity	ASCI_H	1327	332	-0.532	0.108	0.224	0.128	***
Ref30	Calcium	CSCI	364	91	-0.386	0.087	0.228	0.170	***
Ref30	Calcium	ASCI_D	228	58	-0.577	0.159	-0.453	0.268	***
Ref30	Calcium	ASCI_H	193	49	-1.215	0.228	0.939	0.358	***
Ref30	Chloride	CSCI	1414	354	-0.146	0.017	0.348	0.068	***
Ref30	Chloride	ASCI_D	1260	315	-0.183	0.023	-0.007	0.074	***
Ref30	Chloride	ASCI_H	1219	305	-0.183	0.021	0.248	0.074	***
Ref30	Hardness	CSCI	1176	294	-0.375	0.046	0.469	0.092	***
Ref30	Hardness	ASCI_D	1136	285	-0.527	0.067	0.163	0.103	***
Ref30	Hardness	ASCI_H	1097	275	-0.492	0.058	0.464	0.100	***
Ref30	Magnesium	CSCI	288	73	0.000	0.001	-0.545	0.123	NI
Ref30	Magnesium	ASCI_D	152	39	-0.337	0.106	-0.369	0.268	**

					Coefficient		Intercept		
Bio-integrity Goal	Analyte	Index	Train n	Test n	estimate	Std error	estimate	Std error	P
Ref30	Magnesium	ASCI_H	117	30	-0.215	0.075	-0.331	0.301	**
Ref30	Sodium	CSCI	215	54	-0.442	0.132	0.359	0.213	**
Ref30	Sodium	ASCI_D	83	21	-0.908	0.385	0.107	0.413	*
Ref30	Sodium	ASCI_H	48	12	-0.086	0.096	-0.635	0.402	NI
Ref30	Sp.Cond	CSCI	2152	539	-0.466	0.051	0.345	0.076	***
Ref30	Sp.Cond	ASCI_D	1480	371	-0.504	0.068	0.090	0.097	***
Ref30	Sp.Cond	ASCI_H	1437	360	-0.438	0.059	0.318	0.092	***
Ref30	Sulfate	CSCI	1303	326	-0.319	0.037	0.417	0.073	***
Ref30	Sulfate	ASCI_D	1115	279	-0.167	0.033	-0.369	0.077	***
Ref30	Sulfate	ASCI_H	1076	269	-0.143	0.029	-0.126	0.076	***
Ref30	TDS	CSCI	291	73	-0.757	0.132	0.806	0.257	***
Ref30	TDS	ASCI_D	263	66	-0.759	0.176	-0.005	0.291	***
Ref30	TDS	ASCI_H	263	66	-0.487	0.107	0.226	0.237	***

Table S 2. Predicted observed/expected ionic thresholds corresponding to 80%, 90%, and 95% relative probabilities of meeting biointegrity goals. Models for the "Ref10" biointegrity goal are shown in Table 13. NI: Threshold not identified due to poor performance of the biological response model.

			Probability		
Biointegrity goal	**Analyte**	**Index**	**0.8**	**0.9**	**0.95**
Ref1	Alkalinity	CSCI	3.228	2.219	1.645
Ref1	Alkalinity	ASCI_D	1.785	1.406	1.210
Ref1	Alkalinity	ASCI_H	2.065	1.561	1.294
Ref1	Calcium	CSCI	3.955	2.586	1.841
Ref1	Calcium	ASCI_D	1.769	1.384	1.192
Ref1	Calcium	ASCI_H	2.610	1.817	1.408
Ref1	Chloride	CSCI	20.926	11.963	6.852
Ref1	Chloride	ASCI_D	8.852	5.222	3.222
Ref1	Chloride	ASCI_H	27.444	15.148	8.407
Ref1	Hardness	CSCI	4.442	2.902	2.008
Ref1	Hardness	ASCI_D	2.236	1.666	1.342
Ref1	Hardness	ASCI_H	2.788	1.970	1.494
Ref1	Magnesium	CSCI	NI	NI	NI
Ref1	Magnesium	ASCI_D	NI	NI	NI
Ref1	Magnesium	ASCI_H	NI	NI	NI
Ref1	Sodium	CSCI	4.542	2.858	1.958
Ref1	Sodium	ASCI_D	4.687	2.858	1.929
Ref1	Sodium	ASCI_H	6.748	3.932	2.480
Ref1	Sp.Cond	CSCI	3.340	2.289	1.687
Ref1	Sp.Cond	ASCI_D	2.163	1.617	1.308
Ref1	Sp.Cond	ASCI_H	3.340	2.261	1.659
Ref1	Sulfate	CSCI	4.943	3.186	2.171
Ref1	Sulfate	ASCI_D	3.577	2.327	1.703
Ref1	Sulfate	ASCI_H	4.943	3.069	2.093
Ref1	TDS	CSCI	3.116	2.219	1.659
Ref1	TDS	ASCI_D	2.345	1.673	1.336
Ref1	TDS	ASCI_H	2.205	1.617	1.308
Ref30	Alkalinity	CSCI	2.177	1.603	1.294
Ref30	Alkalinity	ASCI_D	1.645	1.322	1.154
Ref30	Alkalinity	ASCI_H	1.743	1.378	1.182
Ref30	Calcium	CSCI	2.634	1.817	1.408
Ref30	Calcium	ASCI_D	1.480	1.216	1.096

			Probability		
Biointegrity goal	**Analyte**	**Index**	**0.8**	**0.9**	**0.95**
Ref30	Calcium	ASCI_H	1.961	1.480	1.216
Ref30	Chloride	CSCI	6.630	3.889	2.481
Ref30	Chloride	ASCI_D	4.037	2.556	1.741
Ref30	Chloride	ASCI_H	6.926	3.963	2.481
Ref30	Hardness	CSCI	2.560	1.799	1.399
Ref30	Hardness	ASCI_D	1.742	1.361	1.190
Ref30	Hardness	ASCI_H	1.932	1.475	1.228
Ref30	Magnesium	CSCI	NI	NI	NI
Ref30	Magnesium	ASCI_D	NI	NI	NI
Ref30	Magnesium	ASCI_H	2.796	1.898	1.429
Ref30	Sodium	CSCI	2.219	1.610	1.290
Ref30	Sodium	ASCI_D	1.348	1.174	1.087
Ref30	Sodium	ASCI_H	3.961	2.451	1.726
Ref30	Sp.Cond	CSCI	2.135	1.575	1.294
Ref30	Sp.Cond	ASCI_D	1.827	1.420	1.210
Ref30	Sp.Cond	ASCI_H	2.107	1.561	1.280
Ref30	Sulfate	CSCI	2.952	2.015	1.508
Ref30	Sulfate	ASCI_D	2.952	1.976	1.468
Ref30	Sulfate	ASCI_H	3.733	2.366	1.664
Ref30	TDS	CSCI	1.897	1.462	1.224
Ref30	TDS	ASCI_D	1.589	1.294	1.140
Ref30	TDS	ASCI_H	1.925	1.462	1.224