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SAN JOAQUIN RIVER HYPORHEC ZONE WATER QUALITY AND TOXICITY TO *DAPHNIA*: IMPLICATIONS FOR CHINOOK SALMON RESTORATION EFFORTS

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Abstract

Toxicity, as measured with a rapid *Daphnia* response test kit, was detected in water samples collected from the hyporheic zone of the San Joaquin River. Little to no toxicity was observed in November and December of 2012, while 64-67% of hyporheic water samples were toxic in January and February of 2013. None of the surface water samples were toxic and these samples typically contained low metal concentrations relative to hyporheic zone samples. Toxicity was correlated with metals that were measured as salmonid Toxic Units (TU's) in water samples. We considered TU's >1 as potentially deleterious to survival of early life stages of Chinook salmon (*Oncorhynchus tshawytscha*). Chemistry samples collected in January and February indicated that 42% of hyporheic zone samples had TU's >1 with the highest TU calculated as 10.02. Metals of concern included high concentrations of aluminum, iron, manganese and copper (maximum concentrations, respectively were 1,970, 4,840, 4,060, and 36.6 µg/L). Information on metal concentrations was only obtained in January and February and concentrations varied between sample locations and months.

Additive TU's indicated metal concentrations could be toxic, or cause deformities, to early life stages of salmon. Literature also suggested metals precipitation effects along with impacts on the ability of salmonids to successfully smolt could take place. Elevated heavy metal concentrations, and toxicity to *Daphnia*, have potential implications for early life-stages of Chinook salmon that prefer these habitats for development.

Introduction

With completion of the Friant Dam in 1942, both spring-run and fall-run salmon were quickly extirpated from the San Joaquin River through elimination of spawning area access and decreased river flows below the dam (Yoshiyama et al. 2001). The San Joaquin River Restoration Program (SJRRP) is a long-term effort to restore self-sustaining Chinook salmon runs from Friant Dam to the Merced River confluence, while reducing water supply impacts. Recovery of federally listed anadromous salmonids requires survival of eggs and alevins in salmon redds (spawning areas of salmon). The incubation period often lasts 40-50 days before hatching occurs (SJRRP 2010). After hatching, alevins remain buried in the gravel while development continues with mostly yolk-sac derived nutrition. In the nearby Sacramento River Basin, spring-run Chinook salmon alevins remain in the gravel for 2 to 3 weeks after hatching and then emerge into the water column (Fisher 1994). This long contact time with the redd environment for these early stages of salmon indicates its importance to salmon populations and is considered a critical period in salmon life history (Gangmark and Bakkala 1960). Degradation of spawning grounds has been implicated as a key cause of salmon endangerment (e.g., Regetz 2003). During spawning activity in freshwater streams and rivers, eggs are buried in gravel substrate, typically to a depth of ca. 30 cm (e.g., DeVries 1997). Environmental conditions, at this depth, may differ markedly from those found at the surface (e.g., Soulsby 2001). This deeper gravel area is often at the interface between surface water and groundwater components, in the hyporheic zone. Survival of salmonids in the redd environment has been related to pH (Lacroix 1985), amount of upwelling (Garrett et al. 1998), quantity of sand in the redd (Kondolf 2000), concentrations of dissolved oxygen (DO) (Ingendahl 2001), and toxicity (Groves and Chandler 2005). Water quality in the hyporheic zone may also be important in salmonid selection of spawning sites (Geist 2000).

Studies examining salmonid egg survival in the intragravel environments of the San Joaquin River have not had uniform results. Green trout egg survival to hatch was relatively low at several sites below Friant Dam (Nelson et al. 2012), while eyed salmon egg survival to hatch was variable (SJRRP 2012). San Joaquin River studies have examined DO and temperature as variables affecting survival (Nelson et al. 2012); however, in this present study we also took the opportunity to augment our data set by collecting some water quality data alongside other sampling.

The primary objective of this study was to evaluate the toxicity of San Joaquin River water acquired from hyporheic zone riffle habitats likely to be utilized for salmon redd creation. Once toxic effects were detected, the secondary objective was to measure sampled water for heavy metals as an initial attempt to determine what water components may contribute to toxicity.

Methods

Water samples were collected from three intragravel locations at each of five unique riffle habitats in the San Joaquin River (Figure 1) on November 27 and December 11 of 2012, and January 23 and February 27 of 2013. Riffles were designated from upstream to downstream as R1 through R5 with surface water samples identified with an "S" (e.g., R1S) and hyporheic samples identified by the three intragravel locations at each set of riffles (e.g., R1L1, R1L2, R1L3). Fused glass airstones and tubing (for discrete water sample withdrawal) were installed at all intragravel locations (ca. 30 cm depth) on October 30, 2012. The airstone was used to prevent clogging of the tubing by sand or other particles during sample collection. Excavations, in which airstones connected to tubing were installed, were made in the stream bed using hand trowels. Water flow at the spot being excavated was blocked, to prevent washing of substrate into the hole, with a bottomless bucket. Substrate from the hole was placed in a nearby bucket, and then returned to the hole subsequent to positioning of the airstone and tubing, after which the bottomless bucket was removed. This disturbance, although limited in extent, mobilizes fine particles and results in cleaning of sediment similar to what might occur from redd construction by salmon (Levasseur et al. 2006). This activity does not simulate a natural redd in all regards because it lacks other features common to redds such as a tail spill. The degree to which these diggings represent intragravel conditions that a salmon might produce is uncertain, with Meyer (2003) concluding from a comparison of artificial and natural redds that it was not possible to confirm how representative artificial redds were to natural redds. In nature, there is no standard redd, but rather a wide variety of egg pocket configurations. During sampling, a 60- ml plastic syringe was connected to tubing to withdraw hyporheic water samples (150-mls) and was also used to collect surface water samples associated with each riffle location. The tubing was initially cleared by withdrawing and discarding 10-mls of fluid, followed by actual sample collection. Water for toxicity testing was then placed in a labeled polyethylene bottle.

Toxicity testing was performed (within a few hours of sample collection) under controlled environmental conditions in Fresno, CA on hyporheic and surface water samples using the IQ Toxicity Test™ system (Aqua Survey, Inc). This is a rapid toxicity test system with results obtained in a matter of hours and comparable to a 24- hour acute toxicity test (e.g., Nelson and Roline 1998). Prior to each experiment *Daphnia magna* neonates were shipped via overnight express from Flemington, NJ. During tests, *Daphnia* were exposed to control and test water for an hour after which a fluorogenically tagged sugar suspension was added to test chamber water. After 15 minutes, chambers were illuminated with black light (longwave ultraviolet [UV]). For the organisms to fluoresce they must ingest the tagged sugar (galactose) and express the enzyme (galactosidase); then the enzyme must successfully cleave the sugar from the fluorogenic marker. This marker, which cannot fluoresce while attached to the sugar molecule, is released and visible under UV light in the organism's circulatory system. Therefore, unaffected organisms, not exposed to toxic conditions, emit bright bluish-white light, while organisms adversely affected do not glow as brightly as those in control water. Toxicity is indicated if there are four or more adversely affected *Daphnia* out of 18 exposed to the test sample. Dilutions, for EC50 (concentration at which 50% of the organisms were affected) calculations, were used where high levels of toxicity were found in the undiluted water sample water.

After toxicity was detected in some samples, chemical analyses using inductively coupled plasma atomic emission spectroscopy scans for metals were elicited. These analyses were performed by the Reclamation Lower Colorado Regional Laboratory using standard methods (AWWA 2005). Water samples for metals analyses were from samples remaining at the conclusion of toxicity testing. Samples were preserved with concentrated nitric acid from individual 0.5 ml glass ampules. In February we also collected some additional sample for measurements of alkalinity and hardness, and also measured pH with a portable meter on site.

Toxic units (TU) related to salmonids were used to characterize detected metal concentrations. A TU was determined for each metal and these were summed to create a final TU for each water sample. Acute and chronic LC50’s (concentration which is lethal to 50% of the test organisms) were obtained from the literature for calculation of TU’s where:

TU=specific metal concentration in water sample/acute or chronic LC50 concentration of specific metal.

It was assumed that metals toxicity was additive (the simplest model), as has often been the case (Finlayson and Verrue 1982, Enserink et al. 1991). There are, however, exceptions to the additive model of toxicity to metal mixtures (Utgikar et al. 2004). We made no attempt to account for water hardness effects on bioavailability of metals (EPA 1986).

Flow data for the study were obtained from USGS gage 11251000 below Friant Dam, California. Precipitation data was acquired from the Department of Water Resources, California Data Exchange Center.

Results

Toxicity test results are presented in Table 1. Toxicity varied temporally, with no toxicity detected in November 2012 and little detected in December. In January and February 2013 ca. 60-70% of "redds" demonstrated toxicity to *Daphnia*. Spatially there was also variability with the furthest upstream and furthest downstream sites consistently having more toxic environments when compared to the other sites. Within single sites there was also variability. Toxicity in artificial redds separated by just a few meters differed, with toxicity measured in some "redds" but not measured in an adjacent "redd" (e.g., R4 in February, Table 1). Overall, if sampling events are combined, 73% of artificial redds demonstrated toxicity at some point. Control water samples were never toxic and surface water samples were rarely toxic (Table 1).

Metals concentrations were measured for water samples collected in January and February (Table 2). TU's were developed for a subset of these metals dependent upon whether concentrations were deemed high and whether literature could be found related to a given element (Table 3). Limited information resulted in additive TU's that combined short-term and long-term toxicity testing of a variety of salmonids. Calculated TU's are presented in Table 4. Although EPA (1991) considers a toxicity level of 0.3 TU's to be protective of aquatic life, we present TU's in red that correspond to TU's $\geq$ 1 as a point at which effects to salmonid early life stages would have a high likelihood to occur (lethality to 50% of exposed early life stage salmon). The dearth of metals data specific to Chinook salmon, and the intermittency of metals presence, also supports this more moderate estimate of impact. While there was not an exact match between TU's for salmonids and % of non-affected *Daphnia* (compare Table 1 and 4), overall these two measures were correlated (r=-0.5997, P=0.0000, n=40). Level of correlation varied between months, with measurements in January more highly correlated (r=-0.8334, P<0.0001, n=21) than those in February (r=-0.5610, P=0.0125, n=19) (Figure 2). It appeared that lower TU's corresponded to a greater *Daphnia* effect in February compared to January (Figure 2), perhaps indicating additional unmeasured toxicants. Chemistry samples collected in January and February indicated that 42% of hyporheic zone samples had TU's >1, with the highest TU calculated as 10.02 (Table 4).

Metal concentrations varied between January and February with aluminum, iron, and manganese high in January and much lower in February. The maximum aluminum concentration of 1,970 µg/L was recorded at R4L1, as was the highest iron concentration of 4,840 µg/L. Highest manganese concentration was detected at R1L2 of 4,060 µg/L, but other locations also had manganese concentrations that were > 2,000 µg/L. In February these metals all declined to concentrations <500 µg/L (Table 2). Other more toxic metals such as copper and zinc seemed to increase in February compared to January with high concentrations of 36.6 µg/L copper and 94.7 µg/L zinc recorded in January (Table 2). Metals at these concentrations could cause effects to early salmonid life stages (Table 3).

Additional water quality measurements taken in February indicated low alkalinity and hardness in both surface [alkalinity =25 mg/L (range 2-88), hardness 10 mg/L (range 6-22)] and hyporheic water [alkalinity=15 mg/L (range 4-24), hardness=5 mg/L (range 2-10)]. Measured hardness values are indicative of very soft water (<60 mg/L) as defined by Briggs and Ficke (1977).

Measured pH's were all circumneutral, ranging from 6.97 to 7.80 for all samples. Low alkalinity values, however, indicate waters are susceptible to rapid pH changes.

Flows below Friant Dam were high in November (ca. 20 CMS) and maintained at about 10 CMS during most other times. Spring run-off at the end of March (Figure 3) resulted in additional higher flows. Most precipitation events occurred in November and December (Figure 4).

Discussion

Toxicity to *Daphnia* was detected in hyporheic samples from intra-gravel environments where salmon eggs might develop. Toxicity was correlated with salmonid TU's derived from metal concentrations measured from water samples. Toxicity varied with month, site, and locations within a site. We measured metals in the hyporheic environment that were at concentrations above what is reported to be toxic to early life stages of salmon. Surface water samples were non-toxic and typically had low concentrations of metals. This large difference in water quality between hyporheic zone and surface waters has been observed in other river systems (Nelson and Roline 2003).

It was ambiguous as to why toxicity increased from November to December 2012 and then again in January and February 2013. Examination of flow patterns does not seem to strongly suggest intrusion of groundwater as an explanation since flow was similar at the four sampling dates (Figure 3). Groundwater intrusion might be expected if surface water flows were diminished.

High flows did occur in the month of November, immediately preceding our first sampling event, and groundwater may have been recharged from the high surface flow, resulting in some dilution (perhaps via metals deposition) of metals in the hyporheic zone. The shallow hyporheic zone often plays a critical role in regulating metal fluxes between surface and groundwater environments (Nelson and Roline 2003). The routine high flows in early November are believed to serve as an attractant for returning adult salmon. Earlier studies indicated these high flows may cause groundwater intrusion into the hyporheic at some locations; however, post-high flow environments indicated decreased groundwater influence (Nelson et al. 2012). This possible dilution of the groundwater by instream surface water following flow events may be important to survival of early life stages of Chinook salmon. The absence of chemistry data from the two initial sampling events leaves this theory untested. It could be argued, however, that hyporheic chemistry had stabilized to more typical constituents (higher metals) with increased groundwater interactions by January and February samplings that were more dissociated temporally from the November high flows (Figure 3). Precipitation events in November and December (Figure 4) may have caused a rise in the water table and increased the groundwater flux through the hyporheic zone. There was decreased variability in hyporheic water temperatures in January that may be indicative of this pattern (Nelson and Reed 2014).

Hyporheic waters are often high in alkalinity and hardness, and these higher levels may protect organisms from metals toxicity because of competition from hardness cations for metal-binding sites on fish gills (Meyer 1999). The extremely low alkalinity and hardness concentrations measured in the San Joaquin River suggest limited protection from metal effects. Protective effects from alkalinity and hardness, however, may vary with constituents, with some metals such as zinc becoming more toxic to salmonids at low hardness levels and unaffected by minor changes in alkalinity (Bradley and Sprague 1984), while copper toxicity has been shown to increase under conditions of low alkalinity but was not significantly affected by increased hardness (Laurén and McDonald 1986). Increased hardness has been shown to protect early life stages of salmonids in the case of other metals, including manganese (Stubblefield et al. 1997).

Correspondence of temporal metal variability with salmon life history—Redds were observed in 2012 that were likely constructed by transplanted fish, truck transported from the lower to the upper reaches of the San Joaquin River during the SJRRP adult trap and haul program. These redds were noticed in late November at several of our sites, and were immediately adjacent to our artificial redds, on the upper San Joaquin below Friant Dam. Life history traits suggest 40-50 days for incubation and another 2-3 weeks where alevins remain in the gravel environment. This would place emergence into the water column at about the third week of January, suggesting that alevins would be in redds when effects to *Daphnia* and high TU's were observed. This timing impacts the life history stage which is typically most sensitive to metals. The least sensitive life history stage to metals appears to be the early egg (Finn 2007). Sensitivity to metals increases as development progresses. Of some solace is the presence of variability in toxicity across redds, with 25% of "redds" considered as non-toxic. Depending upon gravel porosity, alevins may also have some ability to move away (e.g., Dill and Northcote 1970) from deleterious conditions within redds, thus potentially increasing survival rates. We did not collect any direct information on toxicity to eggs/alevins or measure metals in an actual redd, and impacts to salmon are speculative.

Metals source— It is unclear what the metals source is in this part of the San Joaquin River, however, Lee and Lee (2007) indicated that former mining activities in the Sierra Nevada Mountains have resulted in cadmium and copper being introduced into the San Joaquin River along with mercury which was used to help recover gold during processing.

Groundwater quality near gravel mining sites may also be impaired as a result of gravel extraction. It has been suggested that heavy metals that are otherwise retained in soil are introduced into groundwater where gravel extraction occurs (Hatva 1994). Little information is available on this topic and it is unknown whether nearby gravel pits along the San Joaquin River impact river water quality. Large and deep floodplain gravel pits may also change water table elevations in nearby streams (Norman et al. 1998) perhaps altering groundwater/surface water interactions.

Comparisons with other salmon rivers--We found little information on hyporheic metals and potential impacts to salmonids. Bowen and Nelson (2003) examined toxicity (IQ Toxicity Test™) and dissolved trace elements collected from a Chinook salmon redd in Deer Creek, California. No toxicity was detected and trace elements in surface and deep (30 cm depth into the gravel) water samples were all low in concentration (manganese, nickel, and zinc were not detectable). Nelson and Bowen (2004) also tested for toxicity and dissolved trace elements in hyporheic areas associated with Chinook salmon redds on the Yakima and Cle Elum Rivers in Washington. Trace element data from four sampling occasions (October-January) indicated that concentrations of potential toxicants were very low. Cadmium and nickel were not detected in any samples (detection limit 4μg/L and 10 μg/L respectively) while copper was rarely detected with a maximum value of 6.09 µg/L. Iron was often detected but no values were > 50 µg/L. Selenium was observed on four occasions but values were near the detection limit of 2 µg/L. Zinc was the toxicant that was most often detected but was not found at concentrations > 15 ug/L. A single 48 hr toxicity test with *Ceriodaphnia dubia* did not result in any occurrence of mortality. These trace element concentrations were from rivers with successful salmon runs and differ greatly from those measured on the San Joaquin River (but note that total metals were measured on the San Joaquin River).

Indirect effects--Some metals may have other impacts beyond direct toxicity. Teien et al. (2008) indicated that when anoxic iron-rich groundwater enters oxygen-rich surface waters (similar to hyporheic exchange) that oxidation of iron (II) to iron (III) species takes place. They state that while iron (II) is considered the most toxic oxidation state of iron, iron (III) will accumulate on fish gills and result in mortality. In addition, salmonid alevins exposed in the egg stage to non-lethal concentrations of metals, may develop deformities that, while not resulting in immediate mortality, likely decrease survival (e.g., Finn 2007). Salmonid yolk-sac and swim-up larvae are also sensitive to aluminum precipitation onto gills (Finn 2007). Both iron and aluminum were occasionally found at high concentrations in the hyporheic zone of the San Joaquin River. Manganese was also found at high concentrations and will likely precipitate out in the hyporheic as groundwater moves into the hyporheic zone and becomes more oxic (Harvey and Fuller 1998). Iron or metal oxides can precipitate onto the surface of salmonid eggs resulting in suffocation as the diffusion of gases becomes more difficult (see Introduction of Vuorinen et al. 1999). In some cases, seaswater survival can be impacted by exposure to relatively low concentrations of metals such as aluminum (Kroglund and Finstad 2003) which, along with manganese, can impact chloride cells (e.g., Gupta et al. 2012) required for smoltification.

Further research—Water quality information in this report was collected during a limited period on a small number of occasions. More intensive collections with ancillary information such as dissolved metals, pH, hardness, and alkalinity would be desirable to characterize possible impacts to salmon life stages exposed to the hyporheic zone. It would also be of interest to collect chemistry information at various depths in the hyporheic and up into the floodplain to provide information on timing and sources of metals in the system. Comparisons of San Joaquin River water quality with that of nearby tributaries that support runs of adult Chinook salmon might be warranted. It might also be possible to replicate the water quality observed in the hyporheic zone for use in laboratory toxicity testing with early life history stages of salmon for a more direct indication of possible mortality effects. Information on fish exposure to toxicants could be collected from outmigrants captured in screw traps along the San Joaquin River. The present results should be considered preliminary with further research needed.

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Table 1. Percent toxicity of Daphnia exposed to San Joaquin River water from surface (S) or hyporheic (L) environments. In a valid test 15 or more Control *Daphnia* must be non-adversely affected (glowing brightly). If four or more *Daphnia* are adversely affected out of 18 in the test sample, this indicates toxicity. Bolded numbers indicate toxicity in undiluted samples in the table below. Rows highlighted in yellow are surface water samples.

Reach	Date			
	11-27-12	12-11-12	1-23-13	2-27-13
	% positive	% positive	% positive	% positive
Control-initial	16/17 (94.1%)	17/18 (94.4%)	16/18 (88.9%)	16/18 (88.9%)
Control-final	18/18 (100%)	18/18 (100%)	17/18 (94.4%)	15/18 (83.3%)
R1S	**13/18 (72.2%)**[a]	17/18 (94.4%)	17/18 (94.4%)	16/18 (88.9%)
R1L1	16/18 (88.9%)	16/18 (88.9%)	**10/18 (55.6%)**	**13/18 (72.2%)**
R1L2	17/18 (94.4%)	15/18 (83.3%)	**8/18 (44.4%)**	**5/18 (27.8%)**
R1L3	15/18 (83.3%)	17/18 (94.4%)	**2/18 (11.1%)**	17/18 (94.4%)
R2S	15/18 (83.3%)	17/18 (94.4%)	17/18 (94.4%)	16/18 (88.9%)
R2L1	15/18 (83.3%)	16/18 (88.9%)	**11/18 (61.1%)**	**9/18 (50.0%)**
R2L2	15/18 (83.3%)	16/18 (88.9%)	16/18 (88.9%)	**12/18 (66.7%)**
R2L3	18/18 (100%)	17/18 (94.4%)	17/18 (94.4%)	No sample
R3S	15/18 (83.3%)	18/18 (100%)	15/18 (83.3%)	16/18 (88.9%)
R3L1	16/18 88.9%)	16/18 (88.9%)	**11/18 (61.1%)**	**5/18 (27.8%)**
R3L2	15/18 (83.3%)	18/18 (100%)	15/18 (83.3%)	16/18 (88.9%)
R3L3	16/18 (88.9%)	**1/18 (5.6%)**[b]	**7/18 (38.9%)**	**3/18 (16.7%)**
R4S	16/18 (88.9%)	18/18 (100%)	18/18 (100%)	16/18 (88.9%)
R4L1	17/18 (94.4%)	**13/18 (72.2%)**	**6/18 (33.3%)**	**2/18 (11.1%)**
R4L2	16/18 (88.9%)	17/18 (94.4%)	15/18 (83.3%)	18/18 (100%)
R4L3	17/18 (94.4%)	16/18 (88.9%)	16/18 (88.9%)	17/18 (94.4%)
R5S	17/18 (94.4%)	17/18 (94.4%)	17/18 (94.4%)	15/18 (83.3%)
R5L1	18/18 (100%)	**8/18 (44.4%)**[c]	**0/18 (0%)**	**1/18 (5.6%)**
R5L2	18/18 (100%)	18/18 (100%)	**9/18 (50%)**	**5/18 (27.8%)**
R5L3	17/18 (94.4%)	16/18 (88.9%)	**10/18 (55.6%)**	15/18 (83.3%)
Total toxic samples	0	3 (15% or 20% of "redds")	10 (50% or 67% of "redds")	9 (47% or 64% of "redds")

[a]We believe results from this test were erroneous. *Daphnia* appeared to be stuck to the sides of the containers, affecting results. [b]EC50=49.5%. [c]EC50=57.3%.

Table 2. Metal concentrations as measured in surface (S) and hyporheic (L) water samples from the San Joaquin River in January and February of 2013.

Sample													
1/23/2013	As	Be	Cd	Cr	Cu	Mn	Mo	Ni	Pb	Zn	Al	Fe	Se
	all results are in ug/L												
R1S	< 3.6	< 0.06	< 0.16	< 0.6	< 0.9	55.2	1.31	< 0.9	< 2.5	< 0.3	62.5	117	< 12
R1L1	13.1	0.11	< 0.16	1.03	6.16	1380	< 1.2	1.48	3.81	11.1	858	1700	< 12
R1L2	10.8	0.22	0.44	3.10	13.6	4060	< 1.2	4.17	3.86	22.0	1240	2470	< 12
R1L3	11.7	0.12	< 0.16	1.65	8.07	2700	< 1.2	1.65	< 2.5	12.8	921	2510	< 12
R2S	< 3.6	< 0.06	< 0.16	< 0.6	< 0.9	50.0	1.48	< 0.9	< 2.5	< 0.3	59.6	121	< 12
R2L1	< 3.6	0.07	< 0.16	< 0.6	< 0.9	296	< 1.2	< 0.9	< 2.5	1.48	149	419	< 12
R2L2	< 3.6	0.06	< 0.16	< 0.6	< 0.9	219	< 1.2	< 0.9	< 2.5	0.45	141	379	< 12
R2L3	3.97	0.09	< 0.16	< 0.6	< 0.9	727	< 1.2	< 0.9	< 2.5	3.33	258	726	< 12
R3S	< 3.6	0.06	< 0.16	< 0.6	< 0.9	47.3	1.36	< 0.9	< 2.5	0.85	43.9	112	< 12
R3L1	< 3.6	0.07	< 0.16	< 0.6	< 0.9	206	< 1.2	< 0.9	< 2.5	< 0.3	119	360	< 12
R3L2	< 3.6	0.08	< 0.16	< 0.6	< 0.9	206	< 1.2	< 0.9	< 2.5	< 0.3	64.6	238	< 12
R3L3	16.4	0.22	< 0.16	1.83	8.98	2630	< 1.2	2.42	< 2.5	18.9	1380	4370	< 12
R4S	< 3.6	0.07	< 0.16	< 0.6	< 0.9	43.9	< 1.2	< 0.9	< 2.5	< 0.3	56.4	116	< 12
R4L1	22.9	0.33	0.28	2.76	14.7	3430	< 1.2	3.68	< 2.5	26.5	1970	4840	< 12
R4L2	< 3.6	0.09	< 0.16	< 0.6	< 0.9	389	< 1.2	1.00	< 2.5	2.07	153	478	< 12
R4L3	3.89	0.08	< 0.16	< 0.6	< 0.9	237	< 1.2	< 0.9	< 2.5	0.54	148	495	< 12
R5S	< 3.6	0.08	< 0.16	< 0.6	< 0.9	39.2	1.72	< 0.9	< 2.5	< 0.3	57.4	121	< 12
R5L1	19.1	0.25	0.53	1.88	11.1	2640	< 1.2	3.28	< 2.5	19.5	1650	4270	< 12
R5L2	8.78	0.16	0.58	0.81	4.26	829	< 1.2	1.32	< 2.5	7.49	555	1560	< 12
R5L3	< 3.6	0.08	< 0.16	< 0.6	< 0.9	89.6	1.25	< 0.9	< 2.5	0.65	74.4	273	< 12
Sample													
2/27/2013	As	Be	Cd	Cr	Cu	Mn	Mo	Ni	Pb	Zn	Al	Fe	Se
R1S	< 3.60	< 0.06	< 0.16	< 0.60	< 0.92	71.8	1.72	< 0.90	< 2.50	105	62.2	123	< 12.0
R1L1	8.81	0.08	< 0.16	2.18	7.76	49.7	< 1.20	1.74	6.42	14.9	65.5	118	< 12.0
R1L2	14.4	0.59	1.03	9.32	36.6	69.1	< 1.20	11.5	13.2	61.0	50.7	83.2	< 12.0
R1L3	11.0	0.09	0.31	2.64	9.92	184	< 1.20	1.85	2.52	19.6	80.9	187	< 12.0
R2S	< 3.60	< 0.06	< 0.16	< 0.60	< 0.92	37.8	1.47	< 0.90	< 2.50	1.92	37.5	276	< 12.0
R2L1	< 3.60	< 0.06	< 0.16	< 0.60	1.14	133	1.35	< 0.90	< 2.50	0.66	109	60.8	< 12.0
R2L2	< 3.60	< 0.06	< 0.16	< 0.60	1.02	38.8	1.21	< 0.90	< 2.50	0.49	24.1	115	< 12.0
R3S	< 3.60	< 0.06	< 0.16	< 0.60	< 0.92	57.0	1.52	< 0.90	< 2.50	4.81	74.6	222	< 12.0
R3L1	7.69	0.08	< 0.16	1.29	5.45	136	< 1.20	1.03	< 2.50	10.4	74.6	103	< 12.0
R3L2	< 3.60	< 0.06	< 0.16	< 0.60	< 0.92	121	< 1.20	< 0.90	< 2.50	< 0.30	62.5	433	< 12.0
R3L3	16.8	0.10	0.22	3.99	12.9	367	14.2	2.85	5.28	94.7	170	432	< 12.0
R4S	< 3.60	< 0.06	< 0.16	< 0.60	< 0.92	54.2	1.58	< 0.90	< 2.50	< 0.30	45.8	105	< 12.0
R4L1	7.45	0.08	< 0.16	1.49	5.14	155	< 1.20	1.26	< 2.50	10.2	80.0	232	< 12.0
R4L2	< 3.60	< 0.06	< 0.16	< 0.60	< 0.92	95.8	1.80	< 0.90	< 2.50	0.63	58.0	107	< 12.0
R4L3	< 3.60	< 0.06	< 0.16	< 0.60	0.99	116	1.23	< 0.90	< 2.50	< 0.30	80.4	235	< 12.0
R5S	< 3.60	< 0.06	< 0.16	< 0.60	< 0.92	49.8	< 1.20	< 0.90	< 2.50	< 0.30	82.4	151	< 12.0
R5L1	12.5	0.13	0.67	2.25	9.76	114	< 1.20	2.06	2.67	15.4	67.5	193	< 12.0
R5L2	7.83	0.10	0.49	1.12	15.1	110	< 1.20	0.93	< 2.50	9.31	96.2	239	< 12.0
R5L3	< 3.60	< 0.06	< 0.16	< 0.60	0.95	106	1.36	< 0.90	< 2.50	< 0.30	114	266	< 12.0

Table 3. Metal concentrations which affect various salmonid life stages and Toxic Units used for the study.

Metal concentration (µg/L)	Salmonid life stage effects			Concentration used for Toxic Unit
	Egg	Alevin	Swim-up	
Al	1000[a]	500[a]	500[a], 560[b]	500
Cd		>26[a]	1.8[a]	1.8
Cr	>266 for all life stages[c]	205,000[d]	190[e]	190
Cu	400[f]	26[g]	19[g]	19
Fe		1,200[h]		1,200
Mn	2,910[b]			2,910
Ni	50[b]	16,700[d]	50[b]	50
Zn	<1000[e]	>661[g]	97[g]	97

[a]Holtze 1983. Rainbow trout (*Oncorhynchus mykiss*) eyed eggs experienced 14.2 to 21.6 % mortality after eight days exposure (pH 7.2 and 6.5). Post-exposure mortality was approximately 50%. Alevin and swim-up survival significantly reduced at pH 5.5.

[b]Birge et al. 1980. LC50 for rainbow trout embryo-larval assay (28 day test), pH 6.9-7.8.

[c]Patton et al. 2001. Chinook salmon from the eyed-egg stage to swim-up stage (98 days).

[d]Buhl and Hamilton 1991. Coho salmon (*Oncorhynchus kisutch*) 96 hr. LC50 in soft water.

[e]Shazili, N.A.M. and D. Pascoe 1986. 48 hr rainbow trout LC50 hardness at 87.7 mg/L.

[f]Giles and Klaverkamp 1982. 96 hr LC50 rainbow trout embryo.

[g]Chapman 1978. Chinook salmon 96 hr LC50.

[h]Amelung in Loeffelman, et al. 1985. Lowest measured effect on rainbow trout post-hatch larvae after 3 days.

Table 4. Table of additive Toxic Units derived from chemistry data (Table 2) and TU's from the literature (Table 3). Those values in red are $\geq$ 1 Toxic Unit.

Sample	Toxic Units	
	January	February
R1S	0.30	1.40
R1L1	3.94	0.88
R1L2	6.96	3.59
R1L3	5.31	1.31
R2S	0.30	0.41
R2L1	0.81	0.41
R2L2	0.72	0.26
R2L3	1.42	No sample
R3S	0.27	0.46
R3L1	0.66	0.73
R3L2	0.46	0.59
R3L3	7.78	2.65
R4S	0.29	0.27
R4L1	10.02	0.84
R4L2	0.91	0.31
R4L3	0.84	0.49
R5S	0.29	0.37
R5L1	8.57	1.42
R5L2	3.23	1.60
R5L3	0.47	0.57

Figure 1. Map showing locations of riffles where water samples were acquired for toxicity testing and water quality assessments. Millerton Lake impounded by Friant Dam is in the upper right corner.

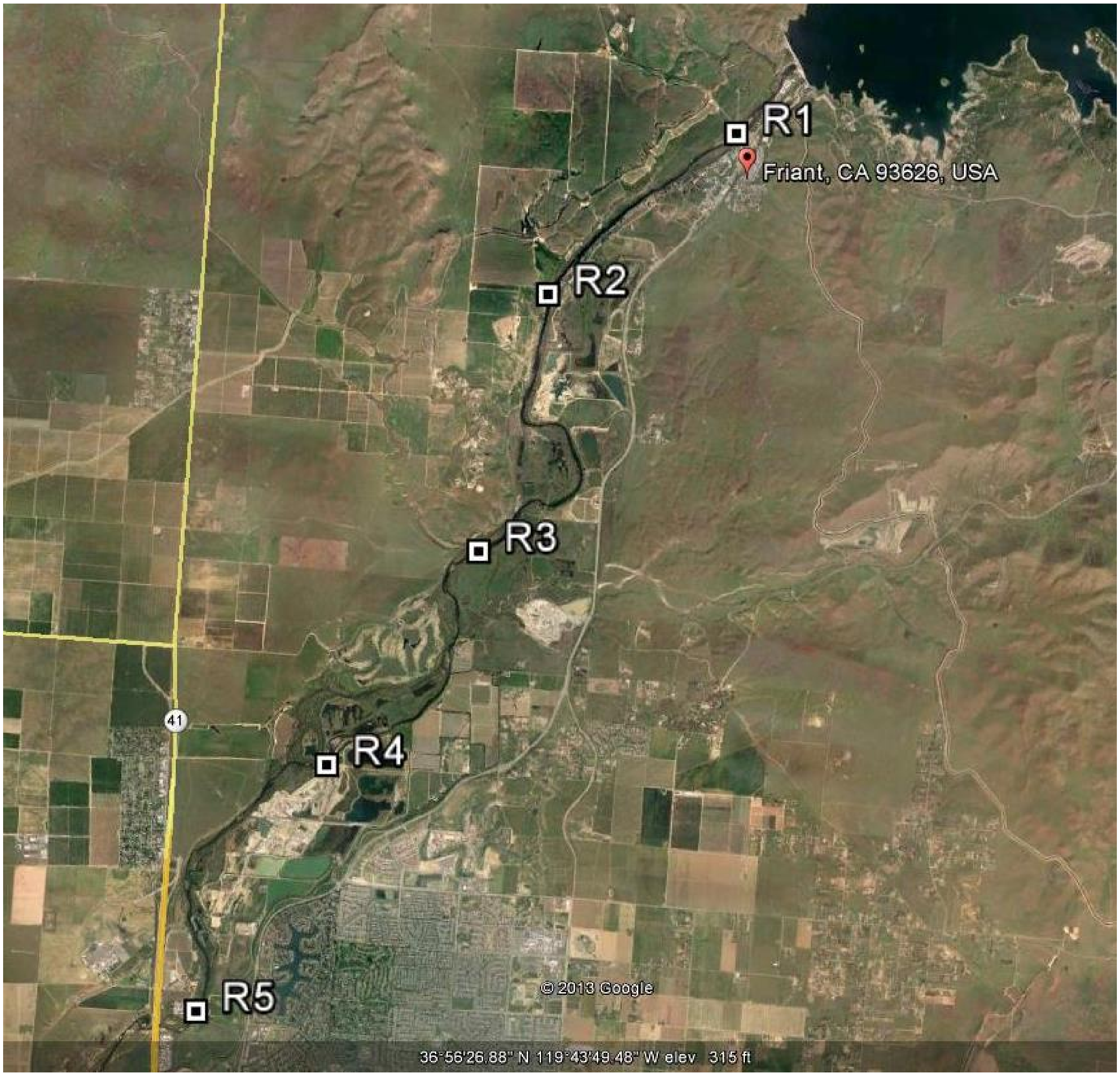


Figure 2. Correlation between affected *Daphnia* and Toxic Units from metals data. Correlation was greater in January compared to February.

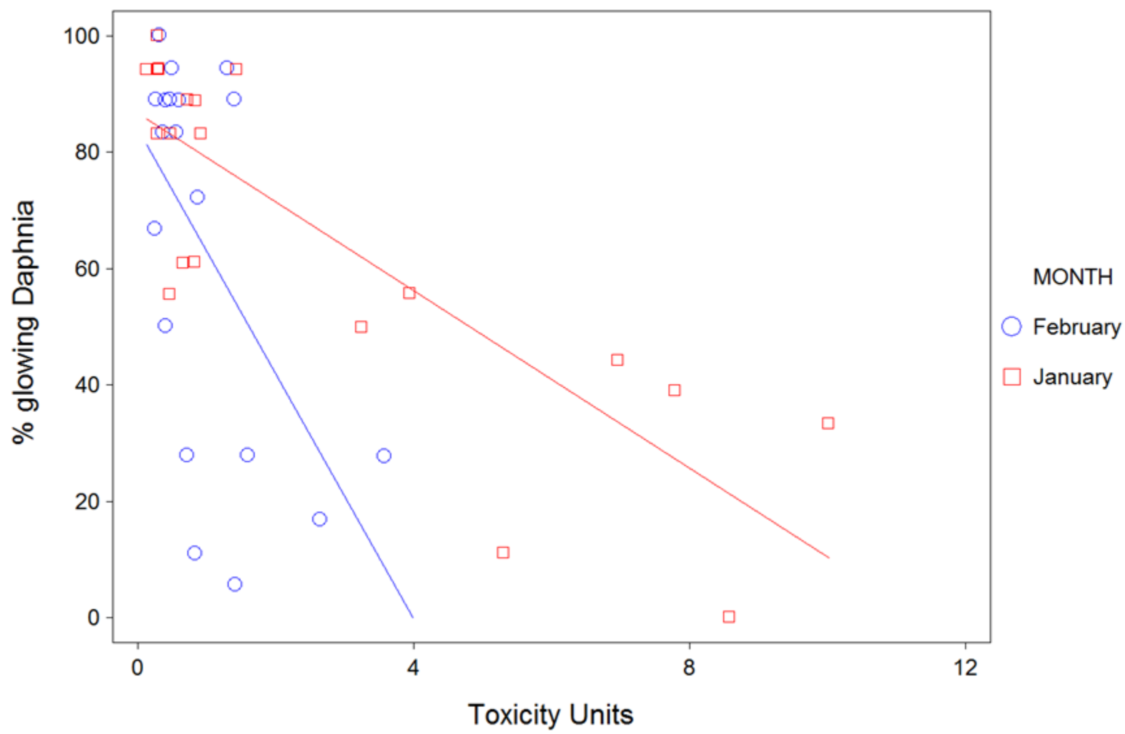


Figure 3. Discharge (cubic meters per second and cubic feet per second) data for the San Joaquin River below Friant Dam. Red triangles indicate water quality sampling dates.

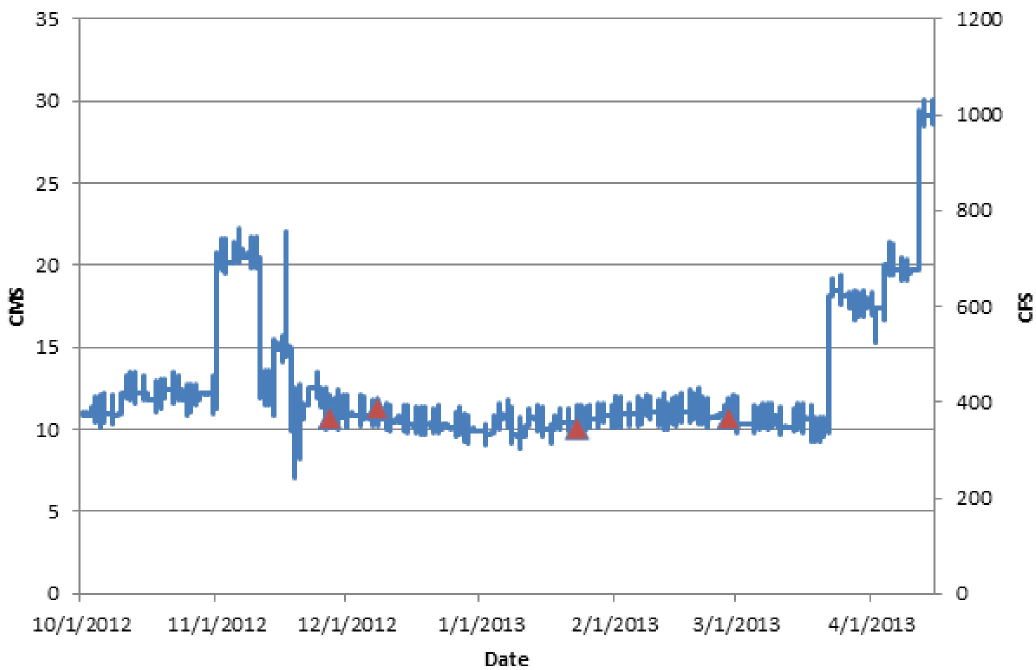
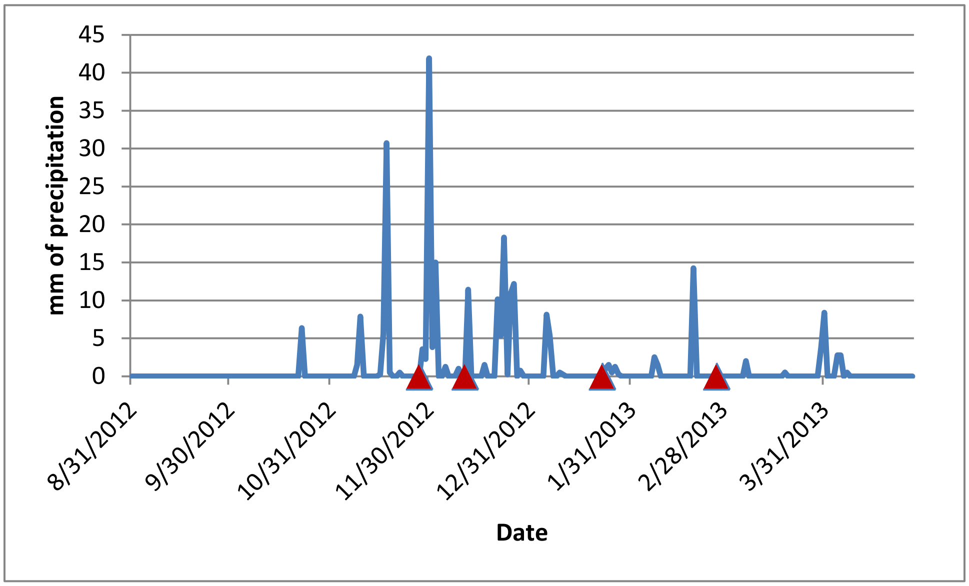


Figure 4. Precipitation events associated with the San Joaquin River near Fresno, CA. Red triangles indicate water quality sampling dates.



PEER REVIEW DOCUMENTATION

PROJECT AND DOCUMENT INFORMATION

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Document SAN JOAQUIN RIVER HYPORHEIC ZONE WATER QUALITY AND TOXICITY TO DAPHNIA: IMPLICATIONS FOR CHINOOK SALMON RESTORATION EFFORTS

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REVIEW REQUIREMENT

Part A: Document Does Not Require Peer Review

Explain

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REVIEW CERTIFICATION

Peer Reviewer - I have reviewed the assigned Items/Section(s) noted for the above document and believe them to be in accordance with the project requirements, standards of the profession, and Reclamation policy.

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Preparer - I have discussed the above document and review requirements with the Peer Reviewer and believe that this review is completed, and that the document will meet the requirements of the project.

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