

Literature Review

I. Historical Summary of Agriculture and Aquaculture on the Eastern Shore

A. Eastern Shore of Virginia Agriculture

Farmers and fishermen have worked and lived in very close proximity to each other ever since colonists settled the Eastern Shore of Virginia in the 1600s. The Eastern Shore varies in width from about five to fifteen miles, and is approximately 70 miles long. Located between the Atlantic Ocean and the Chesapeake Bay, the Eastern Shore's tidal creeks and estuaries reach far into the mainland. This causes the two industries to work in close contact.

Farming has always been an important part of the Eastern Shore's economy. Farmers on the Eastern Shore first began to turn from producing grains and potatoes to more lucrative vegetable crops in the 1840s, but throughout the 1800s, sweet potatoes and Irish potatoes made up the bulk of the agricultural industry. In 1860, Eastern Shore farms produced twice as many potatoes as in 1940. In 1890, seafood placed second behind the sweet potato crop in production value for the region (Turman, 1964).

The turn of the century saw the most productive years for Eastern Shore agriculture, with nearly 50,000 of its acres invested in potatoes. This represented a little under half of the total acres in agriculture for the region. At that time, farmers planted only about 2500 acres in cabbage, onions, and tomatoes combined. The Eastern Shore produced heavily for World War I, and the price of potatoes peaked in 1920, bringing much prosperity to the area (Turman, 1964).

Unfortunately, the Eastern Shore suffered an immense loss with the Great Depression and reverted back to grain crops and self-sufficient farming. The population fell from its highest number ever, over 50,000 occupants in 1940, to much lower levels. Vegetable farming rose to be the most profitable crop in the area, since the price of potatoes never recovered. In 1945, over 12,000 acres of tomatoes grew on the Eastern Shore, and stayed at about that level for several decades (Turman, 1964). Growers estimated that they grew about 3200 acres of tomatoes on the Eastern Shore in 1996 (Wilson and Callendar, 1997).

Since the 1970s, tomatoes and other valuable vegetable crops such as eggplant and cucumber have been grown with the help of plastic ground mulch. This practice is called plasticulture. Combined with trickle irrigation, this has become a powerful tool for farmers on the Eastern Shore to increase their vegetable yields. Primarily, the benefits included minimized herbicide use, soil temperature control, increased disease resistance, moisture control, and fertilizer stabilization, so that fertilizer added to crops will not wash away with rainfall (Gayle, 1996). Approximately 9100 acres were planted using plasticulture on the Eastern Shore in 1996 (Belote, 1996).

Unfortunately, this practice has increased the volume of runoff water produced from the fields engaged in the use of plasticulture (Scott, *et al.*, 1990). Around 55 % of the field covered by impermeable plastic (Gayle, 1996) and the rows in between are compacted by travelling farm equipment. Therefore, less rain penetrates into the soil, producing runoff at a faster rate. Using drip irrigation tubing under the surface of an impenetrable barrier keeps unused fertilizer from being washed off in runoff, which is a desirable effect for those farms in the Chesapeake Bay watershed. On the other hand, crop protectants sprayed on the surface of the crop wash off and have limited chance to interact with the limited soil underneath before being carried from the field in storm water runoff.

B. Eastern Shore of Virginia Aquaculture

The food supplied by the surrounding seas and their tributaries was as important to the early citizens of the Eastern Shore as that provided by traditional agriculture. Fisheries in the area have been a source of income and food throughout the years, starting as early as the 1600s with such industries as commercial fishing and shellfish harvesting. A number of other fisheries related industries have learned to take advantage of the sea's production in the 1900s, including the practice of aquaculture.

Aquaculture is defined in the Virginia Aquaculture Development Act of 1992 as the propagation, rearing, enhancement and harvest of aquatic organisms in controlled or selected environments, conducted in marine, estuarine, brackish, or freshwater (Thacker, 1994). Aquaculturists reported growing clams, oysters, scallops, and soft-shelled crabs in

1995 (Virginia Agricultural Statistics Service, 1996). The aquaculture industry on the Eastern Shore of Virginia amounted to an estimated 6.5 million-dollar industry in 1992 (Thacker, 1994).

In the 1990s, aquaculture on the Eastern Shore has been dominated by estuarine clam aquaculture, specifically the species *Mercenaria mercenaria*, the hard clam. Other common species of shellfish grown on the Eastern Shore include *Crassostrea virginica*, the American oyster, and *Argopecten irradians*, the bay scallop (Thacker, 1994).

The procedure for growing clams is necessarily complex and every stage of growth depends upon the quality of the water in which the clams live (Parks, 1996). All water used in shellfish aquaculture must be natural seawater or estuarine water that has been carefully filtered and irradiated with ultraviolet light. This lowers the chance that the water will contain dangerous biological organisms (Bagwell, 1996). The basic procedure includes carefully selecting a brood stock of adult clams. These clams are conditioned in water obtained from the local Eastern Shore environment, after which they are induced to spawn by carefully controlling the water temperature. The fertilized eggs are collected by filtration of the overflow water from the spawning tank (Castagna and Kraeuter, 1981; Rand, 1981).

The clam embryos, approximately 25 μm in diameter, and the corresponding larvae into which they develop, anywhere from approximately 20 to 75 μm in diameter, are free-swimming or floating without the hard shell of adult clams (ASTM, 1994). This makes them particularly sensitive to poor water quality, including low salinity, low dissolved oxygen, high temperatures, and the presence of toxins. The embryonic and larval clams grow in large tanks within the hatchery where they feed on small algae, approximately five to eight μm in diameter. These algae must be grown for the larvae and added to their water by the aquaculturists to ensure an adequate supply of food. Every two days, the water in the tanks is changed by draining down the tank through a fine mesh small enough to catch the clams. The clams are then added to a clean tank of seawater and the process begins again (Bagwell, 1996).

Seven to fifteen days after spawning, the clams metamorphose into their adult, bottom-dwelling phase. They spend a short time in a screened container within the hatchery through which clean local seawater continuously flows. After they reach a

certain size, the clams are transported to similar screened containers and placed in outside raceways, (Figure 1) where they continue to grow in water piped from the nearby waterway. The clams grow in these raceways until they become large enough to be placed directly in the waterways of the Eastern Shore (Castagna and Kraeuter, 1981). (Figure 2)

C. Economy of the Eastern Shore of Virginia in the 1990s

Unfortunately for the economics of the area, both the farming and the fisheries industries have declined in productivity from their heyday in the 1800s. Around 26% of the Eastern Shore human population lived below the poverty level in 1996 and eight percent were unemployed (McGowan, 1996). Fisheries and farming combined produced only eight percent of the local economy in 1996, but this understates the role these industries have in the manufacturing industry, namely in food processing. The other two large industries on the Eastern Shore, retail and services, rely upon fisheries and farming for much of its customer base (McGowan, 1996).

The people of the Eastern Shore, when surveyed, indicated differing opinions for the future of the Eastern Shore. Because residents had relied heavily upon natural resources for their livelihood in the past, adults indicated retention of their rural lifestyle, and protecting natural resources to be of primary importance (Smutko, 1996). Many high school students indicated that escaping from the rural atmosphere of the Eastern Shore was an anticipated event, but protecting the unique environment of the Eastern Shore concerned them (Danner, *et al.*, 1996).

Residents of the Eastern Shore proved to be very environmentally conscious, even to the point of restricting the economic growth of the area. Sixty-nine percent stated that the environment should be protected above all other concerns (Danner, *et al.*, 1996). Sixty-eight percent of survey respondents indicated that they believed agricultural runoff was the most serious problem with water quality on the Eastern Shore. Only 28% of the residents responded that they felt agriculture did not significantly impact the environment (Falk, 1996).

II. Growing Tomatoes by Plasticulture

Farmers grow tomatoes in two overlapping seasons on the Eastern Shore. Preparation for the first crop starts in March with the tilling of the fields and the installation of drip irrigation and plastic mulch. The black plastic is used for the warming of the soil and the development of the crop. Tomato seedlings are started in the greenhouse, transplanted to the field in April, and harvested in July. The second season begins with preparation of the field in May followed by a late-June planting, and a September harvest. The plastic for the second season is light-colored to cool the ground and prevent heat-damage to the crop. Seaside locations are chosen for the second crop to allay problems caused by the summer heat as well (Gayle, 1996).

First, the land is tilled finely for maximum root growth, and then shaped into long rows of up to 600 feet long, approximately eight inches high (Virginia Cooperative Extension, 1997). Drip irrigation tubing is then laid, with the plastic drawn out over the rows. Row width and plant spacing are determined by the variety of the tomato chosen for the crop. Holes are opened in the plastic at the appropriate intervals for insertion of the tomato plants. Stakes of approximately four feet in height are machine-driven one foot into the earth. The seedling tomatoes are then placed through the hole in the plastic and into the ground next to the stakes (Geisenberg and Stewart, 1986).

The sandy, well-drained soils of the Eastern Shore, and the estuarine waters in some instances used for irrigation, actually increase the flavor of the crop. The tomatoes are irrigated with enough water for them to produce healthy fruit, but not enough so that the plants will store excess water in the fruit. Keeping the tomato plants at this moisture level forces each to produce fruit with higher percent solids and lower water content per volume than normal tomatoes, thus increasing their flavor (Geisenberg and Stewart, 1986). Both the sandy soils, which allow for good water drainage, and the estuarine irrigation water available make the Eastern Shore of Virginia a good location for growing tomatoes under plasticulture.

Farmers prune the tomato plant to maximize fruit production (Virginia Cooperative Extension, 1997), and tie the tomato plant to stakes by hand four times during their growth (Gayle, 1996). The tomato plants are sprayed with a variety of crop

protectants throughout their lifetime, and are manually harvested by workers on three different occasions (Gayle, 1996). After the completed harvest, the leftover plants are chemically desiccated and plant remains removed to aid in disease control. The plastic, stakes, and string are also removed and destroyed, again for disease control (Geisenberg and Stewart, 1986). Some high quality plastic mulches of greater thicknesses can be reused, as well as the drip irrigation tubing, when they are removed from the field carefully and stored indoors throughout the winter season (Virginia Cooperative Extension, 1996).

Tomatoes are susceptible to a number of different diseases. For years, researchers have searched for varieties of tomatoes that are resistant to some of the more damaging tomato diseases. *Fusarium* wilt was one of the more damaging diseases earlier this century, but a resistant variety has been found. Besides variety, other factors play a part in determining a plant's natural resistance to a particular disease. These include the presence of light and moisture, temperature, surrounding gases and the "micro-injuries" that result from the natural contact of the tomato plant with workers during such processes as pruning and tying (Watterson, 1986).

The climate and soil conditions on the Eastern Shore can cause a worsening of the effects from several different crop diseases. For example, the sandy, light soils of the Eastern Shore encourage leaf water soaking and therefore bacterial spot, which thrives in moist conditions. The increase in soil temperatures produced by using plastic mulches helps some warm-weather diseases, while discouraging those favoring cooler temperatures. On the other hand, plastic mulches are considered good at discouraging nematode infestation and soil-borne diseases (Watterson, 1986).

Environmental conditions sometimes cause fruit to become unmarketable. For example, low temperatures cause a condition called catfacing, a scarring and deformation of the blossom end of the fruit. Sunscald and sunburn of tomato fruits are caused by excessive direct exposure to the sun. Too much water sorbed into the fruit causes the tomato to swell and burst its skin, creating an effect called cracking or russetting (Virginia Cooperative Extension, 1997).

Two of the more damaging diseases to the tomato crops of the Eastern Shore are bacterial spot and bacterial speck. Bacterial speck, otherwise known as *Pseudomonas*

syringae pv. *tomato* causes spots to appear on many parts of the tomato plant, including the tomato itself, rendering it unmarketable. Sometimes the disease affects young plants, appears to go away, but then re-appears causing the loss of twenty-five percent or more of the eventual yield (University of California, 1985). These spots associated with bacterial speck appear as a dark coloration, sometimes black or brown, only a few millimeters in diameter with yellowish surrounding tissues. The spots swell slightly out of the fruit. Cool conditions favor this disease, which has been rare when drip irrigation is used, but requires less than a day of moist conditions at the appropriate moment in the plant's development to manifest. Some tomato varieties with resistance to this disease have been developed (Watterson, 1986).

Bacterial spot, also known as *Xanthomonas campestris* pv. *Vesicatoria*, appears in many of the same locations as bacterial speck, but has a slightly different appearance. The spots are black and dry, only a millimeter or so in diameter, occasionally falling off the affected parts. From this small beginning, the spots on the fruit's surface can turn scabby and cover about a centimeter diameter, which is surrounded by a light-colored tissue. Again moist conditions favor this disease, but unlike bacterial speck, this disease thrives in warmer conditions. Some tomato plant varieties are resistant to this disease, but they are not yet marketable (Watterson, 1986). Desiccation and death of the leaves of the tomato plant are signs of either spot or speck infestation (Goode, 1980).

Some other diseases also decrease the yields of tomato crops. These included fungi, such as those causing early blight, late blight, grey mould, and leaf mould, as well as anthracnosis and root galls (Blancard, 1994).

Several strategies have been employed by farmers to reduce the severity of tomato diseases in the field. Scheduling planting and harvesting to avoid optimum conditions for disease development seems to work, as well as crop rotation, using resistant varieties, and application of plastic mulches (Watterson, 1986).

Virginia farmers reported using cultural methods, such as crop rotation and crop timing to help prevent disease in their tomato crop. Eighty-five percent routinely engaged in these practices, while 89% scouted for pests in their crops as well. Farmers reported learning about the use of crop protectants from dealers and extension agents, and

most use gloves and long-sleeved clothing for the application of dangerous crop protectants (Weaver, 1995).

Virginia growers reported very heavy use of crop protectants on their tomato crops. Tomatoes registered second only to soybeans in the number of treatment acres recorded. Herbicide use amongst tomato growers was moderate, with almost half of the growers reporting applying such herbicides as metribuzin, trifluralin, and metolachlor. Insecticide use was reported to be heavier, with over three-quarters of the growers reporting the use of insecticides such as esfenvalerate, endosulfan, methomyl, and carbaryl. Nematicides such as methyl bromide were applied by less than a tenth of the growers responding (Weaver, 1995). The use of fungicides for growing tomatoes was also moderate, with almost two-thirds of the growers reporting their use. Popular fungicides included chlothalonil, mancozeb, maneb, copper hydroxide and copper sulfate, metalaxyl and benomyl (Weaver, 1995).

When these crop protectants enter the surrounding waterways, they are possibly damaging to the water quality and may be toxic to aquatic organisms. Endosulfan, for example, is used as a contact and stomach poison for specific insects. It is considered a very good insecticide because it is very species specific, and does not harm many other beneficial insects. Although it has a reasonably high acute toxicity to rats, about 30 – 160 mg/kg/bw for an oral LC₅₀, few long-term effects were noted, such as carcinogenicity, mutagenicity, or neurotoxicity. On the other hand, endosulfan is considered highly toxic to aquatic life, with a reported 96 hour LC₅₀ of 0.4 ug/L to *C. virginica*. Although this substance sorbs readily to soil particles, if it has little opportunity to interact with the soil before entering the surrounding waterways, it may adversely affect aquatic life. For this reason, the manufacturer recommends that a 300 ft buffer strip be employed when endosulfan is used adjacent to waterways (Volger, 1996).

Metolachlor has a 96-hour LC₅₀ of 2 mg/L for rainbow trout, a much lower toxicity to aquatic life than endosulfan, but it still has potentially damaging effects. Metalaxyl has a 96 hour LC₅₀ of >100 mg/L for Rainbow Trout, whereas chlothalonil has a 96 hour LC₅₀ of 0.25 mg/L for this species (Worthing, 1987). When applied to crops planted using plasticulture in near proximity to waterways, these crop protectants

are potentially dangerous to aquatic life due to the limited interaction with the surrounding soils and short time span before entering the waterways.

III. Copper as a Crop Protectant

Copper is suggested as a bactericide and fungicide for possible treatment of a number of tomato diseases, including bacterial spot and bacterial speck (Watterson, 1986; Blancard, 1994; Jones, *et al.*, 1991). A mixture of copper and mancozeb or maneb (another bactericide) is recommended immediately after transplanting and then once a week afterwards (Virginia Cooperative Extension, 1997). Other sources recommend not treating for bacterial speck beyond the five-leaf stage (University of California, 1985).

Tomatoes are treated for a number of different diseases using copper. Anywhere from one-and-a-half to three pounds per acre per week throughout the approximately three month growing season is recommended for diseases that range from anthracnose to blight to bacterial spot and speck. The application amount is determined by formulation, the crop size, environmental conditions such as rainfall, and the severity of the disease (Griffin, 1996a; Griffin, 1996b; Griffin, 1996c). One pound of free copper added to one-and-a-half pounds of mancozeb, another fungicide, is recommended as an alternative to the copper-only method (Virginia Cooperative Extension, 1997).

Using free copper as a fungicide or bactericide is not restricted to tomato crops alone. Copper is recommended for application to a number of commercially grown crops; some of which are grown on the Eastern Shore. The potato crop that once dominated Eastern Shore agriculture is treatable with copper at a rate of up to four pounds per acre per week for the treatment or prevention of early and late blight. Cucumber, eggplant, and pepper, all of which were grown under plasticulture on the Eastern Shore in 1997, can be treated with copper for a variety of diseases. Cucumber requires one-and-a-half to two pounds per acre per week after the plant begins to vine for the treatment or prevention of angular leaf spot and downy mildew. Eggplant uses two pounds per week “or as needed” for diseases such as anthracnose and alternaria blight. Application of copper is recommended before symptoms of the diseases appear. Farmers use potentially as much as three pounds per week to fight bacterial spot in peppers,

starting the first week of the crop when environmental conditions are good for disease development (Griffin, 1996a; Griffin, 1996b; Griffin, 1996c).

Copper is applied in a number of different chemical compounds for protecting crops. The first copper-based crop protectant was manufactured in 1889, and consisted of copper acetate. Some copper compounds were found effective in protecting wood from decay, including copper arsenite, and led to the now common practice of protecting wood with chromated copper arsenate. The copper compounds that are used primarily on tomato crops consist of hydroxides, basic sulfates, oxides, and oxychlorides (Meister, 1996).

Depending on the compound, these fungicides and bactericides can have very different properties. Copper oxides are very insoluble in water and most organic solvents, as are copper oxychlorides and copper sulfates (Meister, 1996). Copper hydroxide has varying degrees of solubility in water, depending on the formulation, some of which are very soluble, and some of which are not (Griffin, 1996d; Griffin, 1996e; Griffin, 1996f). The possible formulations used to apply copper hydroxide are dry or micro flowables, wettable powders, or water dispersible granules (Meister, 1996). Flowables have their active ingredient already in a liquid form, whereas wettable powders require mixing to stay suspended in the applied liquid (Virginia Cooperative Extension, 1996).

Copper is usually dispersed through a sprinkler system, such as an overhead system or through a traveling sprayer, the type used in plasticulture. It can be applied through an aerial spray, as an alternative method (Griffin, 1996a; Griffin, 1996b; Griffin, 1996c). Staking the tomato crop, and applying copper through the ground-based traveling sprayers is the method found to be most useful in covering the entire crop with fungicide (Gayle, 1996).

Precautions are recommended to growers for preventing the contamination of the surrounding waterways with copper. First, sprayers should not be used whenever the wind speed exceeds five miles per hour, to prevent drift into waterways (Griffin, 1996a; Griffin, 1996b; Griffin, 1996c; North Carolina Agricultural Extension Service, 1988). In addition, farmers should not apply crop protectants whenever the ground is already wet, which encourages runoff (North Carolina Agricultural Extension Service, 1988).

Finally, copper hydroxide should not be applied directly to waterways, or be allowed to enter waterways via runoff, due to its potential toxicity to aquatic life (Griffin, 1996a; Griffin, 1996b; Griffin, 1996c).

IV. Copper in the Environment

Copper as a natural element is found almost everywhere in the environment. Since most copper-containing compounds have very low vapor pressures, copper is not found in the atmosphere as a gas. On the other hand, copper-containing particulates can be carried long distances by the atmosphere. Copper is located in most natural water bodies, as well as in the solid crust of the planet. Copper is also found in most living organisms, and is an essential element for the life and growth of many, including mammals and shellfish. The dose of copper determines whether it is a micronutrient that sustains life or a toxic dose that limits life.

Copper occurs naturally in freshwater, at very low concentrations. This results from the natural weathering of copper containing material of the Earth's crust in the watersheds from which the freshwater originates. Average freshwater copper concentrations in the Amazon watershed, which was mostly unaffected by mankind's activities when the data were collected, appeared to fluctuate from 0.4 to 2.4 ug/L, depending on the underlying rock in the particular tributary being studied. Comparison with the similarly unaffected tributary of the Yukon River yielded similar results, with an average copper concentration of 2.0 ug/L (Boyle, 1979).

Copper concentrations were reported to be between 0.06 and 0.19 ug/L in seawater unaffected by human activity off the south coast of New Zealand (Boyle, 1979). Copper was suspected to be primarily present in complexes, especially closer to the ocean surface where organic matter was more likely to be found (Steeman Nielsen and Wium-Andersen, 1970).

Regardless of location, seawater copper is involved in a natural cycle of surface depletion by biological organisms, and deepwater repletion by the crust underlying the ocean. However, copper concentrations do increase in the top 200 meters of the ocean surface. Copper output from freshwater streams to the ocean does not account for this

surface enrichment, including those streams with elevated copper from anthropogenic activities. Thus, current knowledge cannot fully explain ocean-surface copper concentrations. The most probable explanation pinpoints atmospheric fallout from volcanic activity, or continental aerosols. In the deepest water of both oceans and estuaries, where the water becomes anoxic, copper sulfide's insolubility forces the precipitation of most of the copper present (Boyle, 1979). This precipitation is reversed when the water becomes oxygenated (Greer, 1995).

Copper in estuaries is non-conservative, meaning that estuaries may serve as sources or sinks of copper. As the copper-laden Sacramento River flows through its estuary, the copper content of the estuarine water is twice that of the river, and many times that of the low-copper ocean. This extra copper could be the result of desorption from particles in the river, sources of copper located within the estuary, or copper flux out of the sediments (Boyle, 1979). Another often-noticed estuarine process involves flocculation of copper in certain chemical forms, such as hydrous oxides or organic particulates with the increase in salinity and pH; this flocculated copper is subsequently removed by settling. Estimates of copper adsorbed to particulate matter are high for estuaries, approximately 40-60% of total copper in an aqueous sample, both in organic and in inorganic forms (Batley and Gardner, 1976).

Copper sources to the Chesapeake Bay range from riverine loading to atmospheric deposition, with non-point pollution sources in between, such as agricultural runoff and treated wood used in bulkheading (Greer, 1995; Weis and Weis, 1993; Merkle, *et al.*, 1993). Copper concentrations fluctuate with time for any one location in the Bay due to inconstant sources of copper, such as the application of agricultural crop protectants (Greer, 1995). High copper concentrations do not exist in a simple gradient over time or space in natural waters. They exist in spikes and patches, adding to the difficulty of detecting their presence. Seasonal or cyclical changes make it difficult to analyze Chesapeake Bay copper data (Luoma and Carter, 1991).

The Narragansett Bay has long been beset by anthropogenic sources of copper from military ship-plating activities. After this source of copper had been stopped in 1973, the concentration of copper did not exceed 1.0 ug/L in the Bay (Eisler, 1994). A study was performed on the Patuxent River in Maryland, where an electric station had

provided a point source of copper in years prior to 1987. The level of dissolved copper in the Patuxent River measured from 0.5 to 3.1 ug/L after replacement of copper condensers with titanium condensers (Riedel, *et al.*, 1995).

The measured range of naturally occurring copper in surficial materials of the planet is 2-100 mg Cu/kg of total sediment (Novotny and Olem, 1993). The background level of copper in the sediments depends on watershed characteristics and geology. Copper concentrations can be increased by an anthropogenic source to levels higher than their natural concentration. Sediment copper concentrations can also exceed normal concentrations by increased inputs of copper to the estuarine waters over many years from non-point sources such as agricultural runoff (McIntosh, 1991). Copper, like most heavy metals, shows a tendency to adsorb to finer particles (Novotny and Olem, 1993).

Sediments that are exposed to copper-containing waters do not immediately come into equilibrium with overlying waters. Factors such as the copper concentration and composition of the water and sediment modify the adsorption process, and determine the length of time involved. If the copper concentration of the estuarine water is decreased, then the level of copper in the sediments decreases at a similar rate. In this manner, sediments have the potential to sequester copper for years in estuaries (Turner and Alden, 1996). Some of the sediment contaminated with copper is then buried by other sediments. This process may take as long as a few weeks in the Chesapeake Bay, but takes less time in calm estuarine coves. Storms and bioturbation activities of benthic organisms can reverse this burial and re-expose the copper laden sediment to the water column (Greer, 1995).

A measurement of less than 20 mg Cu/kg sediment is expected in unpolluted sediment (Novotny and Olem, 1993), although higher copper concentrations in natural sediments have been recorded. An example of unpolluted sediment was the Rhine River Basin, where sediment copper concentrations were between 51 and 46 mg Cu/kg sediment (Novotny and Olem, 1993). An example of the potential for sediments to sequester copper for extended periods comes from the before-mentioned ship-plating incident in the Narragansett Bay. Although the concentration of copper in the water column had decreased to unaffected levels, samples of sediment measured as high as 95 mg Cu/kg dry sediment (Eisler, 1994). Alternatively, sediment copper concentrations in

the Patuxent River, Maryland did not show evidence of contamination with excessive copper eight years after the copper inputs to the estuary had been halted. This estuary contained copper concentrations between 20-25 mg Cu/kg sediment, which are expected natural values (Riedel, *et al.*, 1995).

Copper is an essential element for the life and growth of marine organisms. It is found in body tissues and it is involved in natural biological processes. A certain concentration of copper may be harmless to one individual or species and toxic to another (Eisler, 1979). Copper bioaccumulates in certain species, leading to very high internal copper concentrations (Luoma and Carter, 1991). Marine organisms can die from the bioaccumulation of copper due to increased copper concentrations in the surrounding environment (Eisler, 1979).

Species differ in the amount of copper that can be safely ingested, sequestered, and excreted, given their natural biological processes. The size of the organism matters, such that larger organisms are usually able to withstand higher levels of copper in the environment. Similarly, age matters in determining individual size and stage of development, which can also affect an individual's reaction to metal concentrations. Although species may differ in their resistance to copper toxicity, the younger life stages of each species are usually much more susceptible. Some individual organisms adapt to a high copper environment, and can withstand higher concentrations of copper than non-copper tolerant organisms. All of these characteristics, in addition to ambient levels of copper, determine the amount of copper found in an individual organism in its natural environment (Eisler, 1979).

Concentrations of copper in marine organisms vary drastically between sites and organisms. New Zealand scallops, oysters, and clams demonstrate this species variability. Mean copper levels throughout these shellfish were nine, forty-one, and nine mg Cu/kg total organism, respectively (Brooks, and Rumsby, 1965). The widgeon clam, sampled from the Narragansett Bay, exhibited approximately 37 mg Cu/kg dry organism, in an area once contaminated with copper (Eisler, 1994). The Rappahannock River estuary was home *C. virginica* with internal copper concentrations of three to 29 mg Cu/kg field weight of organism (Eisler, 1979).

In the Mussel Watch program, mussels and oysters from the coastline of the United States were sampled for concentrations of potentially toxic compounds from 1986 to 1995. For the area south of Delaware, oysters of the species *Crassostrea virginica* were collected, and exhibited no trend in copper concentrations from Delaware to Florida, including sites within the Chesapeake Bay (O'Connor, 1995).

V. Copper Chemistry

Copper is being added to the world's environment from the Earth's crust at approximately 2×10^9 kg per year by both natural and anthropogenic means. This copper comes from localized inputs such as mines and industry, and widespread inputs such as volcanic and continental aerosols. As this copper enters and accumulates in natural water systems, it becomes increasingly important to understand its effects. The chemistry of copper in natural waters has developed into a science of an interrelated system of several factors, including the physical, biological, and chemical characteristics of the water body, as well as the chemical form of the copper itself (Leckie and Davis, 1979).

Because not all copper species are similarly toxic to aquatic organisms, it is important to be able to determine which species are present in an aqueous sample, and also to know which species of copper are more toxic. Models have been created which use equilibrium equations to estimate speciation in a natural water sample, but determining the speciation of copper in an ever-changing system requires a more dynamic model than simple equilibrium calculations suggest (Boyle, 1979; Brezonik, *et al.*, 1991). Neither analytical methods nor numerical methods have been adequate to determine the exact concentrations of any metal species in natural waters, including copper (Luoma and Carter, 1991).

Functional definitions have been created to circumvent this problem, but the constituents of these functional groups are unknown. The total metals concentration is defined as "the concentration of metals determined on an unfiltered sample after vigorous digestion" (Eaton, *et al.*, 1995). Although this definition would determine the total copper in the sample, not all of that copper is going to be available to organisms, because much of it is adsorbed to sediment particles, which makes it relatively non-toxic. Soluble

or dissolved metals are “those constituents (metals) of an unacidified sample that pass through a 0.45 um membrane filter” (Eaton, *et al.*, 1995). For many organisms, the dissolved copper concentration would be a more accurate indication of toxic copper than total copper, because filtering removes much of the adsorbed copper. Bioavailable metals are those metals which are “available for uptake by living organisms” (Greer, 1995). The bioavailable copper concentration would be the most useful in determining toxic copper, but this concentration varies from organism to organism, and is therefore difficult to determine. The search continues for a more accurate indicator of bioavailable metals.

Differential pulse anodic stripping voltametry (DPASV) separates copper species into several different functional groups based on behavior of the species. One example is labile copper, which is the copper that passes through a 0.45 um filter and is adsorbed onto a Chelex-100 resin. Labile metals are thought to be the most biologically active group determined by this method and the most accurate indicator of bioavailable copper yet. This method can detect the concentrations of labile copper down to 0.005 ug/L (Deaver and Rodgers, 1996). The method is unfortunately not perfect in separating the species of a metal, such that the same metal complex might register in more than one functional group. In addition, this method cannot determine exactly which species are present in any functional group, including labile copper (Batley and Gardner, 1976). Because DPASV is time-consuming, an estimate of labile copper may be useful. The labile to dissolved copper ratio was found to be $0.53 \pm 0.01\%$, throughout the length of an estuary over two different days (Van den Berg, 1993).

Many salts, such as copper sulfate, nitrate and chloride form from the cupric ion and some of these are soluble in water. Copper complexes formed from hydroxide and sulfide are less soluble and under certain conditions, precipitation occurs (USEPA, 1985). In freshwaters, $\text{Cu}(\text{OH})_2$ and CuO , with solubility products of $10^{-19.4}$ and $10^{-20.4}$ respectively (Leckie and Davis, 1979), can become insoluble at higher pHs and copper concentrations (Snoeyink and Jenkins, 1980). Copper sulfide, with a solubility product of $10^{-36.2}$, is insoluble under reducing conditions, commonly found in anoxic deep waters of estuaries (Greer, 1995). Copper forms a number of organic compounds and complexes, with soft acids such as phthalic, pyruvic, glycollic, acetic, and formic, and

other humic and fulvic substances (Leckie and Davis, 1979). Fulvic acid-copper complexes usually exhibit low solubility (Novotny and Olem, 1993). Copper-carbon bonds are possible (Leckie and Davis, 1979).

The processes that contribute most to copper concentrations in freshwater are weathering, adsorption/desorption, and dilution (Boyle, 1979). When aqueous copper is modeled in a freshwater system without considering organic complexes, at very low pH levels, the Cu^{+2} ion is the most important species. The species CuCO_3 dominates from approximately pH six to eight, and Cu(OH)_2 and other hydroxide complexes become the most important species above that (Snoeyink and Jenkins, 1980; Leckie and Davis, 1979). A different modeling effort asserts that over ninety percent of freshwater copper is complexed with organic material, especially in the pH range six to eight with dissolved organic carbon levels between two and seven mg/L (Mantoura, *et al.*, 1978).

Under those circumstances described above, complexes with fulvic acids become the most important species, and can be estimated from a measure of dissolved organic carbon (McKnight, *et al.*, 1983). As the concentration of dissolved organic carbon increases, the concentration of ionic copper decreases. As pH rises above six, for every half a pH increment, the concentration of the Cu^{+2} ion is lowered by approximately one order of magnitude for both freshwater and seawater (Meador, 1991). An increase in freshwater hardness usually corresponds to an increase in alkalinity, causing more copper to be bound in carbonate complexes and less copper to be present in the ionic form (Snoeyink and Jenkins, 1980).

The water temperature affects the kinetics of the system. Even in a continuously altering system like an estuary, where equilibrium is a constantly changing state, and chemical reactions such as complexation occur quicker under warmer temperatures, complexing with strong chelators in natural waters takes hours to months to reach equilibrium (Brezonik, *et al.*, 1993).

The speciation of copper in estuaries and seawater is less certain than that of freshwaters. The most important processes affecting the concentration of copper in seawater are atmospheric and riverine inputs, biological processes, and adsorption/desorption (Boyle, 1979). The complete speciation of copper in seawater has been under dispute, with different researchers offering contrasting theories on the subject.

Earlier researchers attributed the major copper complexes to $\text{Cu}(\text{OH})\text{Cl}$ and $\text{Cu}(\text{OH})_2$ (Boyle, 1979). Complexation with organic ligands is thought to be less important in seawater, because calcium and magnesium ions in the seawater compete for organic bonding sites (Brezonik, *et al.*, 1991). In that case, organic complexation accounts for only about ten percent of the copper species in the seawater (Mantoura, *et al.*, 1978).

Much of the copper flowing through natural waterways is associated with particulates. Particulate copper is less likely to be biologically reactive than aqueous copper (Leckie and Davis, 1979). These particulates are of both inorganic and organic types (Batley, and Gardner, 1976). Several processes alter the percentage of copper in suspended (particulate) form. First, increasing ionic strength in freshwater as it approaches seawater causes coagulation and settling of clays with attached copper. Second, more complexing ligands are present as the freshwater turns into seawater, and copper desorbs from the particulates to form complexes with these new and competing ligands (Leckie and Davis, 1979). Adsorption/desorption processes may provide a buffering effect for the copper concentrations in estuaries (Boyle, 1979).

Copper will bind to sediments according to the chemical and physical characteristics of that sediment. Smaller-sized particles adsorb copper more readily than an equivalent volume of larger-sized particles (Novotny and Olem, 1993). Copper concentrations in the pore water surrounding sediments are often much higher than those in the overlying water column (Eisler, 1994). The concentration of various ligands in the pore water of sediments affected copper partitioning between substrates. Increasing the organic content of sediments increases copper adsorption to sediments (McIntosh, 1991). A low pH of the overlying water discourages adsorption, while at a higher pH, adsorption is almost complete (Novotny and Olem, 1993).

Sediments on the Eastern Shore become buried at a rate of approximately one to two millimeters per year, or about the rate the sea level is rising (Christiansen and Wilberg, 1996). Some areas of Eastern Shore estuaries are increasing in depth, while others are decreasing, dependent upon their location (Greer, 1995). Although certain processes such as precipitation decrease the concentration of copper in the water column, other processes such as resuspension tend to cause increased aqueous copper concentrations. Bioturbation activities of benthic organisms, dredging, and severe

weather uproot contaminated sediments, and contribute to resuspension (Burgess, *et al.*, 1993; McIntosh, 1991).

VI. Copper Toxicity

It is well known that copper can be toxic to many aquatic species at low doses (Hodson, *et al.*, 1979; Brezonik, *et al.*, 1991). The toxicity of copper to humans is orders of magnitude less. Consequently, mammals do not experience the same toxic effects of copper as aquatic organisms. Copper concentrations in natural waters may or may not be ideal for the growth of natural aquatic organisms (Hodson, *et al.*, 1979). Copper, silver and mercury are some of the most toxic metals to aquatic life, although the order of toxicity depends upon species (Bryan, 1971). Values of lethal concentrations (50%) vary among aquatic species from 5 to 100,000 ug/L (Hodson, *et al.*, 1979).

Many aquatic organisms, including *C. virginica* and *M. mercenaria*, bioaccumulate copper in their soft tissues (Sanders, *et al.*, 1991). Bivalve mollusks are known to contain several physical processes that regulate internal copper concentrations, including both removal and uptake mechanisms (Brezonik, *et al.*, 1991). Methods for uptake include membrane-exchange with ambient water, ingestion of copper containing sediments, and ingestion of copper containing biota (Brooks and Rumsby, 1965). Mechanisms that aid in the disposal of copper include metabolizing with subsequent excretion, and sequestering. Sequestering does not actually remove the copper from the tissues, but stores it safely for removal at a future time (Greer, 1995).

Some researchers report that the physical form of copper in the environment is the most important factor in determining its toxicity (Sanders, *et al.*, 1991). Possible physical forms of copper include: sediment-bound in bottom sediments, adsorbed on suspended particles, dissolved in sediment pore water, bound in suspended biota, or dissolved in the water column. Differentiating between toxicity caused by contaminated sediments or a contaminated water column is difficult (McIntosh, 1991). Despite this, some information regarding physical phase and copper toxicity is known. Pore water toxicity in natural sediments is not usually caused by heavy metals (Burgess, *et al.*, 1993). Contaminated suspended sediments are more toxic to aquatic life than

contaminated bottom sediment. The smaller the particle on which the copper is adsorbed, the more toxic the copper is likely to be (Ihsan, *et al.*, 1993). Bivalve mollusks take up more copper from biota than from surrounding sediments (Greer, 1995).

When considering only the copper that is located in the water column, the chemical form of the copper determines its toxicity (Davey, *et al.*, 1973). In natural waters, copper forms complexes with various constituents, and these complexes vary in their toxic effects. Toxicity is related more closely to ionic copper than total copper, (Zamuda and Sunda, 1982) still, some other copper species also affect toxicity. Organic complexes with copper are less likely to be immediately available to aquatic organisms, but are more likely to be bioaccumulated (Brezonik, *et al.*, 1991). Complexes with inorganic material, such as hydroxyl species, sometimes contribute to toxicity, although carbonate complexes are usually non-toxic (Meador, 1991). Because determining the exact copper species present in a water sample is not possible, labile copper can be used as an indicator of biologically available copper. Toxicity to *Hyaella azteca*, an amphipod, occurs between 42 and 142 ug/L total copper, but only between 17.4 and 24.8 ug/L labile copper, measured by DPASV. The smaller range more accurately predicts toxicity, but the exact species included in the labile component are unknown (Deaver and Rodgers, 1996).

The most important factor in determining the toxicity of copper in natural waters is the amount of complexing material present (Hodson, *et al.*, 1979). The organic complexes are of particular importance, especially in soft water. In order to maintain the same LC₅₀ when increasing the dissolved organic carbon concentration, the total copper concentration needs to be increased (Meador, 1991). When clean waters are subjected to contaminated sediments, toxicity is noted, but the addition of EDTA, an organic chelator, decreases this toxicity dramatically. (Burgess, *et al.*, 1993)

Inorganic complexing material ameliorates copper toxicity as well. Calcium and magnesium compete for the same binding sites on organisms, and therefore increasing the hardness of a water decreases the toxicity of copper in that water (Brezonik, *et al.*, 1991). With increasing hardness usually comes increased alkalinity, whose carbonate ions complex copper into generally non-toxic complexes (Snoeyink and Jenkins, 1980). Metals in hard water are always less toxic, given a constant pH (Guthrie and Perry,

1980). In a similar vein, hydrogen ions also compete with copper ions for organism binding sites (Meador, 1991). Seemingly contradictory, a lower pH increased copper toxicity, because increased ionic copper concentration occurs with lower pH values (Guthrie and Perry, 1980). At pH values higher than seven, the same amount of ionic copper is more toxic the higher the pH, indicating that other copper complexes might add to toxicity (Ihsan, *et al.*, 1993; Meador, 1991).

Other environmental factors change copper toxicity, such as salinity and temperature. Salinity is not a significant factor in determining the toxicity of many different contaminants (Guthrie and Perry, 1980). Components of salinity add to the inorganic complexation of copper, which causes a decrease in copper toxicity in saline waters. Salinity facilitates the feeding of bivalve mollusks, increasing uptake of copper in oysters, but salinity's affects on the oyster's ability to process copper are unknown (Greer, 1995). Lower salinities can stress aquatic organisms, lowering their natural defenses against copper toxicity (Hodson, *et al.*, 1979).

Similarly, adverse temperature conditions, generally considered as higher than average temperatures, can stress organisms and add to copper toxicity. A higher temperature lowers the dissolved oxygen concentration, which is another possible source of stress. As with salinity, some physical processes may increase with increasing temperature, possibly resulting in a faster uptake of copper than can be safely removed by the organism (Cairnes, *et al.*, 1975). Temperature's affect on metal toxicity appears to be species dependent (Guthrie and Perry, 1980). Several species of freshwater fish do not experience a change in copper toxicity with changing temperature (Rehwoldt, *et al.*, 1972). On the other hand, *Mercenaria mercenaria* experiences no mortality when subjected to metal-dosed water at six degrees Celsius, but experiences significant mortality when subjected to the same water at twenty degrees Celsius. Of the metals in that metal-dosed water, copper is suspected to be the contaminant that causes toxicity. (Eisler, 1994)

The presence of other potentially toxic metals in natural waters makes determining the effects of any one more difficult (Luoma and Carter, 1991). Little can be inferred from laboratory tests, because most generate toxicity data from single-contaminant experiments. Metals may work synergistically or antagonistically to

increase or decrease toxicity above or below their single-contaminant thresholds (Hodson, *et al.*, 1979). The possibility of organic and inorganic contaminants in the same natural waters presents a situation too difficult for most researchers to consider (Luoma and Carter, 1991).

Toxic effects of copper change dramatically in relation to age or life-stage differences change toxic effects dramatically (Bryan, 1971). In general, younger stages of life are more sensitive than older ones to copper contamination, although eggs are sometimes more resistant than the young (Hodson, *et al.*, 1979). Reproducing puts the mature adults at risk of copper effects as well. The reproductive system is very sensitive to metal contamination in most species, and *Mytilus edulis*, or marine mussel, becomes more sensitive after spawning because its energy reserves are depleted (Luoma and Carter, 1991).

Besides the mortality of an organism, sub-lethal effects of metal contamination can damage aquatic organisms in contaminated environments. No relationship exists between chronic and acute toxicity to an organism, and sub-lethal effects are documented for copper levels between five and 100,000 ug/L (Hodson, *et al.*, 1979). These effects can be unnoticeable in whole animals, becoming significant only at the cellular level (Greer, 1995). Some possible effects of copper on bivalve mollusks include decreases in respiration due to gill damage (Hodson, *et al.*, 1979), greening in oysters, and prevention of settling and attachment in barnacles and scallops (Bryan, 1971). Other effects include poor growth and increased susceptibility to disease (Greer, 1995). Elevated tolerance of higher than ideal copper conditions is noted in certain species (Luoma and Carter, 1991).

The effects of metal contamination in a natural system extend beyond simply killing the most sensitive species. An example is the alga population in the Chesapeake Bay. More sensitive species have been replaced by less sensitive ones, causing shifts in the make-up of the population. If these new algae had been less nutritious to filter feeders, such as bivalve mollusks, ecological catastrophe could have occurred (Greer, 1995). Tracing a system problem to a single contaminant proves to be difficult (Luoma and Carter, 1991). In one stream, copper contamination in sediments was the cause of taxa count reduction, but such examples are rare (McIntosh, 1991).

Due to the economic importance of bivalve mollusks, several species have been utilized to determine copper's toxic effects. The marine mussel, *Mytilus edulis*, demonstrates the extreme sensitivity of these organisms to copper in natural waters. Five to six ug/L total copper and 400 ug/L total copper are the upper limits for embryonic and larval survival, respectively. Over 30 days, the upper limit for adults to experience soft-tissue growth is ten ug/L total copper. The four, ten, fourteen and 30 day LC₅₀s are 200-300, ninety, fifteen, and two ug/L total copper, respectively (Luoma and Carter, 1991).

Argopecten irradians, the bay scallop, is another economically important and related organism. Bay scallops were grown on the Eastern Shore of Virginia in aquaculture facilities in 1996 and 1997. Growth of soft-tissue for this species is stunted at 5.8 ug/L ionic copper, and the scallops detach at that concentration. The 42 day, LC₅₀ for this species was 9.3 ug/L ionic copper. (Pesch, *et al.*, 1979)

Mya arenaria, the softshell clam, was tested for copper toxicity at several different temperatures to determine the effect of season. The summer, seven-day LC₅₀ at 22 degrees Celsius, is 35 ug/L added copper, which proves summer to be the most sensitive season. In the autumn, the LC₅₀ drops to 21 days at seventeen degrees Celsius, and is 86 ug/L added copper. Winter is the least sensitive season, with a fourteen day, four degrees Celsius LC₅₀ of over 3000 ug/L added copper (Eisler, 1994).

Corbicula manilensis, the freshwater clam, is not as sensitive to copper contamination as some of its marine relatives. As larvae develop through their subsequent stages, they become more resistant. The trochophore larvae cannot close their shells to avoid copper contamination, and after one hour in a solution of ten ug/L added copper, 91.5% are dead. The later two developmental stages close their shells upon copper exposure, and have a one-day LC₅₀ of 28 and 600 ug/L added copper. The adult clams are very resistant to copper, with a 96 hour LC₅₀ of over 2,600 ug/L added copper (Harrison, *et al.*, 1984).

C. virginica, the American oyster, is one of the species grown in aquaculture on the Eastern Shore of Virginia. Embryos experience an LC₅₀ of 103 ug/L added copper, determined by those that develop into straight-hinge larvae within normal time limits (Calabrese, *et al.*, 1973). Larvae experience a lower LC₅₀, at twelve days in 32.8 ug/L

added copper. At this concentration, surviving oyster larvae grow only 67.7% of the control group growth.

M. mercenaria, the hard clam, is the last of the species grown in aquaculture on the Eastern Shore of Virginia. Larval clams in eight to ten day trials, experience an LC₅₀ of only 16.4 ug/L added copper. Percent growth compared to controls at this copper level is only 51.7% for this species, showing their greater sensitivity to copper (Calabrese, *et al.*, 1977).

VII. Regulations on Copper

The Commonwealth of Virginia follows the dictates of riparian water rights. Riparian water rights include the ability for every landowner located next to a waterway to use the full extent of the stream's waters. This is true of every landowner along the course of that waterway. Therefore, once the waterway passes beyond the lower edge of the property, it must be in the same condition as when it entered the upper edge. The only restrictions on the use of this water are that the water use be reasonable (Novotny and Olem, 1994).

Federal dictates on the quality of waterways began early in the twentieth century but serious legislation started with the Clean Water Act of 1972, and the Clean Water Act Amendments of 1977 (Novotny and Olem, 1994). Section 307 (a) of the 1972 document created a list of sixty-five toxic pollutants, and section 304 (a) of the 1977 document required the USEPA to publish criteria on these pollutants, evaluating scientific knowledge of health and welfare effects. For copper, the saltwater criteria are 4.0 ug/L as a twenty-four hour average, and not to exceed 23 ug/L at any time, with copper measured in total recoverable copper. The freshwater criteria are 5.6 as a twenty-four hour average, and not to exceed $e^{(0.94[\ln(\text{hardness})]-1.23)}$ ug/L at any time, still as total recoverable copper (USEPA, 1985).

The criteria published under section 304 (a) are not enforceable, but section 303 of the 1977 document provides for the implementation of State water quality standards. Virginia's water quality standards were published in 199, and included an ambient water quality standard for copper in saltwater and freshwater to protect aquatic life. The

saltwater criteria are 2.9 ug/L dissolved copper both as a one hour concentration not to be exceeded more than once every three years, and as a four-day average not to be exceeded more than once every three years. In this case, the acute standard applies to the chronic case as well. The freshwater criteria are different, and state that the acute standard should be $e^{(0.9422[\ln(\text{hardness})]-1.464)}$ ug/L dissolved copper one hour average not to be exceeded more than once every three years. The chronic standard is $e^{(0.8545[\ln(\text{hardness})]-1.465)}$ ug/L dissolved copper four day average not to be exceeded more than once every three years. The hardness in the previous equations is expressed in mg/L as CaCO₃ with a minimum of 25 mg/L and a maximum of 400 mg/L (Virginia DEQ, 1992).

In 1995, the USEPA published a draft for an update on the ambient water quality criteria for copper in saltwater. The acute criteria, here defined as a twenty-four hour average concentration not to be exceeded every three years, is now placed at 4.8 ug/L dissolved copper. The chronic criteria, here defined as a four-day average concentration not to be exceeded every three years on average, is now only 3.1 ug/L dissolved copper. For both criteria, the Virginia State regulatory level is more stringent, although the definition for acute exposure time is different (USEPA, 1995).

A number of programs have been created which aid in the preservation of the Eastern Shore's sensitive water. The 1972 Coastal Zone Management Act, for example, provides a means for States to access funding for the preservation of sensitive coastal areas. The Chesapeake Bay Program, in the 1987 Water Quality Act, aids in the restoration of the Chesapeake Bay to former ecological quality. In the same Act, the National Estuary Program provides funding for research into estuarine areas, mostly conducted under NOAA's Sea Grant. The 1985 Food Security Act aims to reduce agricultural non-point source pollution by providing funding for retiring erodible lands and lands located next to waterways (Novotny and Olem, 1994).

The largest improvement in abating agricultural non-point sources comes from voluntary programs that provide governmental monetary and technical assistance for farmers. This assistance is for implementing programs that protect the environment from the farm's non-point source pollution, and often have beneficial effects for the farmer as well as soil or crop protectant conservation. Most farmers consider themselves good

stewards of the land, and implement these programs, often with their own labor, and occasionally to no benefit of themselves or their farm (Novotny and Olem, 1994).

These programs are called Best Management Programs (BMPs), which range widely in their cost, effectiveness, and scope. A grass filter strip is an example of a vegetative BMP that provides a border between cropland and water body.

Implementation of a filter strip prevents sediment from flushing off the field into the adjacent waterway whenever a heavy rainfall occurs. This helps the farm in providing for soil conservation and preserves the water body by preventing excessive turbidity, which is harmful to aquatic life (Virginia DCR, 1997). Although they are effective tools against soil loss, filter strips have their limitations. Filter strips have a limited life span before their ability to catch sediment is overrun, and using them as a turn-lane or careless spillage of herbicides on the grass sometimes leads to the buffer strip's destruction. They stop sediment-bound crop protectants from leaving the field area, but dissolved crop protectants flow through to the water body. They are effective against sheet flow, but more concentrated flow will carve channels through the strip. In essence, all BMPs have their uses and their limitations in preventing non-point source pollution from agricultural lands (Novotny and Olem, 1994).

Best Management Practices for reducing field loss of crop protectants are classified into categories including application efficiency improvement, integrated pest management, soil and water conservation practices, and substitution of more appropriate crop protectants (North Carolina Cooperative Extension Service, 1984). For metals such as copper, the following BMPs were recommended: crop/plant selection for less metal usage, integrated pest control, reuse or recycle of runoff as irrigation water, filtration of runoff, and an artificial wetland or similar biological filtering system for treatment of runoff. Any or all of these BMPs can be implemented with the government's assistance for the prevention of metal contamination from agricultural areas (Novotny and Olem, 1994).

In some cases, preventing the loss of copper-based crop protectants is not a voluntary choice. Farmers who do not apply crop protectants according to their labeling instructions are in violation of federal law. Water from washing out copper hydroxide application equipment must be carefully disposed of so that none reaches the waterways.

Wind speeds during application must be low enough so that significant drift away from the intended area does not occur. Finally, under no circumstances is copper hydroxide to be applied to waterways themselves (Griffin, 1996a; Griffin, 1996b; Griffin, 1996c) All of these dictates result from an understanding of copper-based crop protectants' extreme toxicity to aquatic life.

VIII. Related Research on the Eastern Shore

Investigators of Chesapeake Bay water quality usually think of the Eastern Shore as a pristine area, and use sites within the Eastern Shore as reference sites when conducting research. Unfortunately for researchers, the Eastern Shore can exhibit changing water and sediment conditions, typical of areas with diffuse pollution sources such as agriculture. For example, the Wye River, actually located on Maryland's Eastern Shore, was tested on several occasions for toxicity to benthic organisms. Although the Wye River exhibited no toxicity throughout most of the tests, significant toxicity was noted on at least one occasion. In addition, variability was noted in some other locations' toxicity values, indicating temporally changing inputs to the estuarine sites. Researchers implied that agricultural activity within the watersheds was the probable reason for this variability (Turner and Alden, 1996).

Several agencies are concerned about the impact that plasticulture may have on diffuse pollution on the Eastern Shore of Virginia. The Commissioner of Agriculture and Consumer Services created a committee in 1996 to investigate complaints from the aquaculture industry that agricultural runoff from fields planted in plasticulture was adversely affecting water quality and therefore the aquaculture industry. A scientific sub-committee was commissioned to report on relevant knowledge on the topic and make suggestions for future research. These suggestions included research into clam mortality, to determine if agricultural runoff is indeed the culprit, and tomato plasticulture, to determine methods for decreasing pollution without harming the agricultural industry (Wilson and Callender, 1997).

The Eastern Shore Soil and Water Conservation District also looked into the effects of plasticulture. They created an inventory of plasticulture tracts and BMP needs,

with over 2,500 acres in the inventory. Their efforts were hampered by the fact that fields can only be investigated after the raised beds have been created, because this tends to change runoff patterns. Some pilot programs of BMPs were implemented with early results. Because plasticulture concentrates runoff from the field, grass buffer strips are not effective with plasticulture, because this BMP works best with sheet flow runoff. Alternative BMPs were therefore investigated, including filters, sediment traps, removing erodible lands from use, and others (Virginia Association of Soil and Water Conservation Districts, 1997).

Concern has been so great that The House of Representatives of the Commonwealth of Virginia passed a resolution in 1997 encouraging the investigation of this problem. The resolution stated that plasticulture does increase runoff, which may impede water quality, and potentially harm aquaculture facilities. Furthermore, several different governmental agencies were responsible for overseeing the problem. Therefore, the resolution created a committee of several agency heads to investigate and report upon the Commonwealth's action in this matter, including the Department of Environmental Quality, and the Commissioner of Agriculture and Consumer Services (Virginia House of Representatives, 1997).

Because tomato growers use several different crop protectants that in high enough doses could cause toxicity to shellfish, investigators have searched for signs of any crop protectants in the waterways of the Eastern Shore in the waterways. Subsequently, researchers from Virginia Polytechnic Institute and State University have found several of the organic crop protectants used in tomato plasticulture on the Eastern Shore. Metolachlor was detected in more than half of the water samples, but in low concentrations no greater than 0.5 ug/L (daCosta, 1997). However, metolachlor is known to be a very leachable chemical, it is possible that it seeps from the fields into the groundwater, and feeds into the tidal creeks and estuaries underground (North Carolina Extension Service, 1988). Researchers have also found traces of metribuzin and trifluralin in waterways, the other two herbicides used in growing tomatoes under plasticulture.

Endosulfan, an insecticide used in tomato plasticulture, was often found in the waterways of the Eastern Shore. Endosulfan is considered highly toxic to aquatic life,

with a reported 96 hour LC₅₀ of 0.4 ug/L to American oyster embryos (Volger, 1996). A puddle by the side of the road yielded 4.17 ug/L endosulfan in March 1997, months after the nearby field had been converted from tomatoes to a grain crop. It is therefore not surprising that concentrations of 2.11 ug/L and 1.96 ug/L were found in the corresponding tidal creek in February. The previous summer, a sample taken at the downstream aquaculture facility registered 0.97 ug/L endosulfan (daCosta, 1997).

The Virginia Institute of Marine Science has investigated this problem from a different perspective. Instead of looking for the agricultural chemicals directly, they used an in-situ bioassay using *Palaemonetes pugio*, or grass shrimp, to determine water body toxicity, and attempted to associate that toxicity to plasticulture acreage in the watershed and rainfall. By monitoring other water properties such as dissolved oxygen and salinity, they were able to rule out toxicity from natural environmental conditions. In several watersheds, toxicity was noted following rainfall, especially in the Gargathy Creek watershed, where 100% of the grass shrimp died after several heavy rainfalls. A MetPADTM assay for metal toxicity indicated that metal toxicity was present in some of the locations and on some of the dates where toxicity was noted. The attempt to associate toxicity to acreage in plasticulture was somewhat successful, but direct correlations could not be made. Researchers indicated that the results were highly influenced by the placement of the shrimp cages within the creek and their relative distance from plasticulture (Luckenbach, *et al.*, 1996a; Luckenbach, *et al.*, 1996b).