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Trends Analysis of Simultaneously Extracted Metal Copper Sediment Concentrations from a California Agricultural Waterbody including Historical Comparisons with Other Agricultural Waterbodies

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Abstract: The objectives of this study were to: (1) assess annual, seasonal and spatial trends in simultaneously extracted metal copper (SEM copper) sediment concentrations in an agricultural California waterbody (Cache Slough) sampled over three years and two seasons (spring and fall); (2) determine the relationship between SEM copper sediment concentrations and precipitation; (3) compare the SEM copper sediment concentrations from Cache Slough with other agricultural streams and (4) compare trends in SEM copper with total copper sediment concentrations previously reported from this waterbody. Sediment samples for SEM copper analysis were collected by boat. Regression analysis, Analysis of Variance, T-test procedure and the Fisher LDS method were used for statistical analysis of data. The results from this study showed that mean seasonal SEM copper sediment concentrations from Cache Slough ranged from 18.6 to 30.1 μg/g dw. SEM copper sediment concentrations were not reported to increase over time in this agricultural waterbody where copper was used as a fungicide, although some spatial differences in SEM copper sediment concentrations were reported. Seasonal analysis showed no significant differences in SEM copper sediment concentrations for both spring and fall for two years, but spring concentrations were statistically higher than fall concentrations for the last year of the study. There were no statistically significant relationships between SEM copper sediment concentrations and precipitation for the three-year period, based on an analysis by year and season. A comparative analysis of total copper and SEM copper from Cache Slough showed that the range of mean seasonal concentrations of SEM copper was much lower, and more sites showed declining trends for SEM copper than for total copper. Increasing trends were not reported at any of the sites for either SEM copper or total copper. A comparison of SEM copper data from Cache Slough was reported to be similar to concentrations reported for other water bodies influenced by agricultural use. Additional multiple year studies in other geographic areas assessing trends in SEM copper sediment concentrations with a comprehensive spatial scale are recommended.

Keywords: SEM copper; sediment; spatial patterns; temporal patterns; agricultural use

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1. Introduction

Sediments in aquatic ecosystems function as an important habitat for benthic communities. They comprise mineral phases of varied particle sizes, including, clay, silt and sand mixed with organic matter [1]. Sediment also serves as reservoir for trace metals introduced in the aquatic environment by geochemical processes and anthropogenic activities [2]. The bioavailability of metals such as copper in sediment is controlled by multiple factors, such as physicochemical (e.g., pH, redox potential, particle size), geochemical (e.g., organic matter, metal dioxide, sulfide) and biological (e.g., feeding behavior, uptake rates) factors [3]. One factor that has been proposed as important in controlling the bioavailability of metals such as copper in sediment is the amount of acid volatile sulfides (AVS) [4]. Metals associated with AVS are called simultaneously extracted metals (SEM). SEM is generally defined as the sum of the molar concentrations of toxicologically important cationic metals (Cu, Pb, Cd, Zn and Ni), which are extracted together with AVS [5]. Di Toro et al. [4] formulated the SEM/AVS model for estimating metal toxicity from contaminated sediments. This model predicts that when AVS concentrations in sediment, on a molar basis, exceeds SEM concentrations all metals will be bound to sulfides and non-toxic. In contrast when sediments contains an excess of SEM metals released into the pore water they are considered potentially, but not necessarily toxic, to aquatic life. Measurements of simultaneous extracted metal copper (SEM copper) or bioavailable copper in the aquatic sediment environment are therefore critical for determining the potential ecological risk of copper.

Copper can be released into the aquatic environment from a number of different sources in both urban/residential and agricultural areas. However, the focus of this paper is copper introduced into the environment via its agricultural use as a plant protection product (PPP). Copper-based compounds, through their stabilized bioavailable copper fraction, are used as a fungicide to protect numerous crops from important diseases. The European Commission (EU) currently considers copper compounds to be both persistent and toxic (PT label) and has designated copper fungicides as a candidate for substitution (CFS) (can be potentially replaced by another PPP). At the EU Commission's request, the European Food Safety Authority (EFSA) outlined a general framework for the environmental risk assessment (ERA) of transition metals, including copper, used as active substances in plant protection products, and this new framework will be considered during the next renewal period for copper compounds [6]. A regulatory need that has been identified for copper fungicides, within the context of this ERA framework is evaluating copper aquatic sediment and monitoring data relevant for European freshwater agricultural streams.

While existing copper monitoring data within the aquatic (water column) compartment are readily available, sediment data for copper are more limited. In a recent study we reviewed the available total copper sediment monitoring data for European water bodies with primarily agricultural use with an adequate spatial and temporal scale and found these data to be limited [7]. In this previous study, a total copper sediment monitoring data set from an agricultural stream in California (Cache Slough) as a surrogate for extensive trends analysis due to the limited copper sediment monitoring data sets for freshwater European agricultural streams, with adequate temporal and spatial scale data [8]. Both climate and soil type in Cache Slough and parts of Europe are similar so using Cache Slough as a surrogate for various areas in Europe is logical. For example, climate conditions for Cache Slough and areas in Europe such as south west Spain and the southern coast as well as south France and most of Italy are classified as Mediterranean/hot summer classification based on the Koppen Climate Classification System [9,10]. In addition the dominant type of soil (vertisols) in both the Cache Slough area and southwest Spain and parts of Italy are also similar [11,12].

Agricultural use of copper as a fungicide has been reported in the Sacramento Delta, Putah Cache Valley and American River Valley watersheds in the Cache Slough, California area [13]. The major crops for copper use within the three watersheds are grapes, cherries, pears, walnuts, rice and peaches [7]. Copper is primarily used for pest control on powdery mildrew, downy mildrew, sour rot, and leaf spot. The high copper use months for all three watersheds occurs in spring and early summer (March, April, May and June). The most dominant type of copper chemicals used for the three Cache Slough watersheds are copper hydroxide and copper sulfate. Therefore, agricultural use of copper in three watersheds located in the Cache Slough area likely contribute to observed copper sediment concentrations in Cache Slough [7].

Although we have conducted trends analysis for total copper sediment concentrations in Cache Slough [7], the recommended next step in this analysis was to also conduct trends analysis for SEM copper (bioavailable copper) in this waterbody in order to provide critical information for assessing the ecological risk of copper. The objectives of this study were to:

(1) assess annual, seasonal and spatial trends in SEM copper sediment concentrations in an agricultural California waterbody (Cache Slough) sampled over three years and two seasons (spring and fall); (2) determine the relationship between SEM cop-per sediment concentrations and precipitation; (3) compare the SEM copper sediment concentrations from Cache Slough with other agricultural streams and (4) compare trends in SEM copper with total copper sediment concentrations from concurrent measurements previously reported from this waterbody.

2. Materials and Methods

2.1. Sites Sampled and Collection Methods

A total of 12 sites were sampled in Cache Slough during both the spring and fall of 2012, 2013 and 2014 in the 18 km study area shown in Figure 1. Site locations were selected to cover different types of habitat from upstream to the downstream confluence within the Sacramento River. Sites were placed near the confluence points of the various water bodies flowing into Cache Slough (i.e., Ulatis Creek, Hass Slough, Shag Slough, Lindsey Slough, Prospect Slough and Miner Slough). Final site selections were made after reconnaissance sampling trips by boat in advance of the spring 2012 sampling. The 12 Cache Slough sites were approximately equally divided into lower (CS 1–CS 4), middle (CS 5–CS 8) and upper (CS 9–CS 12) sections to potentially add power for the statistical analysis presented below.

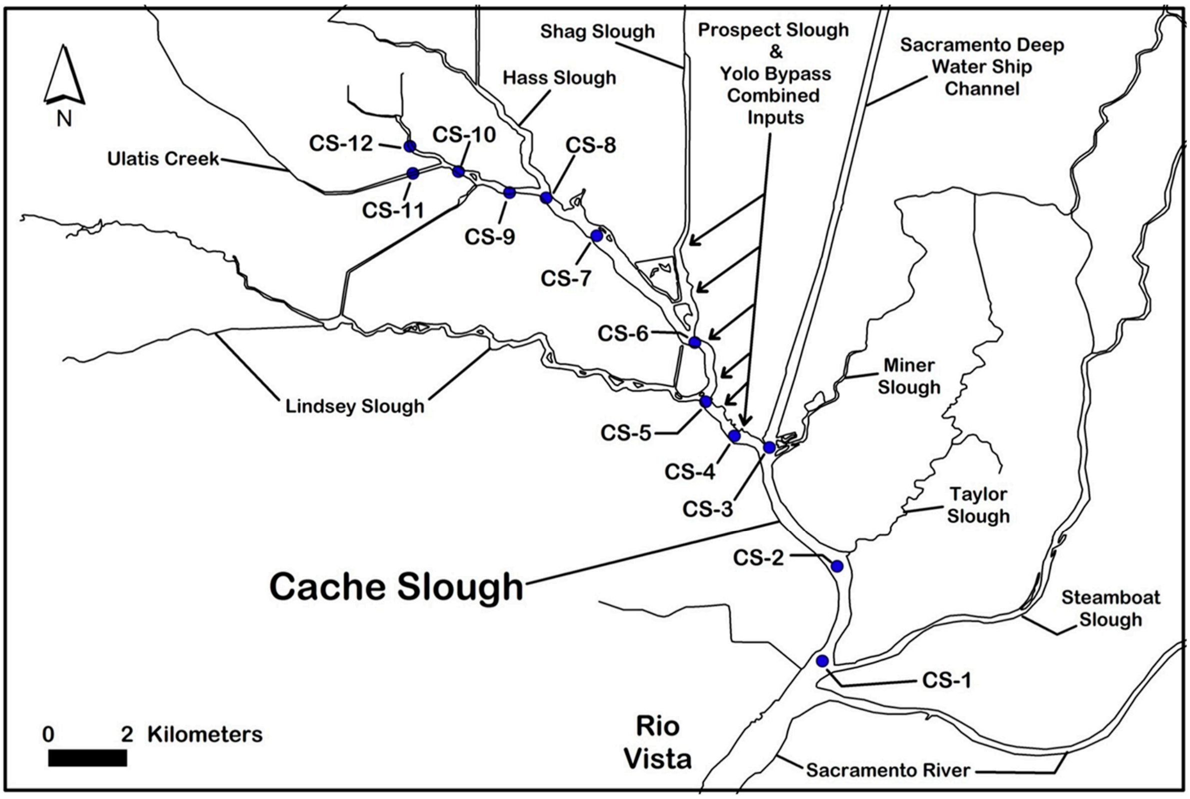

Figure 1. Twelve Cache Slough sites sampled during the spring and fall of 2012, 2013 and 2014.

Sampling in Cache Slough was conducted by boat because this slough is a non-wadeable water body ranging in depth from approximately 1.5 to greater than 9 m depending on tidal cycle. Sediment samples for copper measurements were collected at each site using modified procedures from Delaware River sampling [14]. Sediment from approximately the top 2–5 cm was collected. At each site, a 100 m transect was established and 5 locations were randomly sampled from this transect. Samples from the 5 locations were composited for one sample for copper measurements. Sediment samples were collected using a petite ponar sampler. All sampling equipment was cleaned between sites using nitric acid, ethanol and distilled water.

2.2. SEM Copper Analysis

SEM metals including copper were analyzed from sediment samples using EPA method 200.8. The method detection limit (MDLs) for copper was 0.009 (µmol/g dry weight). AVS were evaluated on sediment samples from each site [15].

2.3. Statistical Analysis

Statistical analysis of the SEM copper sediment data set was conducted using regression analysis, Analysis of Variance (ANOVA), a *t*-test and the Fisher LDS method. Statistically significant trends from regression analysis were defined as a p value < 0.10 and an $r^2 > 0.25$. In some cases simple visual figures plotting the raw data were used.

3. Results

3.1. Summary Statistics

The raw SEM copper sediment data by site, season and year are summarized in Table 1 along with the summary statistics in Table 2. SEM copper concentrations across all sites for the three-year period ranged from 8.9 to 59.1 µg/g dw. Mean seasonal concentrations ranged from 18.6 to 30.1 µg/g dw. Similar median seasonal concentrations ranging from 17.5 to 29.9 µg/g dw were also reported.

Table 1. All Cache Slough sediment copper SEM concentrations (µg/g dry weight) from California sampling by boat for the years 2012–2014.

	2012 Cu SEM (µg/g dw)		2013 Cu SEM (µg/g dw)		2014 Cu SEM (µg/g dw)	
Station	**Spring**	**Fall**	**Spring**	**Fall**	**Spring**	**Fall**
CS-01	28.6	28.0	18.4	17.8	22.3	21.7
CS-02	22.9	13.3	22.2	26.1	19.6	17.2
CS-03	24.1	15.9	15.9	19.1	20.8	18.4
CS-04	32.4	28.6	23.5	22.2	17.8	16.9
CS-05	26.7	34.3	24.1	20.3	34.1	25.2
CS-06	32.4	38.8	29.9	28.0	34.3	27.6
CS-07	29.2	59.1	25.4	27.3	34.2	24.7
CS-08	26.1	46.4	9.5	8.9	25.2	9.8
CS-09	25.4	31.1	20.3	21.0	23.6	13.2
CS-10	17.2	8.9	19.1	11.4	26.2	17.3
CS-11	21.6	25.4	14.0	17.8	27.9	14.0
CS-12	29.9	31.1	33.0	24.1	26.4	17.7

Table 2. Descriptive statistics for sediment copper SEM concentrations (µg/g dry weight) from 12 Cache Slough (CA) sample sites for the years 2012–2014.

Year	Season	*n*	Mean	Std Dev	Range	Min	Max	Median
2012	Spring	12	26.4	4.51	15.2	17.2	32.4	26.4
	Fall	12	30.1	14.0	50.2	8.90	59.1	29.9
2013	Spring	12	21.3	6.59	23.5	9.50	33.0	21.3
	Fall	12	20.3	5.91	19.1	8.90	28.0	20.7
2014	Spring	12	26.0	5.73	16.5	17.8	34.3	25.7
	Fall	12	18.6	5.28	17.8	9.80	27.6	17.5

3.2. Site Trends

SEM copper trends by site are presented in Figures 2–16. There were significant trends by site for Cache Slough sites CS-04 (Figure 14), CS-09 (Figure 15) and CS-12 (Figure 16) and in all cases the trends were declining. The important message from this SEM copper site trends analysis is that none of the sites showed an increasing trend in concentrations over the three-year period and most of the sites showed no statistically significant trends.

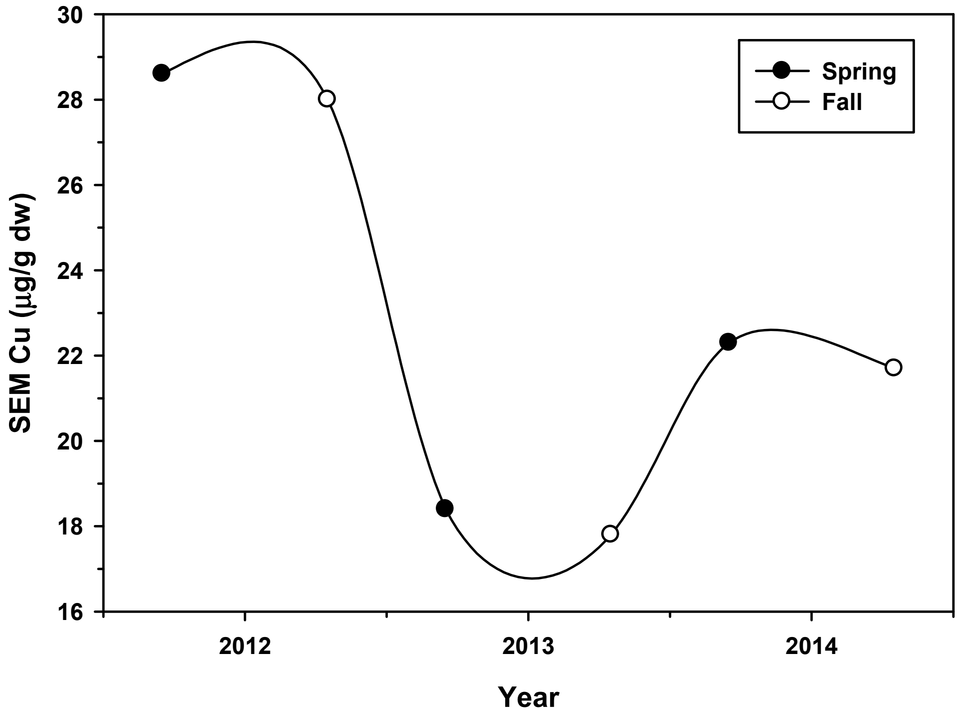

Figure 2. SEM copper concentrations (µg/g dry wt) from spring and fall sediment sampling at Cache Slough site CS-01 for the years 2012, 2013 and 2014.

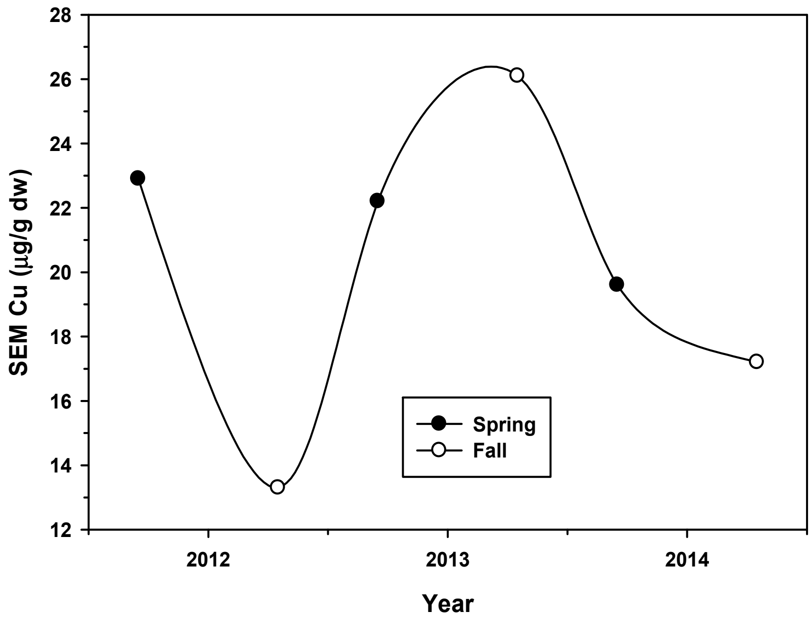

Figure 3. SEM copper concentrations (µg/g dry wt) from spring and fall sediment sampling at Cache Slough site CS-02 for the years 2012, 2013 and 2014.

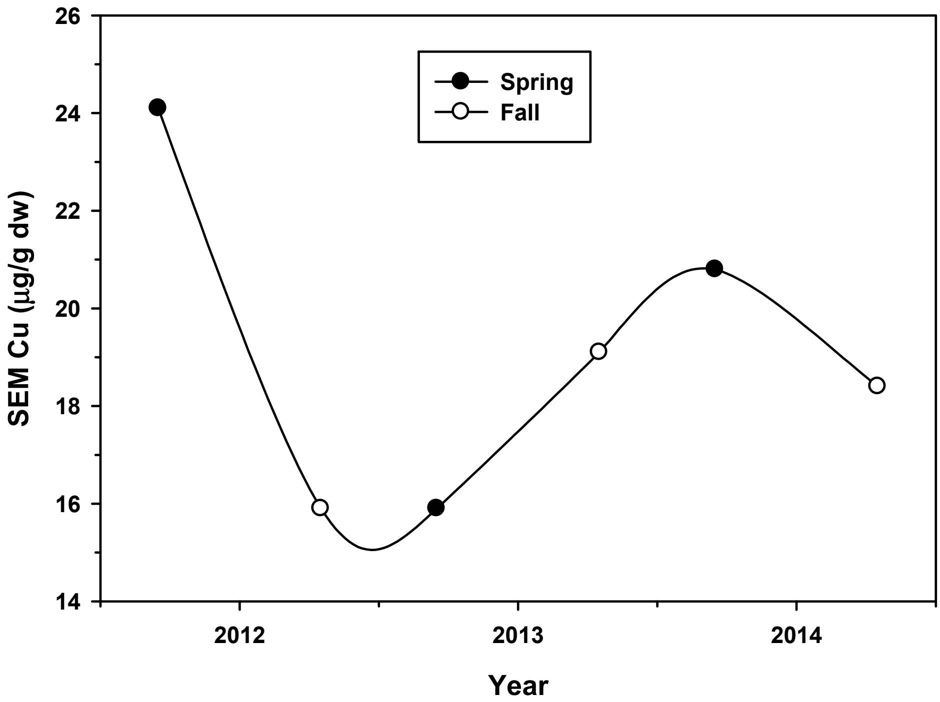

Figure 4. SEM copper concentrations (µg/g dry wt) from spring and fall sediment sampling at Cache Slough site CS-03 for the years 2012, 2013 and 2014.

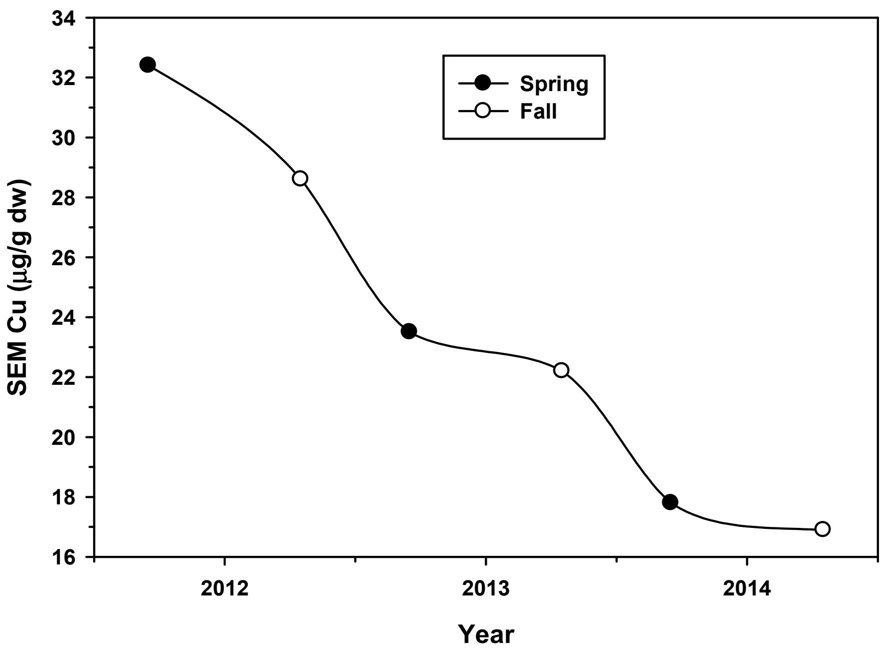

Figure 5. SEM copper concentrations (µg/g dry wt) from spring and fall sediment sampling at Cache Slough site CS-04 for the years 2012, 2013 and 2014.

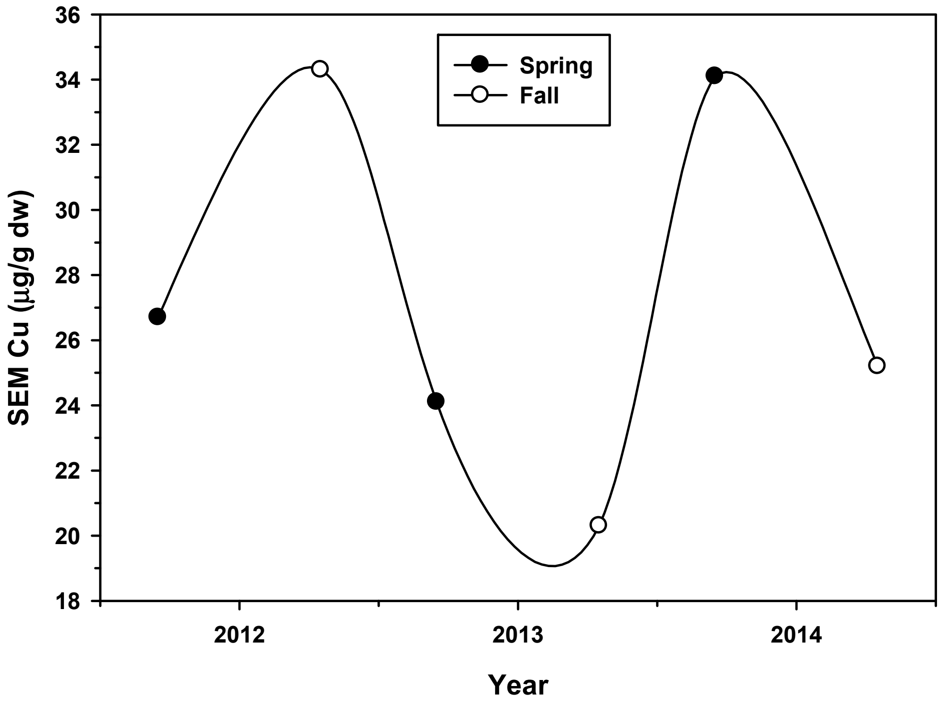

Figure 6. SEM copper concentrations (µg/g dry wt) from spring and fall sediment sampling at Cache Slough site CS-05 for the years 2012, 2013 and 2014.

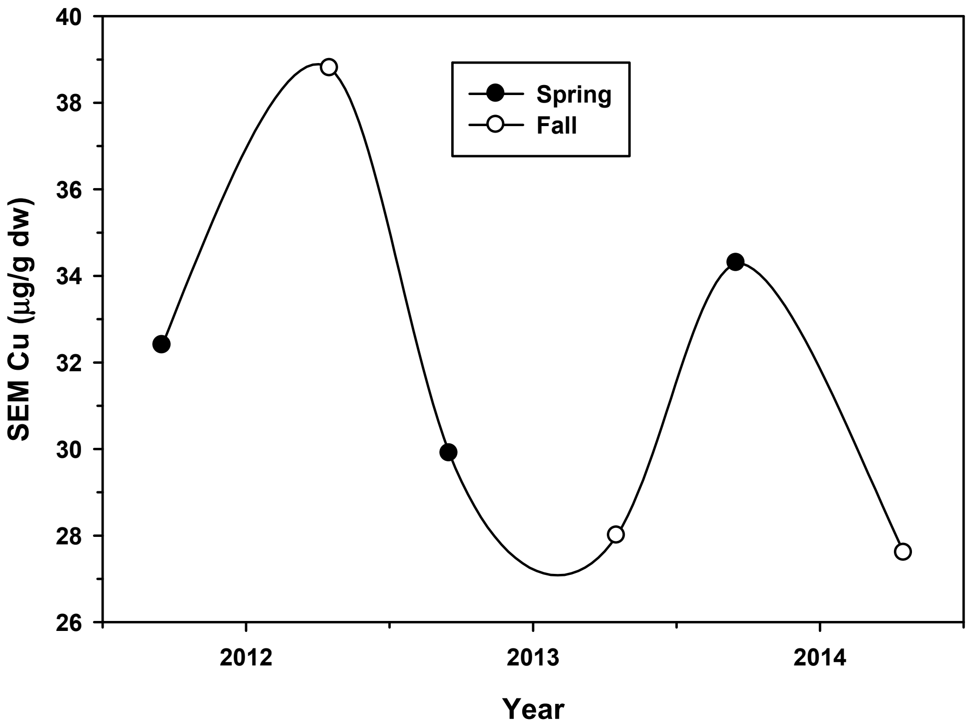

Figure 7. SEM copper concentrations (µg/g dry wt) from spring and fall sediment sampling at Cache Slough site CS-06 for the years 2012, 2013 and 2014.

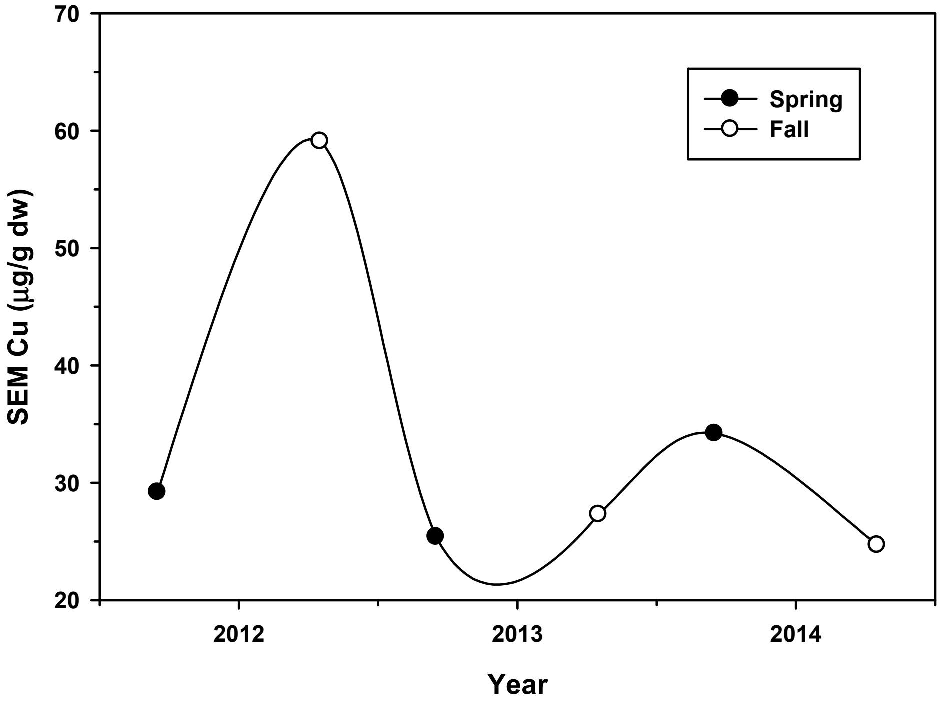

Figure 8. SEM copper concentrations (µg/g dry wt) from spring and fall sediment sampling at Cache Slough site CS-07 for the years 2012, 2013 and 2014.

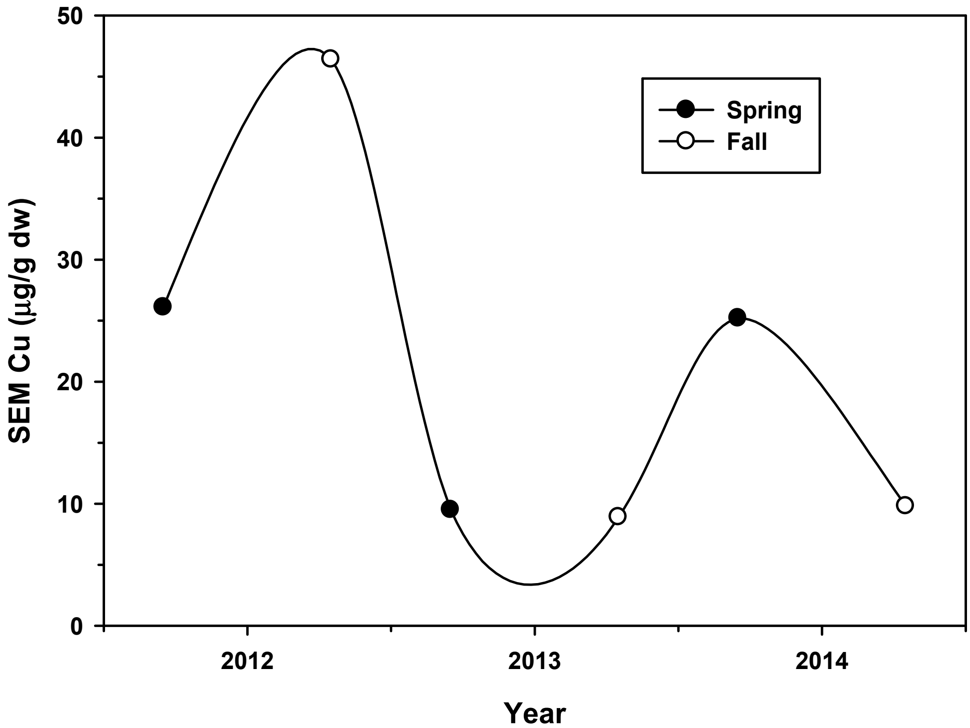

Figure 9. SEM copper concentrations (µg/g dry wt) from spring and fall sediment sampling at Cache Slough site CS-08 for the years 2012, 2013 and 2014.

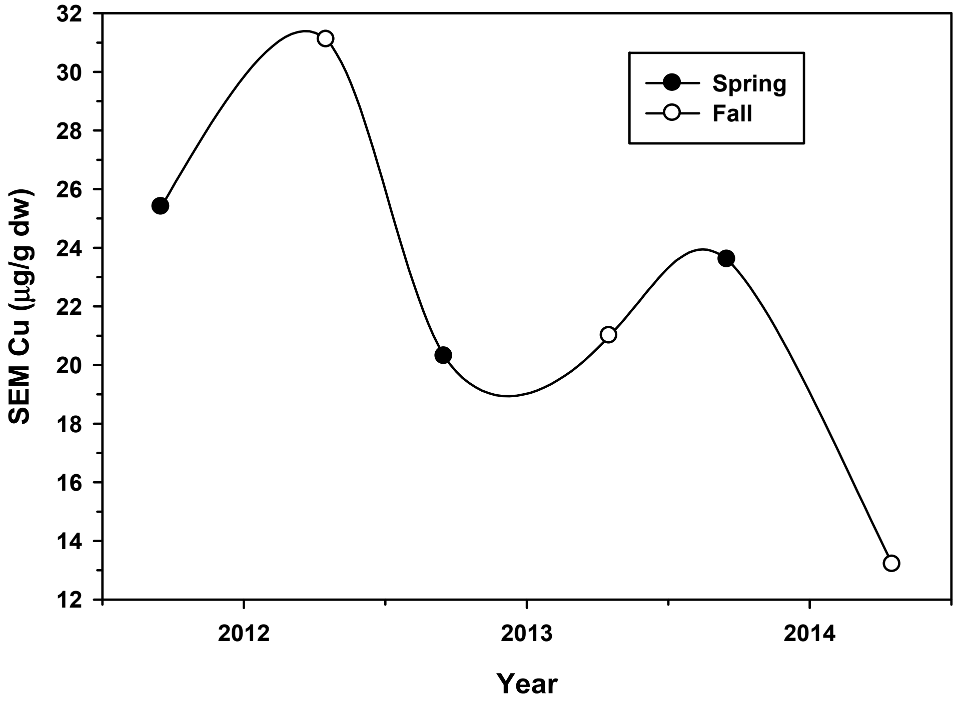

Figure 10. SEM copper concentrations (µg/g dry wt) from spring and fall sediment sampling at Cache Slough site CS-09 for the years 2012, 2013 and 2014.

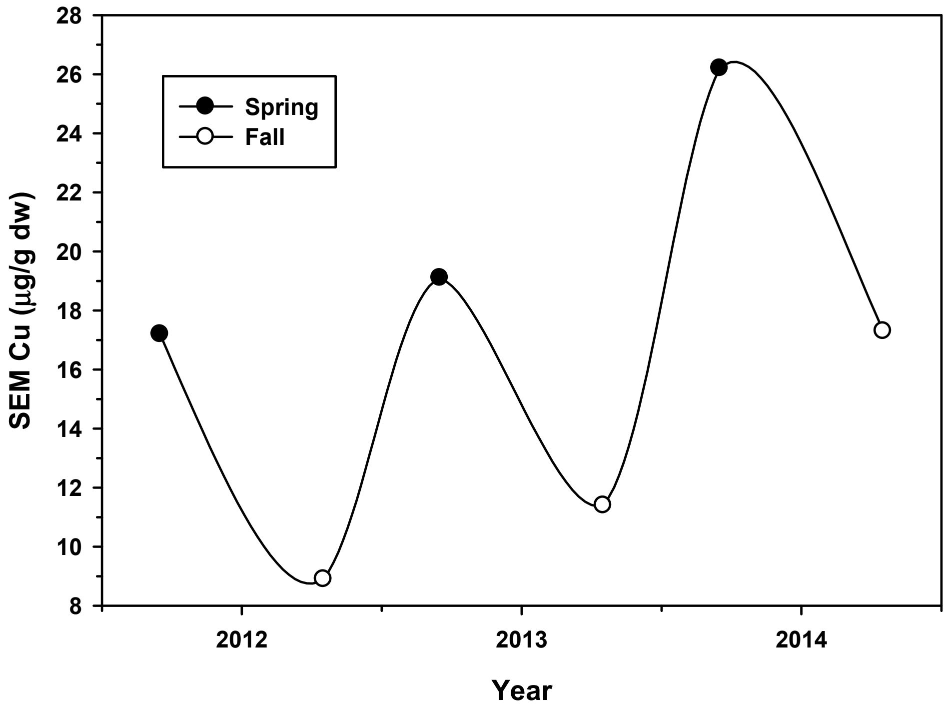

Figure 11. SEM copper concentrations (µg/g dry wt) from spring and fall sediment sampling at Cache Slough site CS-10 for the years 2012, 2013 and 2014.

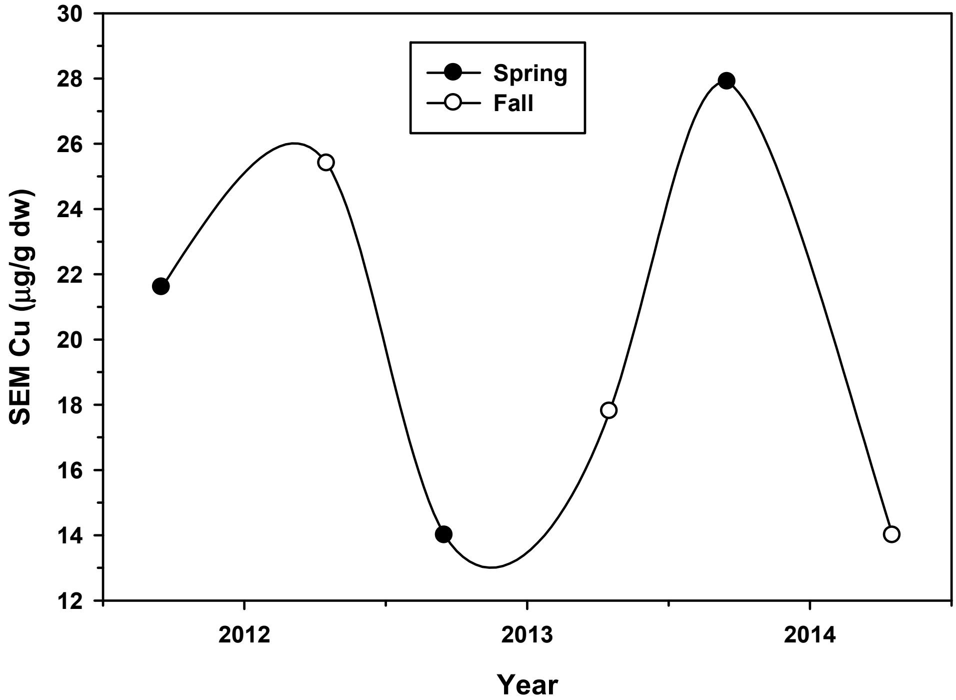

Figure 12. SEM copper concentrations (µg/g dry wt) from spring and fall sediment sampling at Cache Slough site CS-11 for the years 2012, 2013 and 2014.

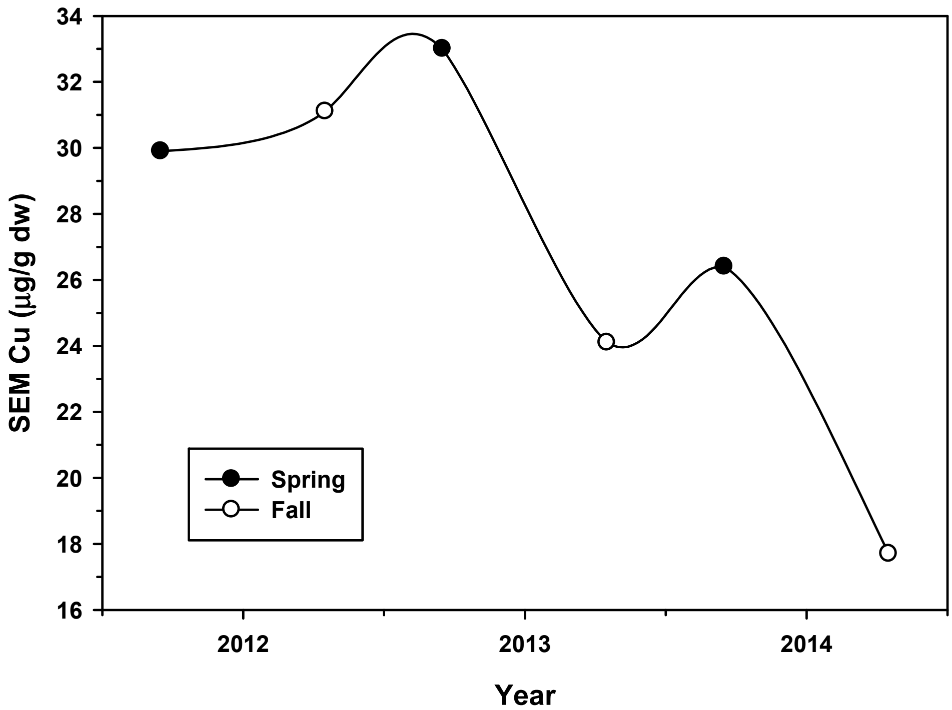

Figure 13. SEM copper concentrations (µg/g dry wt) from spring and fall sediment sampling at Cache Slough site CS-12 for the years 2012, 2013 and 2014.

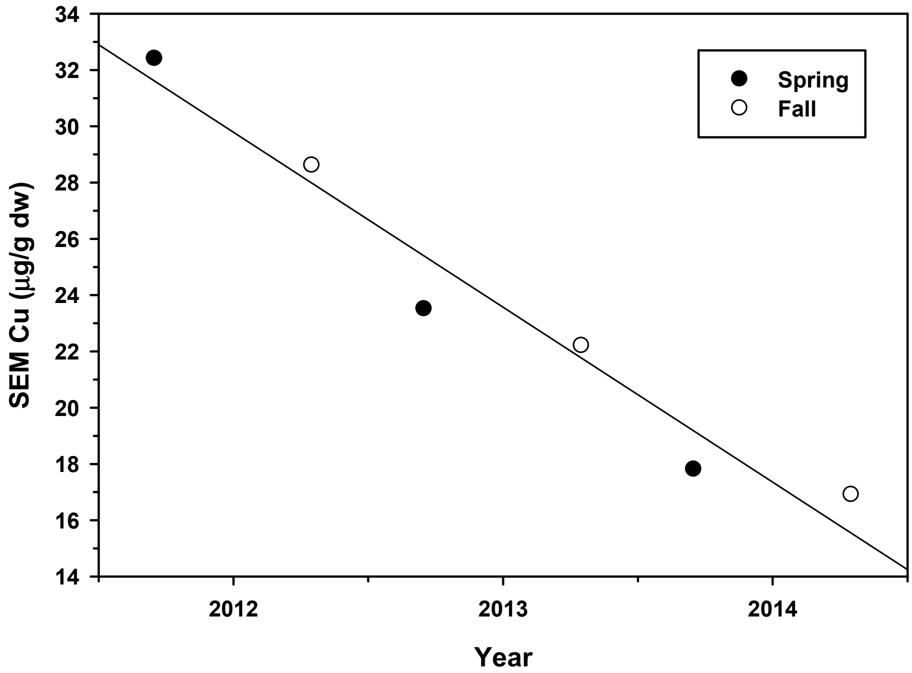

Figure 14. Regression results of sediment SEM copper concentrations (µg/g dry wt) from spring and fall sediment sampling at Cache Slough site CS-04 for the years 2012, 2013 and 2014. ($r^2 = 0.953$, $p < 0.001$).

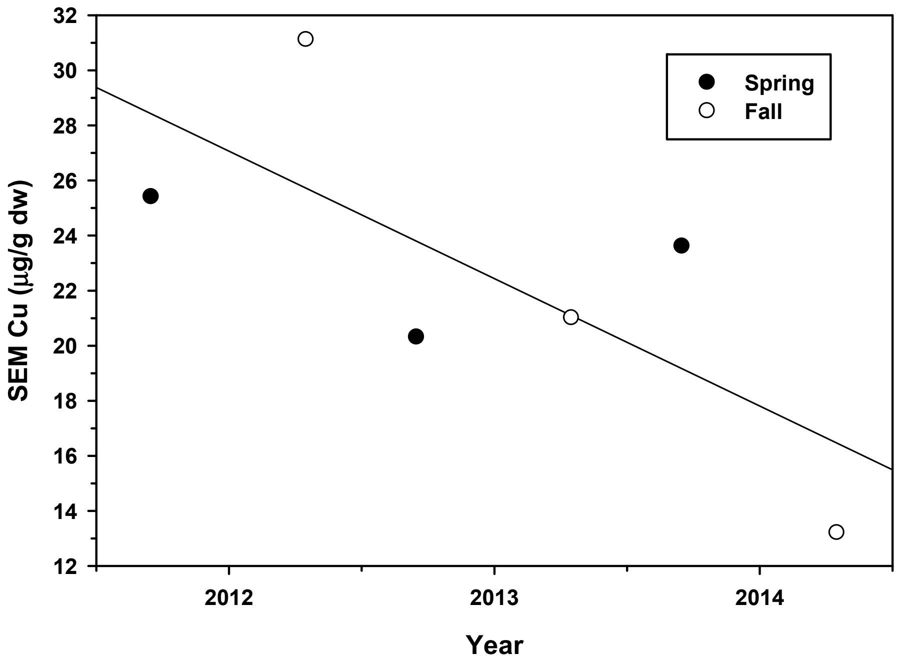

Figure 15. Regression results of sediment SEM copper concentrations (µg/g dry wt) from spring and fall sediment sampling at Cache Slough site CS-09 for the years 2012, 2013 and 2014. ($r^2 = 0.545$, $p = 0.094$).

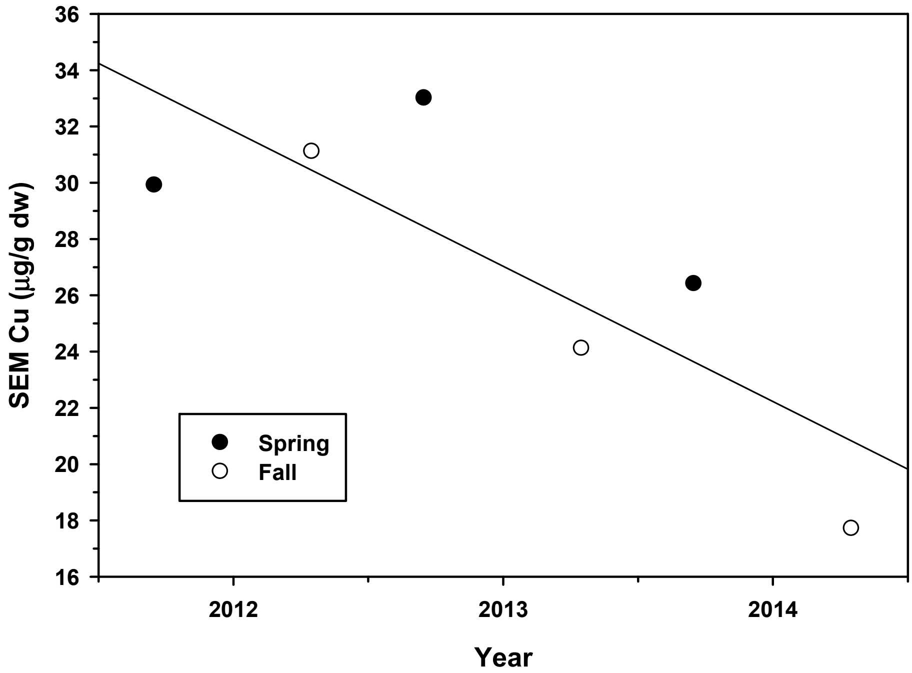

Figure 16. Regression results of sediment SEM copper concentrations (µg/g dry wt) from spring and fall sediment sampling at Cache Slough site CS-12 for the years 2012, 2013 and 2014. (r^2 = 0.666, p = 0.048).

ANOVA was also conducted to compare SEM copper site concentrations with each other using a p value cutpoint of 0.05 (Figure 17). The results from this analysis showed that SEM copper concentrations at CS-07 were higher than CS-10 so there were some limited spatial differences among sites.

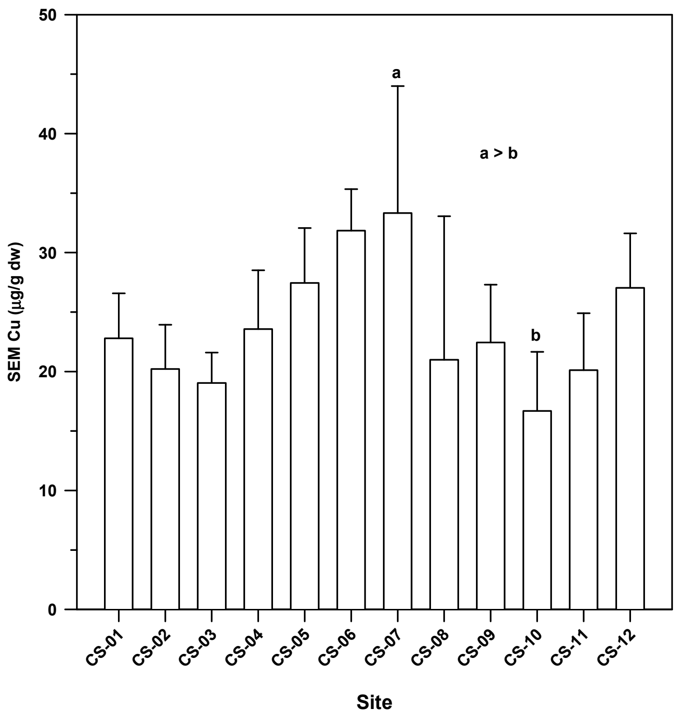

Figure 17. All Cache Slough SEM Cu sediment data by site (ANOVA, p = 0.005). a,b: Site CS-07 is significantly different from site CS-10 (Holm-Sidak method, $p \leq 0.050$).

3.3. Waterbody Section Comparisons

In order to provide more statistical power for a spatial analysis, Cache Slough SEM copper data were analyzed by waterbody section. Sections were defined as lower (CS-01 –CS-04), middle (CS-05–CS-08) and upper (CS-09–CS-12) (Figure 18). The results from this analysis were that SEM copper concentrations in the middle section were higher than both the upper and lower section.

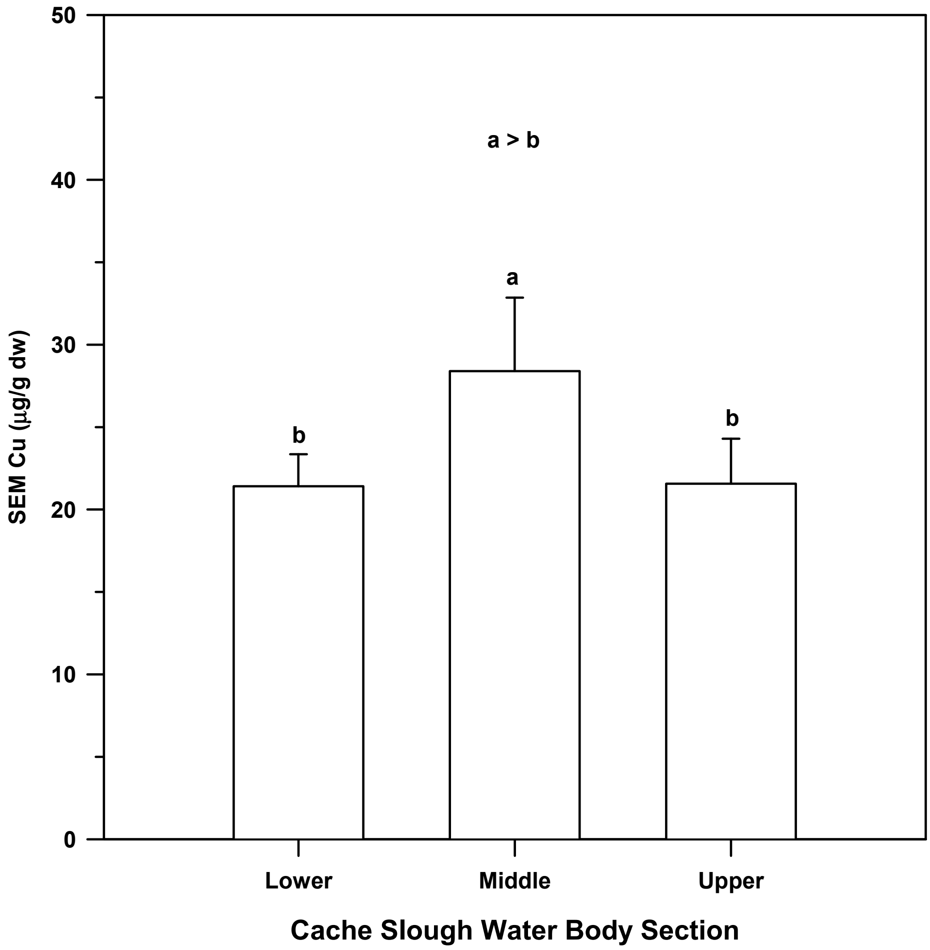

Figure 18. All Cache Slough SEM Cu sediment data by lower, middle and upper (four sites each) water body sections (Kruskal-Wallis ANOVA, $p = 0.004$). a,b: The middle section is significantly different from the lower and upper sections (Holm-Sidak method, $p \leq 0.050$).

3.4. Seasonal Comparisons

Various seasonal comparisons of SEM copper concentration are presented in Figures 19–26. There were no significant differences in SEM copper concentration between spring and fall for 2012 and 2013 (Figures 19 and 20). However, for 2014 SEM copper concentrations were higher in the spring than the fall (Figure 21). It is noteworthy that precipitation was lower in 2014 than the other two years as address below. There were also no significant differences between spring and fall copper concentrations when all years were combined (Figure 22). There were also no significant differences among the three years for all the spring data (Figure 23). However, for the fall data with the three years combined 2012 concentrations were higher than 2014 concentrations (Figure 24). All Cache Slough SEM copper data analyzed by year also showed that SEM copper concentrations were higher in 2012 than in both 2013 and 2014 (Figure 25). A final analysis of all SEM copper data by season and year in Figure 26 showed no significant trend.

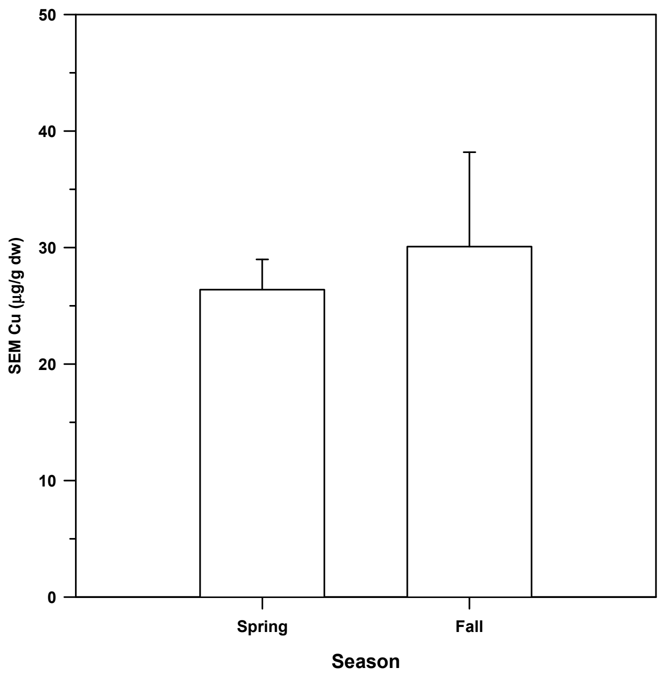

Figure 19. All Cache Slough SEM Cu sediment data for the year 2012 by season (Mann-Whitney Rank Sum Test, p = 0.402).

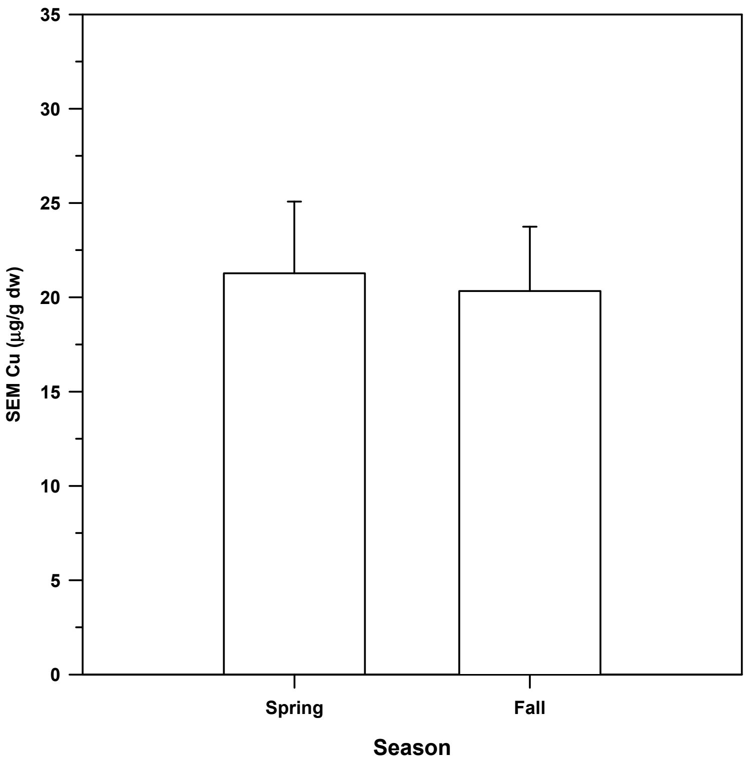

Figure 20. All Cache Slough SEM Cu sediment data for the year 2013 by season (t-test, p = 0.716).

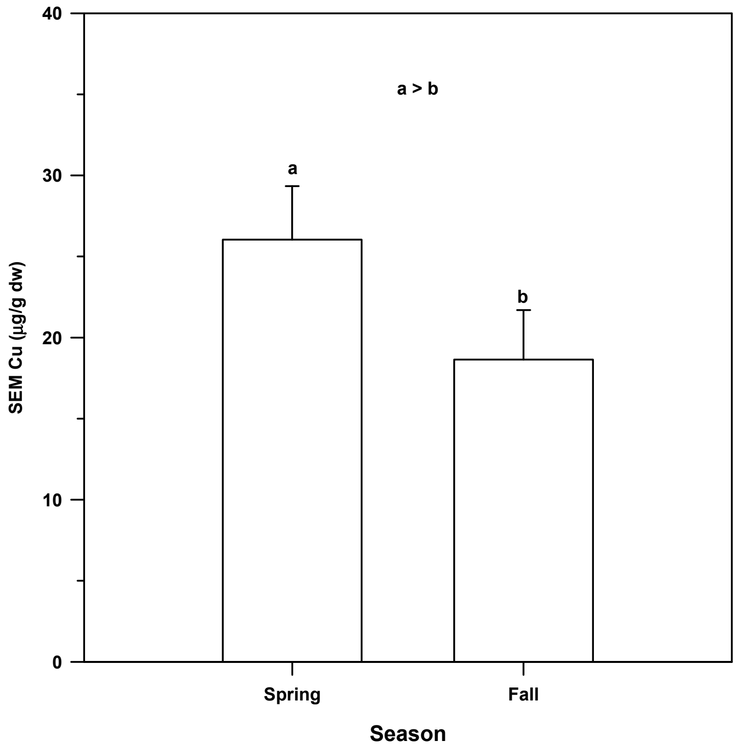

Figure 21. All Cache Slough SEM Cu sediment data for the year 2014 by season. a,b: Spring is significantly greater than Fall (*t*-test, $p = 0.003$).

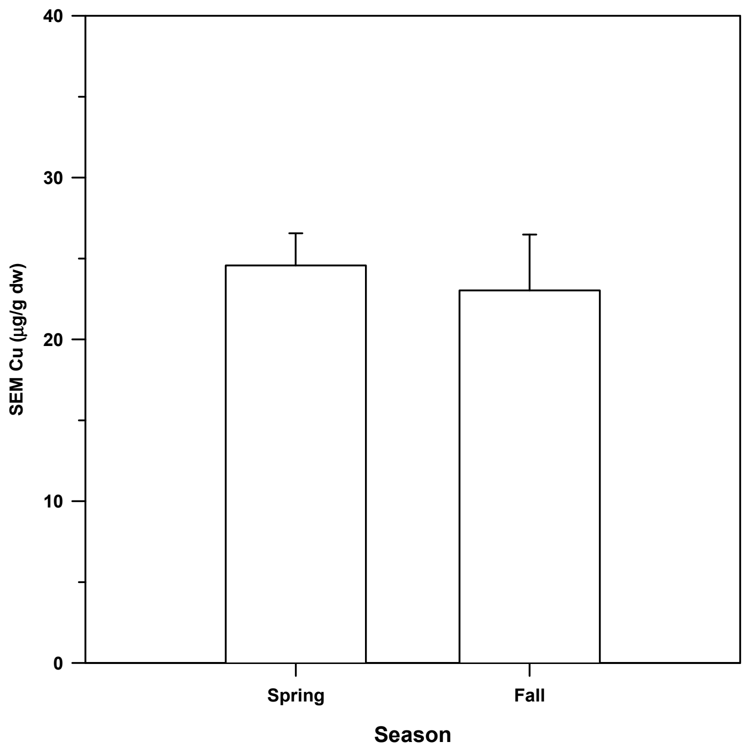

Figure 22. All Cache Slough SEM Cu sediment data for the years 2012–2014 combined by season (Mann-Whitney Rank Sum Test, $p = 0.126$).

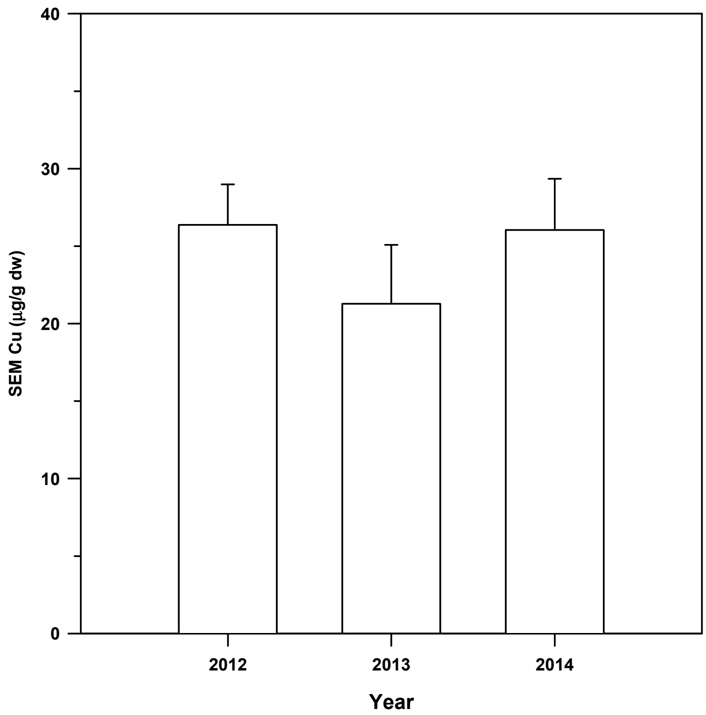

Figure 23. All Spring Cache Slough SEM Cu sediment data by year (ANOVA, $p = 0.062$).

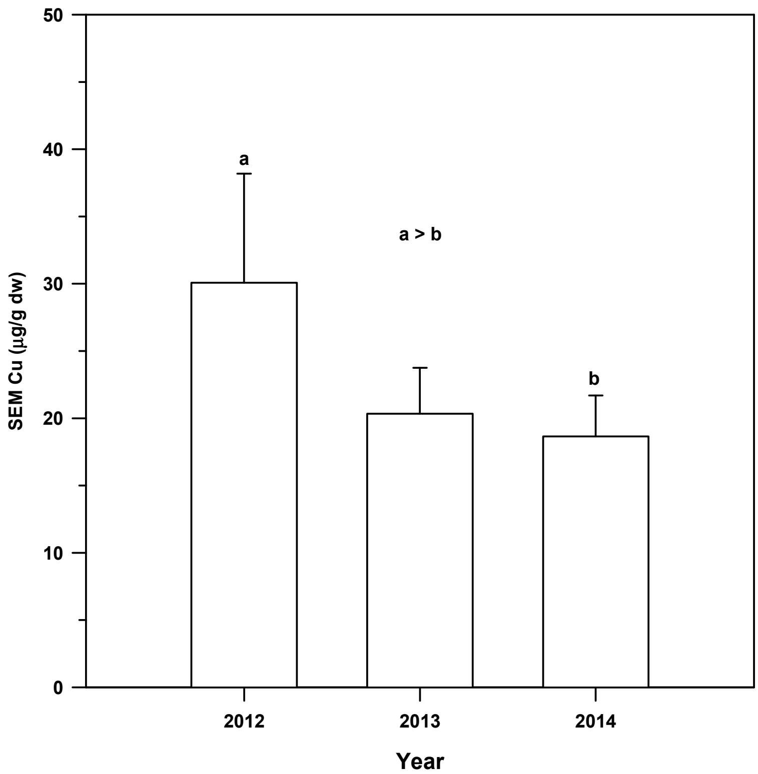

Figure 24. All Fall Cache Slough SEM Cu sediment data by year (Kruskal-Wallis One Way ANOVA on Ranks, $p = 0.026$). a,b: The year 2012 is significantly different from the year 2014 (Tukey Method, $p \leq 0.050$).

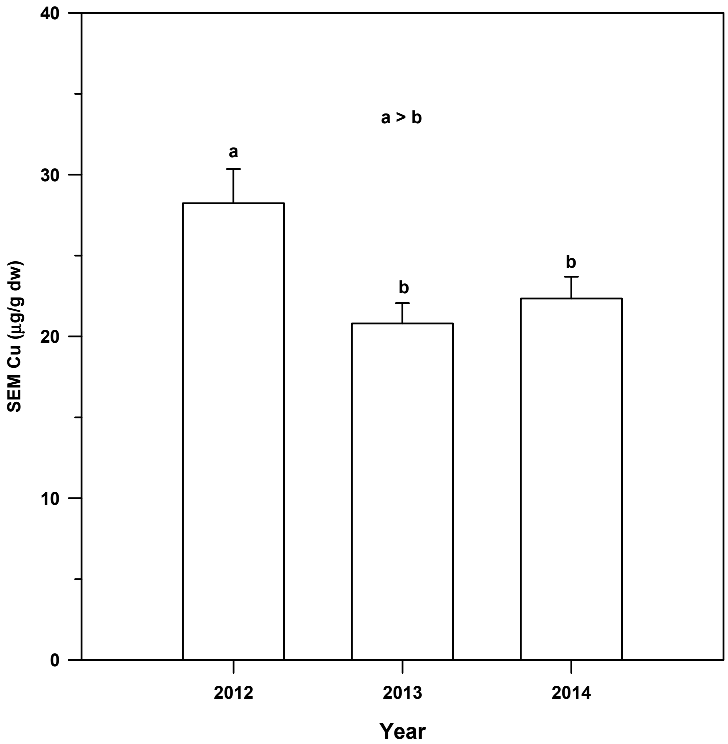

Figure 25. All Cache Slough SEM Cu sediment data by year (ANOVA, $p = 0.004$). a,b: The year 2012 is significantly different from the years 2013 and 2014 (Holm-Sidak Method, $p \leq 0.050$).

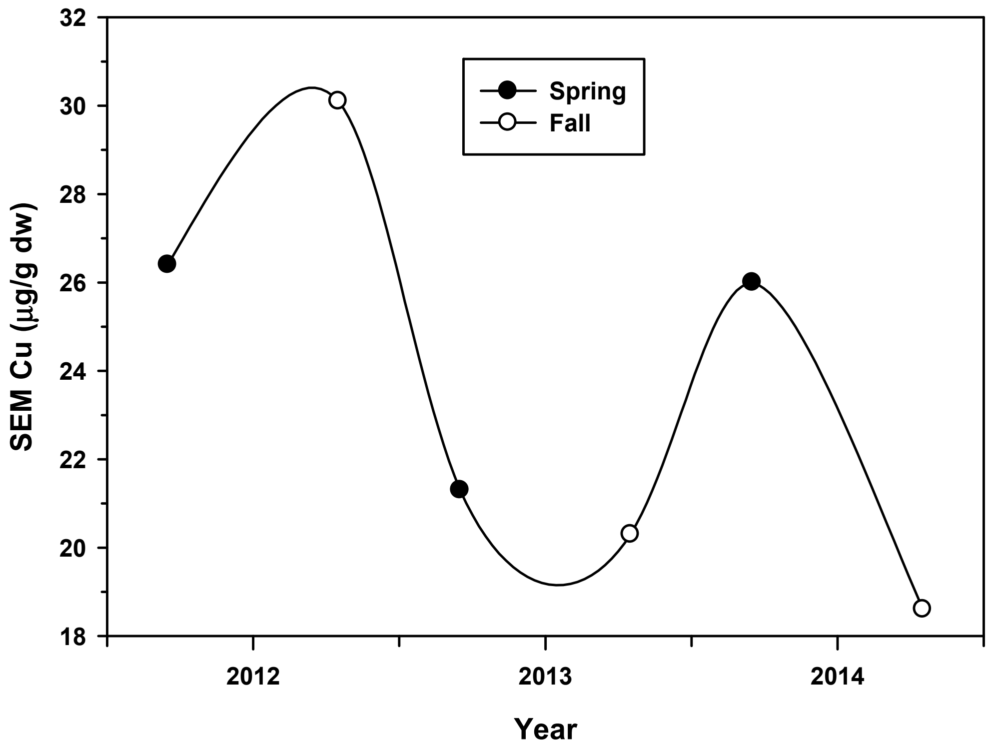

Figure 26. All Cache Slough SEM Cu sediment data for the years 2012, 2013 and 2014 by season.

3.5. Summary of Annual Precipitation Data

A description of the annual precipitation has been previously described in Hall and Anderson [7]. Annual precipitation data (defined as Water Years) from 2011 to 2015 from Cache Slough were summarized to determine the possible influence of precipitation on

SEM copper concentrations (Table 3). The 2011 and 2015 data were included to have annual data both before and after the 2012 to 2014 sampling period. Monthly precipitation summary data for water years 2011–2015 for long-term National Weather Service (NWS) precipitation station SACRAMENTO 5 ESE was used for the analysis. This Station location (Lat: 38°33′ N Lon: 121°25′ W) is approximately five miles east south east of downtown Sacramento. SACRAMENTO 5 ESE is ~25 miles from the center of all 12 Cache Slough sample stations and was chosen because it lies at the approximate center of the near upstream watershed. It was also the closest long-term site in the NWS database with five years of uninterrupted rain data by month. A water year starts on October 1 of the previous reference year and ends on September 30 of the reference year. For example, the 2012 Water Year begins on 1 October 2011and ends on 30 September 2012.

Table 3. Monthly precipitation summary data for water years 2011–2015 for long-term National Weather Service (NWS) precipitation station SACRAMENTO 5 ESE. Station location (Lat: 38°33′ N Lon: 121°25′ W) is approximately five miles east south east of downtown Sacramento.

Water	Precipitation (Inches)												Water Year	Sum % of 30
Year	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	Sum of Rain	Year Mean **
2011	1.75	2.65	5.52	1.36	3.88	7.00	0.08	1.40	1.14	0.00	0.00	0.00	24.78	125
2012 *	1.72	0.87	0.07	2.52	0.94	4.45	2.65	0.00	0.01	0.00	0.00	0.00	13.23	67
2013 *	1.28	4.33	6.46	1.06	0.26	1.59	0.58	0.57	0.31	0.00	0.00	0.55	16.99	86
2014 *	0.00	0.82	0.38	0.20	4.49	1.93	1.97	0.01	0.00	0.02	0.00	0.54	10.36	51
2015	0.37	1.28	7.63	0.01	2.28	0.16	1.81	0.19	0.07	0.00	0.00	0.00	13.80	68

* Water years of Cache Slough study. ** The 30 year mean precipitation for this site over the five years above is 19.85 inches.

Results from the analysis in Table 3 showed that precipitation for all three years of the study (2012–2014) were less than the long term 30 year mean of 19.85 inches. A comparison among study years showed that 2013 was the wettest year followed by 2012. The driest year was 2014. Before the study was initiated in 2012, precipitation was greater than the 30-year long term mean in 2011 that may have influenced copper concentrations in this water body during the first year of the study. Linear regression analysis designed to determine the relationship between rainfall data and SEM copper concentrations by year (Figure 27) and by season (Figure 28) showed no statistically significant relationships.

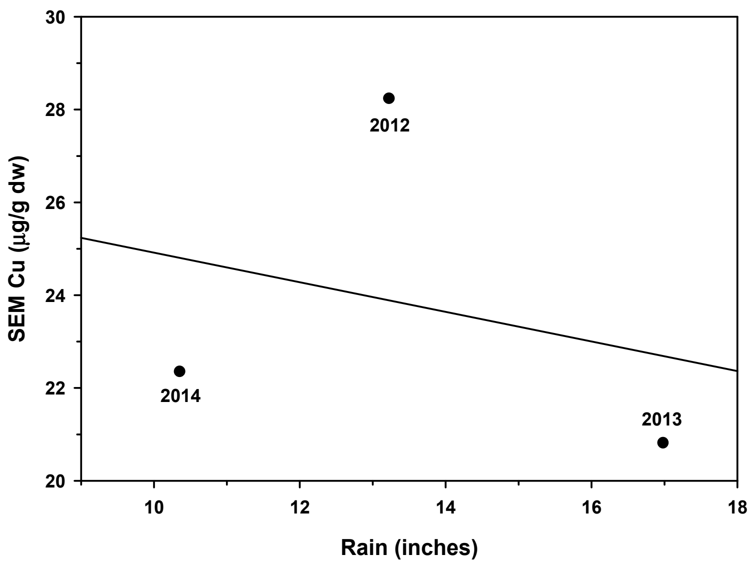

Figure 27. Linear regression results of the total rain in inches at NWS site SACRAMENTO 5 ESE from the water years 2012–2014 versus the mean SEM Cu sediment concentration from all Cache Slough sample sites during the same years ($r^2 = 0.073$, $p = 0.825$).

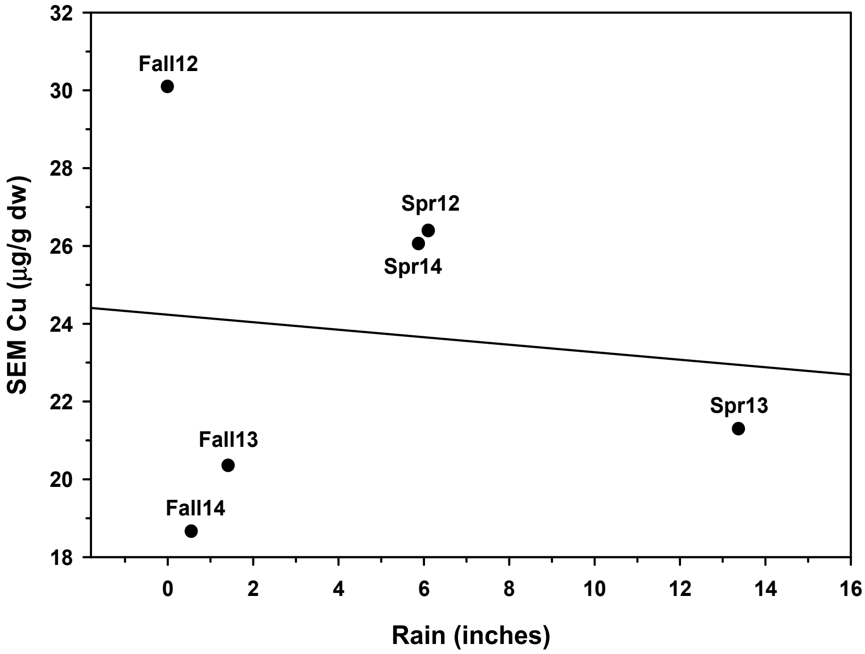

Figure 28. Linear regression results of the total rain in inches at NWS site SACRAMENTO 5 ESE from two different seasons during the water years 2012–2014 versus the mean SEM Cu sediment concentration from all Cache Slough sample sites during the same years (r^2 = 0.012, p = 0.833).

4. Discussion

4.1. Comparison of Sediment SEM Copper Data from Cache Slough with Historical Data

A summary of historical sediment SEM copper data from areas with agricultural influence presented in Table 4 is compared with SEM copper data from Cache Slough. All units for the SEM copper data are presented as µg/g dw to provide a consistent comparison. The information provided for each study in the tabular format was as follows: (1) location; (2) water body and land use (only agriculture considered); (3) Were depositional areas targeted for sampling?; (4) number of sites sampled and frequency of sampling; (5) SEM copper measurements {minimum, maximum and mean in µg/g dw); and (6) reference. The mean SEM copper value from our Cache Slough data set was 23.8 µg/g dw (s.d. = 8.45) and the range was 8.9 to 59.1 µg/g dw. A simple comparison of overlapping ranges was used to determine if the SEM copper data set in Cache Slough is similar to the specific historical data sets. If ranges overlapped, data are considered similar to Cache Slough but if ranges do not overlap and are either lower or higher that the Cache Slough data range the data sets are considered different. Each study in Table 4 is described below.

Besser et al. [16] reported a single SEM copper measurement of 36.2 µg/g dw from a single sample in an agricultural site in the upper Clark Fork river Montana (Table 4). This value is in the range of concentrations (8.9 to 59.1 µg/g) that we reported in Cache Slough.

Burton et al. [17] reported that ranges of SEM copper concentrations from rural sites with suspected with suspected agricultural influence in Sweden (2.3 to 8.9 µg/g) and Italy (3.1 to 3.6 µg/g) that were lower than reported in Cache Slough (8.9 to 59.1 µg/g) (Table 4). The range of SEM copper concentrations reported in Italy was the lowest range reported from this historical summary. The range of SEM copper sediment concentrations from agricultural sites in Denmark (1.8 to 110 µg/g), England/Wales (7.2 to 25.9 µg/g), Finland (1.2 to 41.5 µg/g), Belgium (3.5 to 22.7 µg/g), France (0.06 to 20.8 µg/g) and Germany (1.97 to 76.1 µg/g) have SEM copper concentrations similar to Cache Slough (8.9 to 59.1 µg/g).)

Table 4. Summary of historical sediment SEM copper data (µg/g dry wt) with agricultural influence.

Location	Water Body/Primary Surrounding Land Use	Depositional Areas Targeted?	# of Sites Sampled & Frequency	SEM Cu (Min–Max, Mean)	Reference
Western Montana, USA	Upper Clark Fork River and Milltown Reservoir/Primarily forested but with some inputs from agriculture or Cu mining upstream; some agricultural influence	Not reported	3 sections, 7 total sites sampled once from composite samples (1 of 7 sites agr)	RC (reference): (1.91–1.91, 1.91) [a] Milltown Reservoir: (35.0–902, 265) Upper Clark Fork: (655–655, 655) Upper Clark Fork Agriculture (CF4): (36.2–36.2, 36.2)	[16]
Sweden, Denmark, England, Finland, Belgium, France, Germany, and Italy	SW Sweden/Agriculture [b] E Denmark/Agriculture S England & Wales/Agriculture S Finland/Agriculture S Belgium/Agriculture	Yes (sand grain size and smaller)	Sweden: 3 sites, 1 composited sample each site, sampled once [c] Denmark: 6 sites England/Wales: 16 sites Finland: 5 sites Belgium: 6 sites	Sweden: (2.29–8.90, 4.85) Denmark: (1.84–110.2, 5.28) England/Wales: (7.12–25.9, 15.4) Finland: (1.21–41.5, 13.0) Belgium: (3.50–22.7, 11.2)	[17]
Sweden, Denmark, England, Finland, Belgium, France, Germany, and Italy	N France/Agriculture W & S Germany/Agriculture N Italy/Agriculture	Yes	France: 12 sites Germany: 9 sites Italy: 2 sites	France: (0.064–20.8, 8.23) Germany: (1.97–76.1, 15.7) Italy: (3.05–3.56, 3.30)	
Guadalete Estuary, SW Spain (tidal sites)	Site G1/Harbor/Port Sites G2–G3/Agriculture Sites S1-S7/Mouths of agriculture drains	Yes (most samples < 63 um)	10 sites with 3 replicates/site, sampled twice (Aug 2002 & Mar 2003)	Site G1: (4.4–170, 46.4) Sites G2–G3: (10.8–16.5, 14.0) Sites S1-S7: (5.7–21.0, 14.4)	[18]
Washington State Desert	Hanford Reach (Columbia River)/Desert Priest Rapids Dam (Columbia River)/Agr McNary Dam (Columbia River)/Agriculture Ice Harbor Dam (Snake River)/Agriculture	Not reported	4 sites sampled 2–3 times over 3 years 6 sites sampled 2–3 times over 3 years 6 sites sampled 2–3 times over 3 years 3 sites sampled 2 times over 2 years	Hanford Reach Site (desert): (5.27–12.6, 8.63) Priest Rapids Dam Sites: (4.38–30.5, 17.7) McNary Dam Sites: (6.80–20.9, 15.9) Ice Harbor Dam: (4.64–15.7, 12.3)	[19]
Ravenna, NE Italy (tidal sites)	Pialassa Piomboni (coastal lagoon)/Primary freshwater input from agriculture	Not reported	50 sites sampled once	Pialassa Piomboni: (0.318–89.0, 6.35)	[20]
SE Netherlands	Beekloop (headwater stream)/Agriculture [d]	Not reported	4 sites sampled once with 3 replicates per site	Sites L1–4: (19.1–76.3, 53.2)	[21]

Table 4. *Cont.*

Location	Water Body/Primary Surrounding Land Use	Depositional Areas Targeted?	# of Sites Sampled & Frequency	SEM Cu (Min–Max, Mean)	Reference
N Serbia	Various rivers, canals, streams/Agriculture Various rivers, canals, streams/Urban	Yes	9 urban sites sampled twice in one year 3 urban sites sampled twice in one year	Agriculture: (6.35–96.6, 45.4) [e] Urban: (12.7–23.5, 17.6)	[22]
SW Netherlands	Meuse/Rhine River Delta/Agriculture [f]	Yes	4 sites sampled twice in Nov 1995 and once in Jun 1996	Sites 1–4: (19.1–76.3, 56.7)	[23]
N Netherlands	Lake Ketel/Agriculture (some urban upstream)	Yes (most sediment < 63 um)	4 sites (10 reps per site) sampled once	Sites A–D: (13.3–58.5, 35.3)	[24]
Netherlands/Belgium	Various Coastal Sites (11–20 km offshore) Various Urban Sites	Not reported	8 sites sampled once 10 sites sampled once	Coastal sites: (0.635–2.52, 1.27) Urban sites: (1.27–49.6, 17.1)	[25]
Netherlands/Belgium	Various Agriculture Sites (some urban upstream)	Not reported	3 sites sampled once	Agriculture sites: (10.8–71.8, 34.5)	
Antioch, California State	Lower Kirker Creek/Urban Upper Kirker Creek/Agriculture [g]	Yes	14 sites with composite samples collected once for 2 years	12 Urban Sites: (0.191–12.6, 3.05) 2 Agriculture Sites: (0.191–12.4, 4.21)	[26]
Salinas, California State	Alisal, Gabilon and Natividad Creeks/Urban with some agriculture	Yes	13 sites with composite samples collected once/year for 3 years	11 Urban Sites [h] (3.62–20.6, 8.49) 2 Agriculture Sites: (2.67–8.26, 5.46)	[27]
N Illinois State	Big Bureau Creek/Agriculture	Yes	12 sites with composite samples collected once/year for 3 years	Sites 1–12: (2.54–7.63, 4.63)	[28]
Santa Maria, California State	Santa Maria River, Osco Flaco Creek, Orcutt Creek and unnamed drainages/Agriculture	Yes	12 sites with composite samples collected once/year for 3 years	Sites 1–12 [h] (7.63–20.3, 11.5)	[29]
Pleasant Grove, California State	Upper Pleasant Grove Creek and Tributaries/Urban Lower Pleasant Grove Creek/Agriculture	Yes	21 sites with composite samples collected once/year for 10 years	18 Urban Sites: (0.508–252, 21.5) 3 Agriculture Sites: (0.191–21.9, 6.94)	[30]

[a] Not reported whether sample concentrations were dry weight measurements. [b] All sample sites in this study reported to be wadable streams with no evidence of nearby point source chemical or organic inputs. The map scale was too small to locate specific sites on Google Earth but all appeared to be located in rural areas where agriculture followed by forest was the predominant land use. In addition, sites that appeared to be high quality (as indicated by biological indicators) were targeted for sampling according to the authors. [c] All sites in this study had one composite sample, sampled one time. [d] Authors report soils in region may be contaminated with heavy metals from historic ore smelting activities and manure from intensive livestock farming. [e] Maximum value from a site located at a ship lock in a canal. [f] Authors report that both the aquatic sediments and soils in the delta are contaminated by heavy metals. [g] These sites surrounded by grazing land. [h] All data reported were 3 year mean values by site.

SEM copper sediment concentrations ranging from 5.7 to 21.0 µg/g from various agricultural sites in the Guadalete estuary in Spain presented in Table 4 were reported to be similar to Cache Slough (8.9 to 59.1 µg/g) [18]. The maximum SEM copper value at the harbor/marina site (170 µg/g) sampled during this study was much higher than the agricultural sites.

Patton and Crecelius [19] reported ranges of SEM copper concentrations of 4.38 to 30.5 µg/g for Priest Rapids Dam sites, 6.8 to 20.9 µg/g for McNary Dam sites, and 4.64 to 15.7 µg/g for Ice Harbor Dam located in the State of Washington (Table 4). All of these sites have some agricultural influence and the range of SEM copper concentrations is similar to our Cache Slough data.

SEM copper concentrations ranging from 0.32 to 89 µg/g were reported from 50 sites sampled in the Pialassa Piomboni coastal lagoon in north east Italy [20] (Table 4). Freshwater input from agricultural sources was found in this study area and the range of SEM copper concentrations reported was similar to concentrations in Cache Slough.

Poot et al. [21] reported SEM copper concentrations ranging from 19.1 to 76.3 µg/g from four sites sampled in a headwater stream in south east Neatherlands with agricultural influence, historical smelting activities and manure from intensive livestock farming (Table 4). The SEM copper concentrations reported in this study were similar to concentrations reported in Cache Slough.

SEM copper concentrations ranging from 6.35 to 96.6 µg/g were reported from various rivers, canals and streams in Serbia with agricultural influence [22] (Table 4). However, the maximum concentration from this study was reported from a ship lock in a canal. The range of SEM copper concentrations reported by these authors was similar to concentrations (8.9 to 59.1 µg/g) reported in Cache Slough.

Van den Berg et al. [23] reported SEM copper concentrations ranging from 19.1 to 76.3 µg/g from sites in the Meuse/Rhine River Delta in south west Netherlands with agricultural influence (Table 4). The range of SEM copper concentrations reported from this study was similar to the range of concentrations reported in Cache Slough. Van den Berg et al. [24] also reported SEM copper concentrations in Lake Ketel in northern Netherlands ranging from 13.3 to 58.5 µg/g from sites with agricultural influence. This concentration range was also similar to Cache Slough.

Van den Hoop et al. [25] reported SEM copper concentrations ranging from 10.8 to 71.8 µg/g from stream sites with agricultural influence in the Netherlands/Belgium (Table 4). The range of SEM copper concentrations reported in this study was similar to our Cache Slough values.

SEM copper concentrations ranging from 0.19 to 12.4 µg/g presented in Table 4 were reported from two agricultural sites in upper Kirker Creek in Antioch, California [26]. This concentration range was similar to the range of SEM copper concentrations reported in Cache Slough. SEM copper concentrations from another California streams network in Salinas has a somewhat lower range (2.7 to 8.3 µg/g) than reported in Cache Slough [27].

Hall et al. [28] reported SEM copper concentrations ranging from 2.5 to 7.63 µg/g from 12 sites sampled yearly for three years in an agricultural stream sampled in northern Illinois (Big Bureau Creek) (Table 4), This concentration range of SEM copper values is one of the lowest ranges reported, except for the Italian stream reported by Burton et al. [17], and this range is lower than reported in Cache Slough.

SEM copper concentrations ranging from 7.3 to 20.3 µg/g were reported from an agricultural stream in Santa Maria California based on sampling 12 sites annually over a period of three years [29]. This range of SEM copper concentrations is similar to the range reported in Cache Slough (Table 4).

Hall et al. [30] reported SEM copper concentrations ranging from 0.19 to 21.9 µg/g from three agricultural sites in Pleasant Grove Creek, California (Table 4). Although this creek is primarily influenced by urban/residential land use, the three sites mentioned above had agricultural influence. The range of SEM copper concentrations reported from agricultural sites in Pleasant Grove Creek was similar to the concentration range reported in Cache Slough.

In summary, a total of 25 study areas were found from a historical review of the SEM copper sediment data where agriculture land use was present (Table 4). Depositional areas were targeted for most of the study areas (approximately 80% of the areas) and for the other study areas the investigators did not report if depositional areas were targeted. Depositional areas comprised of fine grain material (clay and silt) would tend to accumulate higher concentrations of AVS and metals such as copper [17] so this is an important consideration when comparing SEM copper data between locations. The range of SEM copper data from 20 of these study areas was similar as determined by overlapping ranges with Cache Slough. However, the range of SEM copper concentrations from 4 of these study areas was lower than reported in Cache Slough. There were no sampling location from agricultural sites where SEM copper concentration ranges were higher than the range reported in Cache Slough. Based on this analysis of historical data it appears that SEM copper concentrations in Cache Slough are similar and representative of other agricultural water bodies sampled throughout the world.

4.2. Comparison of Sediment Total Copper Data with SEM Copper Data in Cache Slough

A comparison of sediment total copper data from Cache Slough from Hall and Anderson [7] with the SEM copper data in this manuscript are presented in Table 5. A total of 7 different metrics were used to compare these data sets: (1) range of mean seasonal concentrations (µg/g dw); (2) statistically significant site trends; (3) significant differences among sites; (4) statistically significant differences by waterbody section; (5); statistically significant seasonal differences; (6) statistically significant differences with seasons combined for all years; and (7) statistically significant relationships with precipitation. A comparison of the range of mean seasonal concentrations showed SEM copper concentrations were substantially lower than total copper. A comparison of site trends showed more sites with declining trends with SEM copper (3 sites) when compared with total copper (only one site) but no sites based on either measurement showed increasing concentrations. Comparisons of concentrations by waterbody section showed that both total copper and SEM copper concentrations were higher in the middle waterbody section (sites CS-05 to CS-08). An analysis of seasonal differences were also similar for total copper and SEM copper as there were no seasonal differences for both spring and fall for 2012 and 2013 but spring concentrations were higher in 2014. Additional seasonal analysis designed to determine statistically significant differences with seasons combined for all years showed no statistically differences for both total copper and SEM copper. For the final metric, no statistically significant differences were reported for both total copper and SEM copper with precipitation.

Key summary points from this comparative analysis of total copper and SEM copper from Cache Slough are that the range of mean seasonal concentrations of SEM copper was much lower and that more sites showed declining trends for SEM copper (bioavailable copper) than total copper. It is also noteworthy that for site CS-04 both SEM copper and total copper showed declining trends. In addition, it is also important to recognize that increasing trends were not reported for either SEM copper or total copper at any of the sites.

Mackie et al. [31] have reported that copper does not degrade in the environment; therefore, if copper use occurs concentrations would be expected in increase in the environment over time. However, despite precipitation and aerial drift as potential routes for entry of copper into the Cache Slough coupled with agricultural use, our results show that SEM copper is not increasing in this water body over time. There are at least four possible reasons that this could occur as discussed below.

Table 5. Comparison of total copper and SEM copper metrics in Cache Slough (2012–2014).

Metric	Total Copper	SEM Copper	Results
Range of mean seasonal concentrations	37–46 µg/g dw	18.6–30.1 µg/g dw	Mean SEM copper seasonal range lower
Significant site trends	CS-04 downward trend	CS-04, CS-09, CS-12 downward trend	More sites show downward trend with SEM copper; no sites showed increasing concentrations
Significant site comparisons	Both CS-06 and CS-05 showed higher values that 2 to 3 upstream sites	CS-07 higher than upstream site CS-10	More significant differences among sites for total copper
Significant water body section comparisons	Concentrations in middle section higher than upper section but not lower section	Concentration in middle section higher than both upper and lower section	Similar results showing higher concentrations in middle water body section
Significant seasonal differences	No seasonal differences for both spring and fall for 2012 and 2013 but spring concentrations higher in 2014	No seasonal differences for both spring and fall for 2012 and 2013 but spring concentrations higher in 2014	Same results
Significant differences with seasons combined for all years	No significant differences	No significant differences	Same results
Significant relationship to precipitation	No relationship to precipitation	No relationship to precipitation	Same results

One reason that may explain a lack of increased SEM copper concentrations over time in Cache Slough is the presence of benthic bioturbating fauna. Bioturbation is the biogenic transport of sediment particles and pore water which destroys sediment stratigraphy, alters chemical profiles, changes rates of chemical reactions and sediment water exchange, and modifies sediment physical properties such as grain size, porosity and permeability [32]. Remaili et al. [33] have reported that the SEM/AVS paradigm used to assess risk to benthic organisms may be incorrect in cases where bioturbating organisms rework and oxidize sediments or for those sediments where AVS has accumulated due to larger bioturbating organisms attempting to establish populations. One of the most dominant benthic species in Cache Slough is the polychaete, *Manayunkia speciosa*, as reported by Hall et al. [8] which is a bioturbating species [34]. Therefore, this polychaete along with other bioturbating species could induce changes in both AVS and metals speciation due to physical changes in the sediment which could impact the concentrations of SEM copper in sediment over time.

Another reason for the lack increased SEM copper over time in Cache Slough is related to the various fractions of copper in sediment. Han et al. [35] have reported that various fractions of copper in sediment such as organic bound, carbonate bound, amorphous iron bound and the soluble/exchangeable component may also accumulate differently over time. Therefore, this set of fraction variables could also impact SEM copper accumulation and may not result in an increase in SEM copper over time.

Resuspension and dispersion of SEM copper in this flowing water body may also impact the sediment concentrations at the various sites and thus prohibit an increase in concentrations over time. This is in contrast to lentic aquatic systems such as constructed wetlands where copper has been reported to increase over time [36].

The last reason for the lack of copper increases over time could be related to the labeled use rates that have been implemented by the grower community in this waterbody. Labeled use rates of copper in the Cache Slough area may simply not impact existing ambient sediment concentrations occurring from a variety of sources. This may be a factor influencing lack of copper increase in sediment over time since copper fungicides have been used since the early 1900s on grapes, walnuts, almonds and peach crops in California [37]. These are crops where copper fungicide use is dominant in the Cache Slough area.

5. Conclusions

SEM copper concentrations in Cache ranging from 8.9 to 59.1 µg/g were similar to ranges reported from 20 different study areas with agricultural influence. Based on this analysis of historical data, it appears that SEM copper concentrations in Cache Slough are representative of other agricultural water bodies sampled in Europe and North America. SEM copper sediment concentrations were not reported to increase over time in this agricultural waterbody where copper was used as a fungicide although some spatial differences in SEM copper sediment concentrations were reported. Seasonal analysis showed no significant difference in SEM copper sediment concentrations for two of the three years sampled. There were no statistically significant relationships between SEM copper sediment concentrations and precipitation for the three-year period based on an analysis by year and season. A comparative analysis of total copper and SEM copper from Cache Slough showed that the range of mean seasonal concentrations of SEM copper was much lower and more sites showed declining trends for SEM copper than total copper. Increasing trends were not reported at any of the sites for either SEM copper or total copper despite reports from other investigators that copper does not degrade in the environment and therefore concentrations would be expected increase over time in the aquatic environment if copper is used. Possible reasons to explain why SEM copper does not increase in Cache Slough are documented presence of bioturbating species impacting physical changes in sediment, various fractions of copper in sediment accumulate differently over time, resuspension and dispersion of copper in this flowing water system and labeled use of copper does not impact historical concentrations used since the early 1900s. Multiple-year studies in other waterbodies designed to assess trends in SEM copper sediment concentrations with an appropriate spatial scale are recommended.

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