

THE ARSENIC CONTENT IN SOIL FOLLOWING REPEATED APPLICATIONS OF GRANULAR PARIS GREEN

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Since Barber and Hayne first reported on the use of paris green as a mosquito larvicide in 1921, very little research has been conducted on the persistence of this material in the soil and water to which it is applied. According to Barber (1941), Misseroli, an Italian investigator, stated in a 1917 publication that an accumulation of arsenic through many applications in the same water does not take place because any dissolved arsenic is volatilized by the microflora of the water. Morin (1933) also stated that there is no accumulation of arsenic in water because aquatic flora convert the arsenic to ethylarsenine. However, de Benedetti (1935) stated that the disappearance of arsenic in water dusted with paris green is due to the fact that it is buried in the mud at the bottom and not to the action of molds or aquatic microorganisms. Bishop (1940) by chemical analysis of soil samples demonstrated the accumulation of arsenic residues at the bottom of reservoirs from routine applications of paris green applied at 1 pound per acre. However, his data were quite variable and in some instances did not seem to support this conclusion. He further stated that areas receiving herbicidal treatment (sodium arsenite) had a greater accumulation of residual arsenic than those receiving only larvicidal treatment (paris green). Bishop also stated that in areas having high residual arsenic content (115 p.p.m.) there was no apparent injury to vegetation or bottom organisms and fish were not rendered unfit for human consumption. Although the preceding is not a complete summary, actually very little research has

been conducted on the fate of arsenic applied as paris green for mosquito control.

METHODS. A series of individual impoundments, each 20 feet long by 10 feet wide, were constructed in the salt marsh on the east coast of Florida. The entire group of impoundments was surrounded by a ditch, the water in which was used to flood the impoundments by means of a pump mounted on a flat bottomed barge. Two treated plots and the untreated check plot were flooded to a level of 18 inches and granular paris green (Rogers and Rathburn, 1960) at a rate of 15 pounds per acre of 5 percent by weight of paris green was applied by hand shaker evenly over the treated plots at each treatment. All plots were kept flooded to a level of 6 to 18 inches for 1 week after treatment. The plots were then allowed to go dry, and at the end of the second week soil samples were taken from each plot. Twelve subsamples, each 1/12 square foot and 2 inches deep, were taken in each plot by means of a circular soil sampler of the same dimensions. The plots were then reflooded, retreated, and after another 2 weeks, resampled. This procedure was followed until 8 applications of granular paris green were made and 8 soil samples were taken in each plot.

The soil samples were obtained uniformly throughout all plots by taking at random 3 subsamples in each of the 4 quarters of each plot. This type of systematic (restricted random) sampling was used since it results in a more adequate representation of all parts of each plot than the completely random sample. The samples, consisting of the 12 subsamples, were then dried in an oven at 90° to 100° F., finely ground in a hand grinder, well mixed by hand and subsampled. Subsampling was accomplished

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by dividing the sample into halves, one of which was mixed and further divided into halves. This procedure was followed until a subsample of approximately 10 to 20 grams remained. From this, two 5-gram portions were then digested with boiling sulfuric and nitric acid (Snell and Snell, 1949) in a microkjeldahl apparatus and analyzed for arsenic by means of the silver diethyldithiocarbamate (AgDDC) method (Anonymous 1960). A soil sample from the treated and untreated plots before treatment and after treatments 2, 4, 6 and 8 were analyzed in July 1963. The remaining samples were extracted,

TABLE 1.—The amount of arsenic in the soil following applications of granular paris green to the water surface of experimental impoundments.

Number of treatments	Micrograms of arsenic per gram of soil—p.p.m.			
	Treated	Untreated	Difference	Calculated
Pre-treatment	1.76	1.08	0.68	0.00
1	0.08
2	1.55	1.38	0.17	0.15
3	3.45	2.69	0.76	0.31
4	2.75	2.02	0.73	0.39
5	2.84	2.13	0.71	0.46
6	3.18	2.78	0.40	0.54
7	2.63	2.13	0.50	0.62
8	2.39	2.03	0.36	0.69

stored and analyzed in May 1965. As a check on extraction and analytical procedures, soil containing 1 microgram of arsenic (as paris green) per gram of soil was prepared from soil obtained from the plots before any treatment was applied.

RESULTS. The amount of arsenic in the soil preceding treatment and following each application of paris green is shown in Table 1. The figures shown for the treated plots are averages of 4 analyses except for treatments number 2 and 3 which are averages of 3 analyses and the pretreatment which is an average of 2 analyses. The difference shown in Table 1 is the amount of arsenic in the treated plots minus the amount in the untreated plots.

From the data obtained there appears to be no evidence of an accumulation of arsenic in the soil following repeated applications of granular paris green to the water surface. However, the amount of arsenic that is added to the soil as paris green even in 8 applications is obscured by the high amount of naturally occurring arsenic and the variations obtained in sampling. By chance, the soil samples from the plots designated to be treated contained a greater amount of arsenic than those designated to be untreated when all the plots were sampled prior to any treatment, and this difference is equal to the theoretical amount of arsenic applied as a result of all 8 treatments. Also, the amounts of arsenic obtained in the treated and untreated plots varied more than this total theoretical amount, as evidenced by the 3.45 micrograms obtained after 3 treatments as compared to 2.75 micrograms obtained after 4 treatments.

Eight applications of granular paris green are more than would normally be applied to an area during 1 year of mosquito control operations. In a normal year 2 or 3 applications may be applied to a single area. Therefore, by applying 3 to 4 years of treatments in a single season, the accumulation of arsenic, if a factor, should be more pronounced.

The accuracy of the analysis is supported by the results of arsenic determinations obtained with samples containing known amounts of arsenic. When the amount of arsenic naturally present in the soil was subtracted from the total amount found to be present in the prepared sample, the difference was the exact amount which originally was added to the soil.

Difficulties were encountered in the analyses performed in 1965. Because of interference from a black precipitate, probably sulfur from the cork stoppers used to seal the samples, only $\frac{1}{3}$ of the extract solution (10 ml.) could be used in these analyses. This small aliquot definitely reduced the accuracy of these analyses. However, no significant differences in the data were noted between these analyses and those performed in 1963.

Therefore, the results of the analyses performed in both years were combined. All the samples obtained after treatment number 1 were lost due to the interference of the black precipitate.

In the last column of Table 1 are shown the calculated amounts of arsenic which theoretically should be present in the samples as a result of the treatments. These calculated amounts of arsenic are cumulative and are based upon an application of 15 pounds per acre of 5 percent paris green by weight of which 40 percent is arsenic and assumes a soil weight of 90 pounds per cubic foot. These figures are offered for comparative purposes and also to demonstrate the small amount of arsenic that is added to the soil as a result of applications of granular paris green.

Between treatments number 2 and 3 an application of granular paris green at the same rate as used in the experiment was applied to the area inadvertently during routine mosquito control operations. This appears to be reflected in the increase in the arsenic content of the experimental plots between treatments number 2 and 3. This application also was taken into consideration in calculating the theoretical amounts of arsenic present in the soil as a result of the treatments.

DISCUSSION. These experiments were conducted on a sandy loam soil on the lower east coast of Florida. Since the type of soil and its underlying structure have a great effect on the accumulation and availability of any chemical, it would not be possible to project the results of

this experiment to include all areas. Also very little is known of the form in which paris green occurs in the soil. It may occur unchanged as cupric acetoarsenite or as various breakdown products caused by hydrolysis and the action of chemicals present in the soil.

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