The Influence of Land Use Patterns on Acid Volatile Sulfide and Simultaneously Extractable Metals in Sediments from Small Tidal Creeks of Charleston Harbor

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Abstract

Surface waters and sediments of small tidal creeks are often the first marine environments to have contact with contaminants associated with urban land use activities. Improved methods for predicting potentially toxic contaminant levels on indigenous living marine resources are needed. Previous work has shown acid volatile sulfide (AVS) is an important controlling factor in the bioavailability of the simultaneously extractable metals (SEM) cadmium, copper, lead, nickel, zinc, and mercury. The AVS approach accounts for the natural assimilative capacities of the sediment whereas more traditional environmental toxicological assessments, such as the AETA and WEA do not. Our work has indicated that cumulative extractable metals (CEM), cumulative metal concentrations obtained from microwave nitric acid digestion procedures, can be used in lieu of SEM in the AVS model with analogous predictive results. The (CEM-AVS) approach accounts for natural metal binding capacities within the sediment and may provide a more relevant estimate of "bioavailable" metal concentrations. The goal of this study was to evaluate AVS and CEM levels in sediment samples from Charleston Harbor and compare the toxicity predictions based on the (CEM-AVS) and the cumulative metal/effects range low ratio (CEM/ERL%) approaches. Sediment samples from small tidal creeks of Charleston Harbor within developed watersheds (urban, suburban, and industrial) and undeveloped watersheds (forested and wetlands) were analyzed for AVS, CEM, and grain size distribution. Both methods predicted a similar number of sites with potentially toxic metal concentrations, but interestingly, poor agreement existed between the two methods on a site by site basis. Additional work is needed to fully evaluate the applicability of each of these assessment protocols.

Introduction

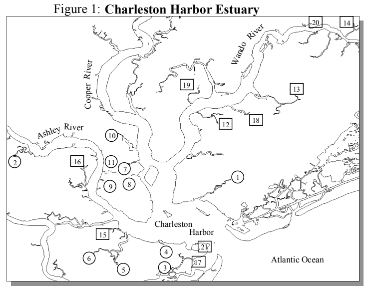
The preservation and protection of the small tidal creeks of estuarine environments and their related marsh lands is vital as they serve as nursery grounds for a wide variety of commercially and recreationally important marine fish and shellfish. They also buffer mainlands against the forces of the oceans as well as providing an important recreational habitat which is more available and exploitable to man via ecotourism. Disruptions to the natural processes in the small tidal creeks and marsh lands as upland areas are developed may lead to pollution and may result in a loss of one or more of their important ecological functional attributes. Trace metal pollution in aquatic environments is primarily associated with urbanization and industrial discharge. This is particularly true in the coastal areas of the Southeastern United States.

Traditional environmental risk assessment approaches for sediment contaminants are based on sediment quality guidelines, such as the Apparent Effects Threshold approach (AET) suggested by Long et al, (1995). The AET approach predicts toxic thresholds termed Effects Range Low (ERL) which are sediment concentrations where 10% of all published studies have found an adverse effect on living marine resources for a given contaminant. The ERLs are designed to set a lower limit above which toxicity is highly probable.

The Acid Volatile Sulfide (AVS) normalized risk assessment approach assess the ability of sediments to naturally bind, complex and precipitate trace metals, thereby providing a more functionally relevant estimate of "bioavailable" metal concentration which may realistically effect the living marine resources. The AVS approach focuses on the bioavailability and ultimately the toxicity of the trace metals (Cadmium, Copper, Zinc, Lead, Mercury, and Nickel) which is largely dependent on the AVS buffering capacities within the sediments by the incorporation of the potentially toxicity lowering sulfide-metal reactions occurring in anoxic sediments. The AVS approach is designed to predict when metals in the environment are potentially bioavailable and therefor a potential risk.

The purpose of this investigation was to evaluate differences in sediment characteristics, grain size distributions, Acid Volatile Sulfide concentrations and metal concentrations from developed and non developed tidal creeks in coastal South Carolina as well as examine the presence and extent of trace metal pollution and the resulting potential risk to living marine resources of tidal creek environment. Creeks from developed watersheds including suburban, urban and industrialized areas and from undeveloped watersheds, forested and salt marshes, were examined and compared (Figure 1).

Figure 1: **Charleston Harbor Estuary**



Developed Tidal Creeks ○

Suburban
1. Shem Creek (L,M,U)
2. Bull Creek (L,U)
3. Parrot Creek (L,U)
4. Yacht Club Creek (L,U)
5. Metcalf's Creek (L,U)
6. Cross Creek (L,U)

Urban
7. New Market Creek (L,U)
8. Vardell Creek (U)

Industrial
9. Diesel Creek (L,U)
10. Shipyard Creek (L,U)
11. Koppers Creek (L,U)

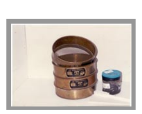
Undeveloped Tidal Creeks □

Forested
12. Rathall Creek (L,U)
13. Horlbeck Creek (L,U)
14. Deep Creek (L,U)

Salt Marsh
15. Dill Creek (L,U)
16. Orange Grove Creek (U)
17. Battery Simkin Creek (L,U)
18. Foster Creek (L,U)
19. Beresford Creek (L,U)
20. Lachicotte Creek (L,U)
21. Grice Cove Creek (L,U)

(L= Lower Reach, M= Middle Reach, U= Upper Reach)

Methods



1. Grain size analysis was performed by the SCDNR using rotap procedure and reported in sand (%), silt (%), and clay (%).

2. Sediment AVS extraction performed under N_2 atmosphere used a cold 6M HCl digestion procedure and a 0.5M NaOH trapping system.

3. AVS samples were quantified by photometric methods against a standard curve.

4. Trace metal analysis were performed using a microwave, nitric acid digestion technique.

5. Quantification of metals employed Induced Coupled Plasma (ICP) and Atomic Absorption (AA) Spectrophotometry methodologies. Results are reported on ug/g dry weight basis.

Results

Figure 2: Grain Size Distributions of Undeveloped Tidal Creeks

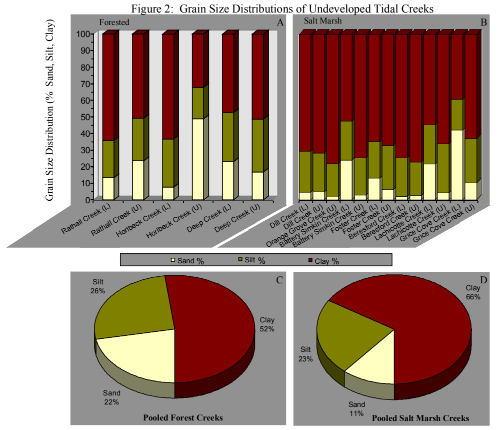


Figure 2: Percent sand, silt and clay composition of sediment samples from undeveloped (forested and salt marsh) tidal creeks. The undeveloped creeks were in general fine grained sediments dominated by clays. The salt marsh draining creeks (B & D) had a mean sand composition of 10.7% which was slightly lower than the forested (A & C) mean sand composition (22.2%).

Figure 3: Grain Size Distributions of Developed Tidal Creeks

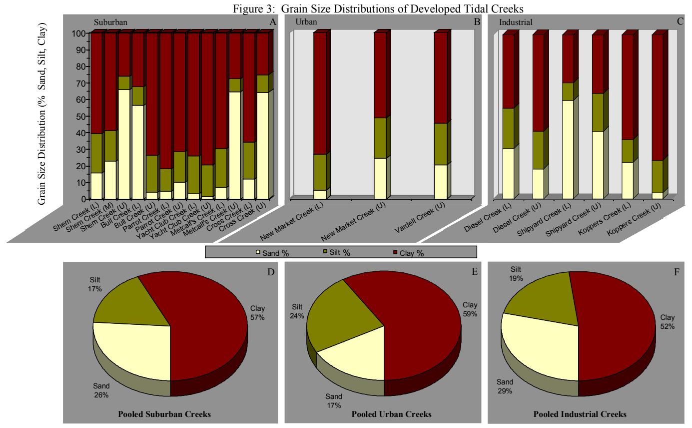


Figure 3: Percent sand, silt and clay composition of sediment samples from developed (suburban, urban, and industrial) tidal creeks. In general the sediments from the developed creeks were dominated by clays with sand making up less than 30% of the grain size distribution. The industrial developed creeks (C & F) had the highest mean sand fraction (29.3%) which was only slightly higher than the suburban (A & D) mean sand composition of (25.6%) and higher than the urban creeks (B & E) (16.8%). No significant differences were observed in comparisons of reference and developeded creeks with the exception of reduced silt at developed watersheds. The forested creeks (Figure 2 A & C) were similar in magnitude to the developed suburban and industrial creeks (Figure 3 A, D, C, & F). These data suggest the development of the drainage basins of tidal creeks had little effect on the grain size distributions measured in this study indicating that the sediment is influenced to a greater extent by the marine forces.

Figure 8: CEM ERL Ratio Toxicological Assessment from Undeveloped Tidal Creeks

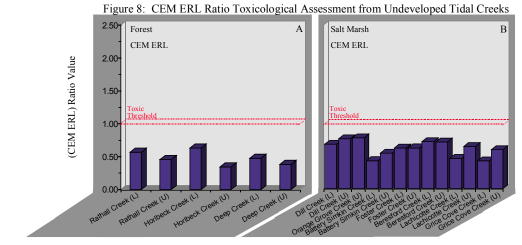


Figure 8: CEM-ERL Risk Assessment Estimate: Cumulative Extractable AVS Metals (Ni, Cu, Zn, Cd, Hg, Pb) - Effects Range Low (ERL=metal concentrations where 10% of all published studies found adverse effects) values from undeveloped (forested and salt marsh) tidal creeks. The undeveloped creeks (A & B) had all samples sites below the cumulative ERL level indicating sediments were non toxic (CEM ERL<1). Generally, the undeveloped creeks were low in metal loading resulting in low CEM ERL ratio values (<1) and low in predicted potentially bioavailable trace metal levels (CEM-AVS<0).

Figure 9: CEM ERL Ratio Toxicological Assessment from Developed Tidal Creeks

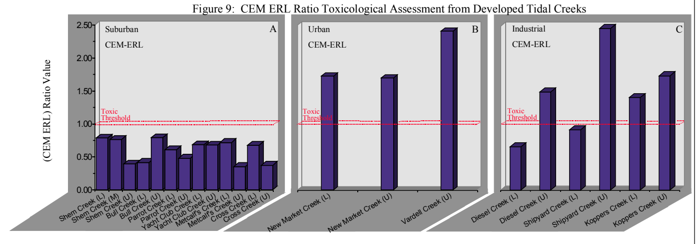


Figure 9: CEM-ERL Risk Assessment Estimate: Cumulative extractable AVS metals (Ni, Cu, Zn, Cd, Hg, Pb) - Effects Range Low (ERL=metal concentrations where 10% of all published studies found adverse effects) values from developed (suburban, urban, and industrial) tidal creeks. Urban (B) and industrial (C) creeks had CEM ERL ratio values >1 indicating potentially toxic sediments in 100% and 67% of the sites, respectively. Interestingly, suburban creeks (A) did not show a potential for toxic sediment conditions (CEM ERL<1). These data suggest greater metal loading in the developed urban and industrial creeks (Figure 9 B & C) in which 78% of the CEM ERL>1 as compared to the undeveloped creeks (Figure 8 A & B) where 0% exceeded CEM ERL>1.

Figure 10: CEM-AVS Toxicological Assessment from Undeveloped Tidal Creeks

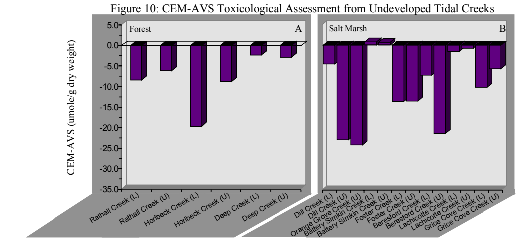


Figure 10: CEM-AVS Risk Assessment Estimates from undeveloped (forested and salt marsh) tidal creeks. Positive CEM-AVS values (>0) indicate sites that are potentially toxic. CEM-AVS difference values indicated only two sites, both from salt marsh stations (B) (e.g. Battery Simpkin Creek upper and lower) in which trace metals may be potentially bioavailable (CEM-AVS>0) and potentially toxic to living marine resources.

Figure 11: CEM-AVS Toxicological Assessment from Developed Tidal Creeks

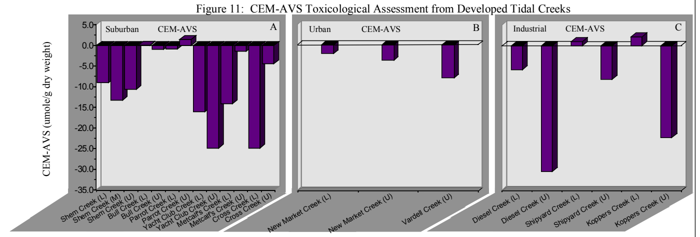


Figure 11: CEM-AVS Risk Assessment Estimates from developed (suburban, urban, and industrial) tidal creeks. CEM-AVS difference values indicated two suburban creeks (A) which showed a potential for bioavailable CEM metals (CEM-AVS >0) in contrast to the CEM ERL ratio risk assessment estimate (Figure 9 A) in which no potentially toxic sites were seen. The urban and industrial creeks (B &C) also showed low predicted potential bioavailability based on the CEM-AVS risk assessment method. Only 33% of the industrial creeks were predicted to have potentially bioavailable CEM concentrations (CEM-AVS>0) compared to 67% by the ERL approach. Interestingly, only one site, Koppers Creek (L), had both CEM ERL and CEM-AVS predictions which indicate potentially toxic and bioavailable metal concentrations. Overall, these data suggested developed and undeveloped creeks are generally low in potentially bioavailable trace metals toxicity potential (CEM-AVS<0).

Figure 4: Metal Concentrations from Undeveloped Tidal Creeks

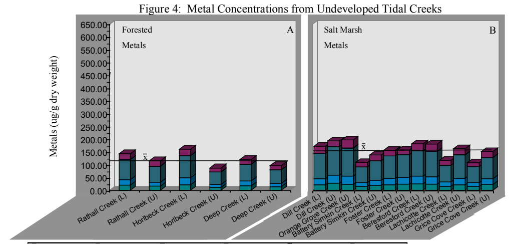


Figure 4: Cumulative Extracted Metal concentrations for Ni, Cu, Zn, Cd, Hg, Pb (ug/g dry weight) from undeveloped (forested and salt marsh) tidal creeks. Metal concentrations from forested (A) and salt marsh (B) draining tidal creeks were similar in magnitudes with mean (x̄-solid line) CEM values of 120.42 and 155.64 ug/g dry weight. These data indicated similar trace metal loading in undeveloped forested and salt marsh tidal creeks.

Figure 5: Metal Concentrations from Developed Tidal Creeks

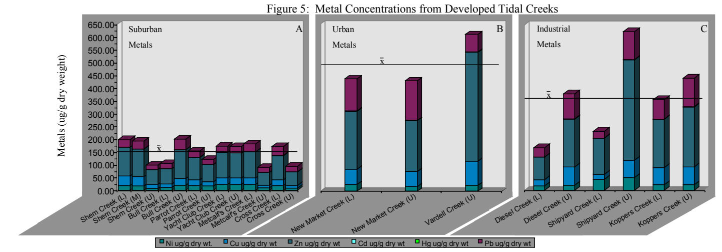


Figure 5: Cumulative Extracted Metal concentrations for Ni, Cu, Zn, Cd, Hg, Pb (ug/g dry weight) from developed (suburban, urban, and industrial) tidal creeks. Note the higher CEM concentrations from the more developed urban (B) and industrial (C) creeks compared to the suburban (A) creeks. A mean (x̄-solid line) CEM of 150.24 ug/g dry weight was observed in the suburban creeks while much higher mean concentrations of 491.57 and 366.99 ug/g dry weight were measured in the suburban and industrial creeks, respectfully. Statistical analysis using Kruskal-Wallis ANOVA on Ranks and Dunn's Test indicated a significant difference in Cd concentrations by land use in the developed creeks (p<.0001). Also, a significant difference between the CEM concentrations was present (p<.0001) using Kruskal-Wallis ANOVA on Ranks analysis although Dunn's Test did not isolate any specific differences (Table 1). Note the large difference between the industrial and urban developed tidal creeks (Figure 5 B & C) CEM mean concentrations as compared to the undeveloped creeks (Figure 4 A & B). The undeveloped creeks mean CEM were similar in magnitude to developed suburban creeks suggesting suburban creeks have minimal additional metal loading due to upland development. Statistical analysis indicates the developed and undeveloped creeks were significantly different (p<.0001) in the metals concentrations of Cu, Zn, Cd, Hg, Pb, and in CEM concentrations using Mann Whitney Rank Sum Test. Generally, urban and industrial creeks appear to have elevated metal loading while suburban, forested and salt marsh creeks all are similar suggesting minimal autogenic metal input.

Figure 6: AVS Concentrations from Undeveloped Tidal Creeks

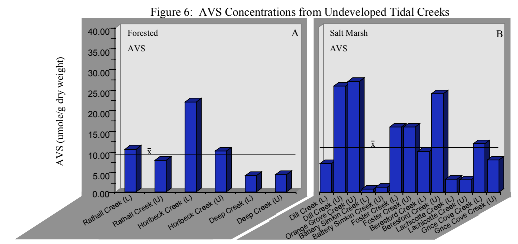


Figure 6: Acid Volatile Sulfide concentrations (umole/g dry weight) from undeveloped (forested and salt marsh) tidal creeks. Individual AVS concentrations in the undeveloped creeks ranged from 0.72 to 26.88 umole/g dry weight. Mean AVS (x̄-solid line) concentrations from the undeveloped forested (A) and salt marsh (B) draining creeks were similar in magnitude with concentrations of 9.70 and 11.74 umole/g dry weight, respectively.

Figure 7: Metal and AVS Concentrations from Developed Tidal Creeks

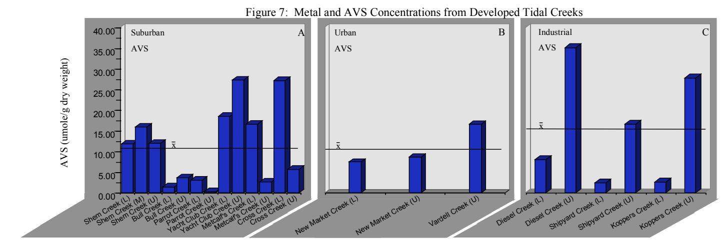


Figure 7: Acid Volatile Sulfide concentrations (umole/g dry weight) from developed (suburban, urban, and industrial) tidal creeks. Mean AVS concentrations (x̄-solid line) from the suburban (11.22 umole/g dry weight) (A) and urban (10.88 umole/g dry weight) (B) creeks were similar in magnitude while at industrial creeks (C) mean concentrations were slightly elevated (15.44 umole/g dry weight). No significant AVS differences were measured in comparisons of suburban, urban, and industrial creeks using Kruskal-Wallis ANOVA on Ranks analysis (Table 1). AVS concentrations from forested and salt marsh undeveloped creeks (Figure 6 A & B) and suburban and urban developed creeks (Figure 7 A & B) were all similar with a range of (9.70 to 11.74 umole/g dry weight), while industrial creeks (Figure 7 C) were slightly elevated indicating possible alteration of the sulfur cycle on the heavily developed creeks. These data suggest metal concentration may be influenced by the developed states of the creeks drainage basins while AVS appears to more intrinsic to natural biogenic factors within estuarine tidal creeks.

TABLE 1: Results of Statistical Analysis.

Kruskal-Wallis ANOVA on Ranks
States of Development: Industrial, Urban, Suburban, Salt marsh, & Forested

Groups	Test Factor	P value	Comments
All states of development	**Ni**	p = .0469	significant
" "	**Cu**	p # .0001	significant
" "	**Zn**	p # .0001	significant
" "	**Cd**	p # .0001	significant
" "	**Hg**	p # .0001	significant
" "	**Pb**	p # .0001	significant
" "	**CEM**	p # .0001	significant
" "	**CEM ERL**	p # .0001	significant
" "	AVS	p = .664	not significant
" "	Sand	p = .419	not significant
" "	Silt	p = .118	not significant
" "	Clay	p = .179	not significant
" "	CEM-AVS	p = .560	not significant

Dunn's Test: Significant results of Kruskal-Wallis analysis (paired comparisons).

	Suburban	Urban	Industrial	Forested	Salt marsh
Suburban		Cd	Cd	Cu, Zn, Hg, Pb	-
Urban			Cd	Cu, Zn, Hg, Pb	Zn, Cd, Hg, Pb
Industrial				Zn, Cd, Hg, Pb	Cu, Zn, Cd, Hg, Pb
Forested					-
Salt marsh					

Mann Whitney Rank Sum Test
Groups: Developed vs Undeveloped

Groups			Test Factor	P value	Comments
Developed	vs	Undeveloped	Ni	p = .6429	not significant
(Suburban, urban, industrial)		(forest, salt marsh)	**Cu**	p # .0001	significant
"		"	**Zn**	p # .0001	significant
"		"	**Cd**	p # .0001	significant
"		"	**Hg**	p # .0001	significant
"		"	**Pb**	p # .0001	significant
"		"	**CEM**	p # .0001	significant
"		"	**CEM ERL**	p # .0001	significant
"		"	AVS	p = .235	not significant
"		"	Sand	p = .513	not significant
"		"	**Silt**	p = .0133	significant
"		"	Clay	p = .810	not significant
"		"	CEM-AVS	p = .713	not significant

Conclusions

Grain Size

X The grain size distributions from developed creeks and undeveloped creeks were generally not significantly different; however a decrease in the mean silt fraction was observed between developed and undeveloped creeks.

X Industrial (mean sand 29%) and suburban (mean 26%) developed creeks showed the highest sand fraction contents while forested (mean 22%) and urban (mean 17%) creeks were only slightly sandier then salt marsh creeks (mean 11%). These data indicate slight alterations of the natural grain size distributions in the more highly developed creeks (industrial and suburban) while urban creeks show no changes as compared to undeveloped creeks.

Sediment Trace Metal Concentration

X Mann-Whitney Rank Sum Test showed significant differences between developed and undeveloped creeks for Cu, Zn, Cd, Hg, Pb, and CEM indicating enhanced metal loading in developed creeks.

X Kruskal-Wallis ANOVA analysis showed significant differences between metal concentrations among the five creek development categories. The Cd, Zn, Hg, and Pb concentrations were significantly different based on Dunn's test between industrial, suburban, urban, and forested creeks. Urban creeks (Zn Cd, Hg, and Pb) and industrial creeks (Cu, Zn, Cd, Hg, and Pb) were also significantly different from salt marsh creeks based on Dunn's test.

Acid Volatile Sulfide

X The AVS concentrations from developed creeks and undeveloped creeks were not significantly different based upon Kruskal-Wallis ANOVA analysis. The industrial creeks showed only a small increase as compared to the other creeks indicating that the sulfur cycle in the creek and marsh sediments has not been influenced by the various levels of development.

CEM ERL and CEM-AVS Risk Assessments

X CEM-AVS differences and CEM-ERL ratio values from developed creeks indicated sediments with increased metal toxicity potential as compared to undeveloped creeks.

X CEM ERL ratio values from developed creeks showed 32% of the sites with ERL exceedences while the CEM-AVS differences indicated only 18% of the sites with potentially bioavailable metals. Urban and industrial creeks had sediments with elevated metal concentrations (CEM ERL>1).

X Suburban, forested and salt marsh creeks were similar in the potential risks associate with metal polltuion as well as the potential bioavailableility of the metals.

X Of the four sites with potentially bioavailable trace metals based on CEM-AVS values, only one coincided with the CEM ERL ratio values exceedences. These data indicate CEM ERL ratio values and CEM-AVS difference values measure different intrinsic properties of the sediments.

X Estuarine environment trace metal toxicological assessments need to incorporate both CEM ERL ratio values and CEM-AVS difference values to account for not only the concentrations of trace metal pollution but to also assess the bioavailability of these trace metal pollutants. This provides a more realistic risk assessment approach for trace metals pollution in estuarine environments.

Acknowledgements

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