

Abstract

Due to the deteriorated water quality seen in the local estuaries of the Eastern Shore in Virginia a study was performed by Virginia Tech to study the causes of this problem. Copper-based protectants are used by tomato farmers on the Eastern Shore of Virginia to primarily fight fungi and bacteria. When runoff occurs, the copper is washed from the plants and fields to the surrounding waterways, effecting the aquatic life in these systems. However, some copper does sorb to the soil in and surrounding the fields and the sediment leaving the field. The fate and transport of this copper onto and off of the soil was investigated through a series of sorption and desorption experiments. The adsorption isotherms showed that as the amount of soil increases, the amount of copper adsorbed also increases. However, over time there was not a clear increase in copper sorption, which indicates that the adsorption is a quick process and that an increase in time does not dramatically change the amount of copper the soil will sorb. For example, the amount of copper sorption at the first time interval of 2 hours is essentially the same as the amount sorbed at each following time interval of 24 hours, 48 hours, and 7 days. At the equilibrium concentration of 200 ppb, a value of 54 mg Cu/kg soil is seen for Bojac Sandy Loam soil. When copper laden soil was used in both 20 ppt saline and pure water desorption isotherms, copper did desorb from the soil into solution. Again this was an immediate process, the 30 minute readings were similar to both the 2 hour and 24 hour readings, thus the increased time did not significantly affect the amount of copper being released. Even though the trend was similar between the two experiments in that time did not have a large role in the amount of desorption, the zero salinity test had slightly higher amounts of copper desorption. On average at both 25 and 75 grams of soil, the zero salinity experiment had 20-25 ppb more copper released than the 20 ppt salinity test.

An Investigation of the Adsorption and Desorption Capacities of Bojac Sandy
Loam Soil from the Eastern Shore of Virginia

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Literature Review

Aquaculture and Agriculture on the Eastern Shore

The plasticulture method of raised beds, which are covered with plastic, is used on Virginia's Eastern Shore by the tomato farmers. This method produces a higher crop yield and reduces the amount of pesticides and irrigation water needed, however, it also increases the rate at which water and pesticides drain from the fields.

A large amount of copper-based pesticide is sprayed on many Eastern Shore tomato farms to combat disease. Approximately one half to three pounds of copper per acre of land is applied with the application of the crop protectants (Kocide labels). With the plasticulture method, high concentrations of copper are seen in the runoff from the fields. In the coastal areas of the Eastern Shore, the agricultural fields directly border the surrounding waterways, making the probability high that the applied pesticides will reach the water by runoff. In any runoff coming from copper treated tomato plasticulture fields, large amounts of copper are present. Dissolved copper concentrations of 20 to 238 $\mu\text{g/L}$ have been found leaving the fields in the runoff (Brady *et al.*, 1999).

When the copper laden runoff enters the surrounding waterways, toxicity can be produced (Klawiter 1998, LaBreche 1998). For example, up to 126 $\mu\text{g/L}$ dissolved copper was found in Gargathy creek, an estuary on the Eastern Shore impacted by tomato runoff (Klawiter, 1998). After runoff, the copper concentrations in the creek were shown to vary with the tide, and then after about 48 hours returned to the background concentrations (Brady *et al.*, 1999). Also, copper continued to be present in the runoff for months after the tomato crop was removed and copper application was stopped (Klawiter, 1998). In addition, copper containing sediments were

shown to desorb copper when entering saline water in estuaries (Stall, 1999). Local shellfish hatcheries take their source water from these estuaries and thus are also seeing the high concentrations of copper. In recent years, these hatcheries have seen an increase in the mortality rates of their shellfish.

Virginia Tech's Study

Virginia Tech performed a project that evaluated the tomato plasticulture runoff and its effects at the Eastern Shore and also modeled the same scenario in a greenhouse scale simulation. This project was undertaken to examine the source of the mortalities seen at the Eastern Shore hatcheries.

In addition to field samples taken at the Eastern Shore, the entire process was reconstructed in an on campus greenhouse to model and examine the interactions occurring between the tomato fields and the estuary waters. Three tomato fields using the plasticulture method were constructed with two receiving copper-based pesticide treatment. The third was a control bed without plasticulture. These beds experienced simulated rainfall events. Also, estuary water tanks were constructed to model the local estuary waters.

Adsorption and Desorption Theory

In a similar study to Virginia Tech's focussing on the copper bioaccumulation in oysters in Taiwan, many of the same adsorption and desorption trends were seen. When sediments from the coastal areas were mixed with seawater in the shaker technique, copper desorption was seen at one hour. However, when shaken for over three hours some copper readsorption was seen (Hung *et al.*, 1995). In addition, the higher the sediment and copper content, the higher the desorption rate (Hung *et al.*, 1999).

In another study, it was noted that the sorption of copper by activated carbon had an initial rapid uptake followed by a slow period to reach equilibrium (Wilczak *et al.*, 1999). In addition, desorption of copper off of activated carbon was rapid, occurring in the first few minutes, and little more desorption was seen after this initial occurrence (Wilczak *et al.*, 1999).

However, in experiments reported by McLaren, little desorption was seen and the reversibility of copper adsorption was poor (McLaren *et al.*, 1999). It was concluded that either the adsorption process is irreversible, very slowly reversible, or requires a high activation energy for desorption since the reversibility of the copper adsorption was not readily occurring (McLaren *et al.*, 1999). When copper is added into an environment, it is likely to sorb to what it comes into contact with first. Since laboratory experiments tend to look at one material that is finely ground with wide solution to soil ratios, they may not be a good representation for the field (McLaren *et al.*, 1999).

Isotherm Theory – Freundlich

Throughout this study, adsorption and desorption isotherms were used to establish boundary conditions of sorption and desorption over time. When a sorbent, Bojac Sandy Loam soil for this research, comes in contact with a solution that contains a metal ion, the ion will sorb onto the surface of the soil. An isotherm represents the equilibrium condition between the sorbent, sorbate and solute. Likewise, when soil that contains a large concentration of a metal ion comes in contact with a solution, the metal ion will desorb from the surface of the soil into the solution.

Isotherms generally used are either the Langmuir or the Freundlich isotherm. However, all isotherms in this report will be reported as Freundlich isotherms, which take into

consideration the heterogeneous nature of the sorbent surface (Fic *et al.*, 1999). These are more suited to soil because of its variable makeup.

The Freundlich isotherms were created on a log base ten scale. The copper concentration in solution, or the equilibrium concentration of copper remaining in solution (C_e), was plotted on the x axis as Log ppm and the y axis consisted of Log mg copper/ kg of soil. This relationship of sorbed to sorbant is represented with the variable q throughout this study. This method was used for both the adsorption and desorption isotherms, however, for the desorption study the q variable was the mg of copper desorbed/ kg of soil.

Introduction

In tomato farming, large amounts of copper-based crop protectants are used to combat disease. Approximately one half to three pounds of copper per acre of land is applied with the application of the crop protectants (Kocide labels). The use of these protectants has been linked to deteriorated water quality on the Eastern Shore of Virginia (Brady *et al.*, 1999; Dietrich *et al.*, 1999; Klawiter, 1998; Dietrich *et al.*, 1996). In the coastal areas of the Eastern Shore, the agricultural fields directly border the surrounding waterways, making the probability high that the applied pesticides will reach the water by runoff.

In any runoff coming from copper treated tomato plasticulture fields, large amounts of copper are present. Dissolved copper concentrations of 20 to 238 $\mu\text{g/L}$ have been found leaving the fields in the runoff (Brady *et al.*, 1999). When the copper laden runoff enters the surrounding waterways, toxicity can be produced (Klawiter 1998, LaBreche 1998). For example, up to 126 $\mu\text{g/L}$ dissolved copper was found in Gargathy creek, an estuary on the Eastern Shore impacted by tomato runoff (Klawiter, 1998). After runoff, the copper concentrations in the creek were shown to vary with the tide, and then after about 48 hours returned to the background concentrations (Brady *et al.*, 1999). Also, copper continued to be present in the runoff for months after the tomato crop was removed and copper application was stopped (Klawiter, 1998). In addition, copper containing sediments were shown to desorb copper when entering saline water in estuaries (Stall, 1999).

The research reported here is a portion of a larger project that evaluated the tomato plasticulture runoff and its effects at the Eastern Shore and also modeled the same scenario in a greenhouse scale simulation. This research project focused on the fate and transport of copper

sorbing and desorbing from soil. Bojac Sandy Loam soil from the Eastern Shore of Virginia was used throughout the entire study by all researchers. The specific objectives of this project were as follows:

- To evaluate the capacity of Bojac Sandy Loam soil to sorb copper.
- To evaluate the desorption of copper from Bojac Sandy Loam soil into saline water which is representative of an Eastern Shore Tidal Estuary.
- To evaluate the desorption of copper from Bojac Sandy Loam soil into Nanopure® water which is representative of rain water.

Methods and Materials

Glassware

All sampling bottles, glassware, and equipment used were soaked in 10% trace metal grade nitric acid for a minimum of 8 hours, rinsed in distilled water three times, rinsed in Nanopure® water three times, and then air dried.

Instrumentation

After all samples were obtained, they were analyzed for copper on either a Perkin Elmer 703 Atomic Absorption Spectrophotometer (Flame AAS), wavelength setting of 324.8 nm and slit setting of 0.7 nm, or a Perkin Elmer 5100 PC Atomic Absorption Spectrophotometer (Graphite AAS). The 703 FAAS was used for samples with copper concentrations above 100 ppb in accordance with US EPA Method 7211 (USEPA, 1996) and the 5100 PC GAAS was used for samples with concentrations below 40 ppb in accordance with US EPA Method 7210 (USEPA, 1996). Dilutions were performed as necessary.

Adsorption

The first part of this experiment focused on the adsorption capacity of Bojac Sandy Loam soil from the Eastern Shore. Several copper isotherm studies were performed on the soil to determine its adsorptive capacity. Each isotherm was set up in the same manner and followed the same methods. However, slight variations in soil amounts and bottle sizes were used in the different experiments in order to determine the optimum adsorption range.

The zero salinity copper solution was prepared by adding 1.8 ml of 1000 ppm CuNO_3 , Fisher Scientific Copper Reference Solution, to six liters of distilled water for a target

concentration of 300 ppb copper. After the solution was stirred, the pH was adjusted to six using about 100 mL of 0.5 N NaOH and a Fisher Scientific Accumet pH Meter.

Each experiment included nine different soil concentrations, typically between 0.02 and 1 gram per 100 ml, and was performed in triplicate. After the solution was added to the bottles using a graduated cylinder, the bottles were then shaken on a rotary end-over-end shaker. One sample, approximately 15 mL, was taken from the corresponding bottles at 2, 24, 48 hours and 7 days using an acid-washed 20 cc plastic syringe. The sample was then filtered through a 0.45 um filter in a Gelman Sciences filter holder. Before filtering the sample, each filter setup was rinsed three times with Nanopure® water. Fifteen ml of sample was removed, filtered, and then placed in a 60 ml Nalgene bottle. Three drops of 1:1 HNO₃:H₂O was added to each sample to keep the copper in solution.

Desorption

The second part of this experiment focused on the desorption of copper from the Bojac Sandy Loam soil. This soil was removed from tomato plant beds in the greenhouse facility, which had been dosed with large amounts of copper over the course of the simulated tomato growing season. Several copper isotherms were performed on the soil to determine its desorptive capacity. The isotherms were set up in the same manner as the adsorption experiments in order to observe the time and amount of copper released from the soil. The first run used a 20 salinity solution while the second run was in a zero salinity solution.

The twenty salinity solution was prepared by adding a total of 96 grams of Instant Ocean, 24 grams of Instant Ocean for each liter of solution, to 4 liters of Nanopure® water. The solution was stirred overnight in a 10 L glass container and then filtered the following day since all of the Instant Ocean does not go into solution. The pH was measured using a Fisher

Scientific Accumet pH Meter 900 and found to be 8.5 which is consistent with salt water. The salinity was measured using the Fisher Model 13-946-27 Hand Held Salinity Refractrometer.

Both experiments included five different soil concentrations, between 10 and 75 grams per 225 ml, and were performed in triplicate. The solution, saline or Nanopure®, was added to each 250 ml bottle and then placed on the rotary end-over-end shaker. 15 mL samples were taken at 30 minutes, 2 hours, and 24 hours.

Each sample was removed from the corresponding bottle using an acid-washed 20 cc plastic syringe and placed into an acid-washed Beckman polypropylene centrifuge tube. All tubes were then weighed to insure that they are within 1 gram of each other and then placed into the JA-20.1 20,000 RPM rotor and centrifuged in the Beckman J2-HS Centrifuge for twenty minutes at 20°C and at 20,000 RPM. After the samples were centrifuged, the supernatant was placed in a 60 ml Nalgene bottle. Three drops of 1:1 HNO₃:H₂O were added to each sample to keep the copper in solution.

Filtration Losses

An additional experiment was performed to examine the copper loss still being seen when the adsorption samples were filtered. Even at the pH of six, a slight copper loss was seen. For this reason, an experiment was performed to determine if the copper loss was due to the filter. Five samples of 300 ppb, zero salinity solution were passed through 0.45 filters and five were collected without going through a filter. In addition, the filters used were rinsed with Nanopure® water that was lowered to a pH of 2 and those samples were also tested for their copper concentration to see if any copper was coming off of the filters.

Results

Adsorption

The first objective of this research was to determine the adsorptive capacity of Bojac Sandy Loam soil to sorb copper. Using isotherm studies, which are reported as Freundlich isotherms throughout this project, the capacity was found for copper in zero salinity water.

The pH of the copper solution influences the effectiveness of 0.45 μ m Fisher Scientific filters. When the solution is passed through the 0.45 μ m filter at pH values below six, some copper remains on the filter. In order to minimize copper loss, the solution was raised to a pH of 6 – 6.5.

For the first three variations of this experiment, the entire experiment was duplicated so that the 2 and 24 hour samples were removed from the first set of bottles and the 48 hour and 7 day samples were removed from the second set of bottles. This design was used because with each sample 15 ml is removed from the 100 ml solution in the bottle. Removing too much volume from the bottle, for example trying to take all four samples out of the 100 ml, would affect the accuracy of the concentration. However, it was determined that much of the variation in the results from the first three experiments was due to the duplicate design. To remedy this problem, larger bottles (250 ml versus 125 ml) were used in the final run so that four 15 mL samples of water and soil could be removed from the same bottle without causing the accuracy of the concentration to be affected.

Table 1: Variations in Adsorption Experiments

<i>Experiment</i>	<i>Soil amounts (g)</i>
Run One (in 125 ml bottles)	0, 0.025, 0.05, 0.1, 0.2, 0.4, 0.8, 1, 1 in H ₂ O
Run Two (Replicate of Run One)	0, 0.025, 0.05, 0.1, 0.2, 0.4, 0.8, 1, 1 in H ₂ O
Run Three (in 125 ml bottles)	0, 0.2, 0.4, 0.8, 1, 1.5, 2, 3, 1 in H ₂ O
Run Four (in 250 ml bottles)	0, 0.4, 0.8, 1.6, 2, 3, 4, 6, 2 in H ₂ O

Only the data from the fourth experiment will be reported in this paper. Although the first three trials provided poor data, they helped to establish the best sampling technique for the sorption isotherms. In addition, they allowed the appropriate soil range for sorption of dissolved copper that appears in the local waters in concentrations of approximately 200 ppb to be determined. Using the information gained from these trials, the best technique was used in trial four.

Four plots, Figures 1 through 4, showing the 2 hour, 24 hour, 48 hour, and 7 day Freundlich isotherms for the zero salinity adsorption experiment are shown below.

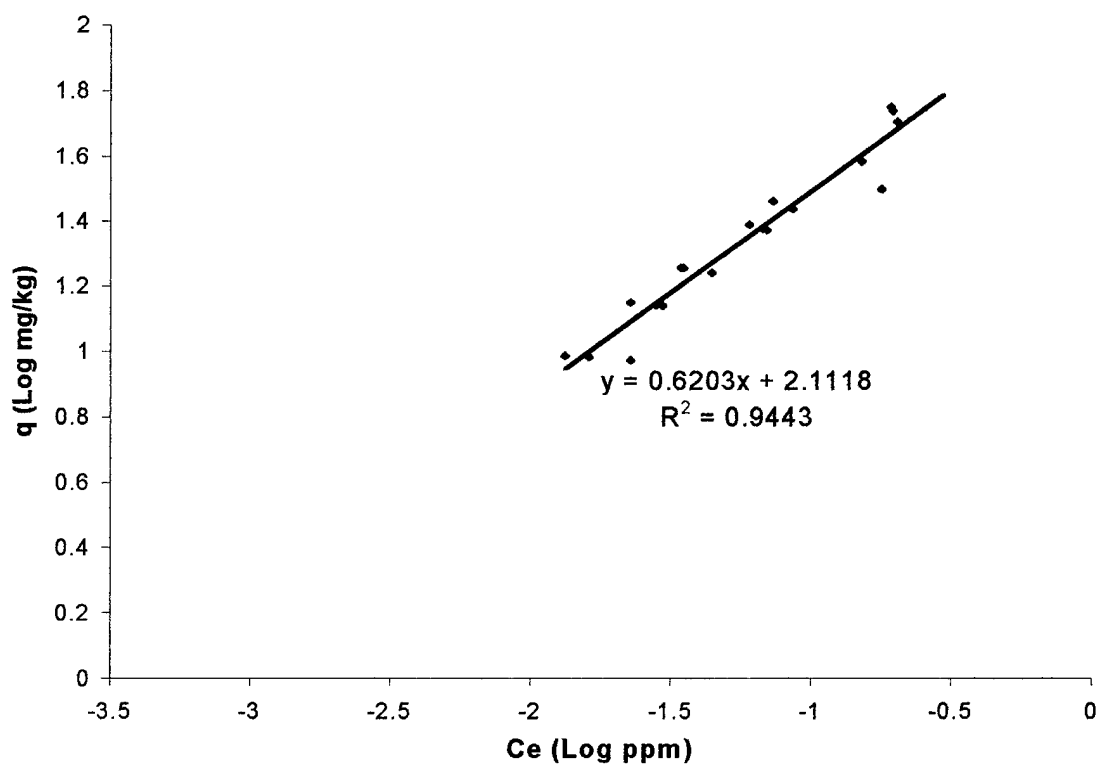


Figure 1: 2 hour Zero Salinity Freundlich Adsorption Isotherm

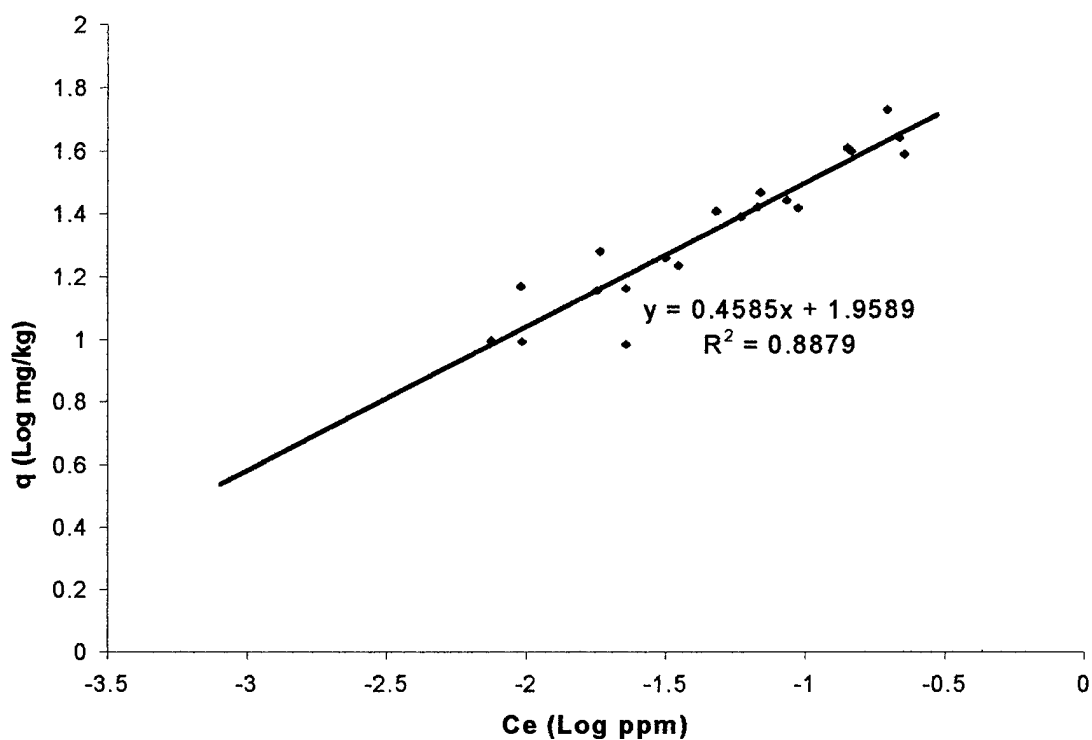


Figure 2: 24 hour Zero Salinity Freundlich Adsorption Isotherm

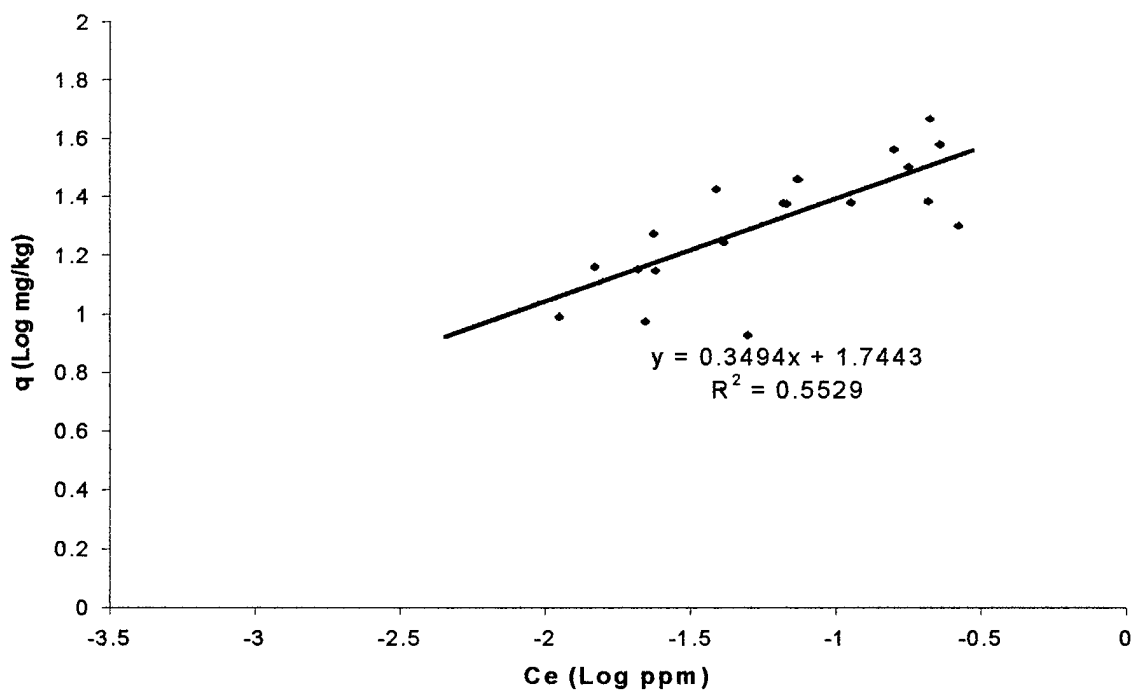


Figure 3: 48 hour Zero Salinity Freundlich Adsorption Isotherm

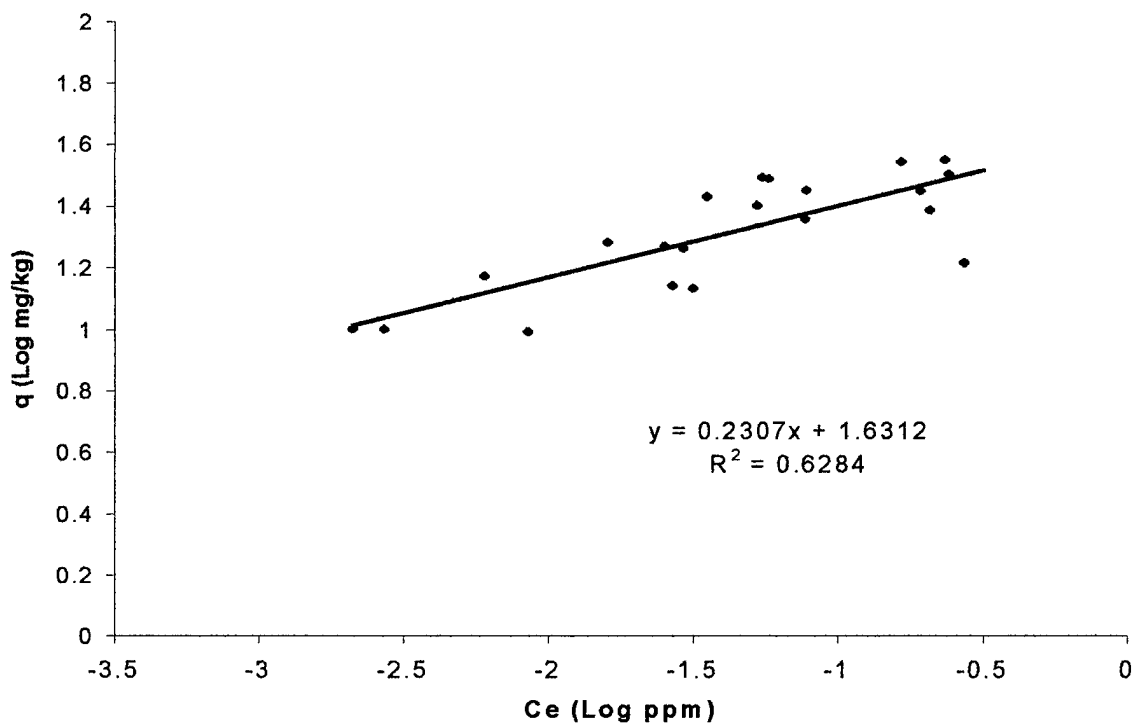


Figure 4: 7 day Zero Salinity Freundlich Adsorption Isotherm

A linear trend of increased copper sorption over the increasing amounts of soil is demonstrated by the high r-squared values from the regression analysis. Below in Table 2 the adsorption capacity for Bojac Sandy Loam is compared based on the time adsorption had been occurring and based on the two different copper concentrations. The first column is showing the results for a copper concentration of 200 ppb, which is a typical value found in the runoff from the tomato fields. The second column shows the values seen at 16 ppb, which is the copper LC₅₀ value for aquatic species.

Table 2: Comparison of Soil Capacities Based on Time and Copper Concentrations

<i>Time (hours)</i>	<i>q (mg/kg) at Ce = 200 ppb or -0.70 (Log ppm)</i>	<i>q (mg/kg) at Ce = 16 ppb or -1.8 (Log ppm)</i>
2	47.9	9.9
24	43.7	13.5
48	31.6	13.2
168	29.5	16.6

Desorption

The second and third objectives of this research involve desorption studies. These objectives were to evaluate the desorption of copper from Bojac Sandy Loam soil into both saline water (representing an Eastern Shore Tidal Estuary) and Nanopure® (representing rain water). Again, these results are reported using Freundlich isotherms where the q value is representative of copper released per kg of soil. The initial q value for the soil was between 20-25 mg Cu/kg soil.

For the first trial of the desorption experiment the 20 salinity water was made with distilled water. However, after observing high amounts of copper in the samples with no soil present, the experiment was performed again using Nanopure® water to make the 20 salinity solution instead of distilled water. This change was made because distilled water has approximately a 20 ppb background copper concentration while Nanopure® has approximately zero background copper concentration. The use of Nanopure® versus distilled water produced a large reduction in background copper concentration in the saline solution.

Based on the adsorption experiments, it was concluded that using larger bottles so that all samples could be removed from one bottle was the best method.

Table 3: Variations in Desorption Experiments

<i>Experiment</i>	<i>Soil amounts (g)</i>
Run One (20 ppt Salinity in 250 ml bottles)	0, 10, 25, 50, 75
Run Two (Nanopure® in 250 ml bottles)	0, 10, 25, 50, 75

Scatter plot showing the relationship between q (Log mg/kg) on the Y-axis and C_e (Log ppm) on the X-axis. The data points are fitted with a linear regression line. The equation of the line is $y = -0.255x - 0.5545$ and the coefficient of determination is $R^2 = 0.7083$.

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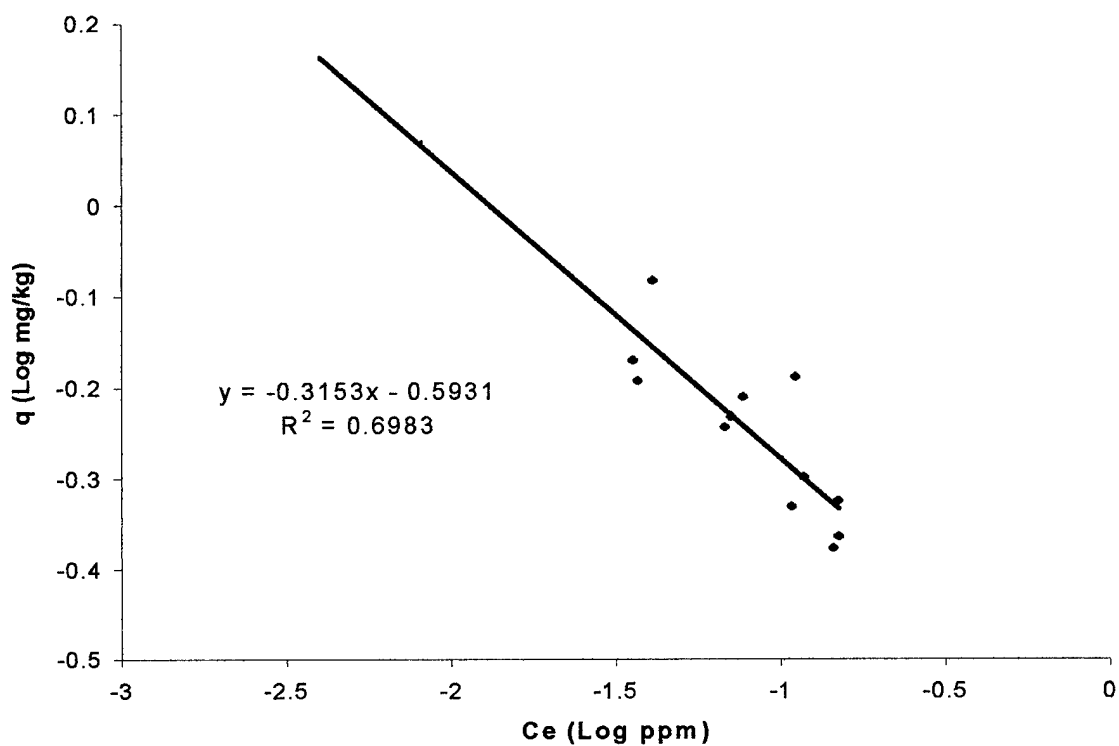


Figure 6: 2 hour 20 Salinity Freundlich Desorption Isotherm

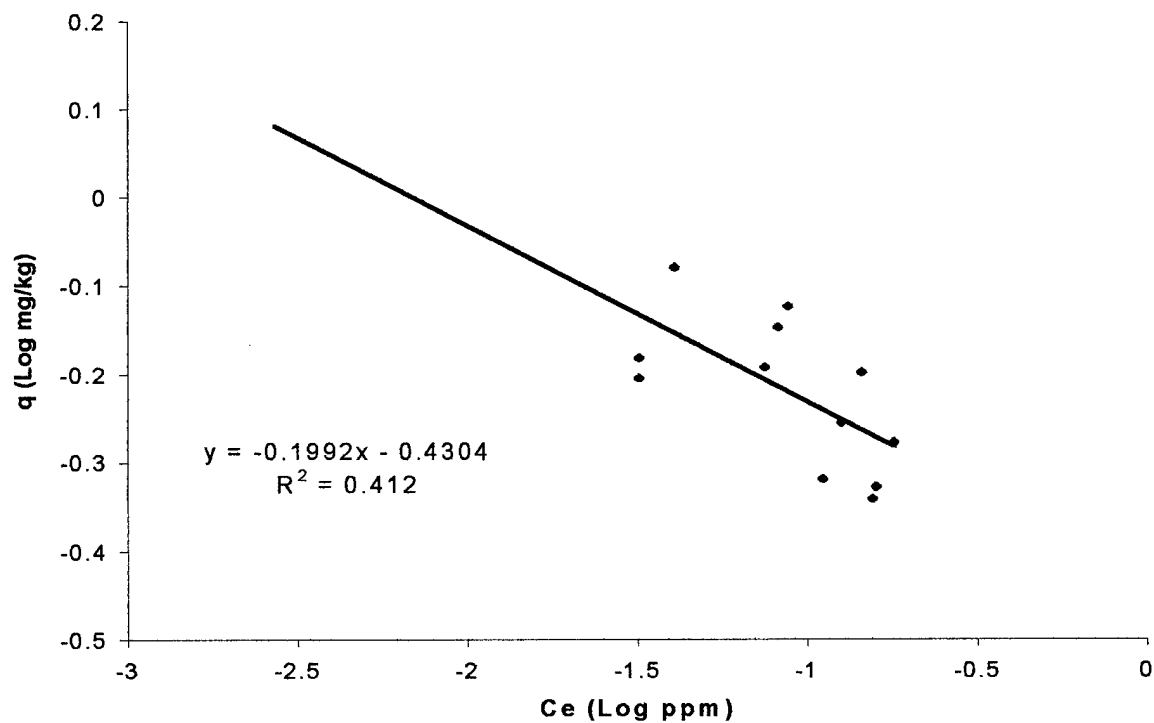


Figure 7: 24 hour 20 Salinity Freundlich Desorption Isotherm

A linear trend of increased copper desorption over the increasing amounts of soil is demonstrated by the r-squared values from the regression analysis. To better demonstrate the increased desorption by increasing the soil concentration, Figure 8 below compares the amount of copper released from 25 grams of soil and 75 grams of soil. It also shows the three time periods at which samples were taken. Clearly, time does make a noticeable difference in the amount of desorption occurring.

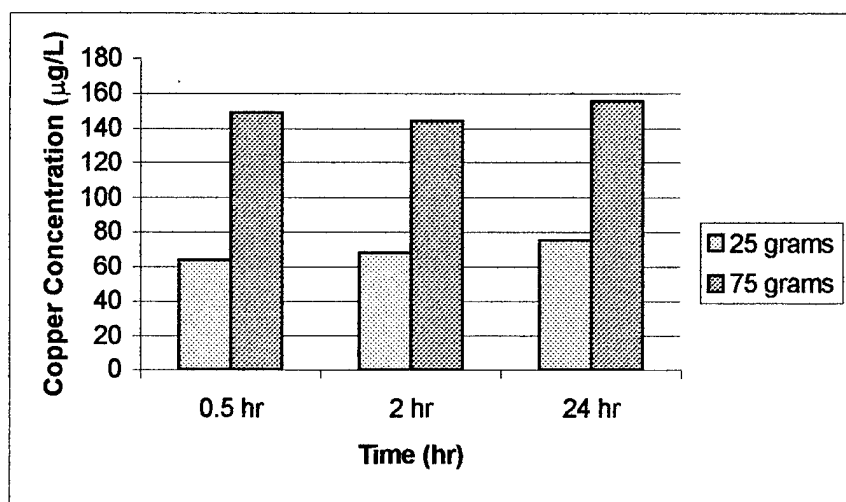


Figure 8: Desorption of Copper from Soil containing 20-25 mg Cu/kg soil into 250 mL 20 ppt Salinity Water

Three plots, Figures 9, 10 and 11, showing the 30 minute, 2 hour, and 24 hour Freundlich isotherms for the zero salinity desorption experiments are shown below.

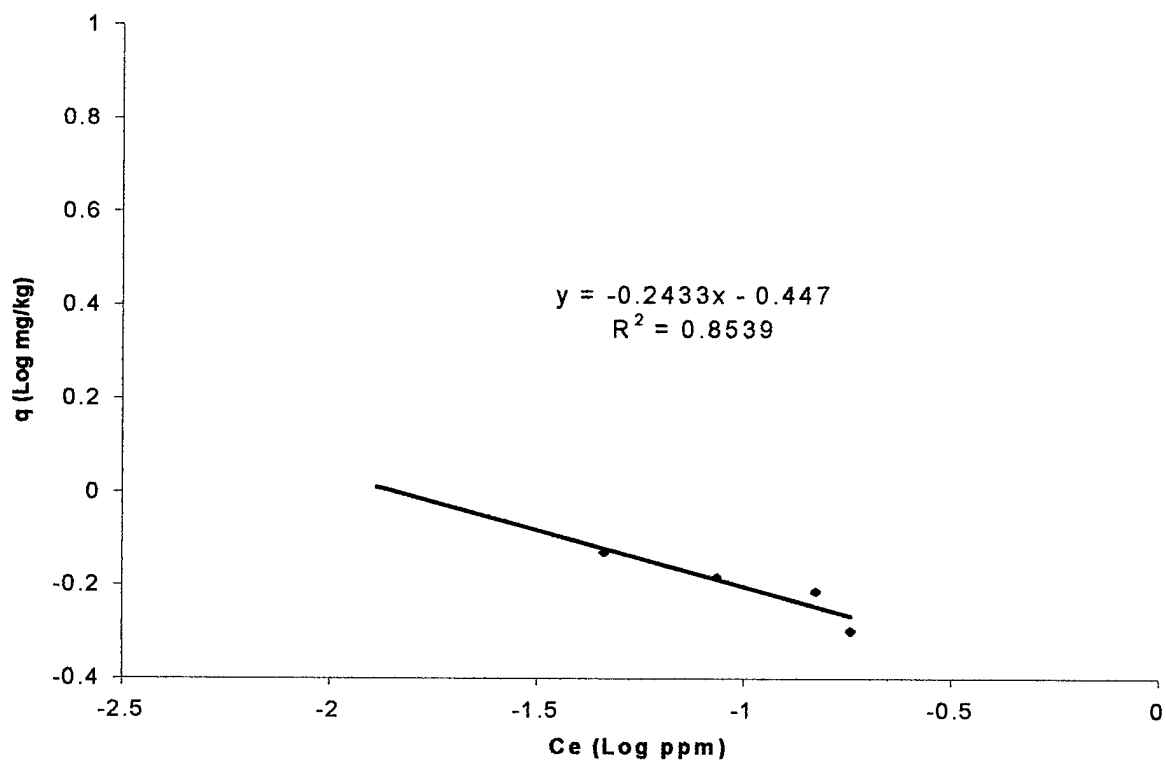


Figure 9: 30 minute 0 Salinity Freundlich Desorption Isotherm

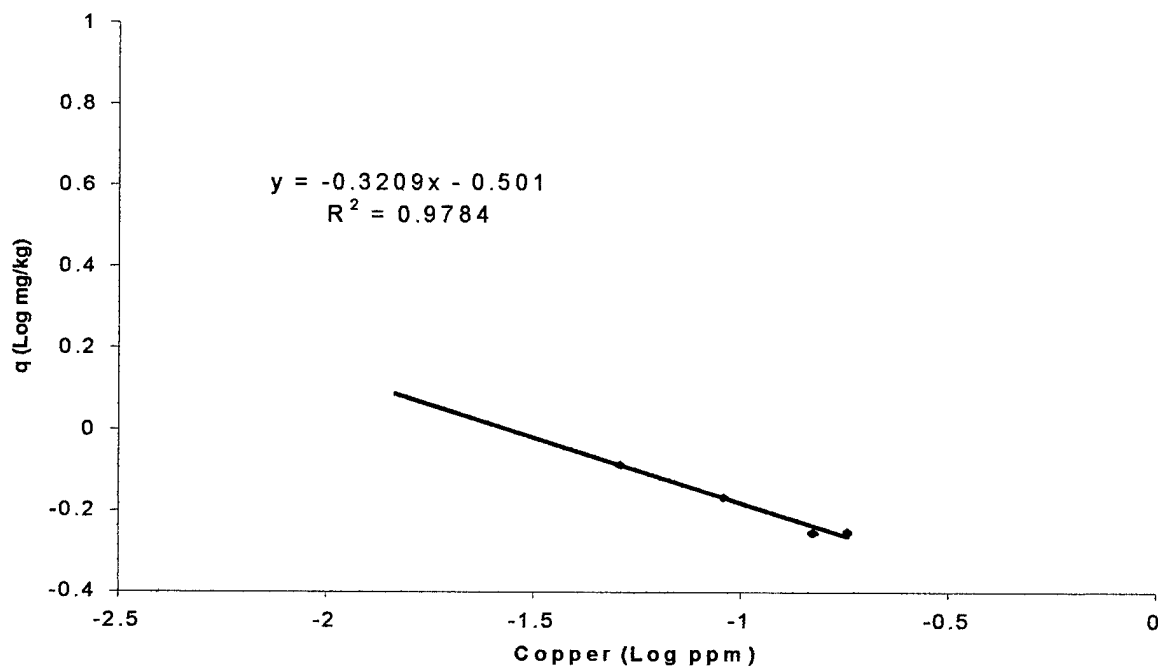


Figure 10: 2 hour 0 Salinity Freundlich Desorption Isotherm

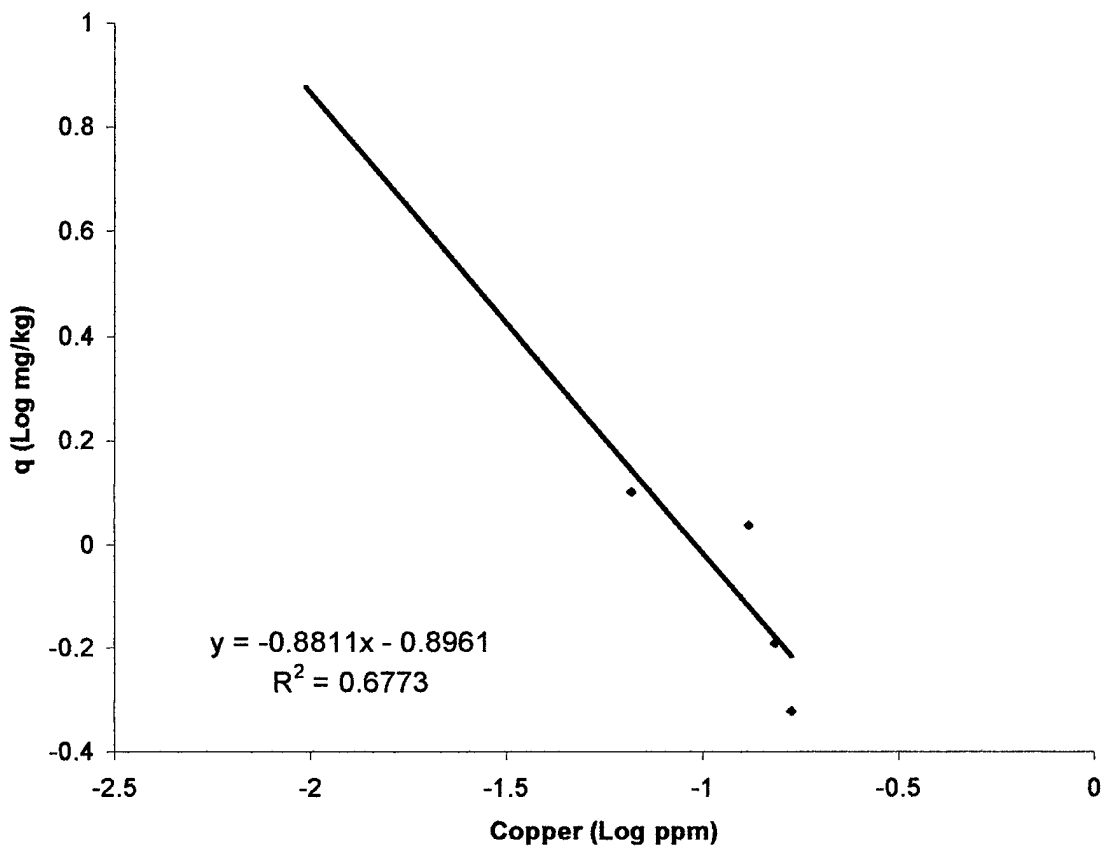


Figure 11: 24 hour 0 Salinity Freundlich Desorption Isotherm

As with the salinity experiment, a linear trend of increased copper desorption over the increasing amounts of soil is demonstrated by the r-squared values from the regression analysis. Again, to better demonstrate the increased desorption by increasing the soil concentration, Figure 12 below compares the amount of copper released from 25 grams of soil and 75 grams of soil. It also shows the three time periods at which samples were taken. Similarly to the 20 ppt salinity experiment, time does make a noticeable difference in the amount of desorption occurring in the zero salinity experiment.

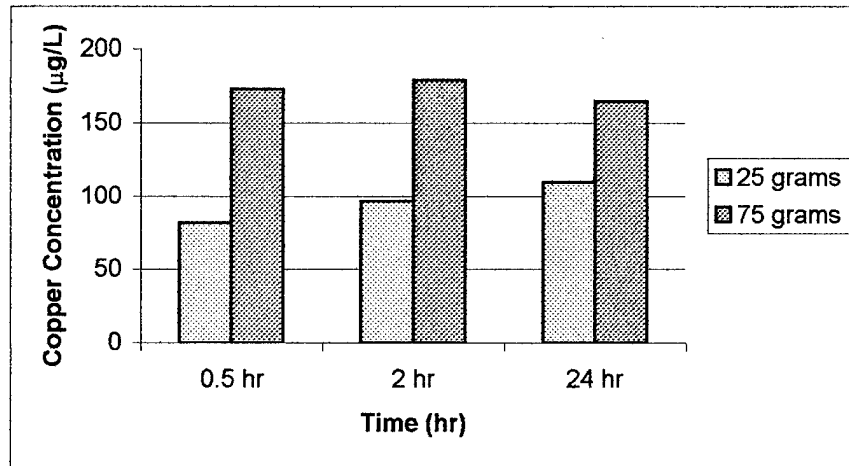


Figure 12: Desorption of Copper from Soil containing 20-25 mg Cu/kg soil into 250 mL Zero Salinity Water

Discussion

Filtration Losses

When performing the adsorption experiments, a noticeable copper loss was seen when filtering the samples. Previous experiments had shown that at pH 6, the 0.45 μm filters would allow the copper to pass through. However, during the adsorption isotherm study with a zero salinity, 300 ppb copper concentration solution at pH 6, a loss was seen. The below figure shows the copper concentrations of the above solution when it was sampled both with and without filters. On average, a 13% loss is seen through the filters. The percent difference for the unfiltered samples was less than 0.1%.

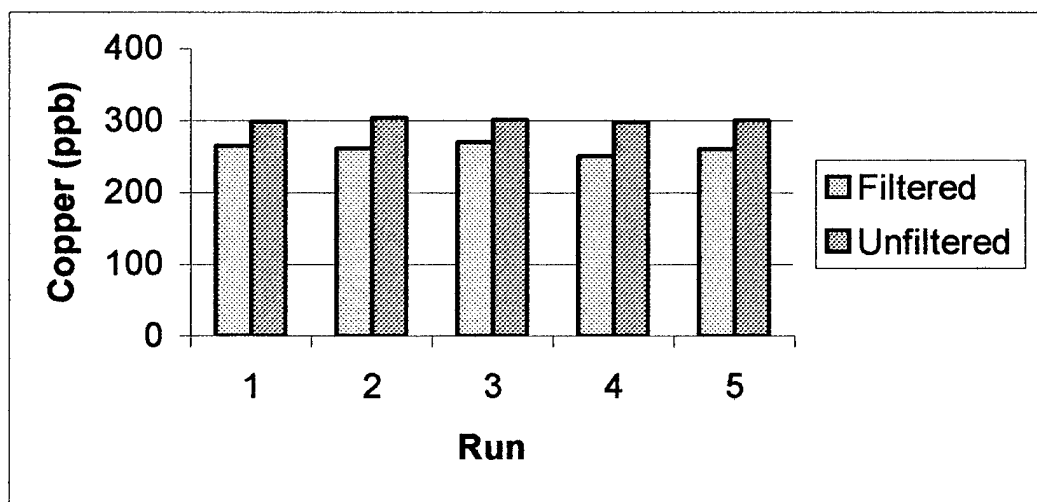


Figure 13: Comparison of Filtered versus Unfiltered Copper Solution

Comparison of Sorbents

Similar isotherm studies were previously performed on resin and granulated activated carbon (Schmitt). In order to determine the ability of these sorbents in comparison to the Bojac Sandy Loam soil, all three are compared below in Figure 14.

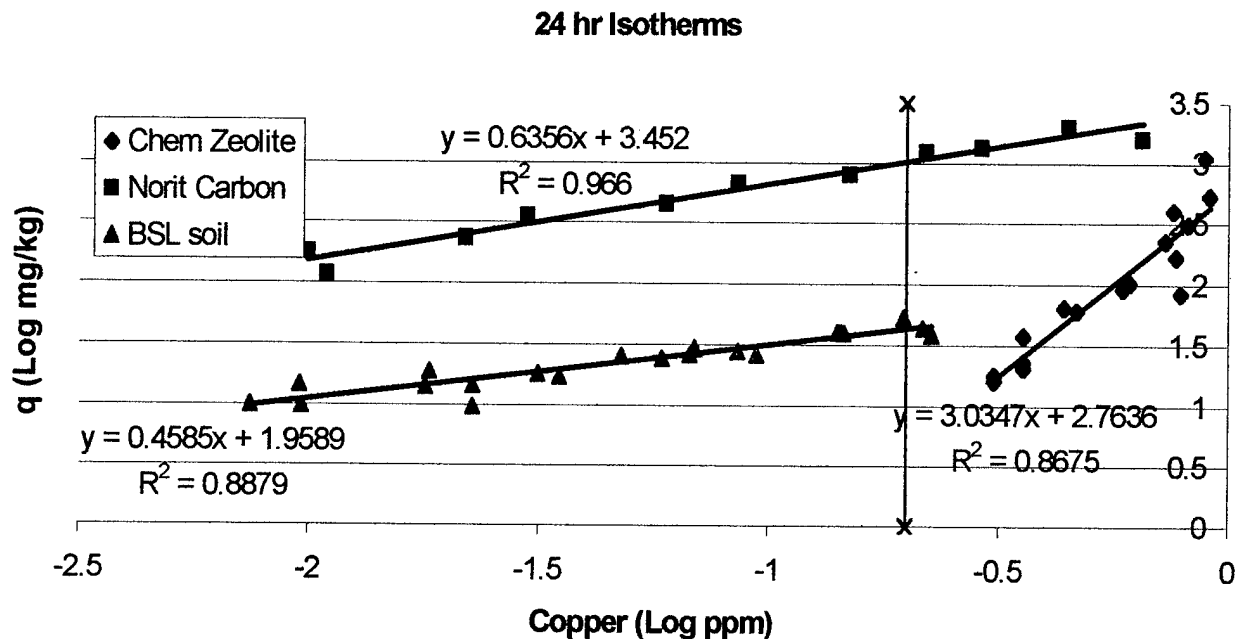


Figure 14: Comparison of Sorbents Ability to Adsorb Copper

The vertical line at $C_e = -0.7$ marks the location of 200 ppb copper concentration, which is a typical value of dissolved copper found in the runoff from the tomato fields (Brady *et al.*, 1999). Table 4 compares the capacities of the three different sorbents at the typical value of 200 ppb and the LC_{50} value of 16 ppb. The table shows these values in terms of q or as mg Cu sorbed/ kg soil sorbent. The activated carbon has the highest capacity for sorption with Bojac Sandy Loam soil being the second most sorbent.

Table 4: Comparison of Sorbent Capacities at Two Copper Concentrations

<i>Sorbent</i>	<i>x mg Cu/kg soil at $C_e = 200$ ppb or -0.70 (Log ppm)</i>	<i>x mg Cu/kg soil at $C_e = 16$ ppb or -1.8 (Log ppm)</i>
Zeolite	4.4	.002
Carbon	1000	200
Soil	43.7	13.5

Agricultural Impact of Copper

During the field sampling taken on the Eastern Shore, desorption was seen over time from soil. This phenomena was recognized because even after the tomato fields were no longer being dosed with crop protectants, significant copper concentrations were found both at the fields and in the local estuaries. This is seen in Figure 15 when looking both at the Kegotank Road tomato field and the Gargathy Creek at Kegotank Landing.

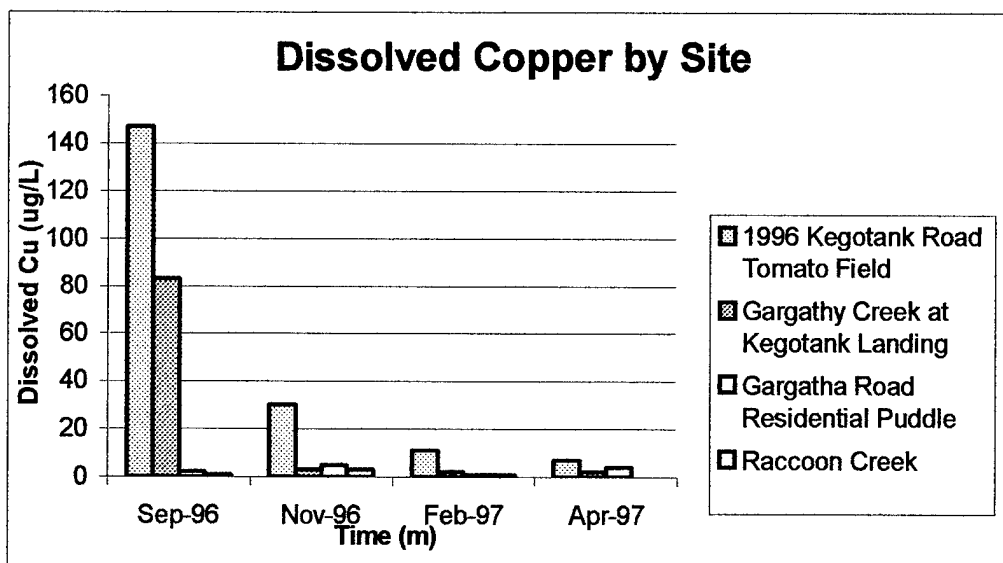


Figure 15: Dissolved Copper Concentrations Found at Various Sites on the Eastern Shore (reprinted with permission of author, Stall, 1999)

Pesticide application stopped before the September 1996 sampling. However even though there is no more application, copper is found not only in September, but also in follow on samples. For this reason, it seemed likely that copper was desorbing off of the soil and sediments either when it enters the saline water of the estuaries or when it is contacted by rainwater.

In the laboratory studies performed in this project the same phenomena was seen. When copper laden soil comes in contact with either 20 ppt salinity water or zero salinity water, copper desorbs from the soil into solution.

Ecological Impact of Copper

In a previous study it was determined that a significant amount of copper is released immediately after time zero when the copper laden soil contacts the saline water of the local estuaries (Cheadle *et al.*, 1999). Comparing the results from a tomato bed with sedimentation versus one without in Figure 16 shows the large copper release only in the bed without sedimentation. The soil is not removed since sedimentation is not used which indicates that the copper is desorbing from the soil when it comes in contact with the saline water.

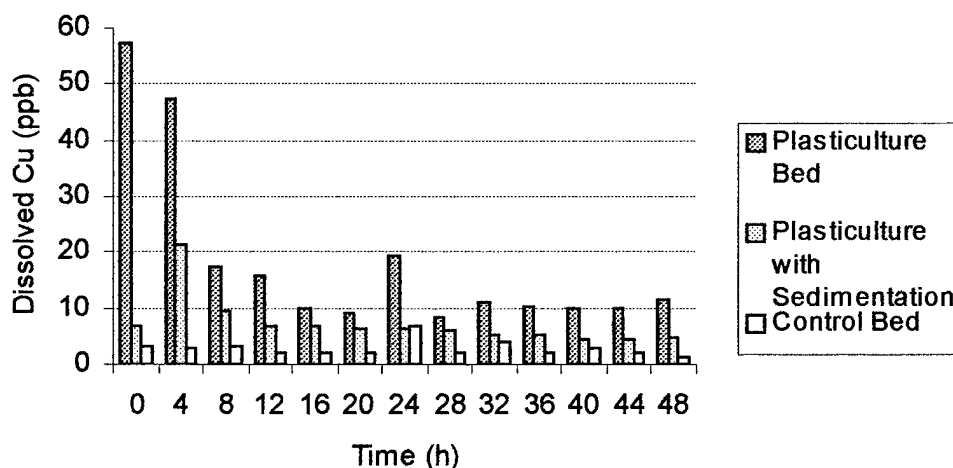


Figure 16: Dissolved Copper in Mesocosms (reprinted with permission of author, Cheadle *et al.*, 1999)

The same effect was seen in the desorption isotherm using 20 salinity water. Copper was seen in the first time interval (30 minutes) and no significant increase of copper release was seen over the next 24 hours which indicated an immediate desorption of copper from the soil.

Conclusions

A study was performed by Virginia Tech to examine the causes of the deteriorated water quality seen in the local estuaries of the Eastern Shore in Virginia. The use of copper-based crop protectants by the tomato farmers, which border the local waterways, was thought to be linked to this drop off in water quality. Due to copper's toxic effect on aquatic life, it became the focus of a large scale investigation. In conjunction with this project, the fate and transport of this copper onto and off of the soil from the Eastern Shore was investigated through a series of sorption and desorption isotherms. The adsorption isotherms showed that as the amount of soil increases, the amount of copper adsorbed also increases. However, over time there was not a clear increase in copper sorption, which indicates that the adsorption is an immediate process and that an increase in time does not change the amount of copper the soil will sorb. When copper laden soil was used in desorption isotherms, both in saline and pure water, copper did desorb from the soil into solution. Again this was an immediate process and the increased time did not significantly affect the amount of copper being released.

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