

Prepared in cooperation with the Bureau of Reclamation

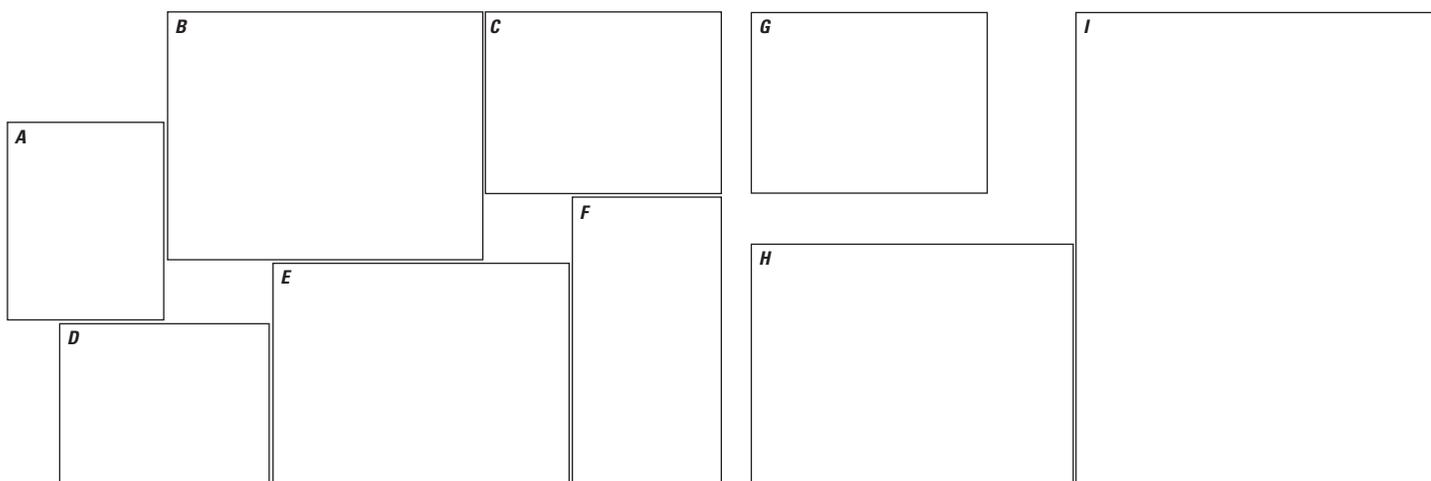
Estimation of Salt Loads for the Dolores River in the Paradox Valley, Colorado, 1980–2015



Scientific Investigations Report 2017–5059

Front cover

Back cover



Cover photographs (front and back). *A, E*, Views of the Dolores River in the Paradox Valley, Colorado. *B, G*, U.S. Geological Survey streamgage 09169500, Dolores River at Bedrock, Colo. *C, D, I*, U.S. Geological Survey streamgage 09171100, Dolores River near Bedrock, Colo. *F, H*, Flow measurements being taken in winter at streamgage 09171100.

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By M. Alisa Mast

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Scientific Investigations Report 2017–5059

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior

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U.S. Geological Survey, Reston, Virginia: 2017

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Suggested citation:

Mast, M.A., 2017, Estimation of salt loads for the Dolores River in the Paradox Valley, Colorado, 1980–2015: U.S. Geological Survey Scientific Investigations Report 2017–5059, 20 p., <https://doi.org/10.3133/sir20175059>.

ISSN 2328-0328 (online)

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Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi ²)	2.590	square kilometer (km ²)
	Flow rate	
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)
	Mass	
ton, short (2,000 lb)	0.9072	metric ton (t)

International System of Units to U.S. customary units

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
	Volume	
liter (L)	33.81402	ounce, fluid (fl. oz)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
	Density	
gram per cubic centimeter (g/cm ³)	62.4220	pound per cubic foot (lb/ft ³)

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C).

Concentrations of total dissolved solids and chemical constituents in water are given in milligrams per liter (mg/L).

Abbreviations

Reclamation	Bureau of Reclamation
PVU	Paradox Valley Unit
R ²	coefficient of determination
SC	specific conductance
TDS	total dissolved solids
USGS	U.S. Geological Survey
VWM	volume-weighted mean

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By M. Alisa Mast

Abstract

Regression models that relate total dissolved solids (TDS) concentrations to specific conductance were used to estimate salt loads for two sites on the Dolores River in the Paradox Valley in western Colorado. The salt-load estimates will be used by the Bureau of Reclamation to evaluate salt loading to the river coming from the Paradox Valley and the effect of the Paradox Valley Unit (PVU), a project designed to reduce the salinity of the Colorado River. A second-order polynomial provided the best fit of the discrete data for both sites on the river. The largest bias occurred in samples with elevated sulfate concentrations (greater than 500 milligrams per liter), which were associated with short-duration runoff events in late summer and fall. Comparison of regression models from a period of time before operation began at the PVU and three periods after operation began suggests the relation between TDS and specific conductance has not changed over time. Net salt gain through the Paradox Valley was estimated as the TDS load at the downstream site minus the load at the upstream site. The mean annual salt gain was 137,900 tons per year prior to operation of the PVU (1980–1993) and 43,300 tons per year after the PVU began operation (1997–2015). The difference in annual salt gain in the river between the pre-PVU and post-PVU periods was 94,600 tons per year, which represents a nearly 70 percent reduction in salt loading to the river.

Introduction

The Paradox Valley is a topographic basin approximately 25 miles (mi) long and 3–5 mi wide located in western Colorado (fig. 1). The valley is a collapsed salt anticline that formed by the upward flow of salts (gypsum, anhydrite, and halite) from the deeply buried Pennsylvanian Paradox Formation (Cater, 1970). The salts were subsequently dissolved, which caused the overlying bedrock to collapse, thereby forming an elongated valley along the northwest to southeast trend of the underlying anticline. The Dolores River, a major tributary of the Colorado River, crosses the Paradox Valley perpendicular to and about midway along the axis of the valley, entering and leaving through canyons incised through as much as 1,000 feet (ft) of Paleozoic and Mesozoic rocks. On

the valley floor, Quaternary alluvial deposits occur along the Dolores River and consist of layers of sand, gravel, and clay that form a water-table alluvial aquifer with a total thickness of up to 170 ft (Bureau of Reclamation, 1978). In the center of the valley, the alluvial aquifer overlies the Paradox Formation where the core of the Paradox Valley anticline and the salt-bearing Paradox Formation are closest to the land surface (Ball and others, 2015). Salt in the Paradox Formation is dissolved by regional groundwater flow that upwells through a brecciated zone at the top of the Paradox and into the alluvial aquifer (Bureau of Reclamation, 1978). Because the brine has a density of nearly 1.2 grams per cubic centimeter, water in the alluvial aquifer is stratified, containing a dense brine layer overlain by a layer of freshwater developed from surficial recharge. The freshwater layer thickens in spring and summer months in response to snowmelt runoff, irrigation return flows, and associated water management in the valley and thins (drains) during winter when recharge from these sources diminishes. Salt concentrations below the freshwater-brine interface have been measured in excess of 250,000 milligrams per liter (mg/L) (Watts, 2000). In the vicinity of the river, where the freshwater-brine interface is very close to the surface, brine discharges through the streambed into the Dolores River. During low-flow conditions in fall and winter, when freshwater recharge is minimal, brine discharge causes salinity concentrations in the river to increase by over three orders of magnitude as it flows across the valley floor.

The Paradox Valley Unit (PVU), which is located in the center of the Paradox Valley adjacent to the Dolores River, is a salinity-control project authorized under the Colorado River Basin Salinity Control Act of 1974 (Public Law 93–320, amended in 1984 as Public Law 98–569) and operated by the Bureau of Reclamation (<http://www.usbr.gov/uc/wcao/progact/paradox/>). The PVU consists of nine production wells, a collection facility, and one injection well that were constructed in the late 1980s to reduce the salinity of the Colorado River, which is a major concern for downstream municipal, industrial, and agricultural water use. The PVU production wells, which are located adjacent to the river (fig. 1), are completed near the base of the alluvial aquifer below the freshwater-brine interface. Withdrawal of brine through production wells reduces brine discharge from the shallow groundwater system into the river, thus reducing the salinity of the river where it exits the valley. Brine is withdrawn from the production wells at a total rate of about 0.5 cubic feet per second (ft³/s) and disposed of through a

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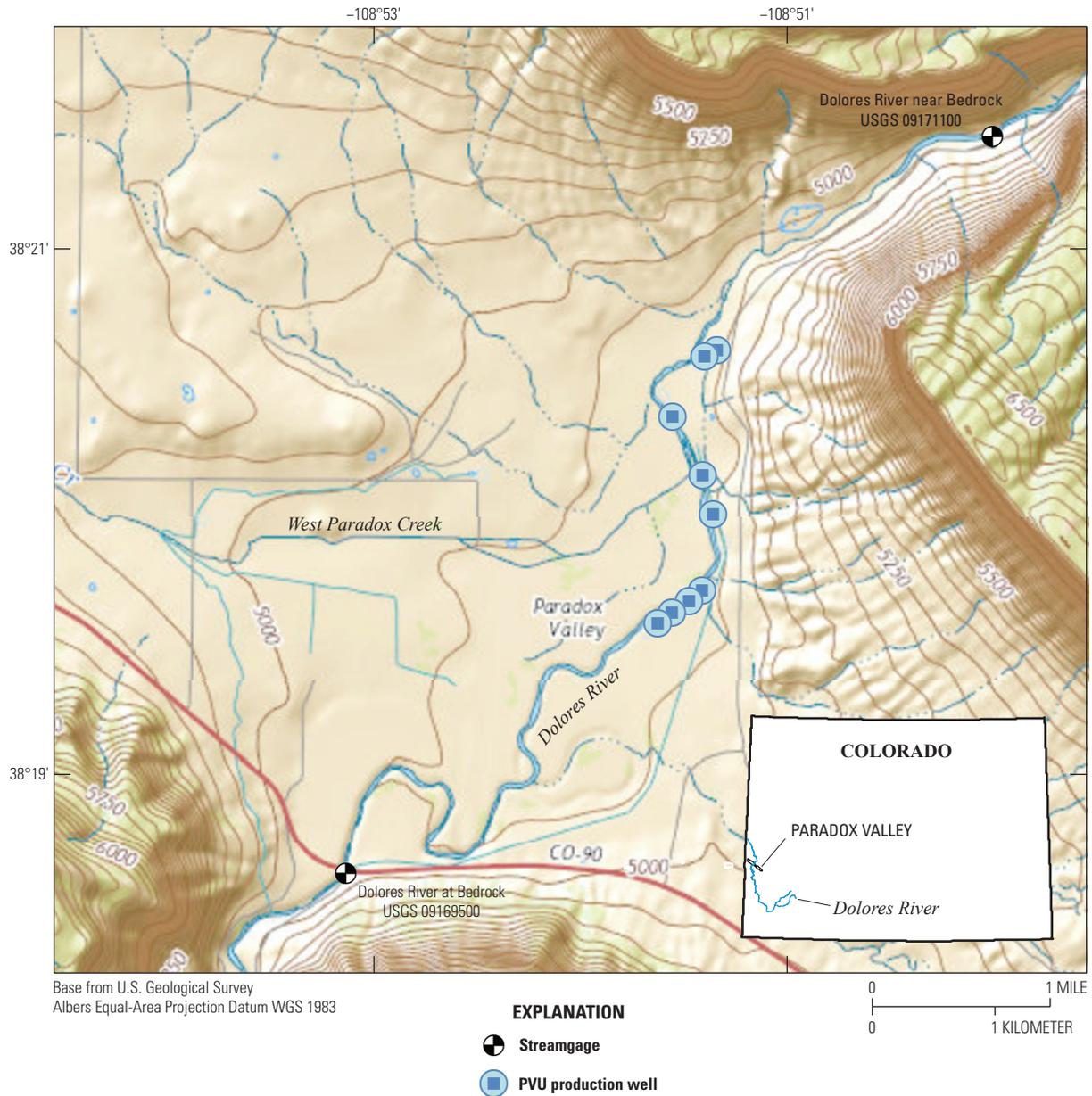


Figure 1. Map of the Paradox Valley and the Dolores River showing locations of U.S. Geological Survey (USGS) streamgages and Paradox Valley Unit (PVU) production wells.

16,000-ft-deep injection well located near the edge of the valley. Testing of the injection well occurred during 1991–1995, and regular operation of the PVU began in July 1996.

The Bureau of Reclamation (Reclamation) evaluates the effect of the PVU on salt loading to the river based on differences between the total dissolved solids (TDS) loads computed at two U.S. Geological Survey (USGS) streamgages on the Dolores River. The Dolores River at Bedrock site (USGS station 09169500) is located upstream from the PVU production wells where the river enters the valley, and the Dolores River near Bedrock site (USGS station 09171100) is located downstream from the PVU where the river exits the

valley (fig. 1). Loads are computed on the basis of continuous measurements (15-minute interval) of specific conductance (SC) and discharge at the two USGS streamgages and monthly water-quality samples, which are used to develop regressions between TDS concentrations and SC. The USGS periodically assists Reclamation with updating the regressions and salt-load estimates as new data become available. The two most recent USGS publications were authored by Chafin (2003), who developed regression models and computed daily salt loads for January 1988 through September 2001, and Linard and Schaffrath (2014), who developed regression models for October 2009 through September 2012.

Purpose and Scope

This report documents and updates regression models developed to relate TDS concentrations to SC for the Dolores River at Bedrock site (USGS station 09169500) and the Dolores River near Bedrock site (USGS station 09171100) using available data through 2015. These results will be used to update the regression equations reported on the USGS National Real-Time Water Quality website (<http://nrtwq.usgs.gov/>), which were originally published by Linard and Schaffrath (2014). The regressions are applied to daily records of SC to estimate the annual gain in salt load to the river as it flows across the Paradox Valley for 1980–2015. Available data-quality information is used to quantify uncertainties in annual salt loads. Annual salt gains are compared between a time period before routine operation of the PVU began (1987–1993; pre-PVU) and three time periods after operation began (1997–2015, 1997–2006, and 2007–2015; post-PVU). Reductions in annual salt load to the river during the post-PVU period are compared to annual salt disposal rates at the PVU injection well.

Study Area

The Dolores River originates in the San Juan Mountains southeast of the study area and drains a 2,024-square-mile (mi²) area upstream from the Paradox Valley. Flow in the Dolores River is largely derived from snowmelt runoff at higher elevations and has been regulated by releases from McPhee Reservoir (90 mi upstream) since March 19, 1984 (Bureau of Reclamation, 1997). Climate on the floor of the Paradox Valley is semiarid, with mean annual precipitation of about 12 inches per year. Major land uses in the valley include rangeland and about 2,700 acres of irrigated cropland and pasture located northwest of the river. Surface water diverted from West Paradox Creek, the only perennial tributary in the valley, and the Dolores River are the primary sources of irrigation water.

Methods

Collection of Streamflow and Water-Quality Data

Streamflow and water-quality data used in this analysis were collected at two sites with USGS streamgages in Colorado: the Dolores River at Bedrock site (USGS station 09169500), herein referred to as the upstream site, and the Dolores River near Bedrock site (USGS station 09171100), herein referred to as the downstream site (fig. 1). Streamflow has been measured continuously at the upstream site since 1918 and at the downstream site since 1971. The streamgage at the upstream site has been operated at the same location over the entire period of record. The streamgage at the downstream site, however, was moved in 1972 to a location 200 ft downstream from its original location and again in August 2000 approximately 600 ft upstream to its current location.

Instream monitors that measure SC and water temperature at 15-minute intervals have been operated at each site starting in 1979. The SC monitor at the downstream site was located 1.2 mi upstream from the streamgage during 1980–1987 and in December 1987 was moved downstream to the current streamgage location. The SC monitor at the upstream site was located 150 ft upstream from the streamgage during 1980–1989 and in July 1989 was moved downstream to the current streamgage location. Instream SC was measured using a USGS mini-monitor (Katzenbach, 1990) prior to winter 1994, a Hydrolab Reporter from winter 1994 to summer 2008, and a YSI 600 series sonde from summer 2008 to present (2015). Because water-quality monitors during all three time periods were operated according to standard USGS protocols (Wagner and others, 2006), and because field, laboratory, and instream SC sensor values agree over the entire period of record, measurements among the three different monitor types are comparable. Daily mean and unit-value (15-minute data) discharge and SC data were retrieved from the USGS National Water Information System (U.S. Geological Survey, 2015). Daily values are available for the entire period of record, and unit values are available starting in 1990.

Water-quality samples were collected at each streamgage by USGS personnel on a monthly schedule and cover a range of streamflow conditions. All samples were collected according to USGS National Field Manual protocol (U.S. Geological Survey, variously dated) and were analyzed at the National Water Quality Laboratory using approved methods (Fishman and Friedman, 1989). Available water-quality data for each streamgage were downloaded from the USGS National Water Information System (U.S. Geological Survey, 2015) including field parameters (SC, water temperature, pH, dissolved oxygen, and alkalinity), major-ion concentrations, and computed TDS for samples with complete major-ion analyses. During the period 1987–2015, 252 samples with TDS and SC were retrieved at the downstream site, and 257 samples were retrieved at the upstream site. In a few cases, the laboratory SC was substituted for the field SC because the field value was either missing or suspect.

Data Analysis

All available unit-value (15 minutes) and daily-value data for discharge and SC at both the upstream and downstream sites for 1980 to 2015 were loaded into the Aquarius® software package (<http://aquaticinformatics.com/products/>), which was used to estimate periods of missing record and to perform load computations. Approximately 9 percent of the daily SC values from each site were missing because of sensor malfunctions, sensor fouling, or power failures. Short gaps (less than 72 hours) in the daily-value SC records were filled by linear interpolation. Longer gaps were filled using tools in Aquarius that build models based on surrogate signals such as discharge or SC at nearby sites to perform corrections on time-series data. Data from 1986 and 1987 were omitted from the analysis because 46 and 92 percent, respectively, of the SC

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records at the downstream site were missing for those years. The complete record of daily SC values showing periods of estimated record are shown in figure 2.

The discrete water-quality samples at each site were used to develop regression models for predicting daily TDS from the daily SC record. Version 3.2.3 of the R Stats package in the R software environment (<https://stat.ethz.ch/R-manual/R-devel/library/stats/>) was used to generate regression statistics and residual plots that aid decisions about model adequacy (Helsel and Hirsch, 2002). Regression models were computed for the entire period of record (1980–2015) as well as for shorter periods including the pre-PVU period (1987–1993) and three different post-PVU periods (1997–2015, 1997–2006, and 2007–2015). The best-fitting regression model was used to estimate daily mean TDS concentrations at each stream site, and daily loads were computed as the product of daily mean discharge (in cubic feet per second), daily mean TDS (in milligrams per liter), and a conversion factor of 0.0026969 to yield results in tons per day. Daily loads were summed over calendar years to yield annual salt loads for each stream site from 1980 to 2015.

Uncertainties in the annual salt loads were quantified to the extent possible with available data-quality information. The measurement uncertainties of daily-discharge values were based on data-quality ratings (excellent, good, fair, poor, or estimated) that are published in annual data reports available at <https://wdr.water.usgs.gov/>. Data-quality ratings for the SC records were

computed by a script that assigns ratings based on data corrections made to the raw SC records using guidance from Wagner and others (2006). The data-quality rating for each daily value was converted to a numeric uncertainty by assigning an uncertainty of ± 2.5 percent to a rating of excellent, an uncertainty of ± 5.0 percent to a rating of good, an uncertainty of ± 7.5 percent to a rating of fair, and an uncertainty of ± 15.0 percent to a rating of poor and to estimated records (Novak, 1985). Because the confidence intervals for the regression models were small compared to the measurement errors in SC, the TDS uncertainty was assumed equal to the SC uncertainty. The uncertainty of the daily load ($\delta Dload$), in tons per day, was then computed using the standard error propagation formula (Taylor, 1997),

$$\delta Dload = Dload \times \sqrt{\left(\frac{\delta TDS}{TDS}\right)^2 + \left(\frac{\delta Q}{Q}\right)^2}$$

where $Dload$ is the daily load, in tons per day; δTDS is the uncertainty in daily TDS, in milligrams per liter; and δQ is the uncertainty in the daily discharge (Q), both variables in cubic feet per second. The daily uncertainties were summed over the year to yield the uncertainty for the annual salt load. These calculations assume that for aggregated uncertainties (such as annual load), systematic errors act in an additive manner, whereas random errors tend to cancel out over longer time scales (Moncrieff and others, 1996).



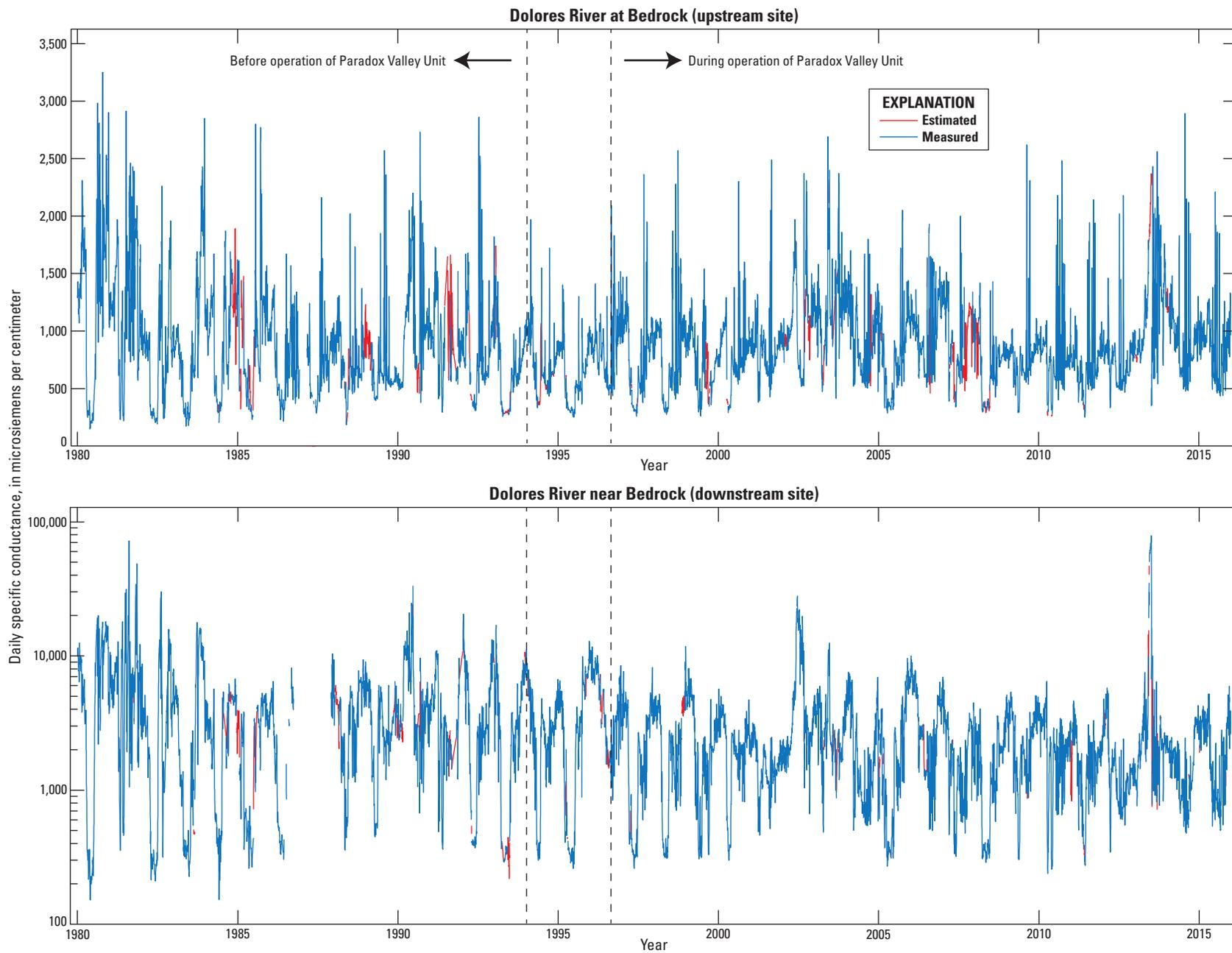


Figure 2. Measured and estimated daily specific-conductance values for the Dolores River at Bedrock site (upstream site) and the Dolores River near Bedrock site (downstream site) for 1980–2015.

Estimation of Salt Loads

Water Quality of the Dolores River

The water quality of the Dolores River changes considerably as it crosses the Paradox Valley because naturally saline groundwater discharges into the river. A synoptic survey of SC in the river between the upstream and downstream sites

illustrates the magnitude and spatial variability of water quality in the river across the valley (fig. 3). The SC survey was conducted by Reclamation in June 2013 (table 1) during an extremely dry period when SC values in the river were much greater than normal, accentuating the influence of brine discharge on the water quality of the river. At the upstream site where the river enters the valley, the SC was 1,990 microsiemens per centimeter ($\mu\text{S}/\text{cm}$) and increased to 31,000 $\mu\text{S}/\text{cm}$ about 2 mi downstream where salty

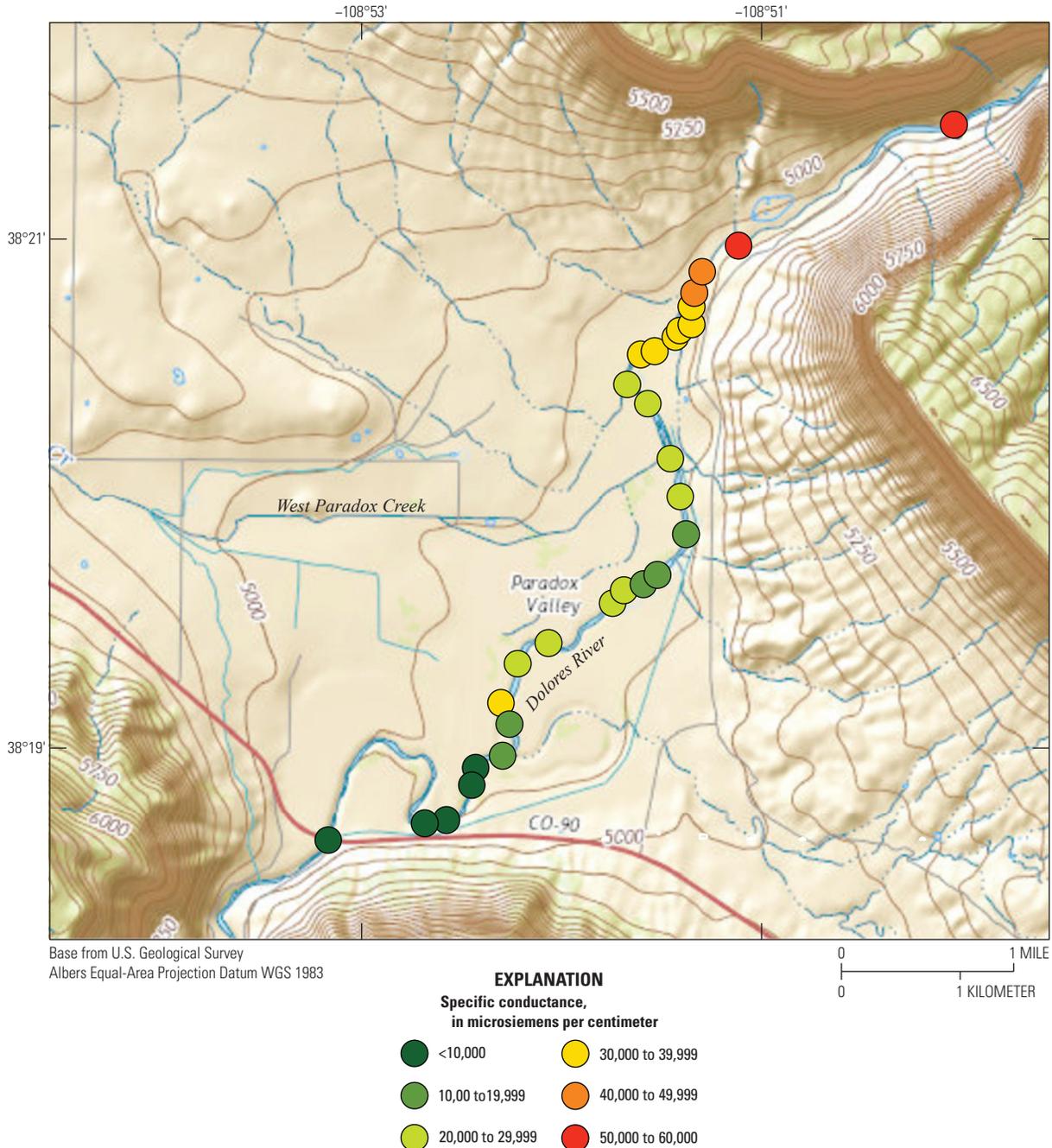


Figure 3. Specific-conductance survey of the Dolores River through the Paradox Valley conducted by the Bureau of Reclamation on June 24–25, 2013. Data shown in table 1.

Table 1. Specific-conductance data collected by the Bureau of Reclamation during a synoptic survey of the Dolores River through the Paradox Valley conducted on July 24–25, 2013.

[Spec. cond., specific conductance in microsiemens per centimeter; date in M/DD/YYYY format; coordinate datum World Geodetic System 1984 (WGS-84)]

Date	Latitude	Longitude	Spec. cond.
6/25/2013	38.31050	-108.88577	1,990
6/24/2013	38.31160	-108.87773	4,310
6/24/2013	38.31180	-108.87588	5,540
6/24/2013	38.31410	-108.87375	4,450
6/24/2013	38.31525	-108.87343	9,740
6/24/2013	38.31603	-108.87122	11,120
6/24/2013	38.31807	-108.87065	16,000
6/24/2013	38.31950	-108.87133	31,000
6/24/2013	38.32205	-108.86997	22,200
6/25/2013	38.32340	-108.86740	23,700
6/25/2013	38.32598	-108.86200	22,800
6/25/2013	38.32687	-108.86108	21,500
6/25/2013	38.32725	-108.85947	19,790
6/25/2013	38.32787	-108.85828	19,050
6/25/2013	38.33045	-108.85628	19,400
6/25/2013	38.33298	-108.85638	20,200
6/25/2013	38.33548	-108.85718	20,000
6/25/2013	38.33905	-108.85910	23,200
6/25/2013	38.34033	-108.86083	28,000
6/25/2013	38.34232	-108.85970	32,700
6/25/2013	38.34253	-108.85855	33,800
6/25/2013	38.34343	-108.85680	34,900
6/25/2013	38.34387	-108.85642	35,000
6/25/2013	38.34423	-108.85545	37,500
6/25/2013	38.34545	-108.85548	39,900
6/25/2013	38.34633	-108.85522	43,000
6/25/2013	38.34772	-108.85455	49,800
6/25/2013	38.34943	-108.85152	52,100
6/25/2013	38.33045	-108.85628	60,000

groundwater likely discharged into the river. Where the river flows past the upper PVU well field, the SC decreased to about 20,000 $\mu\text{S}/\text{cm}$, likely because fresher groundwater discharges into this reach of the river. Downstream from the lower end of the well field, the SC in the river increased to 60,000 $\mu\text{S}/\text{cm}$ (over 30 times greater than at the upstream site) because of additional brine discharge from the alluvial aquifer.

In addition to spatial variability, the river also shows strong seasonal changes in the proportions of major cations and anions as a result of groundwater and surface-water interactions. Figure 4 shows data for the pre-PVU period in order to better illustrate the influence of brine discharge on water quality of the river. During April through June, when streamflow is relatively high, concentrations at the downstream site approach those at the upstream site, where the river is a mixed calcium-sodium-sulfate-bicarbonate-type water. During July through March, when streamflow is relatively low, the downstream site is dominated by sodium and chloride because of the greater influence of brine discharge at low flows. Ranges of sulfate and calcium concentrations are fairly similar between the two sites during most months, suggesting that upstream sources as well as brine discharge contribute these solutes. Tuttle and Grauch (2009) used stable sulfur isotopes to show that sulfate in the Dolores River is derived from the dissolution of gypsum in the Mancos Shale and other sedimentary rocks upstream from the Paradox Valley as well as from anhydrite in the Paradox Formation. In fact, some of the greatest sulfate concentrations (greater than 800 mg/L) occurred during late summer and fall storm events related to monsoonal weather patterns. During these storm events, sulfate concentrations were elevated at both stream sites, suggesting that sulfate under these hydrologic conditions is largely derived from areas upstream from the Paradox Valley.



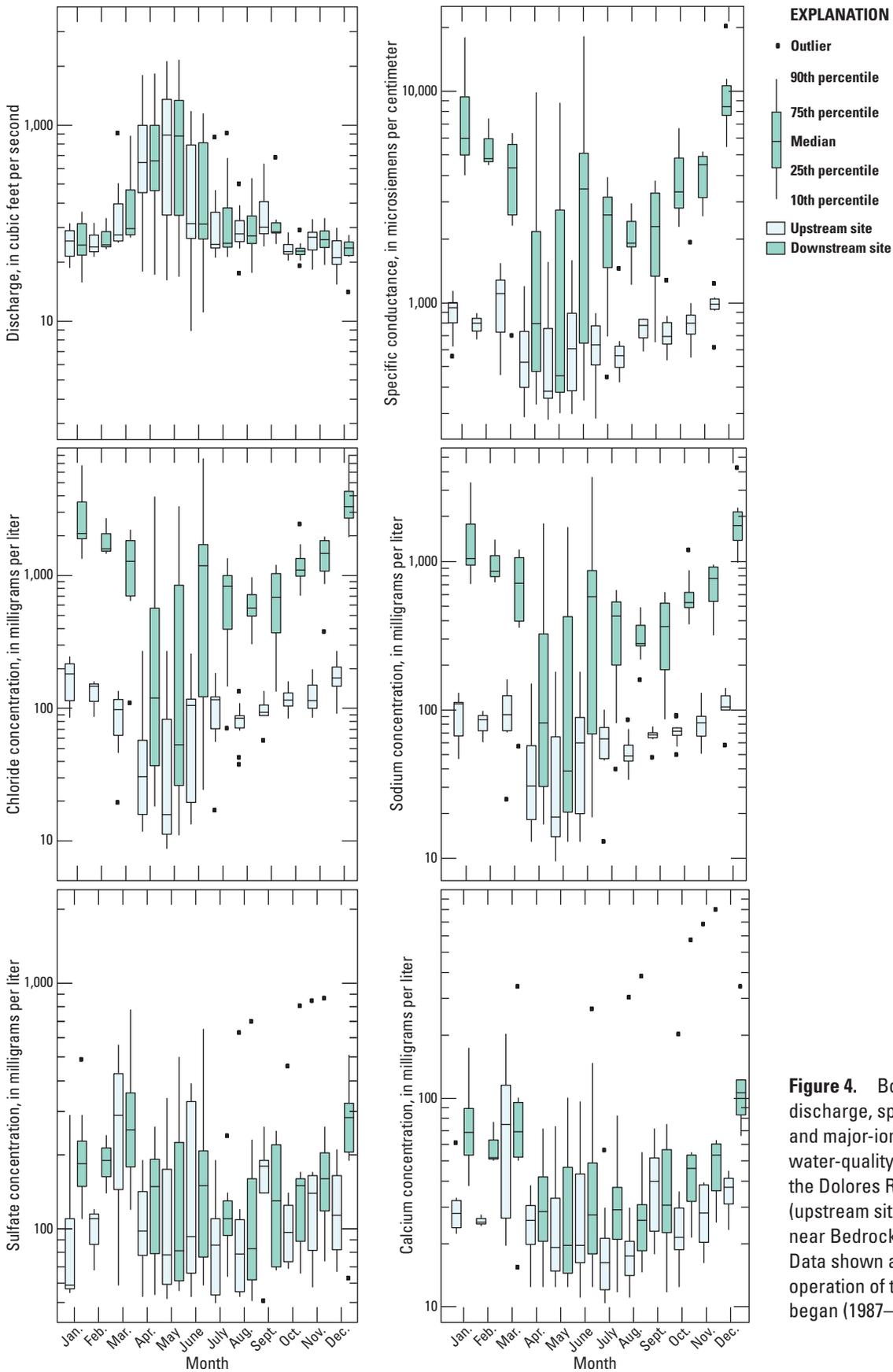


Figure 4. Boxplots comparing discharge, specific conductance, and major-ion concentrations in water-quality samples collected at the Dolores River at Bedrock site (upstream site) and the Dolores River near Bedrock site (downstream site). Data shown are for the period before operation of the Paradox Valley Unit began (1987–1993).

Regression Analysis for Estimating Total Dissolved Solids Concentrations

Regression models were developed using TDS and SC measured in discrete water-quality samples collected from 1987 to 2015; coefficients and statistics for the models are presented in table 2. Initially, all samples at the downstream site were included in a linear model (table 2, model 1); however, a sample collected on July 10, 2013, with an unusually high SC (78,540 $\mu\text{S}/\text{cm}$) leveraged the regression line upward (Cook's Distance = 0.65, which measures the effect of removing an observation; Helsel and Hirsch, 2002) (fig. 5). When this sample was omitted from the regression, both the slope and intercept changed considerably (table 1, model 2), and the fit improved for samples at the lower end of the concentration range. Omitting this sample from the regression, however, limits use of the equation to SC values less than 25,700 $\mu\text{S}/\text{cm}$ (the second greatest value in the dataset). The July 10, 2013, sample was accurately measured during an extremely dry year when discharge in the river fell below 0.01 ft^3/s for several weeks in June and July. Although such dry periods are relatively rare, the daily mean SC at this site also exceeded 25,700 $\mu\text{S}/\text{cm}$ during the summers of 1981, 1982, 2002, and 2013 for a total of 51 days over the period of record. To better accommodate the entire range of concentrations, a second-order polynomial was fit to the complete dataset with a coefficient of determination (R^2) of 0.999 (table 2, model 3). Although the relation between TDS and SC is approximately linear at low to moderate concentrations, the relation becomes increasingly curvilinear at higher concentrations (Hem, 1985), which is consistent with the observed data for the downstream

site. In model 3, the y-intercept was fixed at zero to improve the fit for samples at the low end of the concentration range and because pure water has a conductance less than 1 $\mu\text{S}/\text{cm}$. The plot of residual TDS (observed minus predicted values) versus the predicted TDS concentrations (fig. 6A) illustrates heteroscedasticity because the magnitude of error in the predicted TDS is correlated with the value of predicted TDS. Heteroscedasticity often occurs when there is a wide range between the lowest and greatest values, as is the case for the downstream site where SC varies by nearly three orders of magnitude (note log scale in fig. 6A). Figure 6A also shows that the greatest residuals occur in samples with elevated sulfate concentrations and SC values in the 1,500–3,000 $\mu\text{S}/\text{cm}$ range. Increasing the sulfate-to-chloride ratio in solution will increase the slope of the TDS to SC relation, which is why the regression underestimated TDS for samples with elevated sulfate. The high-sulfate samples accounted for less than 5 percent of the discrete water-quality samples, and nearly all were collected during short-duration storm events in July through October. Given the intermittent nature of these events and the lack of detailed water-quality data during storms, it would be impractical to capture this level of variability in the regression model at this site.

For the upstream station, the fit of the linear model (table 2, model 4) is not as strong ($R^2=0.924$) as the linear fit for the downstream site because a group of samples with sulfate concentrations over 500 mg/L causes the values to diverge at the high end of the concentration range (fig. 7). As shown by the model 4 fit (dashed blue line in fig. 7), the high sulfate samples leverage the regression line upwards, which degrades the fit for low-concentration samples. Samples with

Table 2. Parameters and coefficients of determination of regression models used to estimate total dissolved solids concentrations from specific conductance for the Dolores River at Bedrock site (upstream site) and the Dolores River near Bedrock site (downstream site).

[95% CI, 95 percent confidence interval; SC^2 , coefficient for squared specific conductance term; n, number of samples; R^2 , coefficient of determination; Std. error, residual standard error in milligrams per liter; P, p-value; --, not used in model; <, less than]

Station	Model	Type	Intercept	95% CI	Slope	95% CI	SC^2	95% CI	n	R^2	Std. error	F-statistic	P
Downstream	model 1	linear	-184.3	36.9	0.628	0.005	--	--	252	0.995	257.4	51610	<0.001
Downstream	model 2	linear	-41.3	25.4	0.579	0.005	--	--	251	0.994	151.8	43750	<0.001
Downstream	model 3	polynomial	--	--	0.559	0.005	1.17E-06	8.16E-08	252	0.999	148.5	99630	<0.001
Upstream	model 4	linear	-84.6	22.6	0.696	0.024	--	--	257	0.924	81.35	3133	<0.001
Both	model 5	polynomial	--	--	0.562	0.004	1.13E-06	6.82E-08	509	0.998	126.6	139500	<0.001

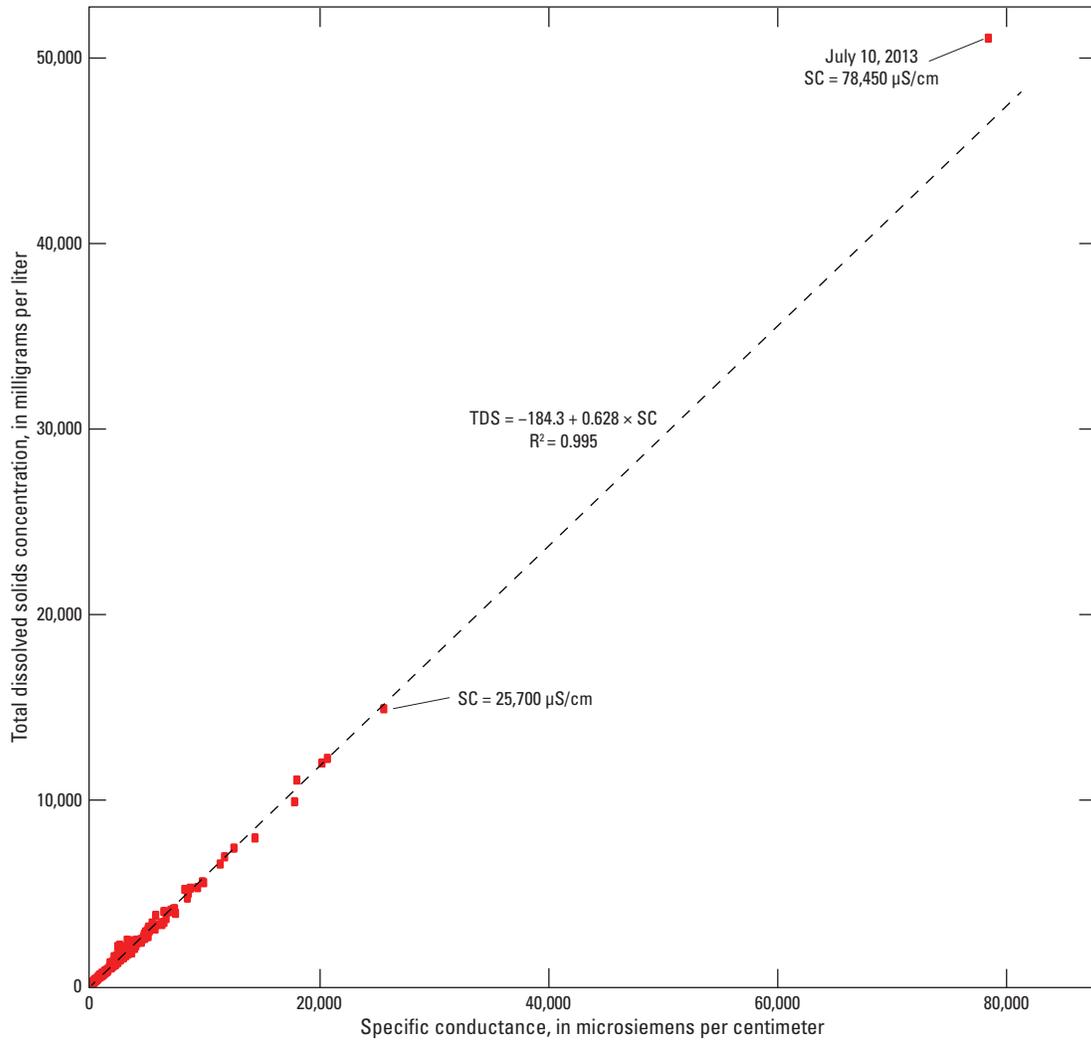


Figure 5. Specific conductance (SC) versus total dissolved solids (TDS) concentrations in 252 water-quality samples collected at the Dolores River near Bedrock site (downstream site) during 1987–2015. Sample collected on July 10, 2013, occurred during an exceptionally dry period when streamflow fell to the lowest level on record. Regression equation is model 1 in table 2. (R^2 , coefficient of determination)

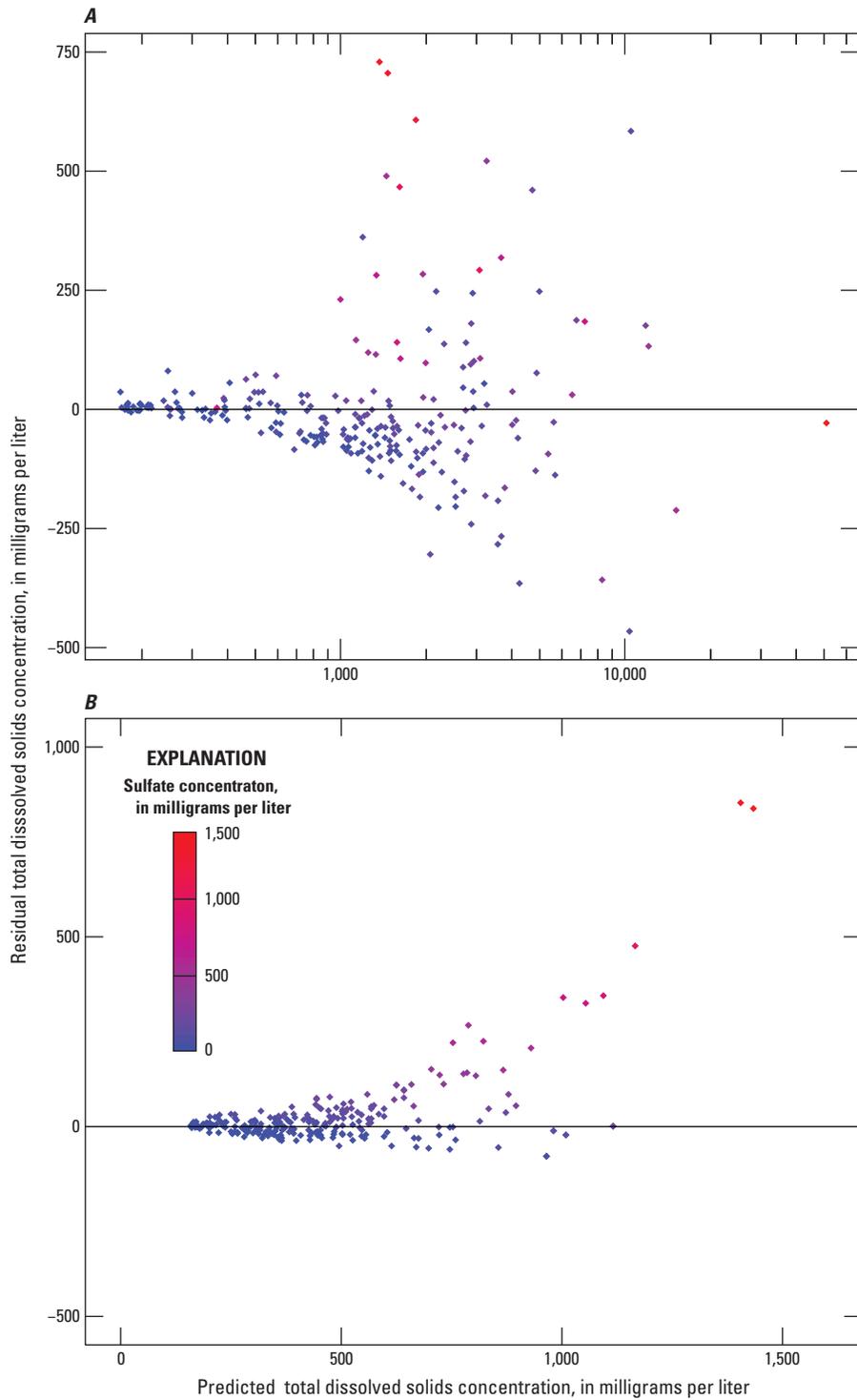


Figure 6. Predicted versus residual (observed – predicted) total dissolved solids concentrations using model 3 for (A) the Dolores near Bedrock site (downstream site) and model 5 for (B) the Dolores at Bedrock site (upstream site). Colors represent range of sulfate concentrations in water-quality samples.

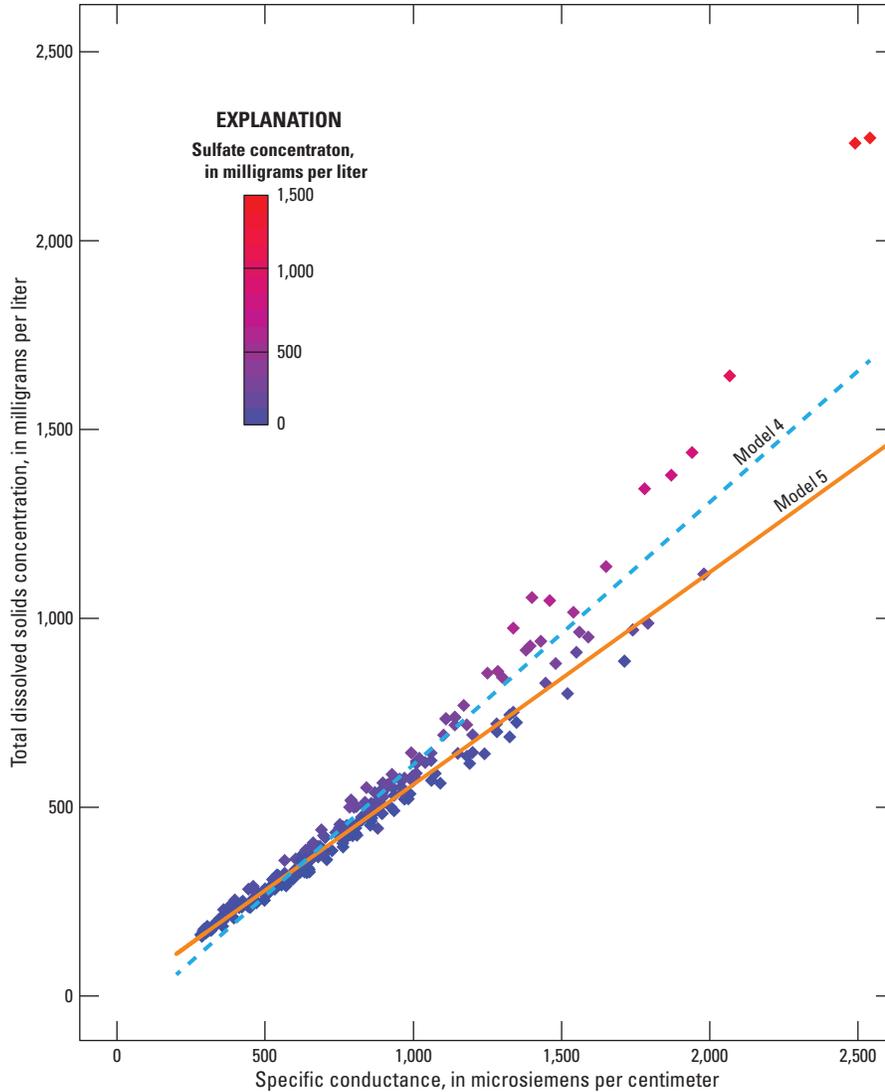


Figure 7. Specific conductance versus total dissolved solids concentrations for the Dolores River at Bedrock site (upstream site). Model 4 is a linear fit of data from the upstream site, and model 5 is a polynomial fit of data from both the upstream and downstream sites (see table 2). Colors represent range of sulfate concentrations in water-quality samples.

elevated sulfate, as observed at the downstream site, typically are associated with storm events in late summer and fall. Samples in the same SC range but with lower sulfate concentrations fall in line with a polynomial model fit to combined data from both the upstream and downstream sites (fig. 7 and table 2, model 5). Because high-sulfate samples account for a small fraction of samples collected, the combined-site polynomial model (table 2, model 5) may be more appropriate than the single-site linear model (table 2, model 4) for estimating TDS at the upstream site. Indeed, the residual plot in figure 6B shows that the polynomial model does a good job of estimating TDS over the entire range of samples, with the exception of samples with elevated sulfate. However, because sulfate concentrations typically are elevated at both stream sites

during storm events, any bias introduced by the regression may be similar at both sites and likely has minimal effect on the net salt load during those events. The polynomial models, therefore, provide the best fit for predicting TDS over a wide range of concentrations at both sites.

To test whether the relation between TDS and SC has changed over time, linear models were fit for the pre-PVU period (1987–1993), the entire post-PVU period (1997–2015), and two subdivisions of the post-PVU period (1997–2006 and 2007–2015). The outlier at the downstream site from July 10, 2013, was excluded from this analysis to avoid biasing the regression for any test period that included this sample. All data at the upstream site were retained for this analysis. Figure 8 compares the slope and intercept for each time

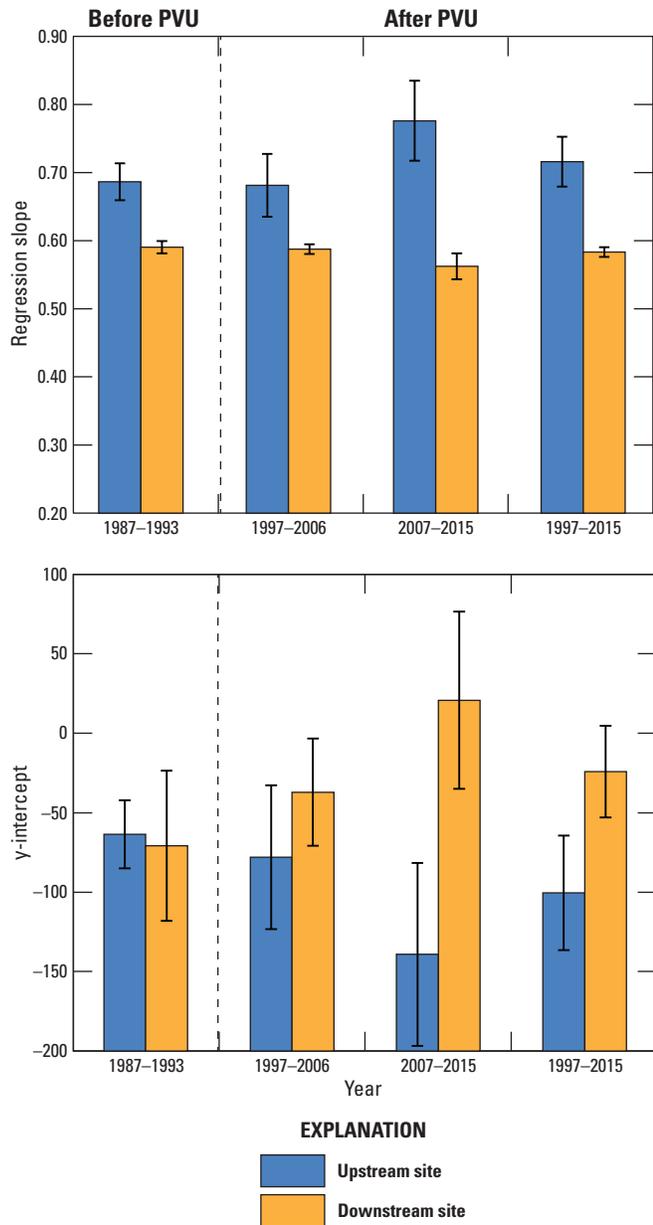


Figure 8. Comparison of slope and y-intercept resulting from linear fit of total dissolved solids concentrations with specific conductance for the Dolores River at Bedrock site (upstream site) and the Dolores River near Bedrock site (downstream site) for periods before and after operation of the Paradox Valley Unit (PVU) began. Error bars represent 95 percent confidence intervals for each regression coefficient.

period, with error bars showing the 95 percent confidence intervals of each coefficient. Although the coefficients differ among the pre- and post-PVU periods, the 95 percent confidence intervals overlap for all four time periods, suggesting that the relation between TDS and SC has not changed substantially over time. There appears to be more variability in the y-intercept than the slope, which may reflect differences in

the concentration ranges of the four time periods and, in particular, greater influence (or leverage) of high-concentration samples on the regression. If the y-intercept is set to zero, the linear-regression slopes for the downstream site are essentially identical between the pre-PVU period (slope = 0.574) and the post-PVU periods (slope = 0.573), suggesting that a single regression equation adequately represents the entire period of record.

Annual Salt Loads for the Dolores River

Based on the regression statistics (table 2) and residual plots presented in the previous section, model 5 was selected to estimate daily mean TDS at both the upstream and downstream sites. Daily loads were computed as the product of daily mean discharge and daily mean TDS (see “Data Analysis” section). Salt gain through the Paradox Valley was estimated as the load at the downstream site minus the load at the upstream site. A plot of daily salt gain for 2015 shows that the majority of the salt gain to the river occurs during winter and early spring (fig. 9). Although most days show large gains, there typically are several days each year with apparent losses (fig. 9). Negative values of daily salt gain often occur during short-duration discharge events, particularly in summer and fall, because of time lags in peak runoff between the upstream and downstream sites (for example, October 22–23 in fig. 9). Apparent salt losses also might result from measurement uncertainty, bias in the regression model, and (or) error associated with estimated SC records.

The computed annual salt load at both Dolores River sites and the annual salt gain through the Paradox Valley are tabulated with uncertainties in table 3. Annual salt gain computed in this study is plotted alongside values estimated using previously developed regression equations (U.S. Geological Survey, 2010) in figure 10. In this study, salt gain was computed back to 1980, whereas the U.S. Geological Survey’s earlier study (2010) only included data back to 1988. The earlier period was not included in the earlier study because the SC monitor at the downstream site was moved in 1988. In this study, the periods 1980–1987 and 1988–2015 were deemed comparable based on data from a nearby SC sensor operated by Reclamation. Salt gain was not computed for 1986–87 because of large data gaps during those 2 years. For 1988–2010, salt gains estimated by the U.S. Geological Survey (2010) average 4 percent less than those computed in this study but are within the ±15 percent average uncertainty estimate of this study. This small bias may be due to differences in the regression models but perhaps also differences in how periods of missing record were estimated.

Although routine operation of the PVU production wells did not begin until July 1996, some brine was removed intermittently during 1991–1995 for testing of the injection well (table 3). Because brine removal during the first 3 years of testing was minimal (less than 4 percent of the annual salt load in the river), these years were included in the pre-PVU period, defined as 1980–1993. Routine pumping did not begin until midway through 1996, so the post-PVU period

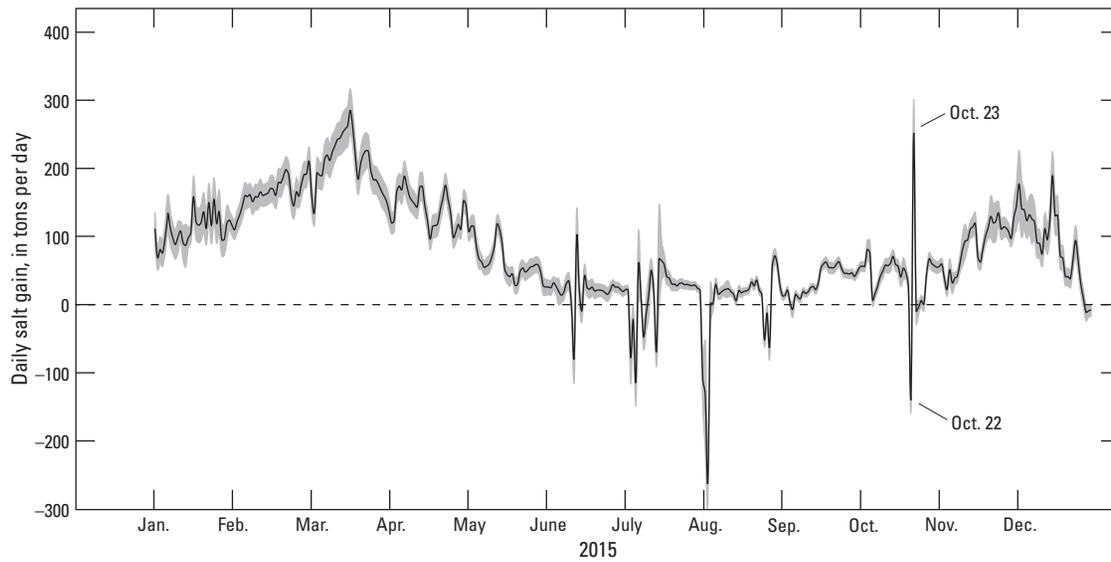


Figure 9. Daily salt gain with measurement uncertainty (gray) for the Dolores River through the Paradox Valley during 2015.

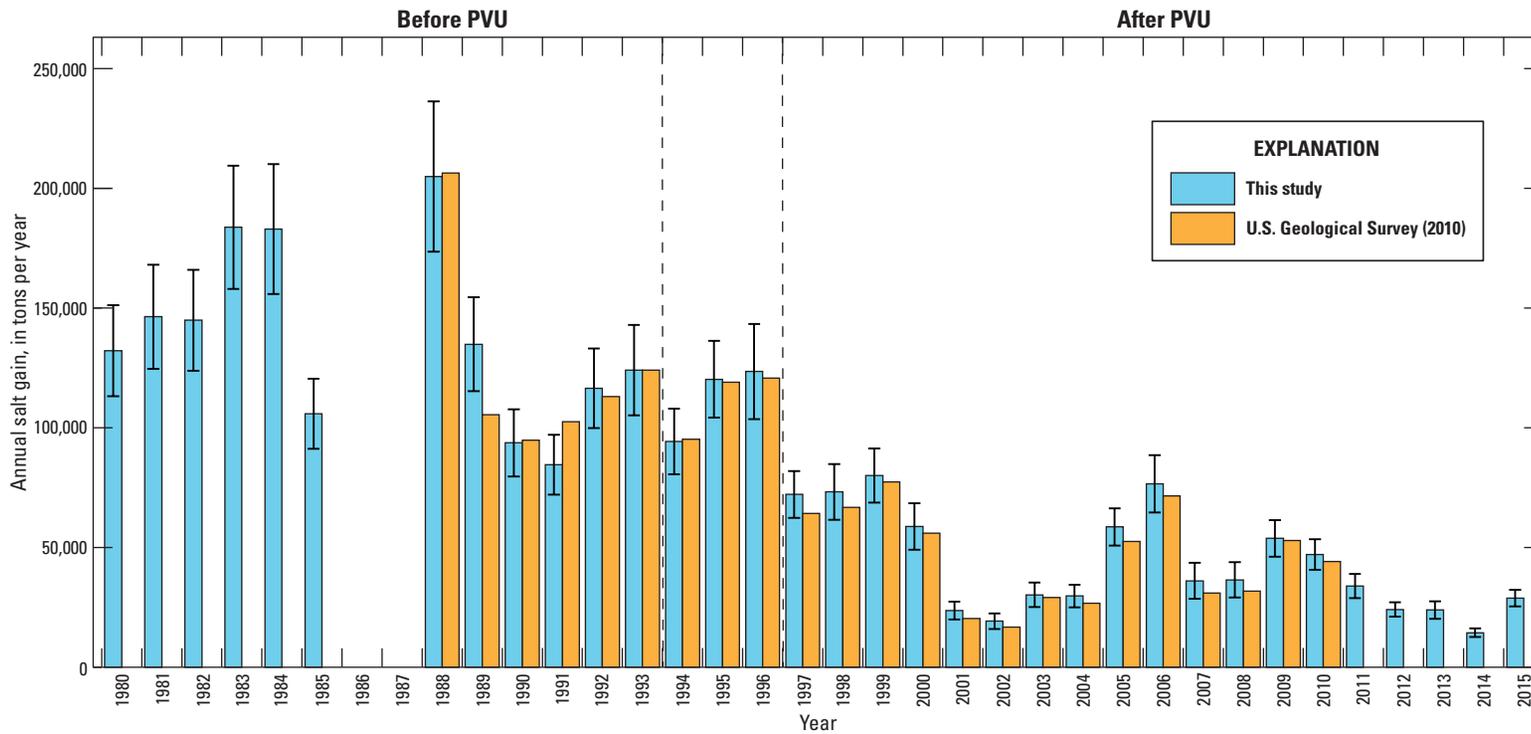


Figure 10. Annual salt gain in the Dolores River through the Paradox Valley with error bars showing measurement uncertainty for periods before and after operation of the Paradox Valley Unit (PVU) began (separated by vertical lines). Annual salt gains reported in the earlier study (U.S. Geological Survey, 2010) are included for comparison.

Table 3. Annual salt removal by the Paradox Valley Unit (PVU), salt loads with uncertainty estimates for the Dolores River at Bedrock site (upstream site) and the Dolores River near Bedrock site (downstream site), and net salt gain through the Paradox Valley for 1980–2015.

[tons/yr, tons per year; net salt gain is load at downstream site minus load at upstream site; --, insufficient data, *, salt removal during testing of PVU injection well]

Year	PVU salt removal	Dolores River at Bedrock		Dolores River near Bedrock		Net salt gain	
	Load tons/yr	Load tons/yr	Uncertainty ± tons/yr	Load tons/yr	Uncertainty ± tons/yr	Load tons/yr	Uncertainty ± tons/yr
1980	--	139,030	13,230	271,220	29,300	132,190	19,030
1981	--	43,800	4,500	190,210	20,400	146,410	21,740
1982	--	93,920	9,300	238,850	25,490	144,930	21,100
1983	--	196,480	18,330	380,250	39,640	183,770	25,710
1984	--	185,330	18,500	368,390	40,320	183,060	27,120
1985	--	176,950	17,480	282,870	27,400	105,920	14,650
1986	--	151,920	14,780	--	--	--	--
1987	--	--	--	--	--	--	--
1988	--	64,540	7,400	269,500	27,290	204,960	31,350
1989	--	56,040	6,070	190,980	18,390	134,940	19,560
1990	--	22,350	2,410	116,130	12,060	93,780	14,040
1991	4,750*	39,430	4,340	124,040	12,280	84,610	12,530
1992	7,090*	75,270	8,360	191,790	17,240	116,520	16,650
1993	11,110*	134,710	17,390	258,840	20,820	124,130	18,880
1994	61,960*	57,900	6,690	152,210	13,530	94,310	13,750
1995	26,100*	104,450	8,690	224,730	23,300	120,280	15,990
1996	33,730	32,270	3,270	155,780	19,420	123,510	19,840
1997	97,030	143,010	14,450	215,210	19,620	72,200	9,830
1998	125,970	91,860	10,520	165,140	18,040	73,280	11,600
1999	112,970	65,370	6,870	145,470	13,850	80,100	11,360
2000	85,230	43,370	5,450	102,240	10,890	58,870	9,700
2001	75,620	31,150	3,360	54,840	6,350	23,690	3,750
2002	111,810	14,970	1,960	34,260	3,760	19,290	3,300
2003	112,700	23,410	2,720	53,660	6,610	30,250	5,120
2004	103,040	29,270	3,140	59,100	6,880	29,830	4,720
2005	101,580	94,860	8,580	153,510	14,870	58,650	7,770
2006	101,700	42,780	5,480	119,440	10,690	76,660	11,980
2007	113,460	44,810	8,020	80,960	8,490	36,150	7,500
2008	111,450	74,670	12,410	111,190	12,890	36,520	7,400
2009	104,850	35,380	3,370	89,230	9,340	53,850	7,620
2010	111,910	42,330	3,620	89,450	9,340	47,120	6,360
2011	111,910	41,510	4,050	75,490	8,520	33,980	5,070
2012	112,690	24,630	1,710	48,820	4,930	24,190	2,960
2013	81,020	25,690	2,420	49,610	6,130	23,920	3,720
2014	100,940	28,240	2,020	42,720	4,250	14,480	1,770
2015	100,310	29,860	2,060	58,810	5,750	28,950	3,460

Table 4. Comparison of mean annual salt gain in tons per year in the Dolores River through the Paradox Valley before and after operation of the Paradox Valley Unit (PVU) began. Adjusted salt gains are based on the regression equation in figure 13. Salt disposal (tons per year) is the average annual salt injected through the PVU injection well during 1997–2015.

	Measured 1980–1993	Measured 1988–1996	Adjusted 1997–2015
Salt load in river before PVU	137,900±20,200 ^a	121,900±18,100 ^a	123,800±21,700 ^b
Salt load in river after PVU	43,300±6,600 ^a	43,300±6,600 ^a	43,300±6,600 ^a
Reduction in river salt load	94,600±21,200	83,200±19,900	80,500±22,700
Salt disposal at PVU	104,000±25,000 ^c	104,000±25,000 ^c	104,000±25,000 ^c

^aMeasurement uncertainty based on standard error propagation equation.

^b95th percentile confidence interval for values predicted using regression equation in figure 13.

^c95 percent confidence interval.

was defined as 1997–2015. The mean annual salt gain in the pre-PVU period was 137,900±20,200 tons per year during 1980–1993 and 121,900±18,100 tons per year during 1988–1996 (the period analyzed by U.S. Geological Survey [2010]) (table 4). The slightly greater salt gain estimated by this study for 1980–1993 may be caused by the wetter climatic conditions during the mid-1980s or exclusion of years during the testing period when some salt removal occurred; however, overlap in the uncertainty estimates suggests that measurement uncertainties also could explain this difference. After the PVU began operation (the post-PVU period), the mean annual salt gain in the river was reduced to 43,300±6,600 tons per year (1997–2015), or about 70 percent less than the salt gain before the PVU began operation.

A potentially important question is whether direct comparison of salt gains in the pre- and post-PVU periods is appropriate given that mean annual discharge was significantly ($p < 0.001$ for Wilcoxon rank-sum test) less in the post-PVU period (169 ft³/s) compared to the pre-PVU period (466 ft³/s) (fig. 11). Declines in streamflow in the Dolores River were caused by flow regulation and diversion at the McPhee Reservoir (completed in 1984) as well as increasing periods of drought in the post-PVU period, as illustrated by the Palmer Drought Index (fig. 11) for the upper Colorado River Basin (National Oceanic and Atmospheric Administration, 2015). Some water also is removed from the system by the PVU production wells; however, the mean annual pumping rate of 0.5 ft³/s is small relative to the change in river discharge between the pre- and post-PVU periods. Although the effect of declining river flows on brine discharge is unknown, the positive relation between annual salt gain and annual mean discharge (fig. 12) suggests that more brine is discharged to the river in wet years, perhaps because greater freshwater recharge to the alluvial aquifer enhances brine discharge into the river.

One approach to adjust salt loads for different flow conditions uses the relation between annual volume-weighted

mean (VWM) TDS and annual mean discharge in the pre-PVU period (fig. 13). The VWM TDS for each year was computed as the sum of the daily TDS times daily discharge divided by the sum of the daily discharge. The relation between TDS and discharge is strong and shows a clear shift between the pre- and post-PVU periods (fig. 13). Using the pre-PVU model in figure 13, VWM TDS was predicted using annual discharge for each year during 1997–2015, and salt loads were adjusted for this drier period as if the PVU did not exist. The drought year 2002 was omitted because discharge was much less than in any year during the pre-PVU period. The salt gain for 1997–2015 was then recomputed from the difference between the adjusted load at the downstream site minus the measured load at the upstream site (fig. 14). This method yielded an adjusted annual salt gain of 123,800 tons per year for the drier 1997–2015 period, which is 10 percent less than the salt gain during the wetter 1980–1993 period. The absolute difference in salt gain between the wetter and drier periods was 14,100 tons per year, which was still within the uncertainty (±20,200 tons per year) of the salt gain for the pre-PVU period.

Annual disposal of brine at the PVU ranged from 75,620 to 125,970 tons per year (table 3) and averaged 104,000 tons per year during 1997 to 2015 (table 4). The change in salt load in the river between the pre-PVU (1980–1993) and post-PVU (1997–2015) periods was 94,600 tons per year, comparing closely (within uncertainty) to the average annual salt disposal at the PVU (table 4). By using the shorter pre-PVU period (1988–1996), the apparent reduction in salt gain was 83,200 tons per year. The difference in these two estimates may be related to changes in streamflow, which declined between the pre- and post-PVU periods because of flow regulation at McPhee Reservoir and increasingly drier conditions. The adjusted average salt load, which accounts for the lower flow conditions of last two decades, is slightly lower at 123,800 tons per year (as described in the previous paragraph), suggesting that around 10 percent of the post-PVU period salt reduction might be due to decreased flow in the Dolores River.

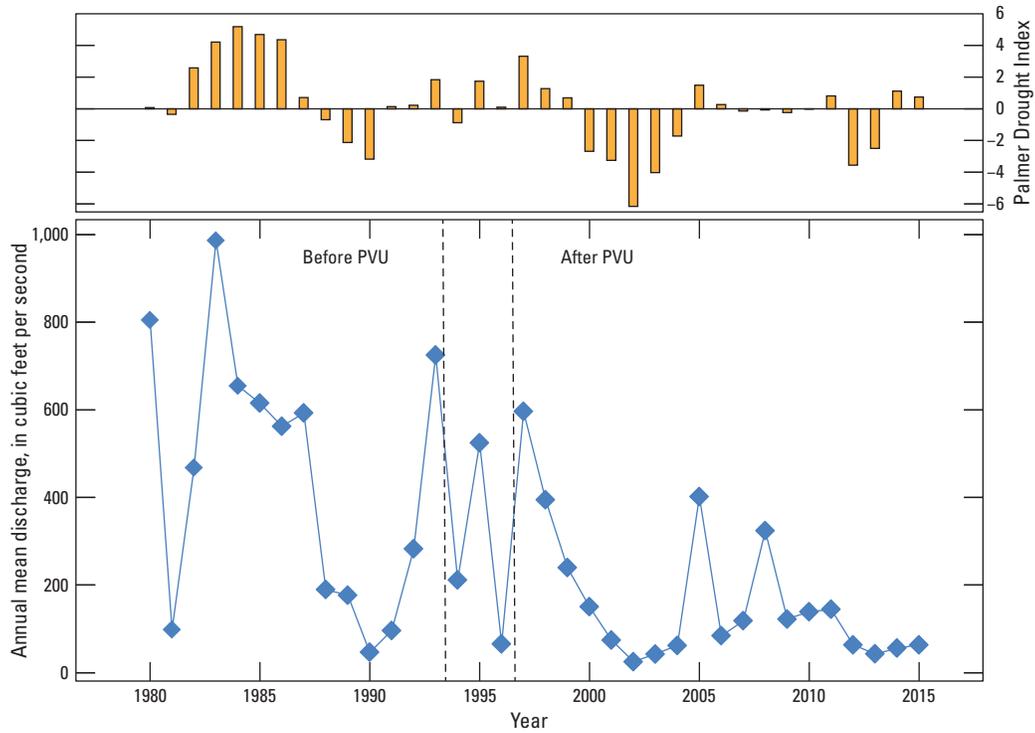


Figure 11. Annual mean discharge at the Dolores River near Bedrock site (downstream site) for periods before (1980–1993) and after (1997–2015) operation of the Paradox Valley Unit (PVU) began (separated by a vertical lines) with the annual Palmer Drought Index (PDI) for the upper Colorado River Basin. Negative values for the PDI indicate drought conditions.

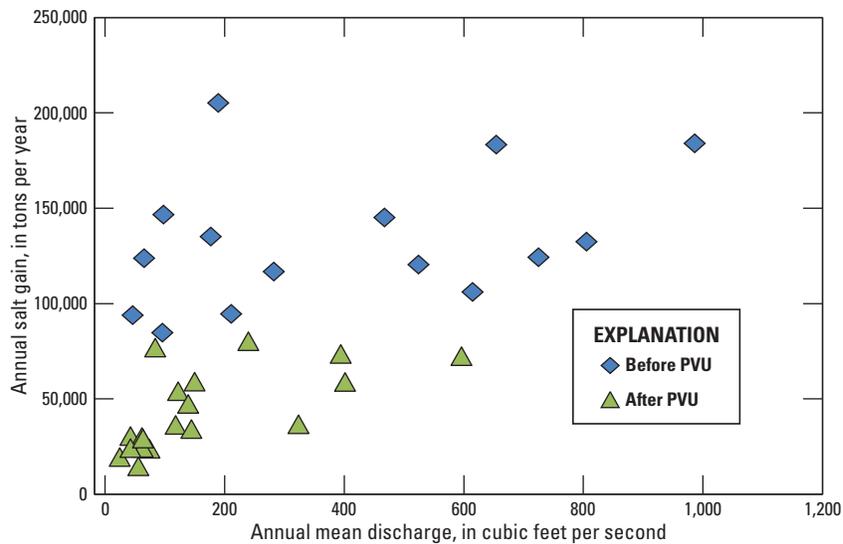


Figure 12. Annual mean discharge at the Dolores River near Bedrock site (downstream site) versus annual salt gain for periods before (1980–1993) and after (1997–2015) operation of the Paradox Valley Unit (PVU) began.

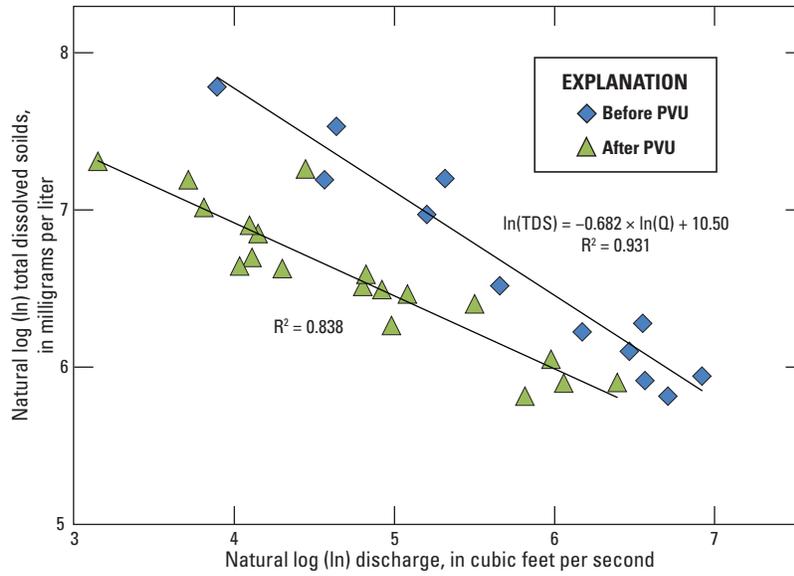


Figure 13. Annual mean discharge (Q) versus volume-weighted mean total dissolved solids (TDS) concentrations for the Dolores River near Bedrock site (downstream site) for periods before (1980–1993) and after (1997–2015) operation of the Paradox Valley Unit (PVU) began. Data for 2002 not included in regression. (R^2 , coefficient of determination)

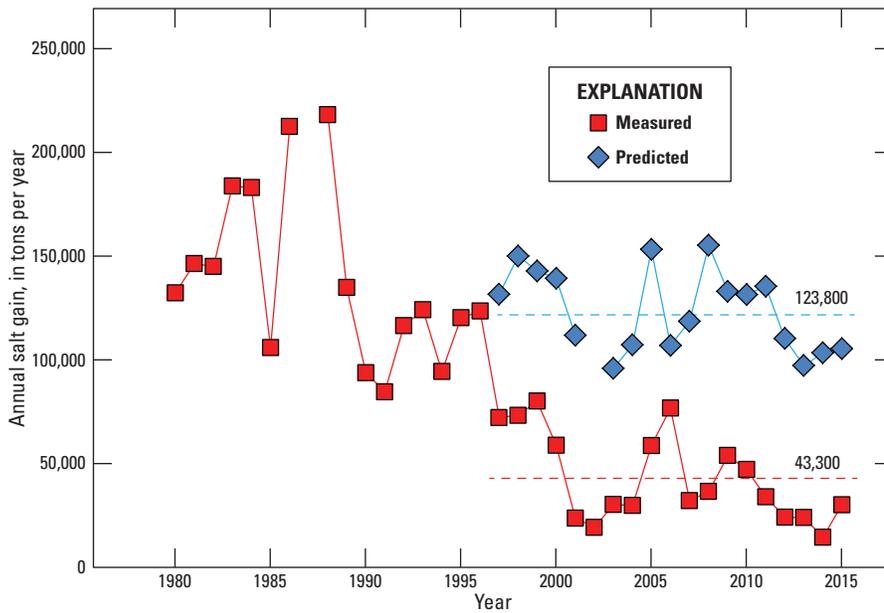


Figure 14. Annual salt gain in the Dolores River during 1980–2015. Predicted values derived from the relation between total dissolved solids and discharge before operation of the Paradox Valley Unit began (shown in figure 13). Data for 2002 not included in prediction.

Summary

This report documents regression models developed to relate total dissolved solids (TDS) concentrations to specific conductance (SC) for the Dolores River at Bedrock site (USGS station 09169500) and the Dolores River near Bedrock site (USGS station 09171100) using available data through 2015. These results will be used to update the regression equations reported on the U.S. Geological Survey National Real-Time Water Quality website (<http://nrtwq.usgs.gov/>). Additionally, the regressions are applied to continuous records of SC to estimate the gain in salinity to the river as it flows across the Paradox Valley for 1980 through 2015.

The water quality of the Dolores River changes considerably as it crosses the Paradox Valley because naturally saline groundwater discharges into the river. For example, during an extremely dry period in June 2013, the conductance of the river increased over 30-fold (1,990 to 31,000 microsiemens per centimeter) between the upstream and downstream sites. During the spring snowmelt period in April through June when streamflow is relatively high, major-ion concentrations at the downstream site approach those at the upstream site. During July through March, when streamflow is relatively low, brine discharge from groundwater has a greater influence on water-quality, and sodium and chloride dominate the major-ion composition at the downstream site with concentrations much greater than at the upstream site. Ranges of sulfate and calcium concentrations are fairly similar between the two sites during most months, suggesting that areas upstream of the valley as well as brine discharge are important sources of these solutes.

A second-order polynomial provided the best fit of TDS versus SC data for both the upstream and downstream sites. The largest residuals occurred in samples with elevated sulfate concentrations (greater than 500 milligrams per liter) that were associated with short-duration storm events in late summer and fall. Because sulfate concentrations often were elevated at both sites on the same sampling date, any bias introduced by the model likely has a negligible effect on the computed net salt load during those events. Regression models were compared between a period before operation of the Paradox Valley Unit (PVU) began (pre-PVU) and three periods after operation began (post-PVU) to test whether the relation had changed over time. Although regression coefficients are slightly different among the pre- and post-PVU periods, the 95 percent confidence intervals overlap for all four tested time periods, suggesting that the relation between TDS and SC has not changed significantly over time and that a single regression equation can be used for the entire period of record.

Salt gain through the Paradox Valley was estimated as the TDS load at the downstream site minus the load at the upstream site. The mean annual salt gain in the pre-PVU period (1980–1993) was 137,900 tons per year. After the PVU began operation (1997–2015), the salt gain in the river was reduced to 43,300 tons per year. The change in salt load in the river between the pre-PVU and post-PVU periods was 94,600 tons per year, which represents a nearly 70 percent

reduction in salt loading to the river and compares closely to the average mass of salt (104,000 tons) disposed of each year at the PVU injection well. However, around 10 percent of this salt load reduction might be attributed to declining streamflow in the post-PVU period.

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