State of California
California Natural Resources Agency
DEPARTMENT OF WATER RESOURCES
Division of Integrated Regional Water Management
North Central Region Office
Water Quality Evaluation Section

South Delta Ion Report

1/21/2021

Introduction:

The Water Quality Evaluation Section (WQES) began collecting standard ion samples at seven stations co-located with continuous water quality equipment measuring salinity conditions in the South Delta on June 20, 2018. Sampled stations are shown in Figure 1 and Table 1.

Increased ion sampling was requested by **BDO** modelers for the purpose of validating and improving the process of volumetric fingerprinting using **DSM2**, or other modeling simulations, in the South Delta. A volumetric fingerprint has been identified by Richard Denton to demonstrate the differing ratios of salinity derived in the Delta from seawater, Sacramento River, San Joaquin River at various stations at a given time (Denton 2015). It is our hope that Dentons fingerprinting methods can be applied to local salinity sources in the South Delta. The results of an ion sample are referred to as the "ionic fingerprint" or concentration of those various ions in a given sample. Increased ion sampling at stations with supporting flow and water quality data collection enables more precise and localized volumetric fingerprinting in the South Delta.

Hypothesis: Sugar Cut and Paradise Cut have unique ionic fingerprints compared to other adjacent South Delta channels.

1. **Local sources** and **long residence times** contribute to <u>higher salinity within Sugar Cut and Paradise Cut.</u> The action of **tidal pumping** in this region causes an unquantified contribution of salinity into Old River downstream of the confluence between Old River, Doughty Cut, Paradise Cut, and Sugar Cut through tidal dispersion. This action can be a contributing factor with significantly higher salinity at the Old River at Tracy Rd Bridge station (OLD) and is a factor to non-compliance with D-1641 Water Quality Objectives for Agricultural Beneficial Uses in the South Delta.
2. If the local sources of salinity within Paradise Cut and Sugar Cut have a unique ionic fingerprint then the samples may be valuable in modeling tidal dispersion and creating more specific volumetric fingerprints in the South Delta. Our hope is that the ion samples will contribute to identifying the impacts of State and Federal water project operations on South Delta salinity versus local contributions.

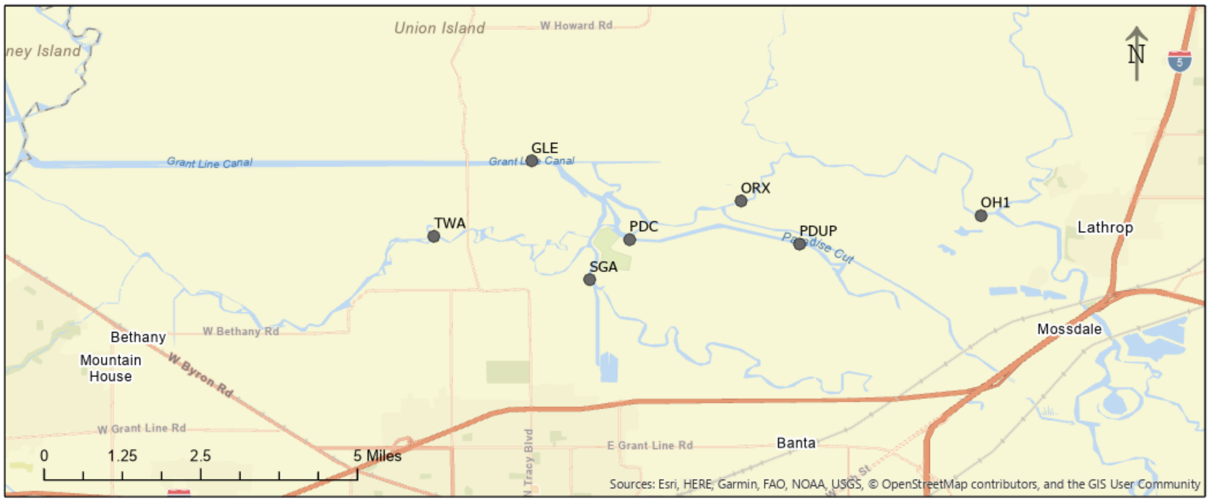

Figure 1: Map of stations with continuous water quality and ion concentration measurements in the South Delta.

Table 1: Station information including Water Data Library discrete water sample station ID and geographic coordinates in WGS 84.

Station Name	Code	Discrete Samples Station ID	Latitude WGS84	Longitude WGS84
Grant Line Canal East	GLE	B9D74921261	37.82025	-121.434861
Old River above Doughty Cut	ORX	B9D74871232	37.8109972	-121.386575
Old River at TWA	TWA	B9D74821274	37.802833	-121.457444
Old River near Head	OH1	B9D74851200	37.807595	-121.331218
Paradise Cut	PDC	B9D74811247	37.8020598	-121.4122564
Paradise Cut Upstream	PDUP	B9D74811224	37.801027	-121.373089
Sugar Cut at Golden Anchor	SGA	B9D74761253	37.79286	-121.421495

Methods:

Salinity is the cumulation of dissolved salts, or ions, and is measured using the electrical conductance of water. Specific conductance (SpCond) is electrical conductance that is corrected to a standard 25 °C temperature. SpCond was collected using **Yellow Springs Instruments (YSI) EXO conductivity** and temperature sensors at seven long-term continuous water quality monitoring stations in the South Delta (Figure 1 and Table 1). **These seven stations were chosen to represent primary South Delta channels. The seven stations represent all of the upstream and downstream channel connections to the Doughty Cut region, where Paradise Cut and Sugar Cut connect.** Paradise Cut and Sugar Cut have previously been identified as sources of salinity (DWR 2020). Grab samples were then collected monthly for ion analysis at 1-meter depth using a Van Dorn sampler during routine station maintenance visits at these seven South Delta stations (Figure 1 and Table 1). The grab samples were filtered using a 0.45 micron filter then analyzed by DWR Bryte Laboratory to determine a suite of thirteen parameters at DWR's Bryte laboratory according to the established methods referenced in Table 2.

Table 2: Bryte laboratory ion constituent, analysis method, and reporting limits.

Parameter	Abbreviation	Method Reference	Reporting Limit	Units
Specific Conductance	SpCond	Std Method 2510-B	1	µS/cm@25 °C
Total Dissolved Solids	TDS	Std Method 2540 C	1	mg/L
Dissolved Chloride	Cl	EPA 300.0 28d Hold	10	mg/L
Dissolved Sulfate	SO4	EPA 300.0 28d Hold	10	mg/L
Dissolved Sodium	Na	EPA 200.7 (D)	1	mg/L
Dissolved Calcium	Ca	EPA 200.7 (D)	1	mg/L
Dissolved Magnesium	Mg	EPA 200.7 (D)	1	mg/L
Dissolved Nitrate	NO3	EPA 300.0 28d Hold	0.1	mg/L
Dissolved Potassium	K	EPA 200.7 (D)	0.5	mg/L
Dissolved Bromide	Br	EPA 300.0 28d Hold	0.05	mg/L
Dissolved Boron	B	EPA 200.7 (D)	0.1	mg/L
Alkalinity	Alkalinity	Std Method 2320 B	1	mg/L as CaCO3
Dissolved Hardness	Hardness	Std Method 2340 B (D)	1	mg/L as CaCO3

The fraction that a particular ion contributes to the overall salinity of a sample is the measured ion's concentration divided by the TDS of the sample. Total Dissolved Solids (TDS) is the combined total of all organic and inorganic substances dissolved in a water sample (APHA 2012). The relative fractions of the all measured ions to TDS is called the ion fingerprint. The ion fingerprint has been shown to be stable for a salinity sources and can be useful in distinguishing between different sources of salinity (Denton 2015). The ion percentage of TDS changes across the range of SpCond, therefore ion fingerprints are presented for ranges of SpCond. Three ranges of SpCond were used to help distinguish how the relationships change across the full range of SpCond. These ranges are low, mid, and high and are defined as SpCond less than 250 µS/cm as low, 250 – 1,000 µS/cm as mid, and SpCond greater than 1,000 µS/cm as high. The break points for the ranges were chosen to highlight the differences at the extreme low and high of the SpCond range while maintain a reasonable number of samples in each group. A total of 186 samples were collected and analyzed for this report, with 33 samples classified as low, 122 samples as mid, and 31 samples as high. The ion fingerprint for each range is estimated to be the average ion fractions of all samples in each particular range.

Regression Analysis

In a report prepared for the State Water Project Contractors Authority, Richard Denton created equations to predict individual ion concentrations from SpCond for water with salinity sources designated as sea water, fresh water, and agriculture dominant (Denton 2015). For the agriculture dominate salinity source, Denton uses San Joaquin River at Vernalis and San Joaquin at Brandt Bridge data. The quality of water in the San Joaquin River is heavily influenced by agricultural drainage, urban drainage, and mixed with relatively freshwater from the Stanislaus, Tuolumne, and Merced Rivers.

The equation used by Denton 2015 takes the form:

$$y = ax^2 + bx + c$$

Where y represents the response variable, or ion of interest and x represents the predictor variable, or SpCond. The regression coefficients *a*, *b*, and *c* were determined using MS Excel regression functions which minimizes the squared sum of the residual values between the modelled concentrations and measured concentrations. Table 3 shows the regression coefficients developed by Denton for the San Joaquin River to predict ion concentration from SpCond. The highest level of SpCond presented at these locations in Denton's report is under 1,700 µS/cm (Denton 2015 Appendix B).

Table 3: Denton equation coefficients for agriculture dominate source water to predict ion concentration from SpCond. (Denton 2015 Table 7.10)

Parameter (y)	**a**	**b**	**c**	**R2**
TDS	3.50E-05	0.56	7	0.994
Cl	1.70E-05	0.13	-8	0.982
SO4	3.50E-05	0.11	-1.2	0.948
Na	1.30E-05	0.109	-3.1	0.984
Ca	1.00E-06	0.045	2.8	0.96
Mg	6.00E-07	0.026	-0.1	0.955
K	0.00E+00	0.0029	0.8	0.63
Br	7.00E-08	0.0004	-0.035	0.894
Hardness	-3.00E-06	0.224	4.3	0.974
Alkalinity	-3.00E-05	0.15	13.5	0.91

Regressions for South Delta data were done for each ion constituent on to SpCond following the same quadratic equation as the Denton report. Regression coefficients were determined using R functions. In this report, comparison to the Denton equations is done graphically by plotting South Delta data and regression equations on the same graph as the Denton agriculture and sea water regression equations. Where appropriate, boxplots are also presented showing the inner quartile range as a box, with the median represented as a line through the middle of the box and vertical whiskers defining points 1.5 times the inner quartile range above or below the 1st and 3rd quartile. Outliers are displayed as dots.

Results and Discussion:

Stations show a gradient of SpCond levels based on channel proximity to the San Joaquin River and direction of flow. Stations further away from the flow path of the San Joaquin River through the South Delta generally have higher SpCond levels, with the exception of GLE. Paradise Cut and Sugar Cut are both dead-end sloughs and the primary mechanism for water exchange is through tidal mixing. Both Paradise Cut (PDC and PDUP) and Sugar Cut (SGA) stations generally have higher levels of SpCond than other South Delta stations, with PDUP having the highest SpCond levels (Figure 2).

Samples from stations were not uniformly distributed across the three established SpCond ranges (Figure 3). Most stations had SpCond levels in the mid-range of 250-1,000 µS/cm, but PDUP differed from all other stations maintaining SpCond concentrations above 1,000 µS/cm during most of the ion sampling period (Figure 2 and 3).

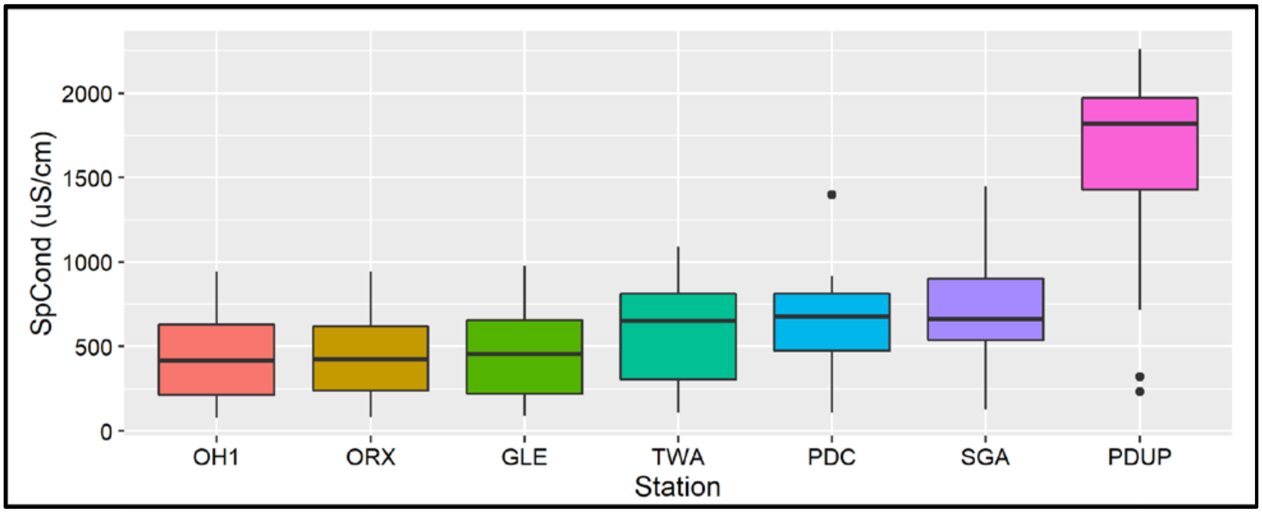

Figure 2: Station SpCond ranges for all samples.

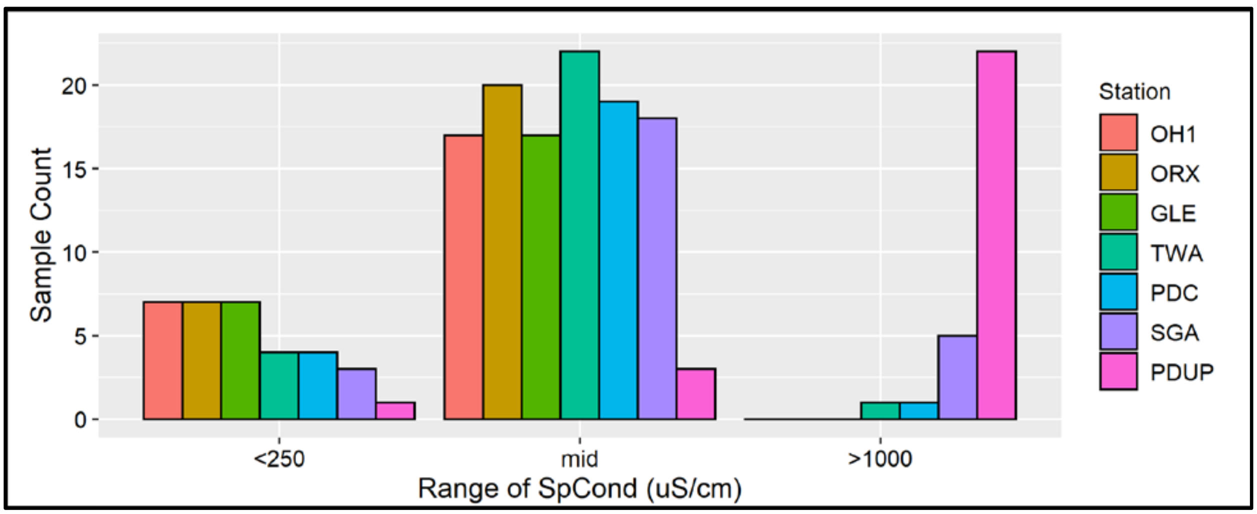

Figure 3: Number of station ion samples collected in each SpCond range.

Ion Fingerprints

The average ion percentage of TDS across all stations and SpCond ranges resulted in the ions chloride (Cl), sulphate (SO4), sodium (Na), and calcium (Ca) being the largest contributors (Table 4 and Figure 4). The fraction that each ion contributes to TDS changes across the range of SpCond values (Figure 5). The greatest change occurs as SpCond levels rise from their lowest values into the mid-range (250-1,000 µS/cm). PDUP was the primary station represented in the high-range (> 1,000 µS/cm) and this resulted in some differing ion percentages from other stations. This included higher chloride (Cl), calcium (Ca), and bromide (Br) and lower nitrate (NO3) and boron (B) ion percentages then other stations (Figure 5).

Table 4: Average ion percentage of TDS across all stations.

	EC Range (µS/cm)		
Ion	**Low (<250)**	**Mid (250 – 1,000)**	**High (>1,000)***
Chloride (Cl)	16.40%	24.21%	30.48%
Sulphate (SO4)	15.77%	18.90%	18.25%
Sodium (Na)	15.57%	19.25%	16.49%
Calcium (Ca)	10.36%	8.95%	10.36%
Magnesium (Mg)	4.64%	4.64%	4.57%
Nitrate (NO3)	1.98%	1.45%	0.25%
Potassium (K)	1.50%	0.97%	0.46%
Bromide (Br)	0.05%	0.07%	0.09%
Boron (B)	0.05%	0.07%	0.05%

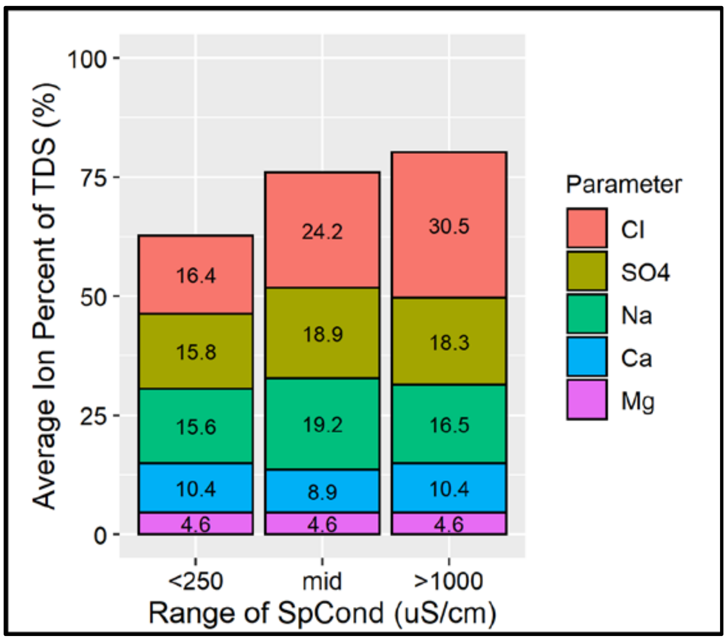

Figure 4: Ion percent of TDS for low (<250), mid (250-1,000), and high (<1,000) SpCond range for the 5 highest ions by percent.

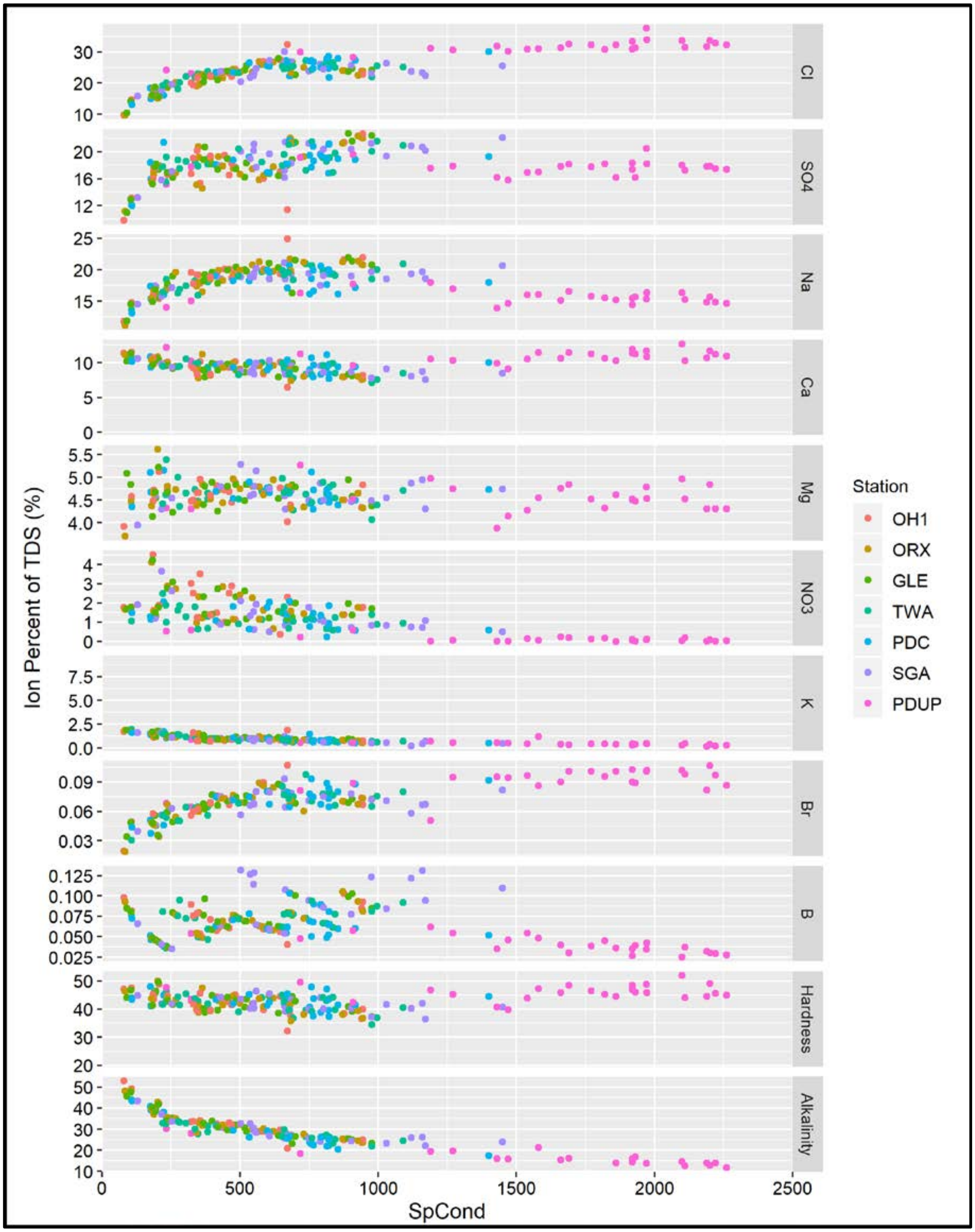

Figure 5: Ion percent of TDS across all stations and the full range of SpCond

Regression Equations

SpCond was a strong predictor for most of the ion constituent concentrations (Table 5 and Figures 6-17). The regression equations do not fit the ion concentration data well for nitrate (NO3), potassium (K), and boron (B) (Figures 12, 13, and 15). These ions are essential nutrients for agricultural crops, local aquatic vegetation, and phytoplankton, which may influence concentrations. Station SGA, located on Sugar Cut, has levels of boron (B) that are generally higher than other stations (Figure 15). The difference in boron levels at SGA, as opposed to lower levels at PDC and PDUP, may be influenced by a shorter water retention period in Sugar Cut than in Paradise Cut. Location of agriculture outfalls in proximity to SGA station may also affect boron concentrations, as boron compounds are often used in agricultural fertilizers. There is uncertainty in using these regression equations to predict ion concentrations for all stations when SpCond is above 1,000 µS/cm because only a few stations are represented at this SpCond range and the regression equations are heavily influenced by the high SpCond at PDUP. See Figure 18 and Figure 19 in the appendix for comparison of model error and regression equations separated by station and parameter.

Table 5: Regression results for a quadratic fit of all South Delta ion data using SpCond. Formula: $y = ax^2 + bx + c$. R^2 represents the squared residuals of the fitted model and N represents the number of data points included.

Parameter (y)	**a**	**b**	**c**	**R^2**	**N**
TDS	3.72E-05	5.37E-01	4.99	0.998	186
Cl	4.14E-05	1.18E-01	-3.77	0.992	186
SO4	-5.89E-06	1.24E-01	-6.73	0.981	186
Na	-1.84E-05	1.35E-01	-7.76	0.985	186
Ca	1.76E-05	2.99E-02	4.96	0.986	186
Mg	1.48E-06	2.46E-02	0.35	0.994	186
NO3	-4.28E-06	8.48E-03	0.93	0.318	186
K	-1.35E-06	4.44E-03	0.89	0.265	186
Br	1.12E-07	3.68E-04	-0.02	0.978	186
B	-2.52E-07	7.74E-04	-0.10	0.746	185
Hardness	5.07E-05	1.75E-01	14.25	0.993	186
Alkalinity	-3.83E-05	1.59E-01	12.56	0.961	181

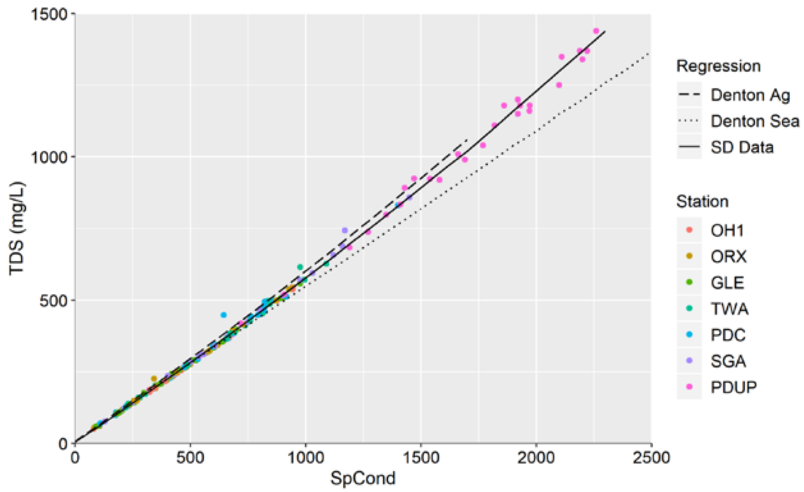

Figure 6: Relationship between TDS and SpCond with fitted South Delta regression line (solid black) and Denton agriculture regression line (dashed).

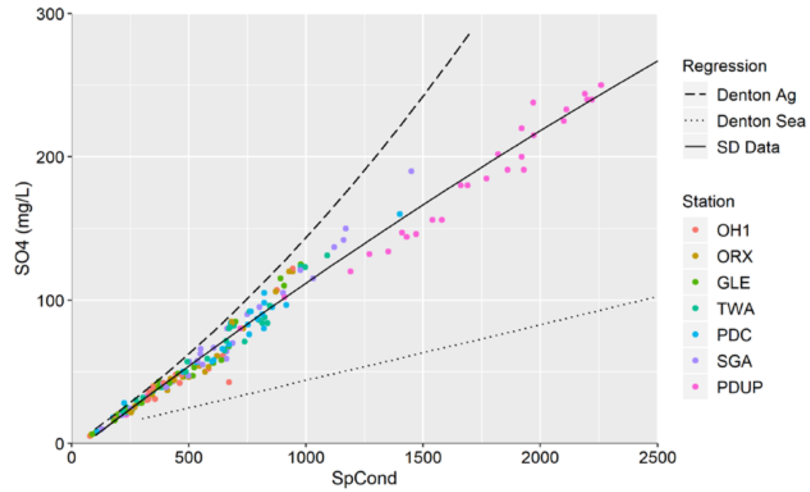

Figure 8: Relationship between sulfate and SpCond with fitted South Delta regression line (solid black) and Denton agriculture regression line (dashed).

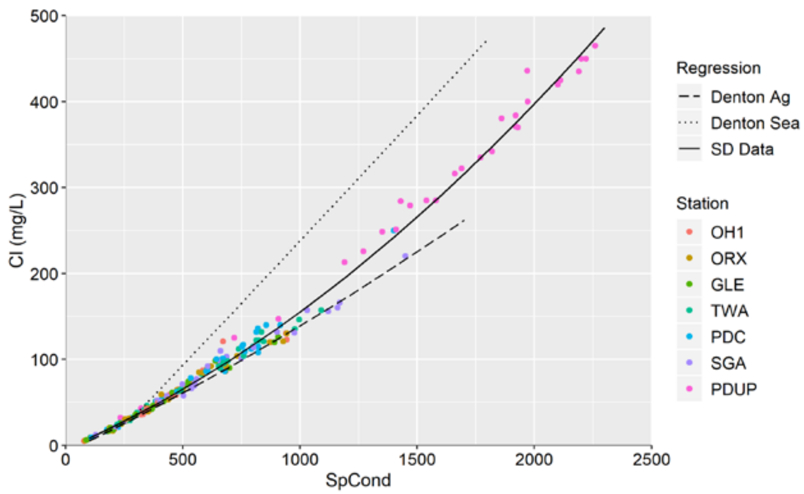

Figure 7: Relationship between chloride and SpCond with fitted South Delta regression line (solid black) and Denton agriculture regression line (dashed).

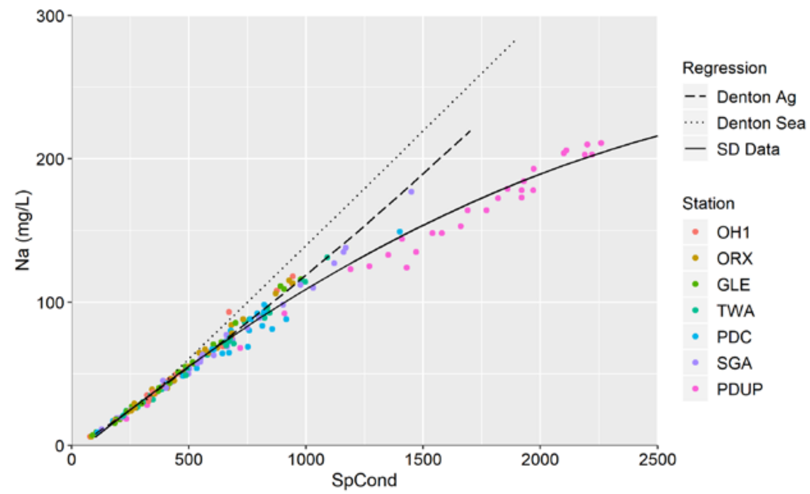

Figure 9: Relationship between sodium and SpCond with fitted South Delta regression line (solid black) and Denton agriculture regression line (dashed).

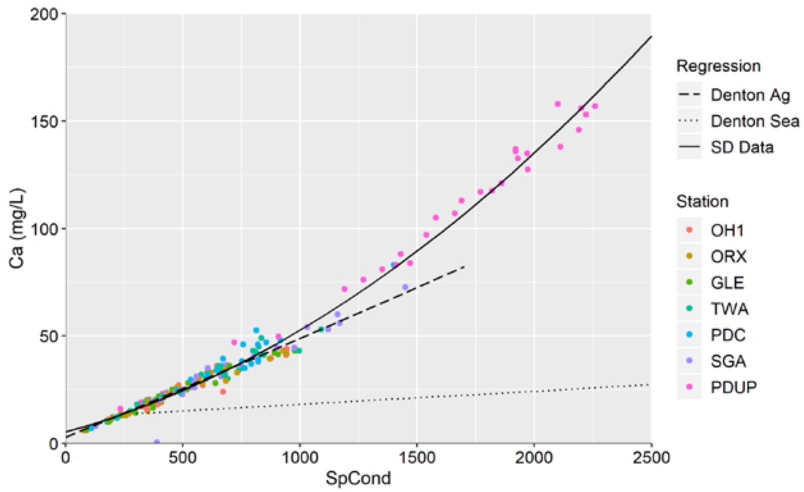

Figure 10: Relationship between calcium and SpCond with fitted South Delta regression line (solid black) and Denton agriculture regression line (dashed).

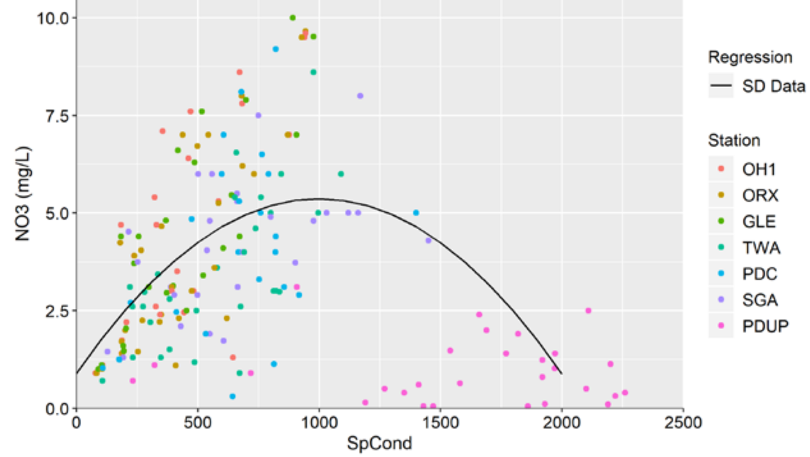

Figure12: Relationship between nitrate and SpCond with fitted South Delta agriculture regression line (solid black).

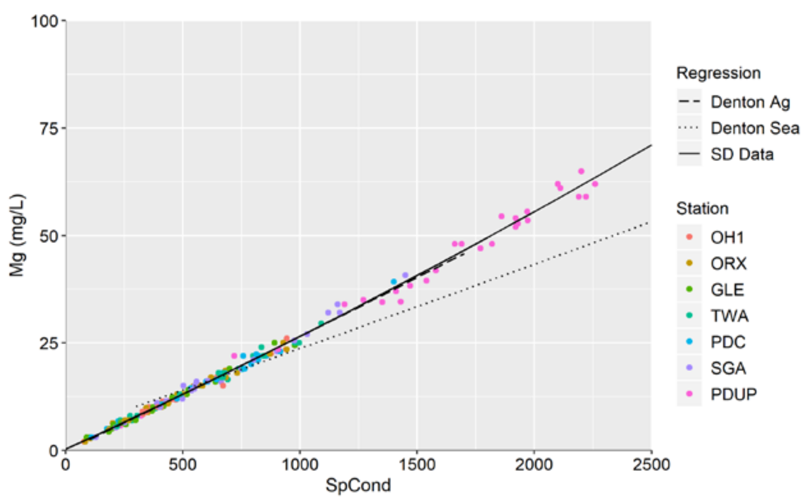

Figure 11: Relationship between magnesium and SpCond with fitted South Delta regression line (solid black) and Denton agriculture regression line (dashed).

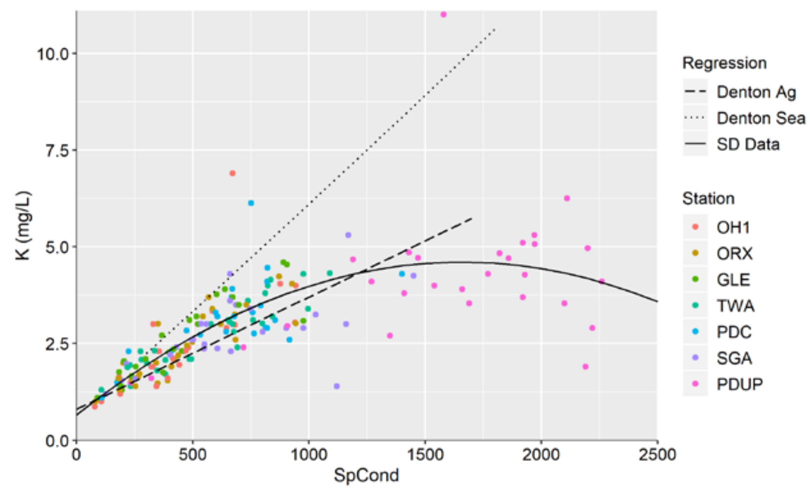

Figure 13: Relationship between potassium and SpCond with fitted South Delta regression line (solid black) and Denton agriculture regression line (dashed.

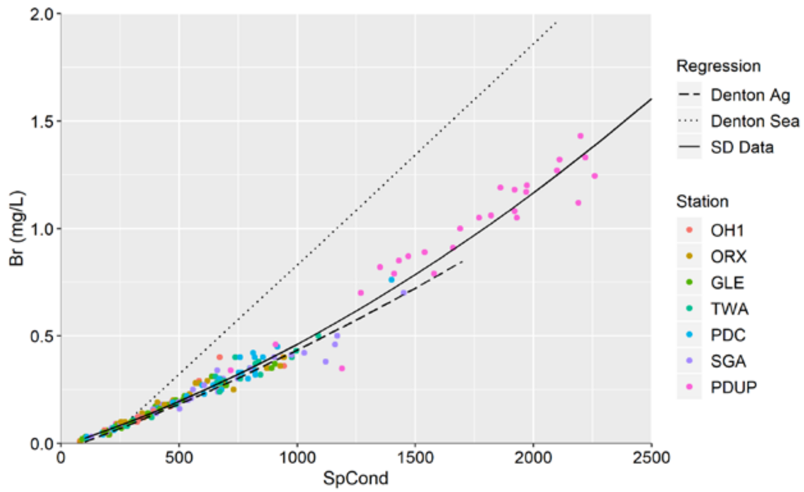

Figure 14: Relationship between bromide and SpCond with fitted South Delta regression line (solid black) and Denton agriculture regression line (dashed).

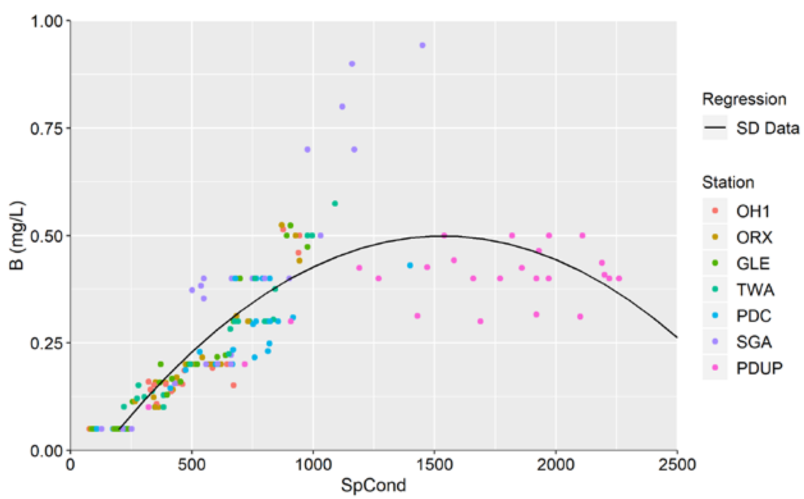

Figure 15: Relationship between boron and SpCond with fitted South Delta agriculture regression line (solid black).

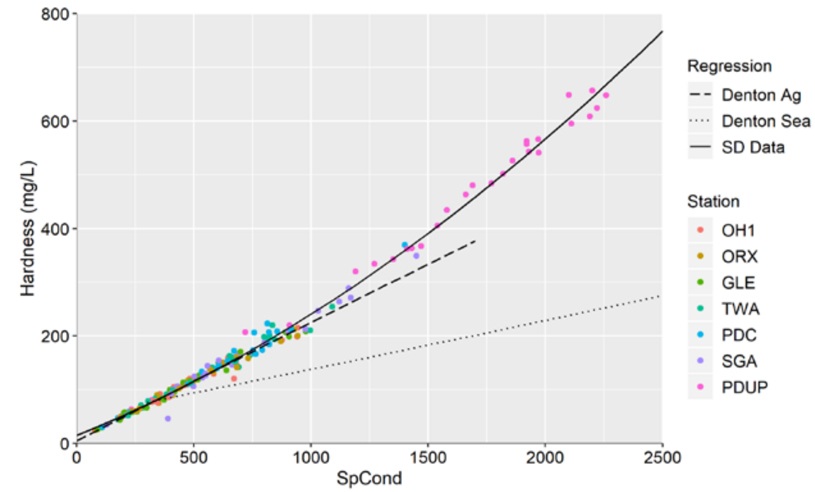

Figure 16: Relationship between hardness and SpCond with fitted South Delta regression line (solid black) and Denton agriculture regression line (dashed).

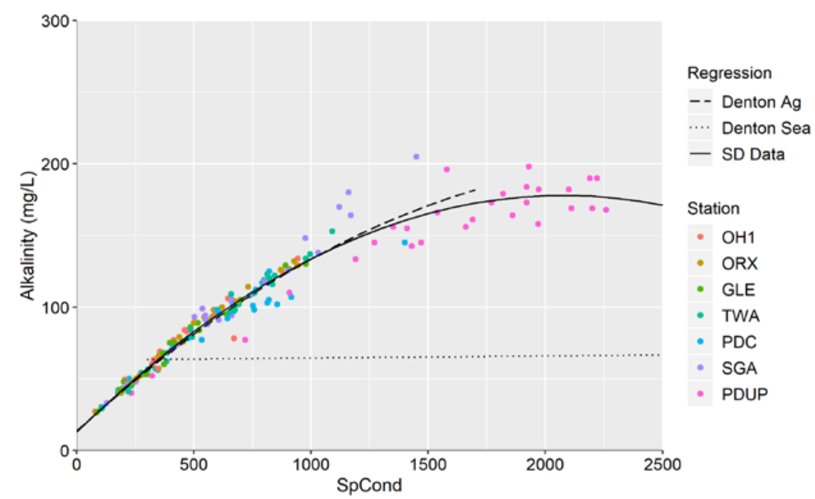

Figure 17: Relationship between alkalinity and SpCond with fitted South Delta regression line (solid black) and Denton agriculture regression line (dashed).

Conclusion:

Differences in ion percentages across the range of TDS concentrations suggests that the ion fingerprint will vary to some degree across the range of SpCond levels and stations. The results did provide support for our hypothesis, showing that both known salinity source channels Paradise and Sugar Cut did have some unique ion fingerprints. The relationship between SpCond and nitrate (NO3), potassium (K), and boron (B) at all stations were less consistent and are likely station dependent and more related to local habitat conditions, especially for Paradise Cut site PDUP that had SpCond values greater than 1,000 µS/cm. PDUP had higher SpCond than all other sites and showed some unique ion fingerprints for chloride (Cl), potassium (K), sulfate (SO4), nitrate (NO3), boron (B), and calcium (Ca). Sugar Cut station SGA had a higher boron (B) fingerprint than all other study sites. The remaining sites OH1, ORX, and GLE all had similar SpCond levels and ionic fingerprints that closely match Denton's San Joaquin River agricultural ionic fingerprint. We took one approach to analyzing this ion dataset but need further input from program managers and modelers to determine if the continuation or modification in the sample design maybe helpful in better tracking South Delta salinity sources beyond ongoing SpCond data collection. Overall, we feel this data may be a valuable tool in modeling tidal dispersion and creating more specific volumetric fingerprints in the South Delta for determining the movement of differing water sources and associated salinity conditions.

Limitations of WQES Analysis of Water Quality Samples (Knowledge gaps/limits):

- Residence time
- Evaporation rates
- Dispersion rates
- Barrier effects on mixing and dispersion
- Pumping effects on mixing and dispersion
- Nutrient uptake by aquatic vegetation
- Land use practices and characteristics of local drainage.
- Analysis on high-tide verses low-tide at SGA, PDC, and PDUP. Essentially two different bodies of water depending on the tide.

Requested Feedback:

WQES is reaching out to our project managers and the BDO and O&M modelers for feedback on this dataset and future sampling. The continuation of this sampling was proposed in the South Delta Comprehensive Operation Plan and Monitoring Special Study required for continued operation of the State and Federal pumping in the South Delta. Processing these samples is relatively inexpensive but is labor intensive. We want to ensure we are collecting useful data in an efficient manner. User feedback will allow us to refine our sampling plans before COP-required work is in full swing. Our questions are:

- Is this data useful?

    - Can it be used to perform more precise volumetric fingerprinting in the South Delta?
    - Will it contribute new evidence for local salt loading/transport?
    - Can it be used to help model or estimate tidal dispersion in the study area? Or would tracer studies be required?
    - Does it provide context that we can't get from SpCond alone?

- Is the geographic location of sampling appropriate?

    - Are there any critical gaps?
    - Are there any sampling sites that are redundant and do not need to be sampled?
    - As we gear up to conduct high speed water quality mapping, the possibility of performing sampling at points between stations is more feasible.

- Do specific sampling events need to be captured?

    - Such as full tidal cycles?
    - Seasonal considerations?
    - Should we spot sample at suspected high-salinity drainages?

Proposed Next Steps:

Further investigations could analyze seasonal and tidal impacts by combining the time-series data collected from continuous monitoring. While this may prove useful, likely the most significant portion of this comparison would be the analysis of SpCond for seasonal and tidal impacts. Due to the regression equations have been fitted to SpCond values, the results of comparing the SpCond seasonal and tidal trends should be the same as predicted ion concentrations. However, there may be a seasonal component to model residuals.

Sampling at station OH1, ORX, and GLE may not be necessary, as no significant differences were found in SpCond and ion concentrations between these locations. In addition, sampling at PDC, and SGA can be redundant during periods of upstream flow because upstream flow is generally water that has come from Old River and sampled either at ORX or TWA. PDC downstream flow can also be redundant because it often represents water that has been sampled at PDUP. The results from this report suggest that the South Delta ion sampling could be reduced to just stations ORX, PDUP, SGA, and TWA and still accurately track changes in expected SpCond ranges and the associated ion concentrations in the South Delta. Sampling at four locations would greatly reduce staff time and resources spent preparing, filtering, and analyzing samples.

References:

ALPHA 2005. Standard Methods for the Examination of Water and Wastewater, 21st edition. American Public Health Association, Washington, DC

Denton, Richard A. February 2015. *Delta Salinity Constituent Analysis.* Richard Denton and Associates, prepared for the State Water Project Contractors Authority.

California Department of water Resources. 2020. *South Delta Salinity Memo, Water Year 2019.* California Department of Water Resources, North Central Region, Water Quality Evaluation Section.

Appendix:

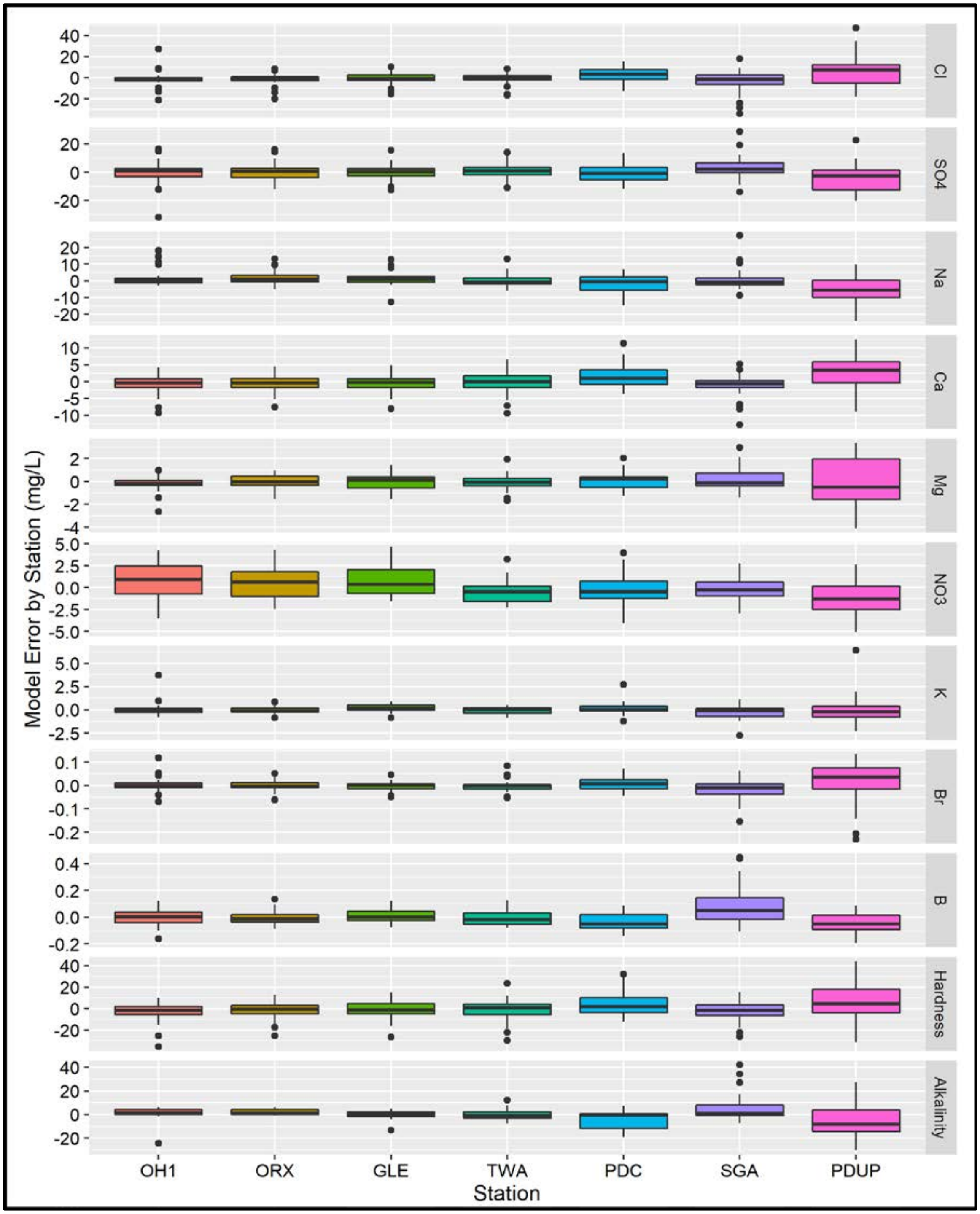

Figure 18: Error between observed ion concentration and model predicted ion concentrations for each parameter and station. Note, if boxplot ranges encompass 0 this provides evidence that individual stations do not have a heavily biased model error, which implies that the model is a good fit for all stations across the range of SpCond and that station specific differences in ion concentration are minimal.

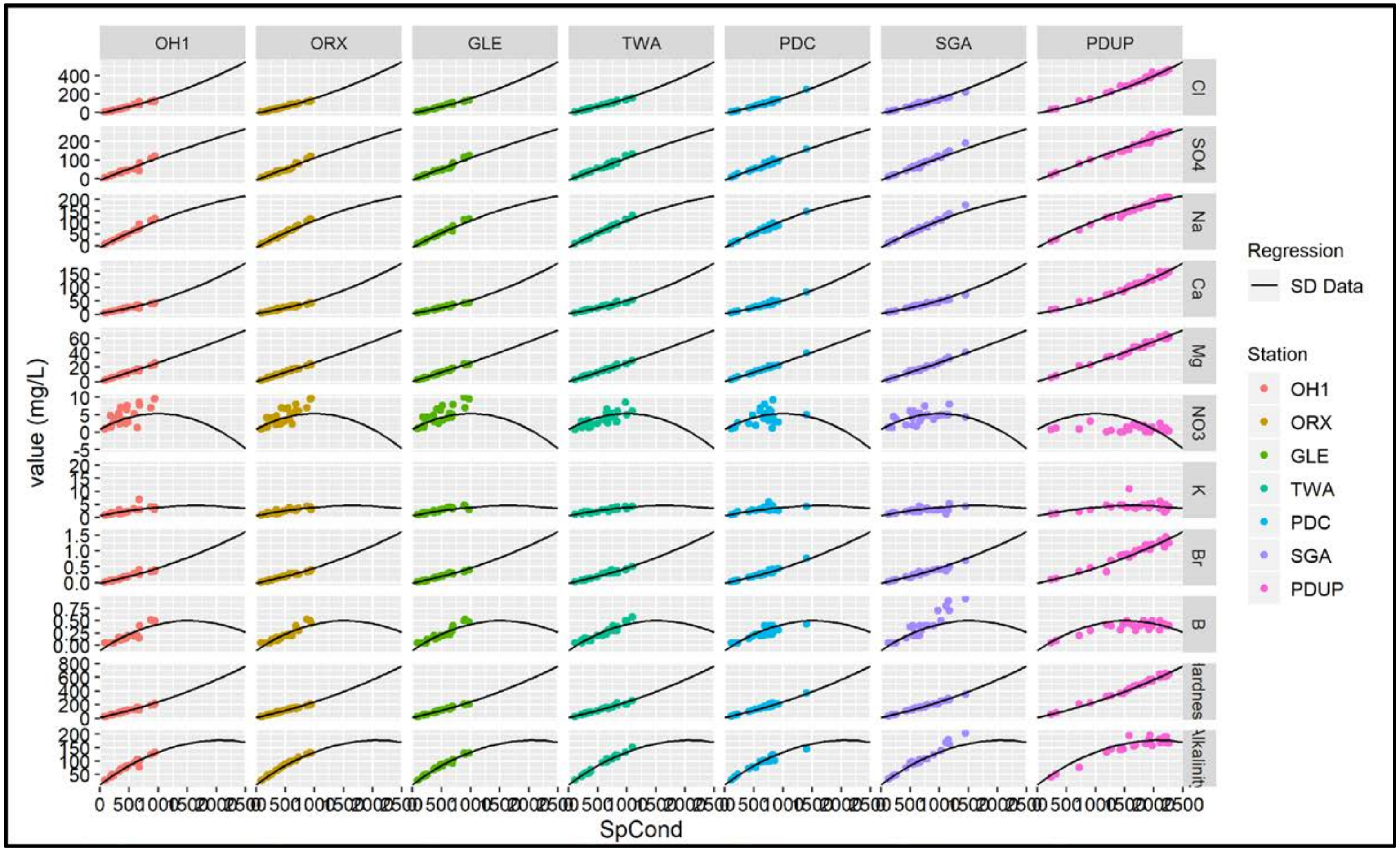

Figure 19: Ion concentration by SpCond separated by parameter.