# Study on the Post-Mortem Identification of Pollutants in the Fish Killed by Water Pollution: Detection of Arsenic

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Arsenic is distributed widely in the environment and any sample of water system will be found to contain a small quantity of arsenic (LEE, 1972) provided that a sample of sufficient of size is analyzed by suitably sensitive method. Arsenic compounds, cacodylic acid (CA), disodium methyl arsonate (DSMA) are still used as pesticides, giving rise to high arsenic levels in soils and air at the time of application. In the cotton growing tract of South and Southeastern United States arsenical herbicides are applied for weed control as well as for defoliation of cotton plants prior to its machine picking. Dimethylarsenic acid (HAMME et al. 1970) is one of the major herbicide used in the United States Air Force Program of restricting forest foliar growth in the area of their interest.

It does not appear that any impairment of human health and damage to the ecosystem, in general, results from the careful use of arsenic compounds in the field of their recommended application. In contrast to these background levels, several community episodes have been reported in which large amounts of arsenic, injudiously applied, gave rise to substantial contamination of the water system, posing a potential hazard to animal and human population. Injury to vegetation and animals occured in the areas adjacent to plants engaged in smelting ores containing arsenic (HAYWOOD, 1907). Water may be contaminated by dumping a large amount of chemicals into water system either by accident or unauthorized disposal. For example, a truck trailer carrying arsenic weed killer was involved in a traffic accident (GOULD, 1970). The contents spilled over the highway and were washed subsequently into the river. An agricultural aircraft operator placed "used" pesticide containers in a ditch, which drained into a large water system where many fish died. Another sprayed a city reservoir with a defoliant. He was treating the surrounding fields and did not shut off his apparatus as he criss-crossed the reservoir. This type of acute accidential contamination from arsenical chemicals has long range and immediate significance. Arsenic poisoning and injury to humans have also been reported from CHILE (OYANGUREN and PEREZ, 1966) and in one of the western states from the United States.

## MATERIALS AND METHODS

The fish in a small reservoir, built on a creek 20Km. Southwest of Orangeburg, were reported dying, following an aerial



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spray of an adjacent field for weed (mainly Amarantha) control and defoliation of plants before machine picking of cotton. This investigation was undertaken to determine the cause of large scale fish killed in this reservoir. It is about 1/2 acre fish pond with an average depth of 4 ft. and 75 ft. wide, located right next to the cotton field and surrounded by cultivated farm land, cropped with soybean, corn, cotton, etc. The creek feeding the reservoir collects the drained and runoff water from the surrounding fields. The surrounding tract of area has a gentle slope into the creek and reservoir. The creek passes through the fish pond and finally discharges into the Edisto River. The acreage of the creek watershed is not precisely known but the water supply through the creek to the fish pond is enough to maintain adequate water level throughout the year. The pond has liberal aquatic vegetative growth and there must be abundant supply of natural food as the aquatic animal population did not receive substantial amount of synthetic food supplements during the year. The reservoir is extensively used for fishing, rowing and other family recreation needs.

Large number of killed fish was seen floating on the surface of the reservoir water. Some dead insects, larvae, and a few mayflies were also noticed. Three killed catfish (Ictalurus punctuaus) approximately of the same size and each weighing about 400 grams were sampled, after about 30 hours of aerial spray of cotton, for the post-mortem identification of pollutants killing fish. No exceptionally characteristic physical visual change was noticable except that the dead fish was in the early state of putrefaction as evidenced by the foul odor from their bodies. Three samples of water were also drawn from three locations of the pond. Two water samples, 1 Km upstream were also drawn as a check against potential killer pollutant.

The sprayed cotton field was carefully inpected. The field was full of all kinds of weeds which practically were over growing the cotton crop. The weed foliar growth was found extremely damaged. The leaves were drooping down and seemed scorched. No appreciable injury to cotton foliar growth was noticed at this state, partially due to the fact that it was almost covered by the weed growth. A rabbit and a few birds were found dead in the field. The attempt was not made to ascertain the cause of their death. Cocklebur (Amarantha) leaves were sampled in triplicate from three different locations where the foliar injury seemed acute. Cocklebur leaf samples, in duplicate were also collected, from a nearby unsprayed soybean field across the fish pond. Another set of cocklebur leaf samples were also collected from an unsprayed cotton field about 8 Km apart. Care was taken to sample plants similar in size and age. Between the spraying of cotton field and sampling there was no rain or irrigation applied.

During the weeks that followed there were heavy rains (10 inches) in this area and the pond became alive again with aquatic animal activity. Another set of samples of reservoir water and catfish were drawn, in triplicate, after a period of seven weeks to evaluate the pollutant's status in fish and reservoir water.

Part of the water samples were preserved with nitric acid and stored at room temperature. The leaves were chopped, dried in an air oven at 70°C overnight and ground to fine powder. One gram of the representative leaf material in duplicate was digested with nitric and perchloric acid (PERKIN-ELMER CORP, 1971) and the final volume diluted to 100 ml with deionized water.

Half a gram of representative fresh fish muscle tissues were transferred to a flask. It was solubilized in concentrated sulfuric acid and incubated (PERKIN-ELMER CORP, 1971) in a shaking water bath at 60°C to get a clear solution. The volume was diluted to 100 ml with deionized water.

The samples thus prepared were directly aspirated into the Atomic Absorption spectrophotometer Perkin-Elmer model 306, under standard conditions, using Argon-Hydrogen flame and three slot burner head.

## RESULTS AND DISCUSSION

The results of analysis are given in Table I. The extensive distribution of arsenic in pond water and weed (Amarantha) vegetation across it showed that the aircraft operator dumped a certain amount of herbicide in the surroundings while criss-crossing the reservoir during the aerial spray of the adjoining cotton field. Runnoff contamination was impossible because of rainless period before and after the spray application of herbicide. All compounds of arsenic are toxic and death to humans, animals or plants may occur from relatively small amounts (LEE, 1972). Threshold limit value (TLV) (as applied to humans) for arsenic and its compounds expressed as arsenic is 0.5 $mg/m^3$ (DINMAN, 1960). In case of arsenic lethal dose (L.D.) 50 for man, bee and rat is 4, 0.8 and 20 PPM, respectively (GIDDINGS and MONROE, 1972). However, the tolerance of arsenic poisoning to man and other animals can be induced through gradual habituation. Effects of arsenic and its compounds on fish and aquatic life are well summarized (MCKEE and WOLFE, 1963) but careful searching of literature does not present a unanimous view, as the experimental conditions in each case were different, on the extent of damage that can be done to fish in general, by the variable concentrations of arsenic. Arsenic concentrations of about 2 parts per million have been found toxic to the fish. Twenty seven parts per million sodium arsenite, expressed as arsenic, was reported lethal (SUBCOMMITTEE ON AIR AND WATER POLLUTION, 1970) to channel catfish when exposed for 24 hours.

Fish pond under natural conditions is an ecosystem of variable heterogenous phenomenon and in the present study no attempt was made to evaluate the aquatic environmental conditions of fish other than the determination of herbicides that could possibly be used for cotton weed control. The average concentration of arsenic in the pond water as reported (Table I) here seemed strong enough for fish killing. In addition, pockets of higher concentration than the average could have been formed, temporarily, near the surface of water as the dispersion of arsenic,

TABLE I

Distribution of Arsenic in Vegetation, Fish and Water

| | Concentration Parts Per Million | |
|---|---|---|
| Amarantha Leaf Tissues | | |
| Cotton Field | Soybean Field Across Pond | Cotton Field 8Km away |
| Sprayed 7.35 | Unsprayed 3.01 | Unsprayed 1.01 |
| Fish Muscle Tissue | | |
| 30 hours 5.09 | | 7 weeks 12.38 |
| Water Samples | | |
| 30 hours | | 7 weeks |
| Pond 2.50 | Upstream 1.44 | Pond 1.91 |

*Averaged over six determinations

A few herbicidal compounds along with certain water parameters, pertinent to the probable cause of fish kill, were also looked into, through detailed water analysis. The result findings did not give any positive support to the investigative objective, so are not reported here.

horizontal or vertical through diffusion mechanism could not have been instantaneous. Moverover, the original arsenic concentration in water may have been higher than the one reported here because some of it was expected to be absorbed by the aquatic vegetation and animal population before water sampling. Sohacki, (1968) reported that the aquatic plants showed variable concentration of arsenic after 2 hours of its application to a fish pond. The fish and other biotic-pond population that became a direct target of herbicide falling from the aircraft along with those that were caught within high herbicidal concentration pockets near the surface of water may be the one that suffered larger degree of casualities. Whatever the case, the killed fish accumulated abnormal level of arsenic and concentration of it in fish was much higher than that of its surrounding water system.

The fish that survived the initial damage or escaped lethal injury became aclimated, with passing time, to their hostile environment and continued bioaccumulation of arsenic. Over a period of seven weeks the ratio of arsenic in fish and pond water became wider (6.5:1). The arsenic absorption by fish population seemed irreversable as the arsenic level in fish increased considerably with time, rather than falling down, though the water arsenic level decreased over the period between samplings. It has been reported that oyster, fish and some other aquatic population are capable of multifold irreversible bioaccumulation of toxicants from the water system in which they live (GOULD, 1970). The long range or indirect effect of bioaccumulation phenomena is most distributing as the herbicidal poison in fish could build to a level high enough to pose a potential hazard to the consumer.

The negative analytical water results for a pollutant may or may not be indicative that the eatable aquatic population is free from injurious chemical, and the arsenic water content, however, meager it may be, cannot be used as a guide to predict its potential accumulation in the fish. The results showed that though the arsenic level of water decreased over a period of seven weeks, the bioaccumulation of it continued to grow in fish.

The decrease in arsenic content of water may be attributed to the flushing of the reservoir due to heavy rains during the period, following the aerial spraying of cotton and before resampling time, and also its probable absorption by bottom sediments. Studies on the dynamics of arsenic in the aquatic environment have been reported by Sohacki,(1968). He found that within 2 months after treatment of a pond considerable amount of arsenic accumulated in the sediments and arsenic was penetrating into the deeper layers of bottom mud. Certain amount of arsenic undoubtedly was also absorbed by the aquatic vegetation.

## SUMMARY

Careless Herbicidal aerial spray of a field for weed control and defoliation of cotton before machine picking, resulted in the contamination of an adjoining reservoir, killing large volume of fish. The dead catfish, along with water and Amarantha weed leaves analyzed contained relatively high levels of arsenic concentrations, indicative of arsenic being the probable cause of fish killing. The arsenic absorbed by fish was irreversable and its bioaccumulation continued in the surviving fish though the water arsenic level fell during the following weeks.

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