Discussion

This sampling project started at the very end of the 1996 growing season, and therefore only sampled one month during the higher than average rainfall growing season illustrated in Figure 14, which clearly illustrated the difference between the magnitude of rain that fell on the Eastern Shore during the growing seasons of 1996 and 1997. Background sampling was performed throughout the non-growing season, extending from October to April, and continued through the much dryer 1997 growing season from May to September.

In the case of plasticulture and copper-based crop protectants, high rainfall such as that experienced in 1996 improved conditions for the outbreak of very damaging bacterial spot and bacterial speck (Watterson, 1986). Farmers were therefore encouraged to apply heavier amounts of copper to their fields under these conditions to prevent the outbreak of disease (Griffin, 1996a; Griffin, 1996b; Griffin, 1996c). Plasticulture already increased the volume of runoff from a field, (Scott, *et al.*, 1990) and the higher than average rainfall totals exacerbated this effect. With an abundance of runoff carrying a larger than average amount of copper from crop protectants off the field, it was expected that concentrations of copper in the tidal creeks and estuaries would be higher during wet seasons as in 1996.

Figure 14 illustrated one of the key problems with investigating non-point source pollution, such as that caused by agriculture. Non-point source pollution is dependent upon rainfall, and rainfall is a variable that cannot be controlled in monitoring studies (Novotny and Olem, 1993). It was therefore very difficult to compare the high levels of copper found in tidal creeks at the end of the 1996 growing season, with the low levels found throughout the growing season of 1997. One example would have compared the 263 ug/L total copper found in September, 1996 in Gargathy Creek at the Kegotank Public Landing, with the 1 ug/L total copper found at the same location in September, 1997.

Rainfall was not the only seasonal variable that changed from year-to-year. The location of plasticulture fields, and the acreage in plasticulture within a particular watershed can change yearly (Gayle, 1996). Rotation of fields in plasticulture was recommended to deter diseases and pests (Watterson, 1986). Although many fields were engaged in plasticulture two years in a row, such as those in The Gulf watershed, in some locations, fields were removed from production and others added, as in the Gargathy Creek watershed. The total acreage of plasticulture was determined by economic reasons including the price and demand of tomatoes (Gayle, 1996).

Changing land-use patterns contributed to the difficulty in comparing copper concentrations from year to year. Although some watersheds did not alter their land-use patterns significantly, such as The Gulf, Raccoon Creek, or Queen's Sound, the location of plasticulture in Gargathy Creek changed with significant results, even though the total acreage stayed approximately the same (Hammer and Boyd, 1997). The large tomato field on Kegotank Road that figured so prominently in 1996 was converted to soybeans for 1997. None of the plasticulture fields in 1997 within the Gargathy Creek watershed was located as close to the waterway as that one had been in 1996. Consequently, the high concentrations of copper found at the Kegotank Public Landing in 1996 were not repeated in 1997.

The lower than average rainfall made the growing season of 1997 an excellent year for both plasticulturists and aquaculturists (Bagwell, 1997; Gayle, 1996). Lack of rain was beneficial to tomato farmers, who carefully supply all of their plants' water needs through irrigation to heighten crop flavor and prevent swelling and cracking (Geisenberg and Stewart, 1986). There was less need in 1997 for additional crop staking due to heavy rains, or for directing pooled rainfall from fields (Gayle, 1996). Less rainfall meant that conditions for dangerous bacterial spot and speck were not favorable, and therefore less bactericide was applied to the crops (Watterson, 1986; Griffin, 1996a; Griffin, 1996b; Griffin, 1986c). Additionally, copper that was applied as a bactericide was not washed off the crop by rainfall, and therefore lasted longer with less need to reapply. All of these effects save the tomato growers money in the form of purchased crop protectants and labor.

Less rainfall reduced the volume of runoff from the fields, and that combined with fewer crop protectants on the crops decreased the volume of toxic crop protectants in the tidal creeks and estuaries. This in turn decreased the probability of aquaculture facilities experiencing mortality due to agricultural-related toxins in the water supply.

A comparison of total copper, dissolved copper, total suspended solids and rainfall were made for Gargathy Creek-Clam Co. in Figure 15, with few apparent trends. It was difficult to compare pollutant concentrations and rainfall data on a watershed basis without having detailed rainfall data (hourly measurements, for example) and a better understanding of the topography and land-use of the watershed (Novotny and Olem, 1993). Therefore, it was not surprising that comparing three-day summed rainfall for weather stations outside of the watershed to copper concentrations found in waterways resulted in no detectable trends. The lack of rainfall associated with many data points resulting from a generally dry summer probably magnified this effect.

Two trends turned out to be exceptions: total copper versus dissolved copper (Figure 16) and total copper versus total suspended solids. (Figure 17) The relationship between dissolved copper and total copper was evident from the definitions of the two parameters (Eaton, *et al.*, 1995). Dissolved copper must be some fraction of total copper depending on the physical characteristics of the water. Although samples were collected throughout the salinity range from freshwater to almost complete seawater, some trend could still be expected.

The weakness of this trend resulted from the continual flux in estuarine conditions, such as salinity and pH. These two water quality parameters have significant effects on the form of copper, and determine whether it is dissolved, or adsorbed to particles in the waterways (Snoeyink and Jenkins, 1980; Leckie and Davis, 1979). Not only was the data set drawn from different tidal creeks and estuaries, each with its own characteristics, but from different locations within the estuaries.

Since 40 to 60% of the total copper in an estuary is associated with particles, a corresponding increase was expected between total copper and total suspended solids, a measure of the particulate matter in water samples (Batley and Gardner, 1976). It has already been established that a greater volume of rainfall increased the amount of copper in waterways. The same should have been true for solids, which were jarred loose by impacting raindrops, and washed away in the subsequent runoff (Novotny and Olem, 1993). Since both concentrations were increased by the same physical process, a correlating increase between the two of them is logical. This correlating increase acted as a buffer system for estuaries, so that the concentration of toxic ionic copper is regulated by adsorption to particles, which makes it less toxic (Batley and Gardner, 1976). Although sediment traps and other Best Management Practices that decrease the particle loading of runoff decrease the total amount of copper flowing to the estuary, they also decrease this buffering effect. A more detailed understanding of shifts in copper speciation between freshwater and estuarine water in needed to fully evaluate the efficacy of BMPs.

The weakness of the trend between total copper and total suspended solids could have been attributed to a lack of data on the high total suspended solids/ high total copper end, caused by the dry growing season. Additionally, although all of the watersheds produced runoff, not all of them contained agriculture, and therefore produced copper and suspended solids in their runoff at the same rates. Additional data collected for each watershed would have allowed a trend analysis on a watershed-by-watershed basis and would most likely have increased the significance of the trend. Growing season and non-growing season data were also analyzed together. Additional data for each season would have allowed separation of the seasons, also increasing the significance of the trend, especially for wet years like 1996.

The two control sites, Raccoon Creek and Queen's Sound at Chincoteague demonstrated and established background copper concentrations between zero and three ug/L dissolved copper, comparable to other natural waterways (Eisler, 1994; Riedel, *et al.,* 1995). Non-agricultural copper inputs to natural waterways can occur, and their contributions to ambient copper concentrations must be determined and accounted for through control sampling. Non-agricultural copper sources can include atmospheric deposition, bulkheading copper-treated wood used in building marine structures (Queen's Sound only,) and marine paint on boat hulls (Weis and Weis, 1993; Novotny and Olem, 1993).

The median concentrations of dissolved copper were the same for all sampling sites investigated. (Figures 38 and 39) As expected, the copper concentrations of the agricultural watersheds remained at background levels throughout the non-growing season between 1996 and 1997. They did not increase with the coming of the summer, a fact that must be attributed to the lack of rainfall received and the placement of the tomato fields in 1997. Even throughout the hardest rainfall event of the summer, from July 22-24, low levels of copper were measured almost everywhere. Even so, spikes of copper were detected as high as 126 ug/L dissolved copper in Gargathy Creek, despite the summer's climatic conditions. Several individual dissolved copper concentrations were determined to be higher than normal. (Figures 40 and 41) None of these higher values occurred at Raccoon Creek or Queen's Sound, reinforcing the fact that copper concentrations in Eastern Shore tidal creeks and estuaries impacted by plasticulture in 1997 were usually equal to background levels, with the occasional high copper spike.

The additional grab sample data confirmed the observation that although roadside pooled rainfall copper concentrations were sometimes higher than those in natural waterways, the concentrations in pooled runoff from plasticulture fields were generally higher still. Copper was applied to both tomatoes and peppers, but not to the other crops: soybeans, grains, cotton, or corn; nor to residential yards (Griffin, 1996a; Griffin, 1996b; Griffin, 1996c). Therefore, copper concentrations from 7 to 57 ug/L for tomato and pepper field runoff, and 1 to 4 ug/L copper for the other locations, appeared reasonable. The only concentration that was unexpected was 9 ug/L found in cornfield runoff, potentially caused by either non-agricultural sources or copper left on the field from a previous year's copper-using crop.

None of the copper concentrations found in the sediments were higher than normal levels, but the concentrations of copper in similar sediments were compared (Novotny and Olem, 1993). Copper concentrations in Gargathy Creek near the landing were higher than those found at the Clam Company and in Queen's Sound, indicating that perhaps the copper-containing runoff entering Gargathy Creek through the landing may have contributed to elevated copper concentrations there.

Short-term high copper concentrations were not necessarily hazardous to adult shellfish, which can close their shell, stop feeding, and wait until the copper slug passes. However, unprotected larval shellfish and embryonic shellfish could have been devastated by them. Remembering that just one hour in ten ug/L added copper will kill 91.5% of *Corbicula manilensis* larvae, the freshwater clam, it is not difficult to believe that 126 ug/L dissolved copper for an equally short period of time will have a significant effect on the survival of estuarine shellfish larvae (Harrison, *et al.*, 1984).

If copper concentrations in a low rainfall year like 1997 were toxic to marine larvae and embryos, then copper concentrations in high rainfall years such as 1996 could have been devastating. In Gargathy Creek at the Kegotank Public Landing, 263 ug/L total copper were measured in September 1996, at the end of the growing season after many tomato crops had been harvested, and in a month that had received about 7.5 inches of rain. In a wet growing season like that which occurred in 1996, high rainfall would have caused substantial runoff and increased the application rate for crop protectants. This would have allowed for high copper concentrations in agricultural runoff entering Eastern Shore waterways. Considering that 16.4 ug/L added copper will kill 50% of clams over the eight to ten day larval stage, and stunt survivors' growth to 51.7% of normal (Calabrese, *et al.*, 1977), larval clams might have had a hard time surviving in Gargathy Creek in 1996. If copper concentrations remained elevated for too long, even the health of adults could have been affected.

Summary and Conclusions

An investigation was completed into the role of plasticulture and copper-based crop protectants on water quality in tidal creeks and estuaries on the Eastern Shore of Virginia. Evaluation of water quality parameters including copper concentrations allowed relationships among parameters to be resolved. Comparing copper concentrations in control and plasticulture-containing watersheds, as well as land-based runoff,- allowed determination of the source of copper spikes found in waterways. Measurement of sediment copper concentrations indicated the degree to which Eastern Shore sediments were sequestering copper from previous inputs. Finally, a comparison was made of measured copper concentrations in tidal creeks and estuaries to known toxicity values for species grown in Eastern Shore aquaculture. The following results were obtained:

- Water quality in the tidal creeks and estuaries of the Eastern Shore of Virginia was affected by copper inputs from crop protectants used in vegetable plasticulture.
- During the relatively low rainfall conditions of 1997, the copper concentration in Eastern Shore waterways remained approximately zero to three ug/L, except during runoff-producing rainfall events in the growing season, when high copper spikes appeared up to 126 ug/L dissolved copper.
- Crops utilizing copper-based crop protectants and planted in plasticulture produced runoff with copper concentrations between 7 and 57 ug/L dissolved copper. Runoff from fields not engaged in plasticulture and not utilizing copper-based crop protectants, as well as pooled rainfall from other residential and natural areas, produced concentrations of ten or less ug/L dissolved copper.
- Dissolved copper was approximately 32% of the total copper in a water sample averaged over all of the samples taken on the Eastern Shore of Virginia, and total copper demonstrated a correlative increase with total suspended solids.
- Sediment copper concentrations in tidal creeks and estuaries of the Eastern Shore were comparable to natural concentrations, although amongst sites with comparable

grain-size distributions, locations closer to agricultural copper sources indicated higher concentrations of copper.

- Although widespread contamination of tidal creeks and estuaries was not evident, occasional high copper concentrations, which existed in spikes, were potentially harmful and toxic to many species of shellfish used in Eastern Shore aquaculture, especially their larval and embryonic stages. These high copper concentrations exceeded the reported LC_{50} for larval clams by an order of magnitude at times.

Recommendations

This research marked the beginning of an investigation into the dynamics of Eastern Shore tidal creeks and estuaries and the impact that non-point source pollution from agriculture may have on estuarine life, particularly those species used in aquaculture. Based on the findings of this research, several recommendations can be made for future research endeavors in many different fields of expertise.

Researchers need to help growers limit copper inputs to tidal creeks and estuaries so that the water bodies will come into compliance with environmental regulations. Non-point source pollution is difficult to prevent because of its diffuse nature. However, several best management practices work to hinder the creation or transport of non-point source pollution. One example would be treating runoff water to remove crop protectants. Grass filter strips or sediment catch basins would take out those pollutants normally adsorbed to particles, along with the particles. A retention pond would give farmers a water source for irrigation, as well as preventing crop protectant containing runoff from leaving the borders of the farm. Integrated pest management or the use of other fungicides and bactericides would decrease the volume of copper used and therefore the amount that would be available to enter the water. Research into testing which types of BMPs are effective is essential.

In order to understand how to prevent non-point source pollution, the form of the crop protectant must be known. If the crop protectant enters the waterway in an adsorbed form, then a sediment catch basin would work. On the other hand, dissolved crop protectants would flow straight through, rendering the catch basin useless. Although this research determined the forms of copper in the tidal creeks and estuaries, different ratios would be expected for runoff water. More runoff samples should be collected to determine this ratio for plasticulture.

A better understanding of the dynamics of the estuaries on the Eastern Shore would provide more information on travel and residence times for crop protectants in the waterways. If the aquaculturists can estimate when contaminated water is in the estuary, then they can use reserve water during those periods, as a contingency for especially heavy rainfalls. Similarly, a simple method or testing device for the presence of dangerous crop protectants in the intake water would be useful for aquaculturists in emergencies.

Another option is to treat intake water to take out those crop protectants that cause mortality, until the sources of toxins reduce their inputs to the water bodies of the Eastern Shore. A method would have to be researched that could treat the large volumes of water used in a shellfish hatchery, clean it to very low concentrations for some of the more toxic crop protectants, and be cost effective.

In order to recommend the use of a treatment method, determining which crop protectant causes mortality is crucial. According to this research, toxic concentrations of copper were found in the tidal creeks and estuaries of the Eastern Shore. According to other research, toxic concentrations of organic crop protectants have also been found. A treatment method to remove toxins would necessarily be very different for copper versus an organic toxin.

More information is necessary on the toxicity of agricultural crop protectants on species used in aquaculture. Although toxicity information is available from laboratory tests for some species and age groups, the influence of several factors remain unknown. These factors include the speciation of copper, and the influence of other environmental characteristics or other toxins.

Lastly, more monitoring data is required. A year’s data is not sufficient to understand the full scope of natural conditions that can exist on the Eastern Shore. Yearly changes in field location and rainfall necessitate the collection of several years of data. Although the background concentrations should not change significantly, the growing season concentrations may, and therefore intensive monitoring during the growing season should be carried out for several subsequent years.

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