A SURVEY OF COPPER IN SEDIMENTS AND AN ASSESSMENT OF POTENTIAL STRESSORS TO RESIDENT BENTHIC COMMUNITIES

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Background and Aims

Copper (Cu) is an essential trace element but can be toxic to biota when present above a certain threshold concentration. Currently, Cu and its compounds have been widely applied in various industries, including as pesticides. It enters the aquatic environment mostly linked to particulate debris which settles and is absorbed into the sediment. The bioavailability and toxicity of Cu in sediments is controlled by multiple factors including Acid-volatile sulfide (AVS). Sediment is likely non-toxic if the concentration of AVS exceeds concentrations of simultaneously extracted metals (SEM). Therefore, accurate and representative measurements of AVS and SEM in sediment are critical for ecological risk assessment of Cu and other metals. This study presents a global survey of AVS and SEM and a focused review of Cu in sediments of a well-studied Californian agricultural catchment (Cache Slough, USA).

Results

Historical Global Review of AVS and SEM monitoring data

- Historical Review of SEM Cu concentrations of agricultural and non-agricultural catchments collated. >1000 SEM Cu measurements from 54 study areas in 16 countries.
- Data indicate that SEM Cu is higher in non-agricultural areas compared with agricultural areas (Table 1).

Study Category	SEM Copper Sediment Concentrations (µg/g dw)					
	n	Mean	STDev	Min.	Max.	90th Centile
All studies	1021	20	47.5	0	902	62
Non-Agricultural	425	26	70.8	0	902	89
Agricultural	384	19.8	16.8	0.06	96.6	55
Control	12	3.9	6.9	0.06	25	17

Table 1. Global SEM Cu concentrations

- 140 AVS measurements were summarized from 21 countries (USA, NL, SWE, DK, UK, FI, BE, FR , DE, IT, CS, CN, CA, ES, BR, EG, IR, PT, AU, IN, TW).

Study Category	Sediment AVS Concentration (µmole/g dw)					
	n	Mean	STDev	Min.	Max.	90th Centile
All studies	140	20.7	53.6	0.01	503	49
Streams/Creeks	21	5.1	8.6	0.01	39.8	27
Rivers	16	27.7	48.7	1.1	197	82
Lakes/Ponds/Reservoirs	29	11.3	233	0.79	127	28
Estuaries/Marine	74	27.2	67.8	0.06	503	68

Table 2. Global AVS concentrations

- A ranking of waterbody types means from low to high AVS measurements showed the lowest mean value was reported for stream/creeks and the highest for rivers.
- Appears that streams/creeks may be more vulnerable to divalent metal toxicity compared to other waters (Table 2).

Copper sediment monitoring data from a California agricultural waterbody (Cache Slough)

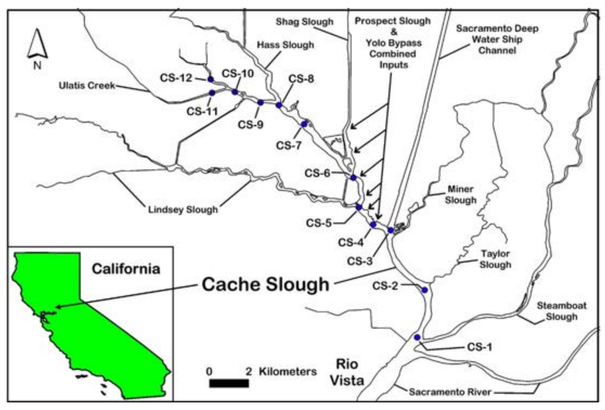

Figure 1. Description of sampling locations on Cache Slough river, California, USA.

Station	2012 Cu (µg/g)		2013 Cu (µg/g)		2014 Cu (µg/g)	
	Spring	Fall	Spring	Fall	Spring	Fall
CS-01	42.3	40.9	52.4	38.4	41.6	39.8
CS-02	36.5	45.8	44.0	46.5	36.8	46.5
CS-03	33.7	34.7	47.8	42.2	46.8	37.9
CS-04	51.5	42.6	49.7	43.6	36.8	31.7
CS-05	42.2	54.6	57.2	50.9	53.8	45.2
CS-06	47.5	60.0	60.7	62.4	52.4	50.7
CS-07	45.4	50.2	48.2	44.2	46.7	40.8
CS-08	47.1	44.4	19.0	19.2	38.5	20.1
CS-09	45.4	36.7	44.4	46.8	42.0	23.4
CS-10	25.4	21.7	36.6	23.4	46.1	30.2
CS-11	38.0	39.1	25.3	34.6	41.5	29.4
CS-12	20.2	47.8	62.7	50.8	50.2	47.4

Table 3. Summary of total sediment Cu concentrations during study period

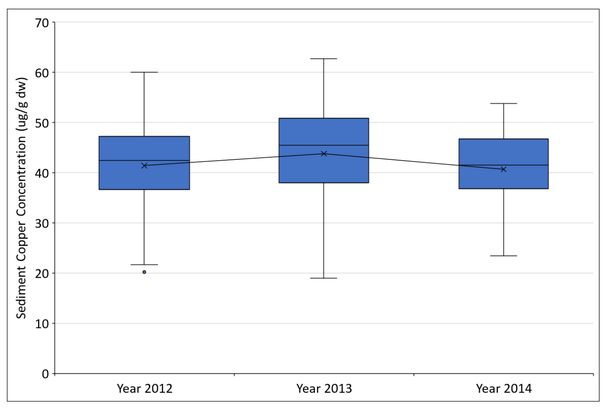

Figure 2. Summary of total sediment Cu concentrations in 2012, 2013 and 2014

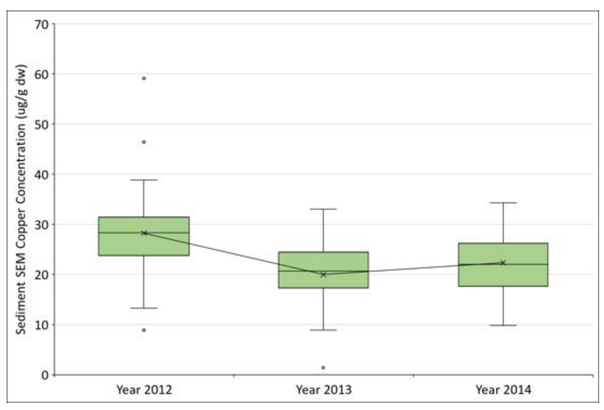

Figure 3. Summary of sediment SEM Cu concentrations in 2012, 2013 and 2014

Benthic Metric	Response to Impairement
Number of collector/filterer and gatherers	Increase
Number of Individuals (abundance)	Decrease
% Amphipoda	Variable
% collector/filterer and gatherers	Increase
% Corbicula	Variable
% Dominant Taxon	Increase
% Oligochaeta	Increase
% Predators	Decrease
% Tolerant Taxa	Increase
Shannon Diversity	Decrease
Taxonomic Richness	Decrease

Table 4. Descriptions of benthic metrics and response to the presence of metals in sediment

Metal	Number of Benthic Metric Relationships	TELs Exceedances for Sites	Agreement with Metric Relationships and TEL Exceedances
As	3	Half of sites	Yes
Pb	3	None	No
Cd	2	None	No
Cu	0	Most sites	No
Ni	0	All sites	No
Cr	0	All sites	No
Zn	0	None	Yes
Hg	0	None	Yes

Table 5. Summary of relationships between metals and benthic community in sediment

- Assessment of Total and SEM Cu sediment concentrations was performed in an agricultural California stream (Cache Slough). Agricultural use of Cu in surrounding catchment is known. Climate and soil type in Cache Slough is similar to parts of Southern Europe.
- 72 samples across 12 sample sites and 3 years collected (Figure 1). The results from this study showed that Total Cu sediment concentrations from Cache Slough ranging from 19 to 63 µg/g dw (Table 2) are similar to reports in European agricultural streams.
- No significant increase in total or SEM Cu in sediments was observed during 3-year study period despite being located in a catchment where Cu is used (Figures 2 and 3).
- Possible reasons for lack of increased Cu over time include the effects of bioturbation and resuspension and dispersion events in the flowing water.
- Relationship between the sediment concentrations of 8 total metals and 5 SEM (Ni, Cu, Zn, Cd, and Pb) with 11 benthic metrics (Table 4) was performed using uni- and multivariate regression analysis.
- Statistically significant and ecologically meaningful relationships with benthic metrics found with As, Pb and Cd only (Table 5).
- Total and SEM Cu were not reported to show any statistically significant relationships with any of the benthic metrics despite most of the sampled sites exceeding the NOAA's (The National Oceanic and Atmospheric Administration) threshold effect level (TEL) (35.7 µg/g dw).
- No agreement observed between benthic metrics and Cu and TEL exceedances (i.e., Cu exceeded TEL at most sites, but effect not observed in benthic community).

Conclusions

- Total and SEM Cu in sediment in an agricultural California stream (Cache Slough) was not observed to increase during sampling period (2012 – 2014).
- Total and SEM Cu were not reported to show any statistically significant relationships with any of the benthic metrics despite most of the sampled sites exceeding the NOAA's threshold effect level.

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