Note that no such set of salinity cycles existed for the autosampling run at Parker's Creek in Figure 35, since Parker's Creek is a non-tidal freshwater creek. This very attribute made Parker's Creek an excellent example of the relationships between total copper, dissolved copper, and total suspended solids. On July 24th from 15:00 to 23:00 hours, a flush of runoff made its way through the creek, resulting in concurrent copper and suspended solids peaks. Similarly, on June 15th from 15:00 to 20:30, the same signature can be seen for Gargathy Creek at the Headwaters in Figure 28. This could be the signature of agricultural runoff from the many surrounding plasticulture fields flowing past the sampler on its way downstream.

The July 22nd through 25th autosampling runs occurred during the heaviest three days of rain during the entire summer of 1997 with about four inches of rain total, a side-effect of Tropical Storm Fran. Many of the sites indicated little copper in the waterways, either in dissolved or total form. Gargathy Creek at the Clam Company, The Gulf at the Clam Company and the Dam Site, and Raccoon Creek all showed background copper concentrations throughout the time period, with copper concentrations between 0 and 3 ug/L. Gargathy Creek at the Gully Site experienced two distinct dissolved copper spikes illustrated in Figure 33, including 126 ug/L, unfortunately unaccompanied by total copper data since the sample was donated for organics analysis. These spikes may have resulted from the location of the sampler, namely at a point where runoff from the 1996 Kegotank Road Tomato Field enters Gargathy Creek from one side of the field.

IV. Grab samples from random sites on the Eastern Shore

Table 2 summarized the dissolved copper concentrations for grab samples collected on the mainland of the Eastern Shore of Virginia. Because these samples were collected from pooled rainfall or runoff on the mainland, they were collected during and immediately after rain events. The samples from Kegotank Landing were taken from runoff that was entering Gargathy Creek from roadside ditches through the landing. The samples were collected before the runoff actually entered the water body.

Table 2. Dissolved copper concentrations for grab samples collected on the mainland. All field samples were of pooled runoff from fields, and all puddle samples were roadside rainfall puddles.

Location	Date	Dissolved Cu (ug/L)
ESWR, Rain Puddle	25-Jul-97	3
Gargatha Road, Cotton Field Runoff	24-Jul-97	1
Kegotank landing, runoff from 1996 Tomato Field on Kegotank Road on the Field Side	01-Nov-96	30
Kegotank landing, runoff from 1996 Tomato Field on Kegotank Road on the Field Side	24-Jul-97	15
Kegotank landing, runoff from 1996 Tomato Field on Kegotank Road on the Landing Side	24-Jul-97	4
Johnson Road, 1997 Tomato Field Runoff	24-Jul-97	52
Johnson Road Non-Agricultural Rain Puddle	25-Jul-97	4
Kegotank Road, 1997 Tomato Field Runoff	24-Jul-97	16
Metompkin Road, 1997 Tomato Field Runoff	24-Jul-97	14
Metompkin Road, Soybean/Wheat Field Runoff	24-Jul-97	1
Route 666, 1997 Tomato Field Runoff	24-Jul-97	7
Route 630, Corn Field Runoff	24-Jul-97	9
Route 630, Forest Puddle	24-Jul-97	1
Route 630, Pepper Field Runoff	24-Jul-97	57
Route 666 Non-Agricultural Rain Puddle	24-Jul-97	1

Notably, the runoff from fields planted in plasticulture, including both tomatoes and peppers, contained high concentrations of dissolved copper, from 57 ug/L at the pepper field to 7 ug/L at a tomato field on Route 666. These high concentrations of copper sometimes reached the waterways, as evidenced by the copper concentrations of runoff flowing into Gargathy Creek from ditches through Kegotank Landing.

Other agriculture, including soybeans and cotton, did not show elevated copper concentrations with the exception of corn, a crop that does not normally use copper as a crop protectant. The copper concentration of the cornfield runoff was 9 ug/L and may have been elevated by roadside inputs, or the field may have been planted in a copper-using crop in a previous year. Other roadside rain puddles indicated varying concentrations of copper, from 1 to 8 ug/L.

Figure 37 demonstrated the geographical scope of copper concentrations in grab samples taken from Gargathy Creek at the Kegotank Public Landing, and the 1996 Kegotank Road tomato field on September 8th, 1996. Copper was measured in acidified copper, which was that copper detected by GFAAS in an unfiltered sample acidified to

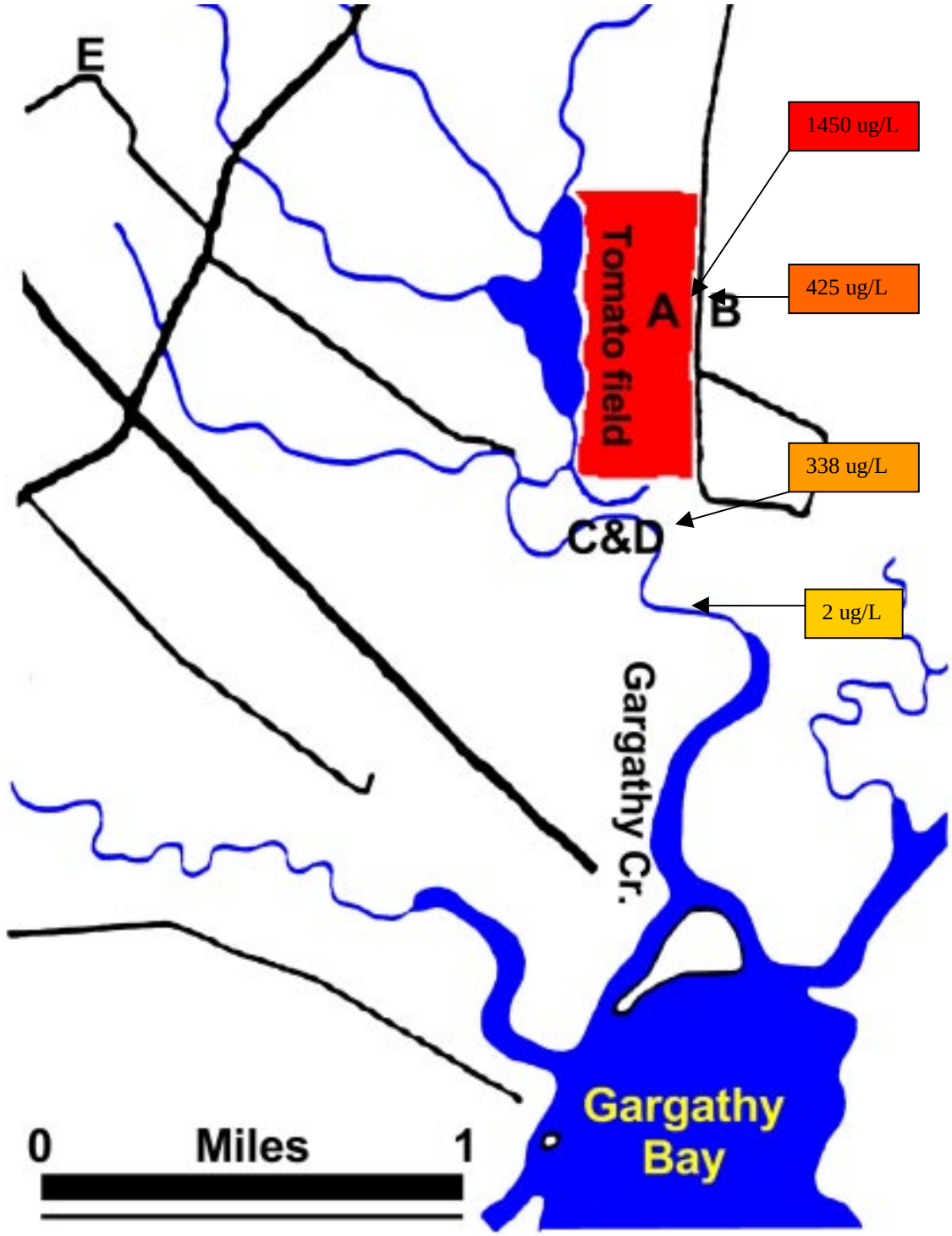

Figure 37. Acidified copper concentrations on September the 8th, 1996 in the Gargathy Creek watershed; copper concentrations notably decreased heading away from the field's pooled runoff (A) across the street (B) into the water at the landing (C) and ending at the aquaculture facility (D)

pH < 2 by the addition of trace metal grade nitric acid. Acidified copper was therefore always higher than dissolved copper and less than total copper.

Copper obviously decreased as it traveled via runoff toward the aquaculture facility from the tomato field. The 1450 ug/L was measured in a sample of runoff flowing directly from pooled runoff in a roadside ditch next to a field planted in tomato plasticulture. The copper concentration decreased to 425 ug/L as the runoff traveled across the road to a rapidly flowing roadside ditch. Once in Gargathy Creek near the Kegotank Landing, the copper concentration further decreased to 338 ug/L, and after traveling to the Clam Company site on Gargathy Creek, the level had subsided to 2 ug/L.

V. Descriptive statistics for dissolved copper in water samples

Statistics describing this set of data were generated by site, including mean, median, standard deviation, minimum, maximum, and number of data points. These statistics were illustrated in Table 3. All sites were listed geographically from upstream to downstream within a particular watershed.

Box plots of the same data set were shown in Figures 38 and 39. The box plots demonstrated the general distribution of the data, including the median, quartiles, and outliers. The median was represented by a horizontal black line, and could have been flush with one edge of the box. The middle two quartiles were represented by the green box, whereas the outer two quartiles were shown by extended black bars. Moderate outliers were indicated by a yellow color, and red indicated a severe outlier. In the box plots, one severe outlier was deleted in order to keep the scale of the plots reasonable. This point was 126 ug/L dissolved copper found in Gargathy Creek at the Gully Site. The datum was included in the descriptive statistics. The approximated data from the monthly grab sampling charts were not included in the descriptive statistics.

The standard deviations and means were sometimes elevated from high spike concentrations, as in the Gully Site, but the median copper concentrations were very similar amongst the stations, indicating a very steady copper concentration with rare high copper spikes. The box plots show very similar distributions in data, with the occasional high copper concentration shown as an outlier, either moderate or severe.

Table 3. Summary of descriptive statistics for dissolved copper by site over the course of study.

	Dissolved Copper Concentrations (ug/L)					
	Mean	Median	Standard Deviation	Minimum	Maximum	# Samples
Gargathy Freshwater Creek	1.6	1	1.506	0	5	8
Gargathy - Headwaters	1.9	2	1.252	0	5	20
Gargathy - Gully Site	8.6	1	28.588	0	126	19
Gargathy - Midstream Dock	0.8	1	0.422	0	1	23
Gargathy - Kegotank	1.7	1	0.947	1	4	13
Gargathy - Clam Co.	1.3	1	1.018	0	6	58
The Gulf - Dam Site	1.7	2	0.557	1	3	25
The Gulf - Clam Co.	1.8	1	1.995	1	12	31
Parker's Creek	1.5	1	1.558	0	7	25
Queen's Sound	1.0	1	0.707	0	2	9
Raccoon Creek	1.1	1	0.843	0	3	33

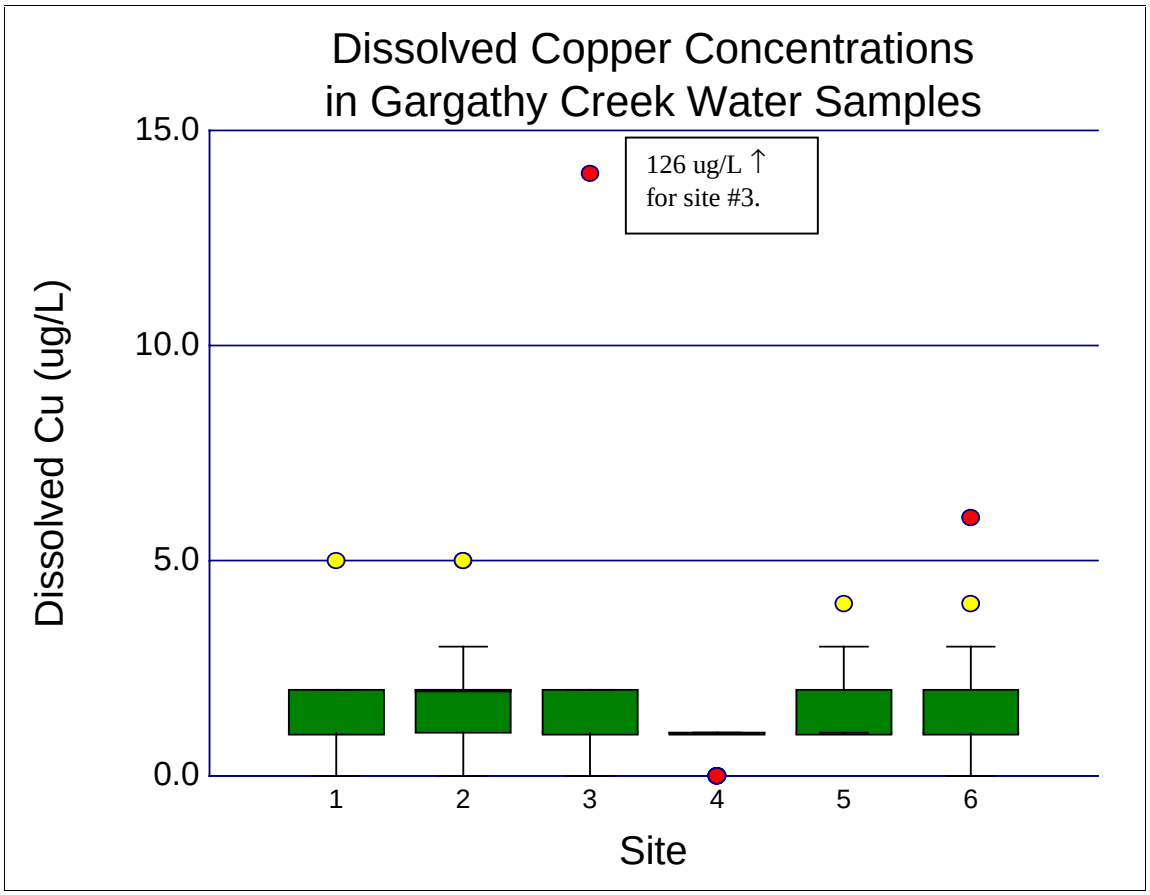

Figure 38. Box plot that summarizes dissolved copper by site for the Gargathy Creek watershed.

1= Freshwater Creek that feeds Gargathy Creek
2= Gargathy Creek at the Headwaters
3= Gargathy Creek at the Gully Site
4= Gargathy Creek at the Midstream Dock
5= Gargathy Creek at the Kegotank Public Landing
6= Gargathy Creek at the Clam Company

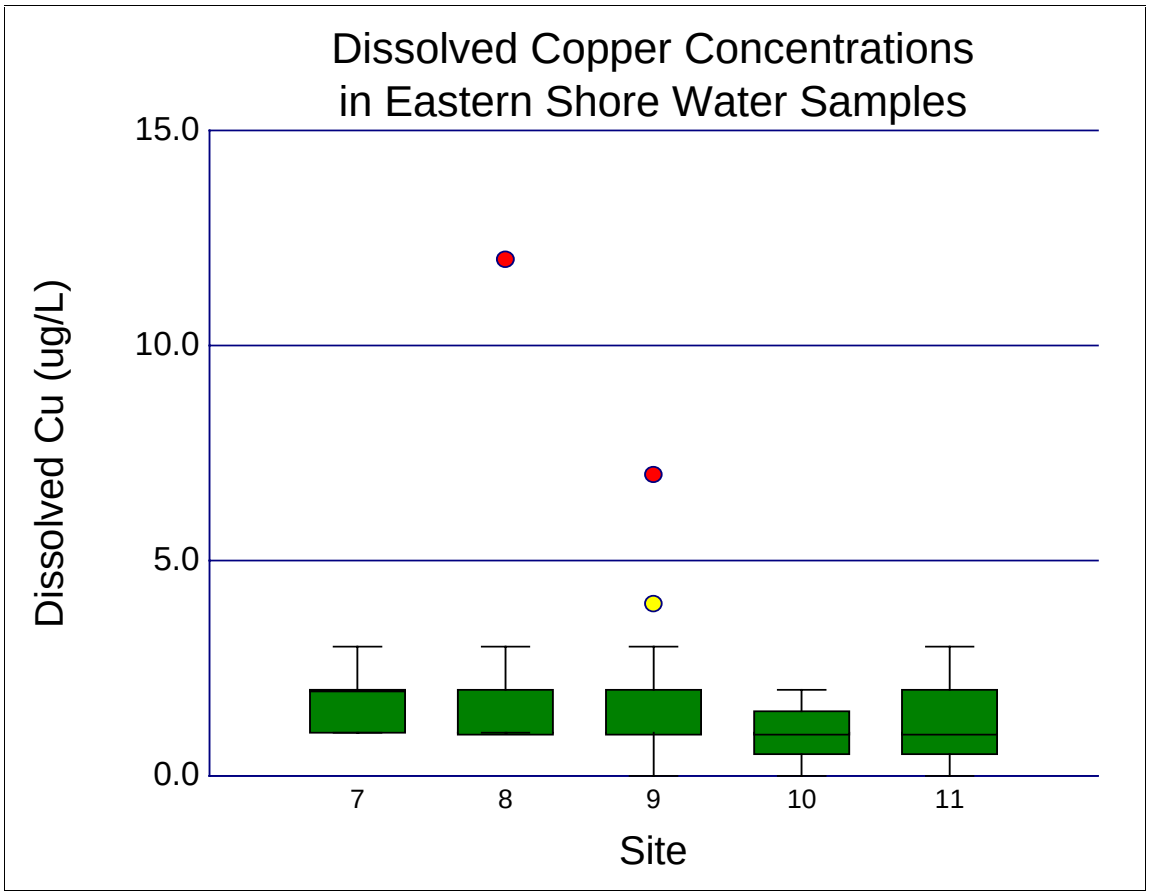

Figure 39. Box plot that summarizes dissolved copper by site for other Eastern Shore locations.

7= The Gulf at the Dam Site
8= The Gulf at the Clam Company
9= Parker's Creek
10= Queen's Sounds at Chincoteague
11= Raccoon Creek

VI. Descriptive statistics for total copper in water samples

Statistics describing this set of data were generated by site, including mean, median, standard deviation, minimum, maximum, and number of data points. These statistics were illustrated in Table 4. All sites were listed geographically from upstream to downstream within a particular watershed.

Box plots of the same data set are shown in Figures 40 and 41. The box plots demonstrate the general distribution of the data, including the median, confidence intervals, and outliers. The median was represented by a horizontal black line, and could have been flush with one edge of the box. The middle two quartiles were represented by the green box, whereas the outer two quartiles were shown by extended black bars. Moderate outliers were indicated by a yellow color, and red indicated a severe outlier. In the box plots, one severe outlier was deleted in order to keep the scale of the plots reasonable. This point was 263 ug/L total copper found in Gargathy Creek at the Kegotank Public Landing. The datum was included in the descriptive statistics.

The means and standard deviations of the stations were high from spikes in the same manner as dissolved copper. In addition, the majority of the total copper data did not settle to one particular concentration the same way that the dissolved copper did. This resulted in widely differing medians, larger ranges of the quartiles in the box plots and fewer values marked as outliers. All of this might have been caused by the smaller set of data for total copper, from noise introduced by additional steps in determining total copper, or from greater fluctuation in total copper values in the waterways.

Table 4. Summary of descriptive statistics for total copper by site over the course of study.

	Total Copper Concentration, (ug/L)					
	Mean	Median	Standard Deviation	Minimum	Maximum	# Samples
Freshwater Creek	6.5	4.5	5.916	2	15	4
Gargathy - Headwaters	6.2	7	2.170	3	8	5
Gargathy - Gully Site	4.8	3	4.166	1	11	8
Gargathy - Midstream Dock	2.0	2	2.000	0	4	3
Gargathy - Kegotank	48.7	5	105.145	1	263	6
Gargathy - Clam Co.	3.0	3	1.323	2	6	9
The Gulf - Dam Site	5.0	5	NA	5	5	1
The Gulf - Clam Co.	3.0	2	1.528	2	6	7
Parker's Creek	7.6	5	6.345	1	21	11
Queen's Sound	1.8	2	0.837	1	3	5
Raccoon Creek	3.4	3.5	1.506	1	6	8

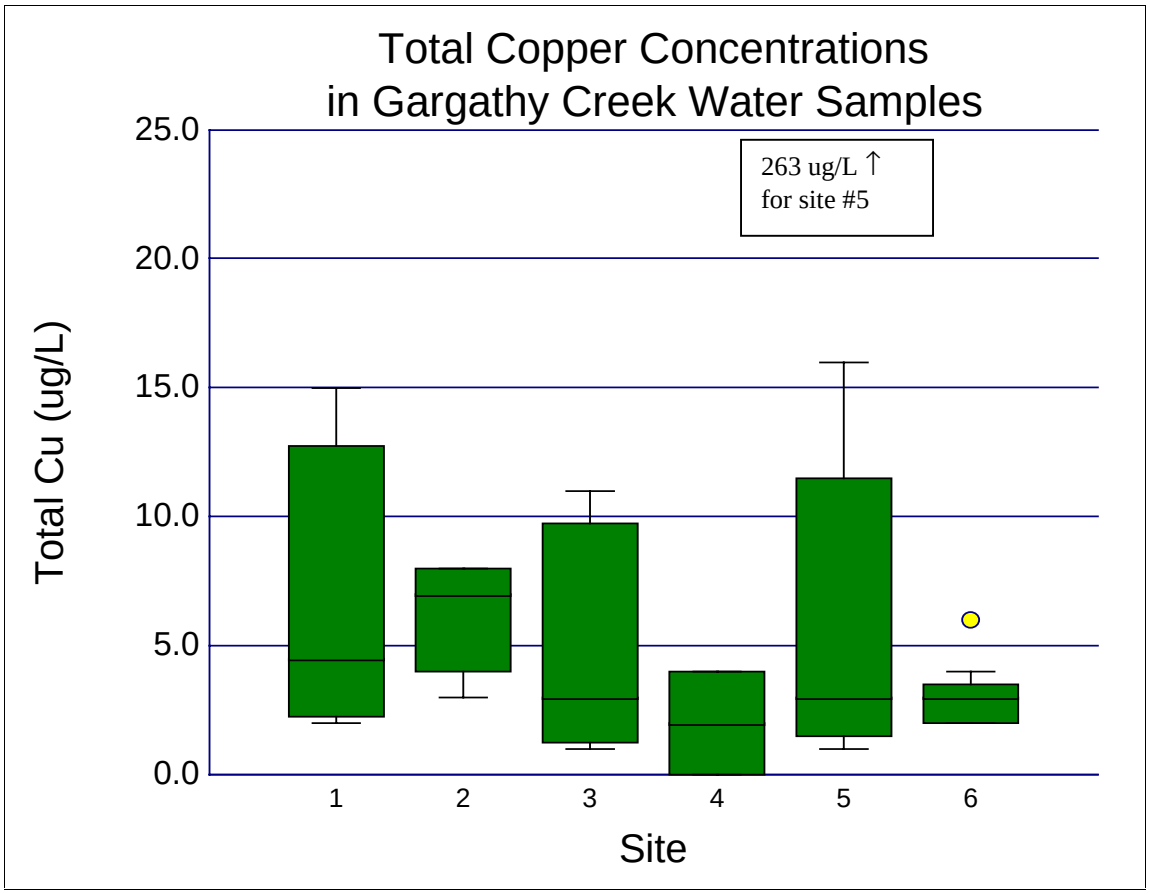

Figure 40. Box plot that summarizes total copper by site for the Gargathy Creek watershed.

1= Freshwater Creek that feeds Gargathy Creek
2= Gargathy Creek at the Headwaters
3= Gargathy Creek at the Gully Site
4= Gargathy Creek at the Midstream Dock
5= Gargathy Creek at the Kegotank Public Landing
6= Gargathy Creek at the Clam Company

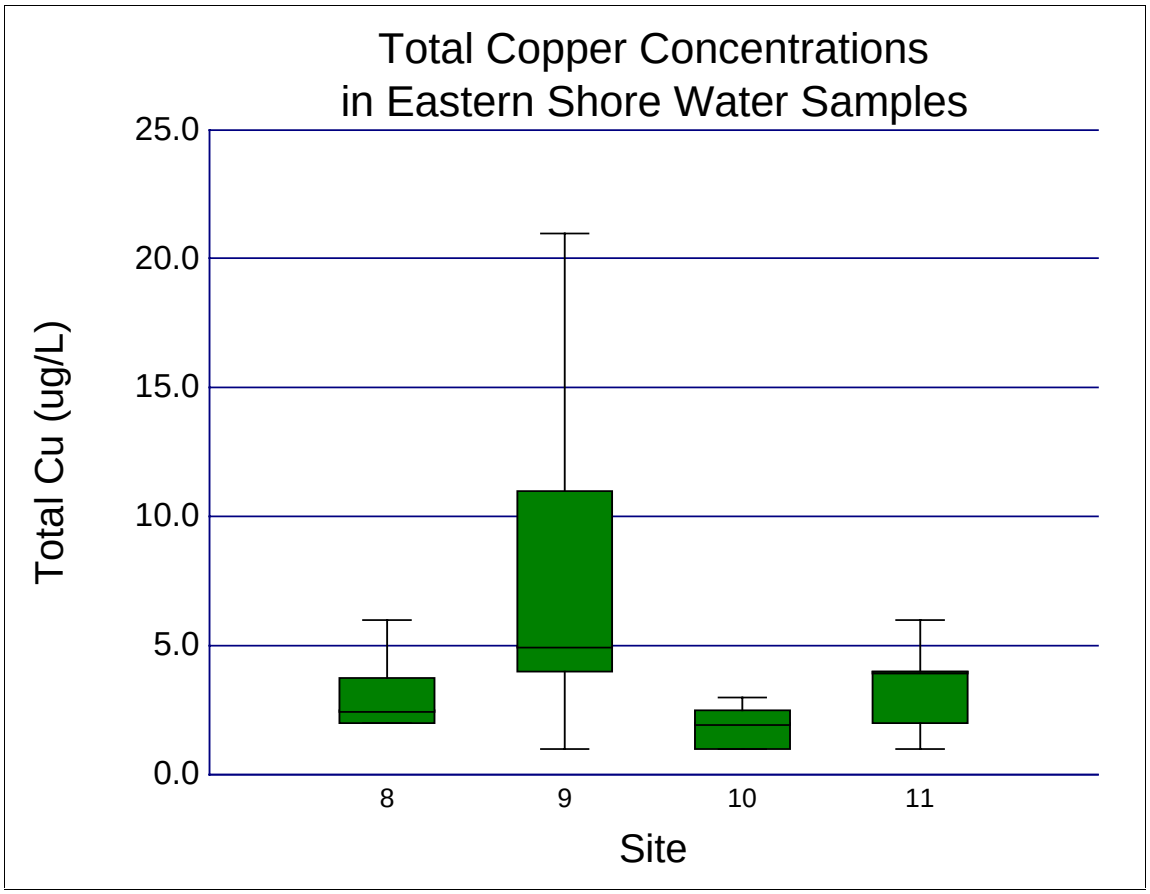

Figure 41. Box plot that summarizes total copper by site for other Eastern Shore locations.

8= The Gulf at the Clam Company
9= Parker's Creek
10= Queen's Sound at Chincoteague
11= Raccoon Creek

VII. Descriptive statistics for sediment samples

The means and standard deviations for the total copper in sediment cores by site and depth were shown in Table 5. Tables 6 and 7 similarly demonstrated the dry weights and volatile solids percentages. All sites were listed geographically from upstream to downstream within a particular watershed. The number of data points was listed in parentheses.

The cores illustrated little detectable trend by depth for total copper. Therefore, all of the total copper values for a site were combined into a set of data. Statistics describing this set of data were generated by site, including mean, median, standard deviation, minimum, maximum, and number of data points. These statistics were illustrated in Table 8. All sites were listed geographically from upstream to downstream within a particular watershed. The grain size distribution for each site was determined by the Virginia Polytechnic Institute and State University Soils Lab and presented in Table 9.

Box plots of the same combined data set were shown in Figure 42. The box plots demonstrated the general distribution of the data, including the median, quartiles, and outliers. The median was represented by a horizontal black line, and could have been flush with one edge of the box. The middle two quartiles were represented by the green box, whereas the outer two quartiles were shown by extended black bars. Moderate outliers were indicated by a yellow color, whereas red indicated a severe outlier.

The distribution of the data indicated that the two samples from Northampton County, The Gulf and Raccoon Creek, contained less total copper than the three stations from Accomac County. These differences were mostly attributable to difference in grain size, with copper adsorbing preferentially to finer particles (Novotny and Olem, 1993).

A non-parametric Kruskal-Wallis one-way analysis of variance was performed to test if the total copper concentrations in sediments were identical among the Gargathy Creek at the Clam Company, Gargathy Creek at the Kegotank Public Landing, and Queen's Sound at Chincoteague locations. These sediments were selected for comparison based on the similar % sand, %clay, % silt measurements. A modified-Levene-Equal-Variance test accepted the null hypothesis that the copper distributions had equal variance

across the three sites, thus allowing for an analysis of variance. The Kruskal-Wallis test rejected the null hypothesis that the medians of copper at the three sites were all equal. (p=0.0005). A non-parametric Kruskal-Wallis Z multiple comparison test indicated that the median sediment copper concentration of the Kegotank Landing samples was statistically significantly higher then the medians of the sediment samples at Clam Company and Queen's Sound at a 95% confidence level. There was no statistical difference between the medians of the Clam Company and Queen's Sound. Thus, even though the measured copper levels could all be considered near background levels, the sediment samples nearest the plasticulture fields did contain statistically higher concentrations than sites farther from the fields.

Table 5. Means, standard deviations, and number of data points for total copper by site and depth in sediment on the Eastern Shore. All data in mg/kg total copper.

Depth of Core (in)	Gargathy - Clam Co.	Gargathy - Kegotank	The Gulf - Clam Co.	Queen's Sound	Raccoon Creek
0 - 1 inches	14.63 +/- 0.21 (n = 2)	18.36 +/- 0.33 (n = 2)	1.19 +/- 0.43 (n = 2)	9.10 +/- 1.26 (n = 2)	4.51 +/- 0.79 (n = 2)
0 - 2 inches	14.20 +/- 0.04 (n = 3)	17.19 +/- 3.56 (n = 3)	1.32 +/- 0.18 (n = 3)	11.13 +/- 1.12 (n = 3)	3.70 +/- 1.61 (n = 3)
2 - 4 inches	13.00 +/- 1.58 (n = 3)	19.62 +/- 3.18 (n = 3)	2.49 +/- 2.50 (n = 3)	18.33 +/- 6.75 (n = 3)	2.95 +/- 0.55 (n = 3)
4 - 6 inches	13.51 +/- 0.64 (n = 2)	16.63 +/- 1.74 (n = 3)	1.70 +/- 0.76 (n = 3)	10.60 +/- 1.00 (n = 2)	2.78 +/- 0.45 (n = 3)
6 - 8 inches	15.66 +/- 5.76 (n = 2)	25.63 +/- 12.42 (n = 2)	1.56 +/- 0.92 (n = 2)	No Data	2.71 +/- 0.89 (n = 2)

Table 6. Means, standard deviations, and number of data points for dry weight percentages by site and depth in sediment on the Eastern Shore. All data in mg/kg total copper.

Depth of Core (in)	Gargathy - Clam Co.	Gargathy - Kegotank	The Gulf - Clam Co.	Queen's Sound	Raccoon Creek
0 - 1 inches	48.21 +/- 1.04 (n = 2)	45.64 +/- 0.40 (n = 2)	83.31 +/- 0.91 (n = 2)	58.72 +/- 6.59 (n = 2)	74.44 +/- 2.02 (n = 2)
0 - 2 inches	46.60 +/- 4.46 (n = 3)	46.35 +/- 1.74 (n = 3)	81.16 +/- 2.37 (n = 3)	56.14 +/- 2.20 (n = 3)	75.58 +/- 2.25 (n = 3)
2 - 4 inches	50.34 +/- 1.63 (n = 3)	47.86 +/- 1.54 (n = 3)	77.08 +/- 4.26 (n = 3)	58.46 +/- 3.03 (n = 3)	80.05 +/- 7.71 (n = 3)
4 - 6 inches	51.47 +/- 5.48 (n = 3)	47.05 +/- 1.68 (n = 2)	74.38 +/- 3.37 (n = 3)	63.66 +/- 3.65 (n = 2)	79.79 +/- 2.37 (n = 3)
6 - 8 inches	46.77 +/- 0.23 (n = 2)	46.61 +/- 8.57 (n = 2)	71.77 +/- 5.61 (n = 2)	No Data	77.70 +/- 4.57 (n = 2)

Table 7. Means, standard deviations, and number of data points for volatile solids percentages by site and depth in sediment on the Eastern Shore.

Depth of Core (in)	Gargathy - Clam Co.	Gargathy - Kegotank	The Gulf - Clam Co.	Queen's Sound	Raccoon Creek
0 - 1 inches	7.22 +/- 0.18 (n = 2)	6.25 +/- 0.13 (n = 2)	0.55 +/- 0.30 (n = 2)	4.32 +/- 0.82 (n = 2)	2.55 +/- 0.14 (n = 2)
0 - 2 inches	7.66 +/- 1.31 (n = 3)	6.48 +/- 0.16 (n = 3)	0.52 +/- 0.18 (n = 3)	5.53 +/- 1.19 (n = 3)	2.30 +/- 0.43 (n = 3)
2 - 4 inches	6.89 +/- 1.12 (n = 3)	6.04 +/- 0.19 (n = 3)	1.59 +/- 0.95 (n = 3)	5.10 +/- 0.24 (n = 3)	2.08 +/- 0.78 (n = 3)
4 - 6 inches	6.24 +/- 1.56 (n = 3)	7.43 +/- 2.21 (n = 2)	2.81 +/- 0.93 (n = 3)	4.11 +/- 0.52 (n = 2)	1.94 +/- 0.36 (n = 3)
6 - 8 inches	7.36 +/- 1.26 (n = 2)	6.27 +/- 1.26 (n = 2)	3.83 +/- 1.80 (n = 2)	No Data	2.04 +/- 0.24 (n = 2)

Table 8. Summary of descriptive statistics for total copper by site in sediment on the Eastern Shore

	Total Copper Concentration (mg/kg)					
Site	Mean	Median	Standard Deviation	Minimum	Maximum	# Samples
Gargathy - Kegotank	19.1	18.1	5.183	13.24	34.41	13
Gargathy - Clam Co.	14.1	14.2	2.098	11.23	19.73	12
The Gulf - Clam Co.	1.7	1.2	1.212	0.89	5.38	13
Queen's Sound	12.8	11.3	5.092	8.20	25.25	10
Raccoon Creek	3.3	3.2	1.037	1.89	5.07	13

Table 9. Classification of each sediment into percentages of sand, silt and clay, and type of soil

Site	% Sand	% Silt	% Clay	Soil Type
Raccoon Creek	75.7	15.5	8.8	Sandy Loam
The Gulf - Clam Co.	95.9	2.6	1.5	Sand
Gargathy - Kegotank	39.5	47.9	12.6	Loam
Gargathy - Clam Co.	40.4	46.7	12.9	Loam
Queen's Sound	42.1	49.1	8.8	Silt Loam

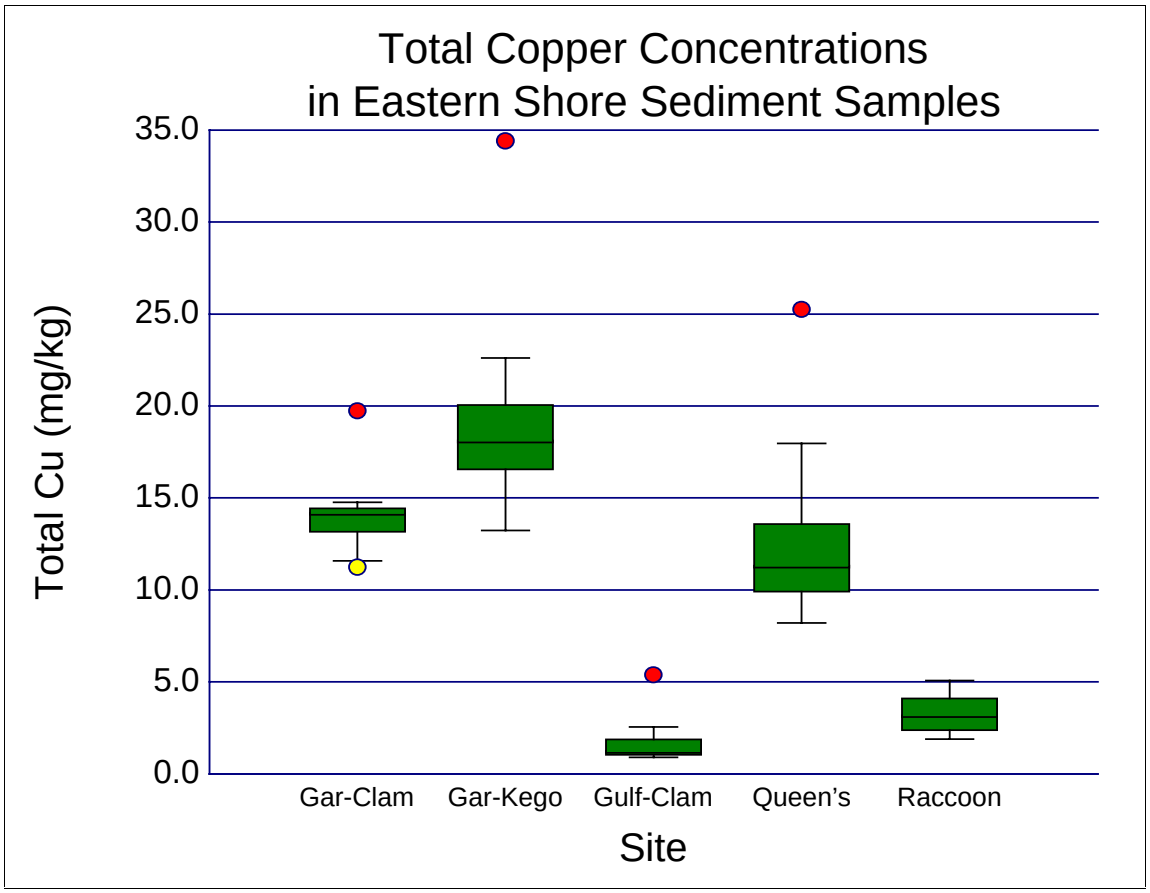

Figure 42. Box plot summarizes total copper in sediment samples for Eastern Shore locations